Chapter 3

THERMODYNAMICS OF INTERFACIAL SYSTEMS

A. The thermodynamics of simple bulk systems

1. *Thermodynamic concepts*

Thermodynamics is in general useful for providing over-arching "rules" that govern the descriptions of macroscopic systems in terms of their properties and their interactions with other systems. The systems usually encountered in textbooks for scientists and engineers are pieces of infinite systems, as pictured schematically in Fig. 3-1(a). Their "boundaries" are completely conceptual and serve only to delineate the extent of the system. Furthermore, it is assumed in formulating thermodynamic descriptions that the systems are in internal equilibrium so that, in the absence of external fields, they are homogeneous with respect to their relevant intensive properties. Specifically, since they are assumed to be in internal thermal, mechanical and diffusional equilibrium, they are uniform with respect their temperature, pressure and composition. This requirement poses problems for solids, in which full internal equilibrium often does not exist. In fluids, molecular mobility often (but not always) guarantees internal equilibrium, whereas in solids, non-equilibrium structures, and hence non-uniform stress fields and compositions, can be frozen in place over time scales of practical interest. (This is clearly the case for many of the purpose-built micro or nano constructions of interest in nanoscience and nanotechnology.) "Textbook chemical thermodynamics" thus focuses on fluids, and the systems commonly encountered are fluid masses delineated by boundaries that are

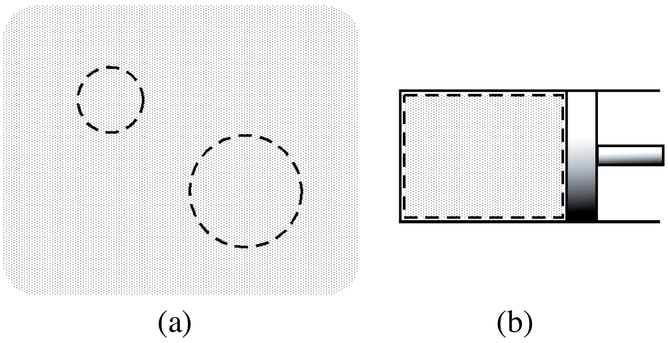

Fig. 3-1: (a) Thermodynamic systems as finite pieces of an infinite homogeneous system, (b) Simple-compressible system as a fluid in a piston-cylinder arrangement.

close to, but not coincident with their actual physical boundaries, as exemplified by the gas contained within the piston-cylinder arrangement of Fig. 3-1(b). Since the physical interfacial region between the fluid and the cylinder wall is only a few Å thick, essentially all of the mass of the fluid is captured by drawing the model system boundary just far enough away from the wall to exclude all the inhomogeneity of the interfacial layer.

2. *The simple compressible system*

In the absence of external fields, the systems of chemical thermodynamics are subject only to the single work mode of compression ("*p-V* work"), and energy added to the system as work is given by:

$$\delta W = -pdV\,. \tag{3.1}$$

This defines a *simple-compressible system*, and the only purely physical processes to which it is subject are those of compression-expansion and heating-cooling. (Mixing or de-mixing can always be deconstructed into compression-expansion processes.) The list of allowable processes can be extended, however, to include ones with respect to which the system is not necessarily in equilibrium, *viz*., chemical reactions or phase changes. The conditions of internal *physical* equilibrium can be envisioned to continue to obtain for individual phases while the system is undergoing one or more of the above physicochemical processes.[1]

The first step in describing purely physical processes consists of writing down the appropriate expression for work. The next step makes use of the State Postulate, which asserts the existence of the internal energy, U, as a property of the system, expressible for a closed system (a system of given mass or set of mole numbers) as a function of two independent relevant variables (one more than the number of independent work modes), *e.g*., using the independent variables T and V:

$$U = U(T,V). \tag{3.2}$$

The First Law of thermodynamics asserts that any change in system energy is given by:

$$dU = dQ + dW, \tag{3.3}$$

where Q is *heat*, defined as energy transfer to the system unaccounted for in macroscopic evaluations of work. The First Law statement is a useful, as opposed to a trivial, statement of the conservation energy because it can be shown that the heat effect Q can be measured independently by *calorimetry*. For systems not undergoing physicochemical processes (phase changes or chemical reactions), the heat effect is associated with a temperature change of the system, *i.e.* $dQ = CdT$, where C is the heat capacity of the system

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[1] Prigogine, I., and Defay, R., **Chemical Thermodynamics**, Longmans Green and Co., London, 1954.

dependent on the thermodynamic state of the system and the nature of the process (constant *V*, constant *p*, *etc.*) during which heat is added. Appropriate scales for both temperature and heat capacity (for reference substances) were established by making use of the mechanical equivalence of heat. Putting the above relationships together allows the development of an explicit expression for the heat effect, *Q*, accompanying any such process, *e.g.*

$$\delta Q = \delta U - \delta W = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV + pdV$$

$$= C_V dT + T\left(\frac{\partial p}{\partial T}\right)_V dV, \tag{3.4}$$

where the heat capacity at constant volume, $C_{\mathrm{v}} = \left(\frac{\partial U}{\partial T}\right)_V$, and the form of the coefficient in the second term of Eq. (3.4) is obtained by ordinary thermodynamic reductions; in this case:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p. \tag{3.5}$$

One may proceed from this point to the expression for entropy change, *dS,* for a quasi-static process, *viz. dQ*/*T*, substituting from Eq. (3.4):

$$dS = \frac{\delta Q_{\mathrm{rev}}}{T} = \frac{C_{\mathrm{v}}}{T} + \left(\frac{\partial p}{\partial T}\right)_V dV, \tag{3.6}$$

and thence to the Helmholtz free energy function: $F = U - TS$:

$$dF = d(U - TS) = -SdT + \delta w = -SdT - pdV. \tag{3.7}$$

The Second Law of Thermodynamics states that for the spontaneity of a proposed process in an isolated system, $dS \geq 0$, or $dF \leq 0$ for systems constrained to constant *T* and *V*. Independent variables *T* and *p* may be chosen instead of *T* and *V*, in which case it is convenient to introduce the system enthalpy, $H = U + pV$ and the Gibbs free energy (or free enthalpy), $G = H - TS$. The enthalpy is a useful function for describing heat and work effects accompanying constant pressure processes, and the Gibbs free energy is a useful function for describing system equilibria and stability with respect to processes at constant temperature and pressure. In this set of variables, the descriptive equations become:

$$\delta W = -p\left(\frac{\partial V}{\partial T}\right)_p dT - p\left(\frac{\partial V}{\partial p}\right)_T dp \tag{3.8}$$

$$\delta Q = C_{\mathrm{p}}dT - T\left(\frac{\partial V}{\partial T}\right)_p dp \tag{3.9}$$

$$dH = d(U + pV) = C_{\mathrm{p}}dT + Vdp \tag{3.10}$$

$$dS = \frac{\delta q_{\mathrm{rev}}}{T} = \frac{C_{\mathrm{v}}}{T} + \left(\frac{\partial p}{\partial T}\right)_V dV = \frac{C_p}{T} - \left(\frac{\partial V}{\partial T}\right)_V dp \tag{3.11}$$

$$dG = d(H - TS) = -SdT + Vdp \tag{3.12}$$

In all cases, mathematical reductions have been made which put the expressions in a form such that the coefficients can be evaluated from quantities obtainable in the laboratory.[2] For systems modeled as "simple-compressible," the list of such quantities includes only:

- volumetric data (p-V-T equations of state)
- calorimetric data (heat capacities, latent heats)
- composition (whose changes allow one to follow a physicochemical process)

From the above type of development, much can be done toward describing the behavior of real systems. In particular, expressions for heat and work effects are made available, and expressions for the "driving forces," whose sign and magnitude determine the spontaneity of various processes, are derived.

B. The simple capillary system

1. The work of extension

In constructing a model for systems that includes their interface(s) with adjacent systems, it is first recognized that if it is to be a piece of an infinite system, the piece must include one or more interfaces within its conceptual boundaries. Since the latter are finite, the interfacial area in the system is also finite,[3] and the extensive properties of the system can no longer be obtained by simply multiplying the corresponding intensive properties by the system mass. Such a system will be termed in general an *interfacial system*, and if the bulk phase states involved are fluids, it is a *capillary system*. As stated earlier, because of their greater simplicity, it is useful to first set forth the thermodynamic description applicable to capillary systems and to point out and discuss later the ramifications of extending the description to fluid-solid interfacial systems.

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[2] Recall that absolute entropy, S, is obtainable (using the Third Law of Thermodynamics) calorimetrically or spectroscopically.

[3] Hill, T. L., **Thermodynamics of Small Systems**, Part I, W. A. Benjamin Publ., New York (1963).

The simplest model one may use is that of the *simple capillary system*, pictured in Fig. 3-2. It consists of three parts in internal equilibrium: two portions of bulk phase, of volumes V' and V'', which are "simple compressible," and the interface itself, of area A, regarded mechanically as a membrane of zero thickness in uniform, isotropic tension. It is not possible to choose any simpler model, such as the interfacial layer by itself, because the latter is not "autonomous," *i.e.* it is inextricably connected to at least small adjacent portions of the bulk phase on either side.[4]

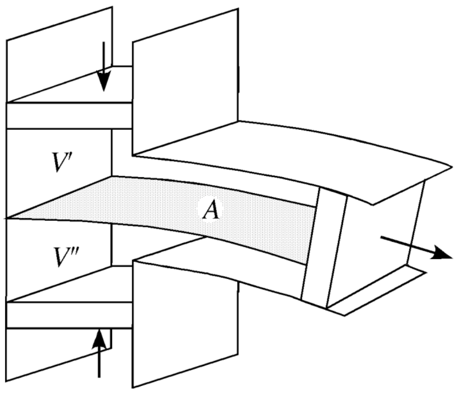

Fig. 3-2: The simple capillary system.

Work may be done on a simple capillary system in accord with:

$$dW = -p'dV' - p''dV'' + \sigma dA, \tag{3.13}$$

where the last term on the right is the "work of area extension."[5] In writing Eq. (3.13), it is clear that the membrane model of Young has been incorporated into the simple capillary system model. Recall that the difference between p' and p'' is related to the interfacial tension and the local curvature of the interface, κ, in accord with the Young-Laplace Equation, Eq. (2.29):

$$p'' - p' = \sigma\kappa. \tag{3.14}$$

The pressure difference is usually not significant for purposes of computing work unless the surface is of high curvature ($R_m = 1/\kappa \leq 1$ μm). One thus generally uses the approximation of a flat surface system, so that:

$$dW \approx -pdV + \sigma dA. \tag{3.15}$$

2. *Heat effects; abstract properties; definition of boundary tension*

Starting with the above work expression, and using the State Postulate in the form, for a closed simple capillary system:

$$U = U(T, V, A), \tag{3.16}$$

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[4] Defay, R., Prigogine, I., Bellemans, A., and Everett, D. H., **Surface Tension and Adsorption**, pp. 2-3, Longmans, London, 1966.

[5] If the interface resists bending deformations, as mentioned in Chap. 2, G.4, an additional work term may be required.

together with the First and Second Laws of thermodynamics, one can derive the equations for the heat effect and the various thermodynamic property changes for simple capillary systems, which are as follows:

$$\delta Q = C_{\mathrm{V,A}} dT + T\left(\frac{\partial p}{\partial T}\right)_{V,A} dV - T\left(\frac{\partial \sigma}{\partial T}\right)_{V,A} dA \tag{3.17}$$

$$dU = C_{V,A} dT + \left[T\left(\frac{\partial p}{\partial T}\right)_{V,A} - p\right] dV + \left[\sigma - T\left(\frac{\partial \sigma}{\partial T}\right)_{V,A}\right] dA \tag{3.18}$$

$$dS = \frac{C_{\mathrm{v}}}{T} dT + \left(\frac{\partial p}{\partial T}\right)_{V} dV - \left(\frac{\partial \sigma}{\partial T}\right)_{V,A} dA \tag{3.19}$$

$$dF = -SdT - pdV + \sigma dA \tag{3.20}$$

Integration of the expression for dF at constant temperature and volume gives:

$$F = F_0 + \sigma A, \tag{3.21}$$

where F_0 is a constant with respect to system area changes at constant T and V. Such equations show how one can evaluate heat and work effects and other property changes for simple capillary systems from laboratory data obtainable for such systems, the list of which now consists of

- volumetric data,
- calorimetric data,
- composition, AND
- interfacial tension data (as a function of T and composition)

Comment needs to be made regarding the derivatives $\left(\frac{\partial p}{\partial T}\right)_{\mathrm{V,A}}$ and $\left(\frac{\partial \sigma}{\partial T}\right)_{\mathrm{V,A}}$ in Eqs. (3.17)–(3.19) above. A *pure-component* simple capillary system is just a liquid against its equilibrium vapor, so that the pressure is the vapor pressure at the given temperature, and the surface tension is also fixed when the temperature is fixed. Thus in this case, both expressions should be written as total derivatives. For closed multicomponent capillary systems, both the system pressure and surface tension have to be regarded as functions of volume and surface area as well as temperature because changes in those variables at constant temperature will result in a redistribution of the components amongst the system parts, *i.e.*, between the liquid phase, the vapor phase and the interface.

It may be desirable to change the independent variable set to (T, p, A) or (T, p, σ), but for single-component simple capillary systems this is not possible because once temperature is fixed, p and σ are fixed, as mentioned above. These variable sets may be used for multicomponent capillary systems, in which variations in p and σ would be accompanied by redistribution of the components between the various parts of the capillary system. Multicomponent as well as open capillary systems are discussed more explicitly below.

The above equations have been developed under the assumption of internal equilibrium. Internal diffusional equilibrium in a simple capillary system means that during any process, an equilibrium distribution of the components between the various parts of the system (the two bulk phase portions and the interface) exists. This amounts to maintaining phase equilibrium and adsorption equilibrium, as discussed in more detail below.

The important new terms in the above expressions express the consequences of making interfacial area changes, *viz.*

- work of extension: $\sigma\, dA$
- heat of extension: $-T\left(\frac{d\sigma}{dT}\right)dA$, and
- entropy of extension: $-\left(\frac{d\sigma}{dT}\right)dA$, *etc.*

In particular, the free energy of extension at constant (T,V), *i.e.*, $-\left(\frac{\partial F}{dA}\right)_{\mathrm{T,V}}$, provides a thermodynamic definition of the boundary tension, σ.

What one learns upon inserting realistic numbers from surface or interfacial tension measurements into the above equations for δQ and δW is that the heat and work effects associated with interfacial area changes, such as might accompany the subdivision of ordinary bulk matter into particles in the colloid size range, are quite small. For example, if at 300°K a droplet of diameter 1 cm (with A = 3.14 cm^2) is broken up into droplets of diameter one μm (there will be 1.33 x 10^{12} such droplets), the surface area will have increased to A = 4.19 m^2. If the surface tension is σ = 35 erg/cm^2, and its temperature derivative is taken as –0.1 erg/cm^{2}K, we have:

$$W = \int_{3.14}^{4.19\cdot 10^4} \sigma\, dA = (35)(4.19\cdot 10^4) = 1.47\cdot 10^6 \text{ erg} = 0.035 \text{ cal}, \tag{3.22}$$

and

$$Q = -\int_{3.14}^{4.19\cdot 10^4} T\left(\frac{d\sigma}{dT}\right)dA = -(300)(-0.1)(4.19\cdot 10^4) \text{ erg} = 0.030 \text{ cal} \tag{3.23}$$

These values are almost negligibly small. One might have anticipated the smallness of these effects as they were not taken into account in the early experiments of Clausius, Rumford, Joule, *etc.*, leading to the establishment of the First Law principle, *i.e.*, a statement of the conservation of energy.

The failure to account for them never led to any apparent violation of the principle.

The above type of development also leads to the expression of important driving forces affecting the spontaneous behavior of capillary systems. Most importantly, it shows from the thermodynamic point of view, that systems with positive values of σ will always tend to spontaneously contract their interface. A spontaneous process will occur (at constant T,V) if F can thereby be made to decrease, *i.e.*, dF is negative. This will obviously occur if the change in area, A, is negative.[6]

It is to be noticed that the key properties involved in describing the interfacial effects in pure-component systems or systems of constant composition are the boundary tension and its temperature derivative, the experimental determination of which we have already discussed.

C. Extension to fluid-solid interfacial systems

1. *The work of area extension in fluid-solid systems*

Next consider how fluid-*solid* interfacial systems differ from the fluid-fluid (capillary) systems described above. The first observation is that solids, and in particular interfacial zones between solids and fluids, are often not in states of full internal equilibrium. Stress relaxation times may be large relative to times scales of practical interest so that, dependent on their history, solid specimens may be supporting significant residual stresses. Nonetheless, provided appropriate precautions are taken, such systems can often be qualitatively and even quantitatively described in terms of the thermodynamics of capillary systems.[7] The "tension" σ at a solid-fluid interface represents, analogous to that in a capillary system, the integral effect of a reduced lateral stress component across the zone of inhomogeneity between the fluid and solid phases. The difference is that the stress field in the solid is in general not known and may not be in a relaxed, *i.e.*, internal equilibrium, state. Even in the absence of residual stresses, the boundary tension at a fluid-solid interface can be defined only when the total free energy density tensor in the solid phase reduces to a uniform value. Fortunately, this restriction may not be critical, because the elastic (stress)

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[6] There are cases where this statement must be amended. The process of breaking up a mass of liquid into droplets, as described above, produces a *configurational* entropy change in addition to the term: $-\int\left(\frac{d\sigma}{dT}\right)dA$, as discussed in Chap. 9 in the context of emulsification. This also affects the free energy changes, which have entropy content.

[7] Hering, C., *in* **Structure and Properties of Solid Surfaces**, R. Gomer and C. S. Smith, Eds., pp. 5-82, Univ. Chicago Press, Chicago (1953).

energy density is usually only a small (often negligible) component of the total energy density.[8]

The evaluation of the work associated with area extension for fluid-solid interfacial systems depends on how the area is created. One way this may be effected is through direct interface creation, as occurs, for example when new solid material precipitates out of a solution. In this case, the (reversible) work effect is given by

$$\delta W = dF = \left(\frac{\partial F}{\partial A}\right) dA = \sigma dA, \qquad (3.24)$$

the same result as for capillary (*i.e.*, fluid interface) systems. On the other hand, new solid-fluid interface may be produced by the mechanical *stretching* of a pre-existing solid-fluid interface, a process that changes the structure and properties of the interfacial layer. In capillary systems such changes are instantly relaxed out, and the work expression is the same as that for interface creation, but in solid-fluid systems they may be frozen in indefinitely, or at least for significant periods of time. The isothermal quasi-static mechanical work required to stretch the interfacial area is given in general by[9]

$$\left(\frac{\delta W}{dA}\right)_{\text{int. dilation}} = \sigma_{\text{m}} = \frac{dF}{dA} \equiv \frac{d(f^{\sigma} A)}{dA} = f^{\sigma} + A\frac{df^{\sigma}}{dA} = \sigma + A\frac{d\sigma}{dA}, \qquad (3.25)$$

where σ_{m} is the mechanical boundary tension (or total stretching tension), and f^{σ} is the surface free energy per unit area, equal to the thermostatic "tension," σ, defined above. The last term must be included because the structure of the surface is being changed. Finally, work may be associated with both bulk and surface shear strain in the solid. The work terms associated with these processes would be[10]:

$$\text{Work of bulk shear strain} = V(\mathbf{s}^{\beta} : \delta\varepsilon^{\beta}), \text{ and} \qquad (3.26)$$

$$\text{Work of surface shear strain} = A(\mathbf{s}^{\sigma} : \delta\varepsilon^{\sigma}), \qquad (3.27)$$

where $\mathbf{s}^{\beta}$ and $\mathbf{s}^{\sigma}$ are the bulk and surface stress tensors, respectively, and $\delta\boldsymbol{\varepsilon}^{\beta}$ and $\delta\boldsymbol{\varepsilon}^{\sigma}$ are the corresponding bulk and surface displacement tensors. In processes involving surface area extension in fluid-solid interfacial systems, the work of surface shear strain is usually negligible, but the work associated with the accompanying bulk shear strain is often the dominant component of the actual total work effect. It is generally not possible to calculate this effect

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[8] Defay, R., Prigogine, I., Bellemans, A., and Everett, D. H., **Surface Tension and Adsorption**, pp. 286ff, Longmans, London, 1966.

[9] Tabor, D., **Gases, Liquids and Solids and other States of Matter**, 3rd Ed., pp. 166-168, Cambridge Univ. Press, Cambridge, UK (1996).

[10] Benson, G. C., and Yun, K. S., *in* **The Solid-Gas Interface**, Vol. 2, E. A. Flood, Ed., pp. 203-269, Marcel Dekker, New York (1967).

quantitatively, but it is one of the reasons that the energies associated with size reduction (crushing and grinding) of solids are usually much larger than those suggested by the above equation for ($\delta W/dA$).

2. *Compound interfacial systems; Young's equation*

Another method for changing the area of a given fluid-solid interface is by advancing or retracting the fluid phase across the solid, as when a liquid drop is advanced or retracted across a solid surface, pictured in Fig. 3-3. In such a case, a given fluid-solid interface is created or destroyed at the expense or benefit of another fluid-solid and fluid- fluid interface. What is required to describe such processes are *compound* capillary or interfacial systems, *i.e.*, systems with more than a single type of interface. Consider the (reversible) work associated with the process shown in Fig. 3-3, whereby the liquid drop expands its base at constant temperature and volume (in the absence of gravity) to cover more of the solid surface. This is given by

$$\delta W = dF = \left(\frac{\partial F}{\partial A_{\mathrm{SG}}}\right)_{\mathrm{T,V}} dA_{\mathrm{SG}} + \left(\frac{\partial F}{\partial A_{\mathrm{SL}}}\right)_{\mathrm{T,V}} dA_{\mathrm{SL}} + \left(\frac{\partial F}{\partial A_{\mathrm{LG}}}\right)_{\mathrm{T,V}} dA_{\mathrm{LG}}$$

$$= (\sigma_{\mathrm{SG}} - \sigma_{\mathrm{SL}})dA_{\mathrm{SG}} + \sigma_{\mathrm{LG}}dA_{\mathrm{LG}} \tag{3.28}$$

Expressions of this type are the thermodynamic basis for the computation of the work associated with such processes as adhesion and wetting discussed in the next chapter.

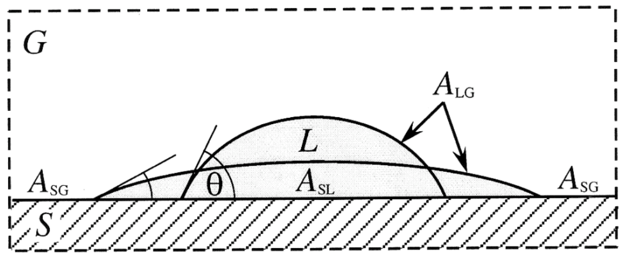

Fig. 3-3: A compound capillary system consisting of a drop of liquid (L) resting on a solid (S) surface in the presence of a gas (G). If the liquid drop is flattened, its interfacial area against the solid, A_{SL}, increases while that of the solid surface against the gas, A_{SG}, decreases by a corresponding amount, and the liquid-gas interface, A_{LG}, increases.

The thermodynamically preferred configuration for a compound capillary system of the type shown in Fig. 3-3 is obtained from the minimization of the free energy, F, with respect to variation of the interfacial areas in an isothermal, constant volume process of the type suggested in the figure[11]:

$$F = F_0 + \sigma_{\mathrm{LG}}A_{\mathrm{LG}} + \sigma_{\mathrm{SL}}A_{\mathrm{SL}} + \sigma_{\mathrm{SG}}A_{\mathrm{SG}}, \tag{3.29}$$

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[11] Sheludko, A. **Colloid Chemistry**, pp. 90-92, Elsevier, Amsterdam, 1966.

where F_0 is a constant. If the drop is sufficiently small that gravity can be neglected ($Bo \rightarrow 0$), it may be regarded as spherical cap,[12] allowing its liquid-gas surface, A_{LG}, its volume V and the contact angle θ to be expressed in terms of its height h and its base radius R. Consider the construction shown in Fig. 3-4, with the slice dV of the spherical segment of radius R shown. The element of segment area dA is the width of the slice, $Rd\psi$, times its circumference, $2\pi r' = 2\pi R \sin\psi$. Thus, integrating over the segment, *i.e.*, from $\psi = 0$ to $\psi = \theta$, one obtains:

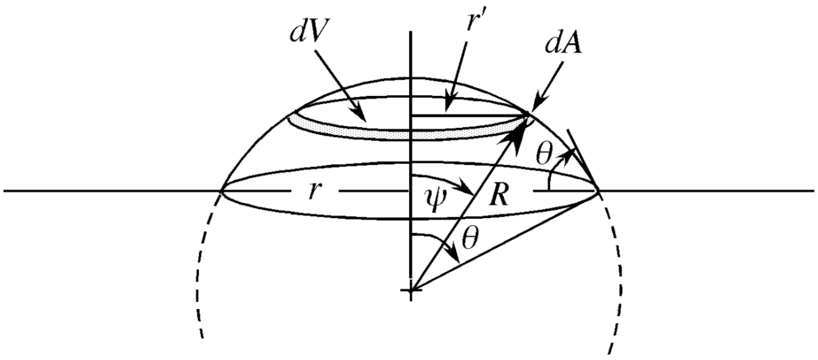

Fig. 3-4: Diagram showing computation of the area and the volume of a spherical segment.

$$A_{\mathrm{LG}} = \int dA = \int_0^\theta 2\pi R^2 \sin\psi \mathrm{d}\psi = 2\pi R^2(1-\cos\theta). \qquad (3.30)$$

The volume of the slice dV is its area: $\pi r'^2 = \pi R^2 \sin^2\psi$, times its thickness, $R\sin\psi d\psi$, which upon integration gives:

$$V = \int \mathrm{d}V = \int_0^\theta \pi R^3 \sin^3\psi \mathrm{d}\psi = \frac{1}{3}\pi R^3\left[2-\cos\theta(\sin^2\theta+2)\right]. \quad (3.31)$$

Then both $\cos\theta$ and R may eliminated in terms of r and h using the relationships:

$$r = R\sin\theta \text{ and } h = R(1-\cos\theta), \qquad (3.32)$$

as suggested by Fig. 3-5. After some algebra, one obtains:

$$A_{\mathrm{LG}} = \pi\left(r^2+h^2\right), \qquad (3.33)$$

$$V = \frac{1}{6}\pi h\left(3r^2+h^2\right), \text{ and} \qquad (3.34)$$

$$\cos\theta = \frac{(r^2-h^2)}{(r^2+h^2)}. \qquad (3.35)$$

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[12] If gravity is to be taken into account, the situation is more complex in that the shape is less easily expressible, and gravitational potential energy must be added in. The derivation follows the same lines, however, and the results are identical.

The Helmholtz free energy of the system may then be expressed as

$$F = F_0 + \pi\left(r^2 + h^2\right)\sigma_{\mathrm{LG}} + \pi r^2\sigma_{\mathrm{SL}} + \left(A_{\mathrm{S\text{-}total}} - \pi r^2\right)\sigma_{\mathrm{SG}} \qquad (3.36)$$

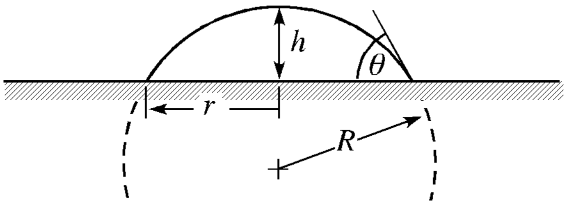

Fig. 3-5: Diagram for derivation of Young's equation by minimization of system free energy.

If F is to be minimum, any variation of it upon variation of r and h (subject to the constraint of constant V) must vanish, *i.e.*,

$$\delta F = \pi(2r\delta r + 2h\delta h)\sigma_{\mathrm{LG}} + 2\pi r\delta r\sigma_{\mathrm{SL}} - 2\pi r\delta r\sigma_{\mathrm{SG}} = 0, \text{ and} \qquad (3.37)$$

$$\delta V = \frac{\pi}{6}(6rh\delta r + 3h^2\delta h + 3r^2\delta h) = 0, \text{ or, simplifying:} \qquad (3.38)$$

$$h\sigma_{\mathrm{LG}}\delta h + r(\sigma_{\mathrm{LG}} + \sigma_{\mathrm{SL}} - \sigma_{\mathrm{SG}})\delta r = 0, \text{ and} \qquad (3.39)$$

$$2rh\delta r + (r^2 + h^2)\delta h = 0. \qquad (3.40)$$

Using the Lagrange method for finding the extremum of a function subject to auxiliary constraints, we multiply Eq. (3.40) by the arbitrary constant $-\lambda$, add it to Eq. (3.39), and set the resulting coefficients of both dr and dh equal to zero, giving:

$$\sigma_{\mathrm{LG}} + \sigma_{\mathrm{SL}} - \sigma_{\mathrm{SG}} - 2\lambda h = 0, \text{ and} \qquad (3.41)$$

$$\sigma_{\mathrm{LG}}h - \lambda(r^2 + h^2) = 0. \qquad (3.42)$$

Elimination of λ between the above equations, and substituting for $\cos\theta$, gives:

$$\cos\theta = \frac{(\sigma_{\mathrm{SG}} - \sigma_{\mathrm{SL}})}{\sigma_{\mathrm{LG}}}. \qquad (3.43)$$

This important result is known as *Young's Equation*,[13] and it appears to confer upon the contact angle the status of a *thermodynamic property*, *i.e.*, it should have a fixed, unique value for a given physical system at a given temperature and pressure at equilibrium. As seen in Chap. 4, however, experimental values for it depend upon many *non*-thermodynamic quantities, and its use as a thermodynamic property (*e.g.*, to infer "surface energies") must be made only with caution.

A compound capillary system is also exemplified by an oil drop floating at a water-air interface. The total system is made up of three simple capillary systems, involving the water-air, oil-air and oil-water interfaces,

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[13] Young, T., *Phil. Trans.*, **95**, 65, 82 (1805).

respectively, in mutual equilibrium, as shown in Fig. 2-28. Minimization of the system's free energy in this case leads to the force balance of Eq. (2.48):

$$\underline{\sigma}_{\mathrm{w}} + \underline{\sigma}_{\mathrm{o}} + \underline{\sigma}_{\mathrm{o/w}} = 0, \tag{3.44}$$

i.e., Neumann's triangle, where $\underline{\sigma}_{\mathrm{w}}, \underline{\sigma}_{\mathrm{o}}$, and $\underline{\sigma}_{\mathrm{o/w}}$, the boundary tensions of the water-air, oil-air and oil-water interfaces, respectively, are treated as vectors.

For a sessile drop on a flat *solid* surface, Neumann's triangle reduces to the set of scalar equations:

$$\sigma_{\mathrm{SG}} - \sigma_{\mathrm{SL}} = \sigma_{\mathrm{LG}} \cos\theta, \text{ and} \tag{3.45}$$

$$\sigma_{\mathrm{LG}} \sin\theta = E_{\mathrm{S}}, \tag{3.46}$$

where θ is the contact angle. The first equation above is the horizontal component of the force balance, *viz.* Young's Equation, while the second shows that the vertical component of the interline force must be balanced by an elastic force E_{S} in the solid phase.

As pointed out in Chap. 2, three-phase interlines that exist in a compound interfacial system may be imbued with a line tension, τ_{ℓ}. For the case of a sessile drop on a flat surface, the horizontal force must then be augmented by τ_{ℓ}/R (where R is the base radius of the drop), so that Young's Equation becomes

$$\cos\theta = \frac{\sigma_{\mathrm{SG}} - \sigma_{\mathrm{SL}}}{\sigma_{\mathrm{L}}} - \frac{\tau_{\ell}}{R\sigma_{\mathrm{L}}}. \tag{3.47}$$

With a maximum plausible value of $\approx 10^{-9}$ N for τ_{ℓ}, the final term is seen to be generally negligible, except possibly for micro or nano droplets that may be encountered in hetero-nucleation processes or capillary condensation into micro or nano pores.

D. Multicomponent interfacial systems

1. *The Gibbs dividing surface and adsorption*

To study the effects of composition on the behavior of multicomponent capillary systems (*e.g.*, the dependence of surface tension on composition, *etc.*), one must first recognize that the various components in such a system do not distribute themselves uniformly at equilibrium amongst the various parts of the system. An example is shown schematically in Fig. 3-6, where the circles represent a solute component. It is evident that the concentration of the component in the lower bulk phase is higher than it is in the upper bulk phase, and that in this case it is especially high in the interfacial region. The figure also shows a representation of the solute concentration profile through the interfacial region. If we wish to examine the distribution of this component or others within the system, the simple capillary system model must be developed further. It thus far considers the system *only as a whole* (with the assumption that there is maintenance of component distribution equilibrium) as it undergoes various processes.

As mentioned earlier, an attempt to actually "split up" the system into its parts to identify properties with these parts alone, leads to quantities difficult (or impossible) to address in the laboratory, or even to define unambiguously. What can be done, however, is to develop an extension of the model of a simple capillary (or interfacial) system that reflects all of its measurable properties. A number of devices have been proposed for this, but the one most commonly used is that of the *Gibbs Dividing Surface*. Gibbs replaced the interfacial layer by a (zero-thickness) "dividing surface," oriented normal to the density gradient in the interfacial zone, up to which *all* of the intensive variables describing the bulk phase portions of the system are taken to be uniform at their bulk-phase values. This is pictured schematically in Fig. 3-7 for the concentrations of the solvent (1) and solute (2) in a binary simple capillary system. (Once again, the solute is shown to be concentrated in the interfacial zone, but this of course need not be the case.) The bulk phase concentrations of the species are C_1', C_1'', C_2', and C_2''. Depending on the dividing surface location, the model requires an addition (or subtraction) of a particular number of moles of each species to the surface, n_1^σ and n_2^σ, respectively, to exhibit mass equivalence with the real system, *i.e.*,

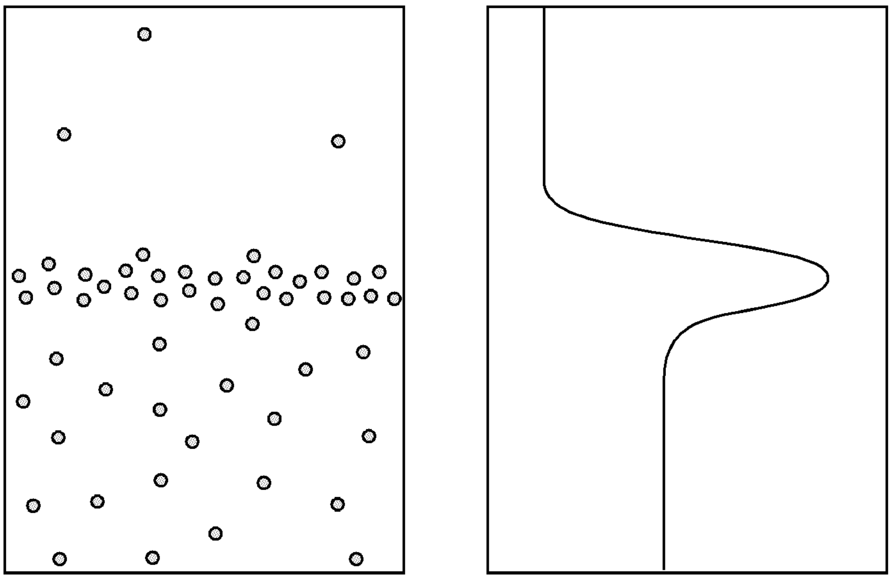

Fig. 3-6: Schematic representation of the variation of a solute concentration in moving from one bulk phase, through the interfacial zone into the adjacent bulk phase.

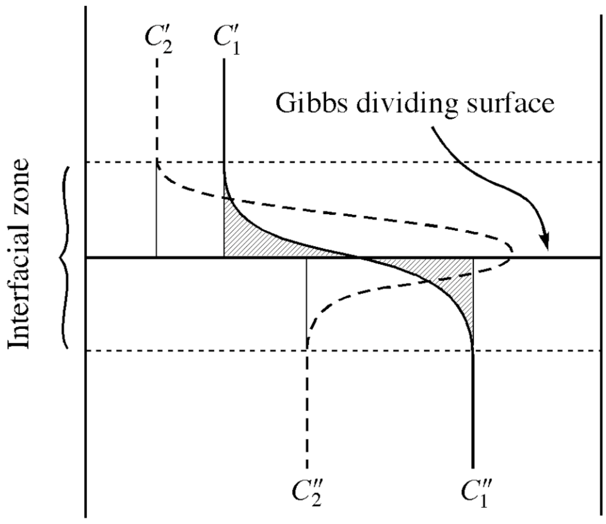

Fig. 3-7: Gibbs Dividing Surface drawn in a binary liquid-gas capillary system.

$$n_1^\sigma = (n_1)_{\text{real}} - (n_1)_{\text{model}}, \text{ and} \tag{3.48}$$

$$n_2^\sigma = (n_2)_{\text{real}} - (n_2)_{\text{model}}. \tag{3.49}$$

The terms n_1^σ and n_2^σ are called "surface excesses" and are examples of "properties of the dividing surface," as distinct from properties of the capillary system. They are the numbers of moles of the components *ascribed* to the dividing surface. One may define surface excesses for other extensive thermodynamic properties of the system as well, such as "surface excess enthalpy," "surface excess entropy," *etc.*

The location of the dividing surface (for a quasi-flat surface) is arbitrary, but it is clear that both the magnitude and the sign of the n_i^σs are extremely sensitive to where it is placed. (When the surface is curved, mechanical equilibrium considerations require in principle that the dividing surface be located at a specific position called the *surface of tension.*[14] This cannot, in any case, be located experimentally.) A shift of the dividing surface location by just a few Å may change the sign of any surface excess, and may alter its value by many orders of magnitude. The Gibbs dividing surface is clearly of no value for describing mass distribution in the case of a pure-component system, but for a binary system, one may first notice that while the surface excess for either component can be made any value desired by judicious location of the dividing surface, the *relative positions* of the actual concentration profiles of different components are not at all arbitrary. The relationship is fixed by Nature, even if the details of the profiles are not known. One seeks to define a quantity that expresses the *relative* surface excess of one component (usually the solute, 2) *with respect to another* (usually the solvent, 1). *This* quantity is independent of dividing surface

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[14] Defay, R., Prigogine, I., Bellemans, A., and Everett, D. H., **Surface Tension and Adsorption**, p. 3, Longmans, London.

location and should, at least in principle, be subject to unambiguous determination in the laboratory. Such a quantity can be derived for a binary system by writing material balances for the solvent and solute components with reference to Fig. 3-8:

$$1.\ n_1^\sigma = n_1 - V'C_1' - V''C_1''\ \text{(substitute } V' = V - V''\text{)}$$

$$= n_1 - VC_1' + V''(C_1' - C_1''),\ \text{and} \tag{3.50}$$

$$2.\ n_2^\sigma = n_2 - VC_2' + V''(C_2' - C_2'') \tag{3.51}$$

The quantities n_1^σ, n_2^σ and V'' are dependent upon dividing surface location, but the other quantities are independent of it and measurable. Eliminating V'' between the above two equations, and putting both the surface excesses on the left side of the equation gives:

$$n_2^\sigma - n_1^\sigma\left[\frac{C_2' - C_2''}{C_1' - C_1''}\right] = \left\{(n_2 - VC_2') - (n_1 - VC_1')\left[\frac{C_2' - C_2''}{C_1' - C_1''}\right]\right\}. \tag{3.52}$$

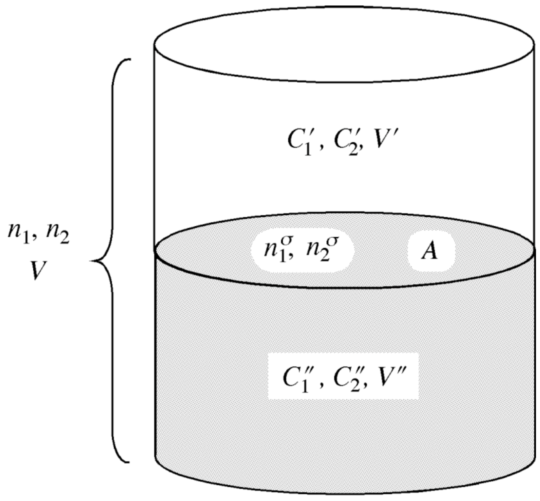

Fig. 3-8: Binary simple capillary system.

Finally, dividing through by the interfacial area A gives:

$$\Gamma_{2,1} = \Gamma_2 - \Gamma_1\left[\frac{C_2' - C_2''}{C_1' - C_1''}\right] = \frac{1}{A}\left\{(n_2 - VC_2') - (n_1 - VC_1')\left[\frac{C_2' - C_2''}{C_1' - C_1''}\right]\right\}. \tag{3.53}$$

where the surface excesses on a per-unit-area basis, Γ_1 and Γ_2, are known as the *adsorptions* of those components, and $\Gamma_{2,1}$ is known as the *relative adsorption of 2 with respect to 1.* This quantity meets the requirements called for above, since all of the quantities on the right hand side of the equation are independent of dividing surface location and, in principle, measurable in the laboratory. (The extension to solutions of more than one solute is evident. One may express, for example, the relative adsorption of any of the solutes with respect to the solvent.) Its physical significance may be better appreciated by noting that it is *the adsorption of component 2* *(regarded as a solute) when the dividing surface is located in such a way as to make the adsorption of component 1 (the solvent) equal to zero*. One may also appreciate it better by considering the situation when one of the phases (say phase′) is a gas. In this event, the concentrations of both components in the gas are generally very small compared with those in the liquid (or solid), and may be neglected. Thus in such a case

$$C_1' << C_1'', \text{ and } C_2' << C_2'', \text{ so that} \tag{3.54}$$

$$\Gamma_{2,1} \approx \Gamma_2 - \Gamma_1\left(\frac{C_2''}{C_1''}\right). \tag{3.55}$$

Dividing through by Γ_1 gives:

$$\frac{\Gamma_{2,1}}{\Gamma_1} = \frac{\Gamma_2}{\Gamma_1} - \left(\frac{C_2''}{C_1''}\right) , \tag{3.56}$$

from which it can be seen that the relative adsorption of 2 to 1 is zero when the components are in the same proportion in the interface as they are in the bulk. When component 2 is relatively *enriched* in the interface,

$$\Gamma_{2,1} > 0 \quad \text{(termed } \textit{positive} \text{ adsorption)}, \tag{3.57}$$

and when it is relatively *less* concentrated in the interface than in the bulk,

$$\Gamma_{2,1} < 0 \quad \text{(termed } \textit{negative} \text{ adsorption)}. \tag{3.58}$$

The relative adsorptions of the various solutes in a solution thus describe the distribution of components between the interface and bulk phases.

2. *Immiscible interfacial systems*

One of the most important simplifications of the current model is that of the *immiscible* simple interfacial system, which occurs when the phases forming the system are completely immiscible, as pictured in Fig. 3-9. This simplification applies in particular to most of the fluid-solid interfacial systems encountered in practice, and amounts to requiring that the solid be non-volatile or insoluble in the adjoining fluid, and that none of the components of the fluid phase dissolve into the solid. Capillary system examples would also include aqueous solutions in contact with an oil or with mercury, in which all components of the solution are assumed to be completely insoluble, or a solution of completely non-volatile components in contact with a gas which does not dissolve in the solution. The most important immiscible interfacial system is that of a solution in contact with an insoluble solid that itself cannot dissolve any of the components of the solution. For immiscible interfacial systems, the Gibbs dividing surface may be located without ambiguity so as to separate all of the atoms or molecules

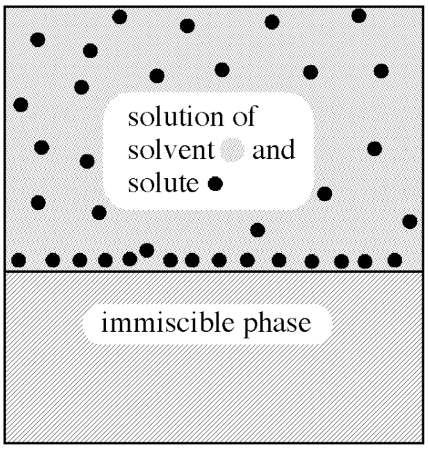

Fig. 3-9: An immiscible interfacial system. The bulk phase portions are completely immiscible, and Gibbs Dividing Surface is made coincident with the actual boundary between the phases. In the system shown, the upper phase is a binary solution, whose components compete for space at the phase boundary.

of the immiscible phases from one another, and the relative adsorption of the solute is given by

$$\Gamma_{2,1} = \Gamma_2 - \Gamma_1\left(\frac{C_2}{C_1}\right), \tag{3.59}$$

where the (′) and (″) may be dropped from the concentration variables since the components appear in only one phase. It is evident from the above equation as well as Fig. 3-9 that the solute and solvent *compete* for space on the adsorbent surface. Under conditions in which the solution is dilute (*i.e.,* $C_2 \rightarrow 0$) or for adsorption of a component from a non-adsorbing gas (so that $\Gamma_1 \rightarrow 0$), one may identify the relative adsorption of the solute with its actual adsorption, *i.e.*, $\Gamma_{2,1} \approx \Gamma_2$.

A special case of an immiscible interfacial system occurs when the "solute" is not soluble in *either* bulk phase portion of the system. This is exemplified by the insoluble or Langmuir monolayers discussed briefly in Chap. 2. The monolayer component is spread at the surface. This may also pertain to a spread non-volatile (or insoluble) monolayer at a solid-fluid interface. In such cases, $C_2 = 0$, and

$$\Gamma_{2,1} \approx \Gamma_2. \tag{3.60}$$

3. *The measurement of adsorption*

To measure adsorption, first consider the right hand side of the general expression for it given earlier in Eq. (3.53):

$$\Gamma_{2,1} = \frac{1}{A}\left\{(n_2 - VC_2') - (n_1 - VC_1')\left[\frac{C_2' - C_2''}{C_1' - C_1''}\right]\right\}. \tag{3.61}$$

It at first seems a straightforward thing to do, since all the quantities on the right hand side are measurable. In reality, however, this calls for computing the difference in two terms that are so close to the same value that it cannot in general be determined with any certainty. This derives from the fact that proportionally so little of the solute inventory resides at the interface. The most successful direct attempt at measuring the relative adsorption in a capillary system has been the *microtome* method of McBain and coworkers[15], shown schematically in Fig. 3-10. A very thin slice (0.05 - 0.1 mm thick, 1 - 2 m^2 in area) of solution was scraped from the surface by a knife traveling along a set of rails. Some results from their experiments are shown in Table 3-1. Interferometry was used to measure the ratio of (n_2/n_1) in the scraped-off layer and compared with the ratio of concentrations for a sample taken from the bulk. The idea was that the scraped-off layer was sufficiently thin that its composition would reflect the different ratio of components at the interface, and the relative adsorption could be determined from the general expression (with C_1' and $C_1'' \approx 0$):

$$\Gamma_{2,1} \approx \frac{1}{A}\left[n_2 - n_1\left(\frac{C_2''}{C_1''}\right)\right]. \tag{3.62}$$

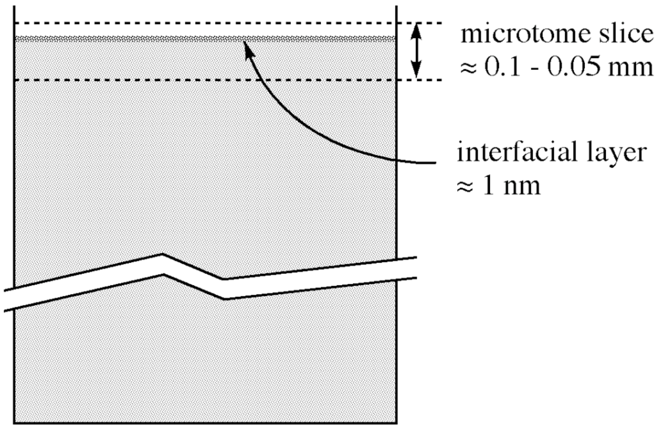

Fig.3-10: Schematic of McBain's microtome method for measuring relative adsorption at a gas-liquid interface.

The measured values give the order of magnitude of typical adsorption. Radioactive tracers[16] and bubble fractionation techniques[17] have also been used to measure $\Gamma_{2,1}$, although they are both fraught with difficulties in interpretation. At any rate, one may consider $\Gamma_{2,1}$, to be a measurable (albeit sometimes with difficulty), unambiguous property of fluid interface systems.

Table 3-1: Relative solute adsorption from aqueous solutions obtained by the microtome method. 1 μmol/m^2 = 10^{-10} mol/cm^2.

Solute	C_2 (M)	$\Gamma_{2,1}$ (μmol/m^2)
Phenol	0.218	4.4
n-Hexanoic acid	0.0223	5.8
NaCl	2.0	- 0.74

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[15] McBain, J. W. and Humphreys, C. W., *J. Phys. Chem.*, **36**, 300 (1932);
McBain, J. W., and Swain, R. C., *Proc. Roy. Soc. (London)*, **A154**, 608 (1936).

[16] Adamson, A. W., **Physical Chemistry of Surfaces**, 4th Ed., pp. 80 ff, Wiley-Interscience, New York, 1982.

[17] Adam, N. K., **The Physics and Chemistry of Surfaces**, pp. 113 ff, Dover Publ., New York, 1968.

For some immiscible interfacial systems, however, determination of adsorption can be made fairly easily, as in the case of adsorption onto the surface of finely divided, high-surface-area solids from either a gas mixture or a solution. These systems are usually immiscible so that C_1'' and C_2'' (concentrations in the solid phase) are both 0, and one may simplify the expression for $\Gamma_{2,1}$ to:

$$\Gamma_{2,1} = \frac{1}{A}\left\{(n_2 - VC_2) - (n_1 - VC_1)\left[\frac{C_2}{C_1}\right]\right\}. \tag{3.63}$$

The second term in the brackets is negligible, following from the assumption that the number of moles of sol*vent* 1 adsorbed, n_1^σ, is negligible relative to the total number of moles of solvent, n_1, in the system. Then one has:

$$C_1 = \frac{n_1 - n_1^\sigma}{V - \bar{v}_1 n_1^\sigma} \approx \frac{n_1}{V}, \tag{3.64}$$

from which the second term in the brackets above is zero. For the case of adsorption out of a liquid solution, a common method is to measure the concentration of solute in the bulk phase before, C_2^0, and after, C_2, adsorption equilibrium has been established, as shown in Fig. 3-11(a). Then:

$$\Gamma_{2,1} \approx \frac{1}{A}\left[n_2 - VC_2\right] = \frac{V}{A}\left[C_2^0 - C_2\right]. \tag{3.65}$$

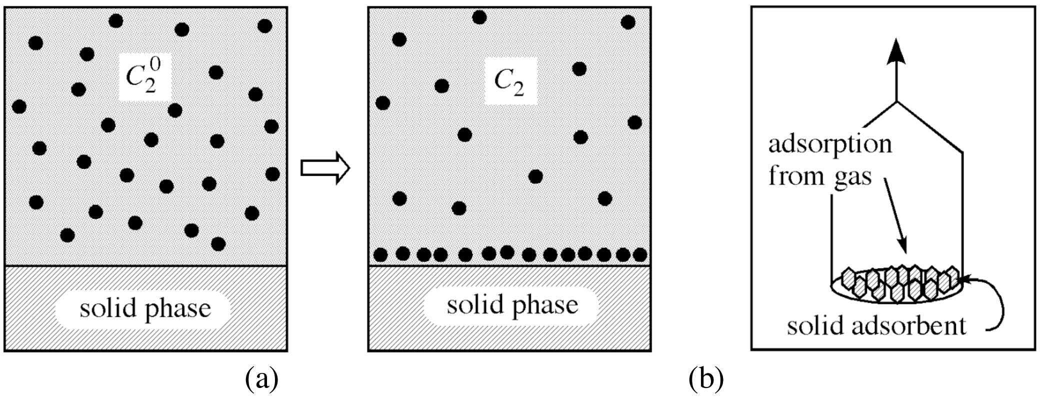

Fig. 3-11: Adsorption onto finely divided and/or porous solids (a) from a liquid phase, or (b) from a gas phase.

This will be a measurable difference if the total amount of adsorption is sufficiently large, a condition which often exists because the area *A* of the solid-fluid interface is large - often several hundred m^2/gram of solid adsorbent.

For adsorption of a component 2 from a gas mixture with a non-adsorbing component 1, measurement can be made directly from the increase in weight (Δw) of the adsorbent (of molecular weight *MW*) upon adsorption, as shown in Fig 3-11(b). The computation for the relative adsorption is:

$$\Gamma_{2,1} = \frac{1}{A}\frac{(\Delta w)}{(MW)g}, \tag{3.66}$$

where g is the gravitational constant.

Chromatography also provides a powerful means for the measurement of adsorption at solid-fluid interfaces, often even when the specific area of the adsorbent is not especially large. High performance liquid chromatography (HPLC)[18] and gas or inverse gas chromatography (IGC)[19] are used for adsorption from solution and from gas mixtures, respectively.

Another case in which "adsorption" is readily determined is that of an insoluble (Langmuir) monolayer spread on a liquid surface. In such a system, we have:

$$\Gamma_{2,1} = \Gamma_2 = \frac{n_2}{A}. \tag{3.67}$$

A given number of moles of the surfactant, n_2, is deposited on the surface using a micrometer syringe containing a dilute solution of the compound in a volatile "spreading solvent," which evaporates from the surface quickly after it is spread.

Both adsorption at the solid-liquid interface and Langmuir monolayers are discussed in more detail later in this chapter.

4. *The phase rule; descriptive equations for binary interfacial systems*

Capillary systems, divided up into parts as we have done, may appear to have more variables describing them than do "ordinary systems." For a two-phase, c-component system we have in addition to p, T and $\mathsf{c} - 1$ concentration variables, the surface tension and $\mathsf{c} - 1$ relative adsorptions, $\Gamma_{1,i}$ ($i = 2 \rightarrow \mathsf{c}$), *i.e.*, a total of c additional variables. This does not mean, however, that the variance of the system has increased, because there is a new equation for each new dependent variable, *viz.*, the adsorption equilibrium equation, $\mu_i^{\mathrm{ads}} = \mu_i^{\mathrm{bulk}}$, for each component, the μ_i's being the chemical potentials of the components.

Consider a binary two-phase system consisting of solvent (1) and solute (2). The phase rule is:

$$\mathsf{F} = \mathsf{c} - \mathsf{p} + 2 = 2 - 2 + 2 = 2,^{20} \tag{3.68}$$

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[18] Sharma, S. C., and Fort, T., *J. Colloid Interface Sci.*, **43**, 36 (1973); Wang, H. L., Duda, J. L., and Radke, C. J., *J. Colloid Interface Sci.*, **66**, 153 (1978).

[19] Lloyd, D. R., Ward, T. C., and Schreiber, H. P., Eds., **Inverse Gas Chromatography**, ACS Symposium Ser. 391, Washington, DC, 1989.

[20] The variance goes up by one if the curvature of the interface is high ($R_{\mathrm{m}} \leq 1$ μm), with the additional variable being a measure of the curvature.

where in general **c** is the number of components, **p** is the number of phases, and **F** is the "variance," or number of independent intensive variables required to fix the intensive state of the system. If one fixes, for example, T and the mole fraction of the solute in the liquid, x_2, the state of the system is fixed, specifically the values of σ and $\Gamma_{2,1}$ are fixed. More generally, for a binary *isothermal* system, one can express any variable as a function of any other independent variable. At constant T, *e.g.*, $p = p(x_2)$; $y_2 = y_2(x_2)$, *etc.*, or bringing in the capillary properties, we have:

$$\sigma = \sigma(x_2) \quad \rightarrow \quad \text{the } \textit{surface tension equation} \tag{3.69}$$

$$\Gamma_{2,1} = \Gamma_{2,1}(x_2) \quad \rightarrow \quad \text{the } \textit{adsorption isotherm} \tag{3.70}$$

$$\sigma = \sigma(\Gamma_{2,1}) \quad \rightarrow \quad \text{the } \textit{surface equation of state} \tag{3.71}$$

These three types of relationships (named as indicated) each describe the binary capillary system. What is observed, however, is that for a given type of system, usually only one of them is readily accessible in the laboratory. The surface tension equation is easily obtained for fluid interface systems, since both σ and x_2 (or C_2) are readily measured. $\Gamma_{2,1}$, however, is not easily measured for these kinds of systems (recall the microtome method), and therefore neither the adsorption isotherm nor the surface equation of state is generally obtainable directly. The adsorption isotherm is readily determined for solid-liquid or solid-gas systems (if the specific area is large), since $\Gamma_{2,1}$ and C_2 are both accessible. The surface tension, however, cannot be measured for these systems, and so the surface tension equation and surface equation of state are unobtainable. The surface equation of state is readily determined for insoluble monolayers, since for such systems both σ and $\Gamma_{2,1}$ are measurable, but the immeasurability of C_2 precludes getting the other two types of relationships.

E. The Gibbs Adsorption Equation

We are often interested in one of the "inaccessible" relationships for a given system. For example, we may wish to obtain the adsorption isotherm for a liquid-gas system, or the surface pressure (equilibrium spreading pressure, π) of an adsorbing solute at a solid-liquid interface. Thermodynamics solves this problem by providing a rigorous relationship amongst the above equations. (This is one of the most important general things that thermodynamics does for us, *i.e.*, yielding quantities we cannot measure in terms of quantities we *can* measure.) The rigorous relationship referred to is the capillary system analogue of the Gibbs-Duhem Equation. It is called the *Gibbs Adsorption Equation.* At constant T it takes the form:

$$d\sigma = -\sum_{i=2}^{m} \Gamma_{i,1} d\mu_i = -\Gamma_{2,1} d\mu_2 - \Gamma_{3,1} d\mu_3 - \ldots \tag{3.72}$$

for a solution consisting of a solvent (1) and any number of solutes (2), (3), *etc*.

Its general derivation follows. The objective is to develop a relationship amongst the variables describing a capillary system in full adsorption equilibrium. To do this, one starts by generalizing the thermodynamic description to *open* multicomponent simple capillary systems. Specifically:

$$dF = -SdT - p'dV' - p''dV'' + \sigma dA + \sum \mu_{\mathrm{i}} dn_{\mathrm{i}}, \tag{3.73}$$

where

$$\mu_{\mathrm{i}} = \left(\frac{\partial F}{\partial n_{\mathrm{i}}}\right)_{T,V',V'',A,n_{\mathrm{j}\neq \mathrm{i}}}.$$

As is done in bulk phase thermodynamics, we define a potential function whose differential is expressed in terms of differentials of *intensive* properties. In this case, such a function is

$$G = F + p'V' + p''V'' - \sigma A \tag{3.74}$$

Then:

$$dG = -SdT + V'dp' + V''dp'' - Ad\sigma + \sum \mu_{\mathrm{i}} \mathrm{d}n_{\mathrm{i}}. \tag{3.75}$$

This can be integrated under conditions such that the intensive state of the system remains constant, *i.e.*, constant T, p', p'', σ and μ_i, leading to:

$$G = \sum \mu_{\mathrm{i}} n_{\mathrm{i}}, \tag{3.76}$$

for which a general differentiation yields:

$$dG = \sum \mu_{\mathrm{i}} dn_{\mathrm{i}} + \sum n_{\mathrm{i}} d\mu_{\mathrm{i}}. \tag{3.77}$$

Comparison of the two expressions for *dG* gives:

$$SdT - V'dp' - V''dp'' + Ad\sigma + \sum n_{\mathrm{i}} d\mu_{\mathrm{i}} = 0. \tag{3.78}$$

This is the form of the Gibbs-Duhem Equation for simple capillary systems. We may subtract from it the Gibbs-Duhem Equation for each of the bulk phase portions (in the Gibbs model), *viz*.,

i) $S'dT - V'dp' + \sum n'_{\mathrm{i}} d\mu_{\mathrm{i}} = 0$, and (3.79)

ii) $S''dT - V''dp'' + \sum n''_{\mathrm{i}} d\mu_{\mathrm{i}} = 0$, leaving: (3.80)

$$\underbrace{(S - S' - S'')}_{S^\sigma}dT - \underbrace{(V' - V')}_{0}dp' - \underbrace{(V'' - V'')}_{0}dp'' + Ad\sigma + \sum \underbrace{(n_{\mathrm{i}} - n'_{\mathrm{i}} - n''_{\mathrm{i}})}_{n_{\mathrm{i}}^\sigma} d\mu_{\mathrm{i}} = 0 \tag{3.81}$$

and dividing through by *A*:

$$s^{\sigma}dT + d\sigma + \sum \Gamma_{\mathrm{i}} d\mu_{\mathrm{i}} = 0, \text{ or} \tag{3.82}$$

$$d\sigma = -s^{\sigma}dT - \sum \Gamma_{\mathrm{i}} \mathrm{d}\mu_{\mathrm{i}}, \tag{3.83}$$

where $s^{\sigma} = S^{\sigma}/A$. By virtue of the Gibbs-Duhem Equations for the bulk phase portions (which we have so far just used once, *i.e.*, their sum), not all of the μ_{i}'s are independent. Dividing Eqs. (3.79) and (3.80) through by V' and V'', respectively, and subtracting yields:

$$C's'dT - dp' - \sum C'_{\mathrm{i}} d\mu_{\mathrm{i}} = 0$$

$$C''s''dT - dp' - \sum C''_{\mathrm{i}} d\mu_{\mathrm{i}} = 0$$

$$(C's' - C''s'')dT - 0 - \sum (C'_{\mathrm{i}} - C''_{\mathrm{i}}) d\mu_{\mathrm{i}} = 0\ . \tag{3.84}$$

C' and C'' refer to the total molar concentrations of phase $'$ and $''$, and s' and s'' refer to molar entropies. In carrying out the above subtraction, it has been assumed that the interface is quasi-flat, so that $dp' \approx dp''$. We may now solve for $d\mu_1$ in terms of the remaining variables:

$$d\mu_1 = \left[\frac{C's' - C''s''}{C'_1 - C''_1}\right] dT - \sum_{\mathrm{i=2}}^{\mathrm{m}} \left[\frac{C'_{\mathrm{i}} - C''_{\mathrm{i}}}{C'_1 - C''_1}\right] d\mu_{\mathrm{i}}, \tag{3.85}$$

and substituting into Eq. (3.83) gives:

$$\begin{aligned} d\sigma &= -s^{\sigma}dT - \sum_{\mathrm{i=1}}^{\mathrm{m}} \Gamma_{\mathrm{i}} d\mu_{\mathrm{i}} \\ &= -s^{\sigma}dT - \Gamma_1 \left\{ \left[\frac{C's' - C''s''}{C'_1 - C''_1}\right] dT - \sum_{\mathrm{i=2}}^{\mathrm{m}} \left[\frac{C'_{\mathrm{i}} - C''_{\mathrm{i}}}{C'_1 - C''_1}\right] d\mu_i \right\} - \sum_{\mathrm{i=1}}^{\mathrm{m}} \Gamma_{\mathrm{i}} d\mu_{\mathrm{i}} \\ &= -\left[s^{\sigma} - \Gamma_1 \left(\frac{C's' - C''s''}{C'_1 - C''_1} \right) \right] dT - \sum_{\mathrm{i=2}}^{\mathrm{m}} \left[\Gamma_{\mathrm{i}} - \Gamma_1 \left(\frac{C'_{\mathrm{i}} - C''_{\mathrm{i}}}{C'_1 - C''_1} \right) \right] d\mu_{\mathrm{i}} \\ &= -(s^{\sigma})_1 dT - \sum_{\mathrm{i=2}}^{\mathrm{m}} \Gamma_{\mathrm{i,1}}\, d\mu_{\mathrm{i}}. \end{aligned} \tag{3.86}$$

In the above, $(s^{\sigma})_1$ is the *relative* surface entropy (with respect to the adsorption of component 1), and $\Gamma_{\mathrm{i,1}}$ is the *relative* adsorption of component i (with respect to that of component 1). At constant temperature, we recover the Gibbs Adsorption Equation, as stated in Eq. (3.72). For a binary system, it takes the form:

$$d\sigma = -\Gamma_{2,1} d\mu_2. \tag{3.87}$$

Since $d\mu_2 = RTd\ln\gamma_2 x_2$, where x_2 is the mole fraction and γ_2 is the activity coefficient, one may write out the Gibbs Adsorption Equation for a binary, Eq. (3.87), as:

$$\Gamma_{2,1} = -\frac{1}{RT}\frac{d\sigma}{d\ln\gamma_2 x_2} = -\frac{1}{RT}\frac{d\sigma}{d\ln\gamma_2 + d\ln x_2}. \tag{3.88}$$

Multiplying and dividing the denominator by $d\ln x_2$ (and recalling the condition of constant T), yields:

$$\Gamma_{2,1} = \frac{-\frac{x_2}{RT}\left(\frac{\partial\sigma}{\partial x_2}\right)_T}{\left[\left(\frac{\partial\ln\gamma_2}{\partial\ln x_2}\right)_T + 1\right]}. \tag{3.89}$$

For ideal or ideal-dilute binary solutions ($\gamma_2 \to 1$, or $\gamma_2^{\mathrm{H}} \to 1$, resp.) Eq. (3.89) becomes:

$$\Gamma_{2,1} = -\frac{x_2}{RT}\left(\frac{\partial\sigma}{\partial x_2}\right)_T, \tag{3.90}$$

or in terms of molar concentration:

$$\Gamma_{2,1} = -\frac{C_2}{RT}\left(\frac{\partial\sigma}{\partial C_2}\right)_T. \tag{3.91}$$

Thus it may be seen how the adsorption isotherm can be obtained from surface tension data (together with bulk phase activity data, if the solution is non-ideal). One can similarly interchange amongst the various equations for capillary systems, such as obtaining a surface tension equation from an adsorption isotherm, or a surface equation of state, *etc*. It is seen from any of Eqs. (3.89)-(3.91) that in general, a surface tension reduction implies positive adsorption, and *vice versa*. Recalling Fig. 2-4, one may note that most organic solutes are positively adsorbed at the water surface, while ionizing salts are negatively adsorbed. It is to be noted also that there are interesting cases of extrema in surface tension, corresponding to zero adsorption, or "surface azeotropy."

Figures 3-12 and 3-13 show the derivation of an adsorption isotherm from surface tension data for the acetone-water system, a case when bulk phase non-ideality must be taken into account. The isotherm computed on the assumption of an ideal solution is also shown for comparison, and it is noted that the strong positive deviations from ideality in the acetone-water solution strongly enhance the relative adsorption of acetone at intermediate concentrations. At very low concentrations, the effects of non-ideality are less severe. The reduction in *relative* adsorption at higher solute concentrations is commonly observed. Our greatest interest in what follows will be dilute solutions, particularly those of surface active agents in water.

The cases studied by McBain and coworkers generally corresponded to sufficiently dilute solutions that the ideal form of the Gibbs Adsorption Equation was applicable. (For ionic solutes, some special considerations must be taken, as discussed later.) We may now compare the derived adsorptions with those measured by the microtome method, as shown in Table 3-2. Agreement is seen to be reasonable.

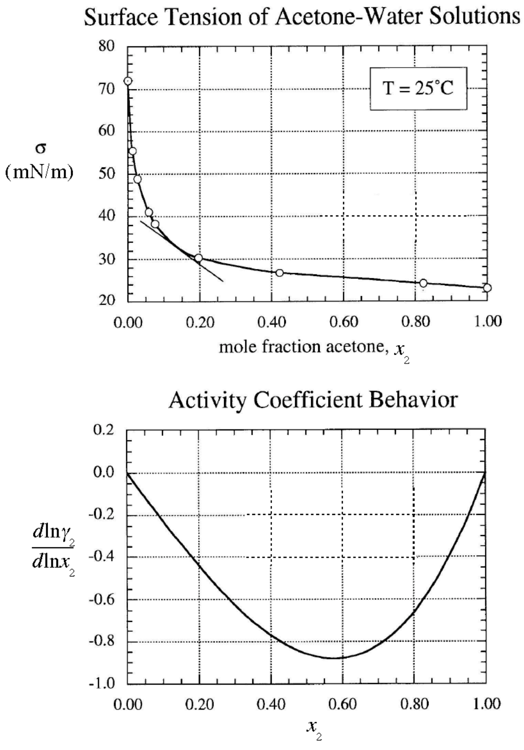

Fig. 3-12: Data needed to derive adsorption isotherm for acetone-water system. Surface tension data from [Howard, K. S., and McAllister, R. A., *AIChE J.*, **3**, 325 (1957).] Activity data from [Gmehling J., Onken, U, and Arlt, W, **Vapor-Liquid Equilibrium Data Collection Vol. 1, Part 1a**, p. 193, Dechema. Frankfurt, Germany, 1981.]

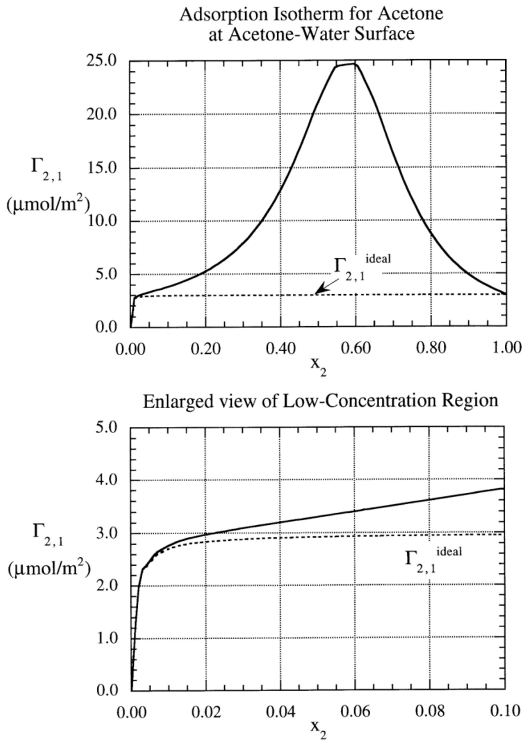

Fig. 3-13: Derived adsorption isotherm for acetone at the acetone-water surface.

Table 3-2: Comparison of relative adsorption from aqueous solutions obtained by the microtome method (obs) and computed using the Gibbs Adsorption Equation (calc).

Solute	C_2 (M)	$\Gamma_{2,1}$ (μmol/m^2)^{obs}	$\Gamma_{2,1}$ (μmol/m^2)^{calc}
Phenol	0.218	4.4	5.2
n-Hexanoic acid	0.0223	5.8	5.4
NaCl	2.0	-0.74	-0.64

It is now evident how, through the use of the Gibbs Adsorption Equation, one may obtain the surface pressure π of an adsorbate at a solid-fluid interface by integration of the appropriate adsorption isotherm. For example, the surface pressure of an adsorbing vapor at a solid-gas interface, as might be required in the interpretation of contact angle data, is computed from the adsorption isotherm, $\Gamma_{2,1} = \Gamma_{2,1}(p_2)$, where p_2 is the partial pressure of component 2 in the gas (assuming ideality in the gas phase), as follows:

$$d\pi = -d\sigma = \Gamma_{2,1}RT\,d\ln x_2 = \Gamma_{2,1}RT\,d\ln p_2, \text{ so that} \tag{3.92}$$

$$\pi = RT\int_0^{p_2}\Gamma_{2,1}\frac{dp_2'}{p_2'}\,. \tag{3.93}$$

The gas-solid isotherm, $\Gamma_{2,1}(p_2)$, is conveniently obtained by the direct weight-gain measurements described above or by using inverse gas chromatography, as described in Chap. 4. It should be noted that the surface pressure is not the surface tension (or energy) σ, but merely its reduction upon adsorption, *i.e.*

$$\sigma = \sigma_0^1 - \pi\,, \tag{3.94}$$

where σ_0^1 in immiscible interfacial systems is the "tension" (or energy) of the solute-free interface between the substrate phase and the pure solvent component phase 1.

Similar to the above, the surface pressure (interfacial free energy reduction) for detergents adsorbed at solid-liquid interfaces, believed to be responsible for the roll-up mechanism in detergency, may be obtained from the measured adsorption isotherm, $\Gamma_{2,1}(C_2)$, which is integrated using the Gibbs Adsorption Equation, *viz.*:

$$\pi = RT\int_0^{C_2}\Gamma_{2,1}\frac{dC_2'}{C_2'}\,. \tag{3.95}$$

Certain caveats must be observed in applying the Gibbs Adsorption Equation to solid-fluid interfaces.[21] First, the adsorption process cannot be accompanied by any irreversible interfacial stretching, as described earlier. More importantly, it cannot, in the form derived, describe *chemisorption*, *i.e.*, situations in which an adsorbate-adsorbent covalent bond is formed, or even most cases in which an acid-base interaction or electrostatic attraction provides the dominant driving force for adsorption. This has been identified later in this chapter as *amphiphilic adsorption,* and the result of such a process may be an *increase* in the solid-liquid interfacial energy.

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[21] Molliet, J. L., Collie, B., and Black, W., **Surface Activity**, pp. 94-98, van Nostrand, Princeton, NJ, 1961.

F. Surface tension of solutions

1. *Ideal-dilute capillary systems*

Most solutions whose interfacial properties are of interest are dilute. Recall that for bulk solutions, it is convenient to define *ideal-dilute solutions* and then refer real solution behavior to them. Ideal dilute solutions are defined as those obeying Henry's Law

$$f_2 = x_2\mathcal{H}_{2,1}, \tag{3.96}$$

where f_2 is the fugacity of component 2 in the solution, and $\mathcal{H}_{2,1}$ is Henry's constant. For the case in which the solution is in equilibrium with an ideal gas mixture:

$$p_2 = x_2\mathcal{H}_{2,1}, \tag{3.97}$$

where p_2 is the partial pressure of component 2 in the gas. Real solutions could be described by inserting an activity coefficient, γ_2^{H}, so for example:

$$p_2 = x_2\gamma_2^{\mathrm{H}}\mathcal{H}_{2,1}\ . \tag{3.98}$$

All solutions obey Henry's Law when they are sufficiently dilute, *i.e.*, $\gamma_2^{\mathrm{H}} \rightarrow 1$ as $x_2 \rightarrow 0$.

In a similar fashion, one may define an *ideal-dilute capillary system* as one obeying Henry's Law as above, both in the bulk solution *and* in the interfacial layer. Such a system exhibits linear surface tension behavior, *viz.*

$$\sigma = \sigma_o - \alpha C_2; \quad \text{where } \alpha = -\left(\frac{\partial\sigma}{\partial C_2}\right)_{C_2\rightarrow 0}. \tag{3.99}$$

$\alpha > 0$ refers to positive adsorption. For cases of positive adsorption, a greater degree of dilution is required for a system to be ideal-dilute with respect to capillary behavior than to obey Henry's Law in the bulk solution because of the greater concentration in the surface layer, *i.e.*, greater mutual proximity of solute molecules.

One may deduce the corresponding isotherm for an ideal-dilute capillary system, using the Gibbs Equation.

$$\Gamma_{2,1} = -\frac{C_2}{RT}\left(\frac{\partial\sigma}{\partial C_2}\right)_T = -\frac{C_2}{RT}(-\alpha) \equiv \left(\frac{\alpha}{RT}\right)C_2, \tag{3.100}$$

termed Henry's Isotherm. The surface equation of state, $\sigma = \sigma(\Gamma_{2,1})$ is obtained by eliminating C_2 from the isotherm using the surface tension equation to get

$$\sigma_0 - \sigma \equiv \pi = RT\Gamma_{2,1}. \tag{3.101}$$

Note that α disappeared, and it is therefore evident that all ideal dilute capillary systems have the same surface equation of state. It can be put into a familiar form by defining the "specific area" of the solute as: $a_{2,1} \equiv 1/\Gamma_{2,1}$, so that

$$\pi a_{2,1} = RT, \tag{3.102}$$

a two-dimensional analogue of the ideal gas law. Equation (3.102) is also analogous to the osmotic pressure equation in ideal dilute solutions, *i.e.*, the van't Hoff equation.

It is evident that if one started with the surface equation of state, it would not be possible to regenerate either the surface tension equation or the adsorption isotherm, except to within an additive constant of integration.

2. *Moderately dilute capillary systems*

As solution concentrations increase beyond the range of the "ideal-dilute," for capillary systems showing positive adsorption, the initial linear surface tension decrease moderates to one that decreases less steeply. This is illustrated by some data for carboxylic acids shown in Fig. 3-14. These data were found by Szyszkowski[22] to be well fit by the two-parameter equation:

$$\pi = RTB\ln(1 + C_2/a), \tag{3.103}$$

now known as the *Szyszkowski Equation.* It reduces, as $C_2 \rightarrow 0$, to the linear surface tension equation, with $\alpha = RTB/a$. For homologous series' of compounds, the constant B was found to be the same for the series, while the parameter "a" was characteristic of the particular member. Adherence to the Szyszkowski equation format at modest solute concentrations is the basis for

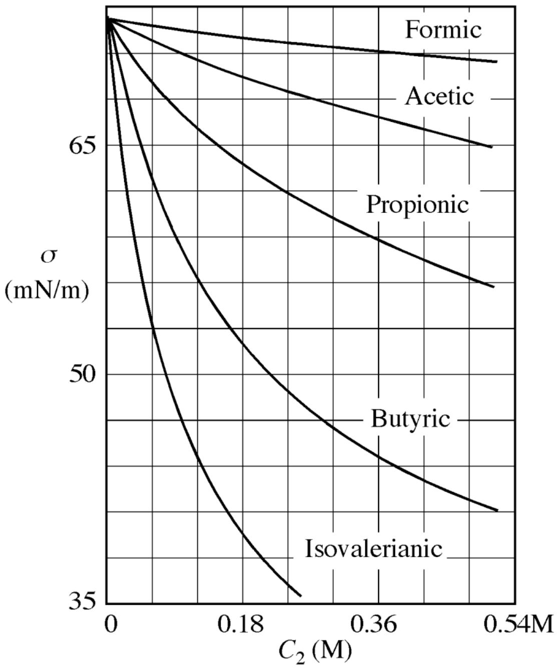

Fig. 3-14: Szyszkowski surface tension data for a homologous series of carboxylic acid solutions. Data from [Szyszkowski, B., *Z. Physikal. Chem.*, **64**, 385 (1908).]

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[22] Szyszkowski, B., *Z. Physikal. Chem.*, **64**, 385 (1908).

the definition of what might be termed "moderately dilute" capillary systems. These are solutions that are sufficiently dilute to obey Henry's Law with respect to the bulk solution properties, but not dilute enough to be ideal dilute in the surface layer. The surface tension behavior of dilute aqueous solutions of many surface active agents are described by this model. A summary of Szyszkowski parameters for a large number of compounds is given by Chang and Franses.[23]

The Szyszkowski equation can be converted, using the ideal solution form of the Gibbs Adsorption Equation, into the corresponding adsorption isotherm and the equation of state for what might be termed *moderately dilute capillary systems*, as shown in Fig. 3-15. The resulting isotherm is in the form of the well-known *Langmuir Isotherm*,

$$\Gamma_{2,1} = \frac{BC_2}{a + C_2}. \tag{3.104}$$

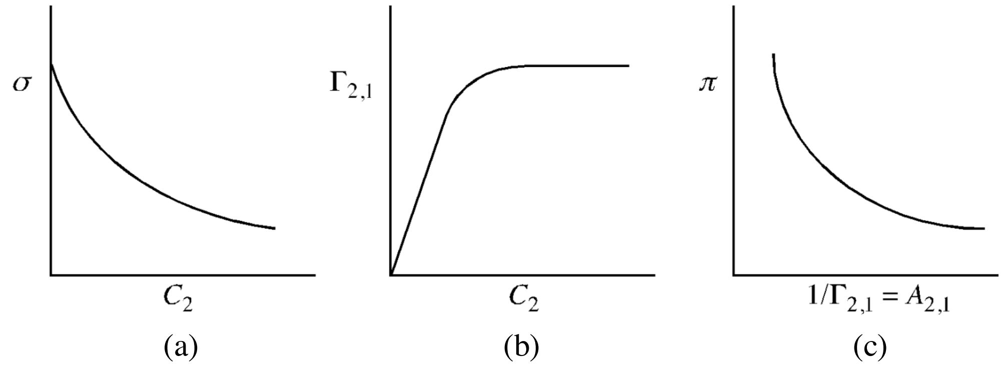

Fig. 3-15: Functional form of thermodynamic equations for a binary moderately dilute capillary system: (a) Szyszkowski surface tension equation, (b) Langmuir adsorption isotherm, (c) Frumkin surface equation of state.

At low C_2, Henry's adsorption isotherm is recovered, with: $\Gamma_{2,1} \rightarrow (B/a)\, C_2$, and at sufficiently high concentration, the surface becomes saturated, *i.e.*, $\Gamma_{2,1} \rightarrow B = \Gamma_\infty$, yielding the maximum molar packing density Γ_∞ of a monolayer of solute at the surface. The equation of state that is derived from the Szyszkowski Equation is termed the Frumkin surface equation of state:

$$\pi = -RTB\ln\left(1 - \frac{\Gamma_{2,1}}{B}\right) \equiv -RTB\ln\left(1 - \frac{\Gamma_{2,1}}{\Gamma_\infty}\right), \tag{3.105}$$

from which it is seen, the constant "*a*" has disappeared. This suggests that any member of a given homologous series obeying the Szyszkowski Equation has the same surface equation of state.

The type of "surface phase" non-ideality exhibited by systems described by the Szyszkowski Equation *et seq.* is that which is attributable

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[23] Chang, C.-H., and Franses, E. I., *Colloids Surfaces A*, **100**, 1 (1995).

solely to the space occupied by the adsorbing molecules. It does not account for lateral attractive or repulsive interactions between them (*i.e.*, cooperative effects). While this simple description appears to be satisfactory for many alkane-chain (up to C_{18}) ionic surfactants at both the water/air and water/oil interfaces,[24] it appears to fail for many nonionics. Frumkin[25] had earlier proposed a modification to the Langmuir Isotherm to account for such interactions, *viz.*

$$\Gamma_{2,1} = \frac{\Gamma_\infty C_2 \exp\left(A\frac{\Gamma_{2,1}}{\Gamma_\infty}\right)}{a_F + C_2 \exp\left(A\frac{\Gamma_{2,1}}{\Gamma_\infty}\right)}, \tag{3.106}$$

The bulk concentration has been augmented by the factor $\exp\left(A\frac{\Gamma_{2,1}}{\Gamma_\infty}\right)$, in which "*A*" is an empirical constant accounting for lateral, or solute-solute, interactions in the surface. For $A > 0$, the adsorption is influenced by favorable interactions, such as chain-chain cohesion, whereas for $A < 0$, adsorption is disfavored by solute-solute repulsion in the surface. The implicit nature of the Frumkin Isotherm (as it is termed) precludes the derivation of an analytical expression for the corresponding surface tension equation, but it can be obtained numerically. The surface equation of state can be obtained in closed form. This three-parameter representation is adequate for the representation of data for most dilute surfactant solutions, still in the context of moderately dilute capillary systems.

G. Surface active agents (surfactants) and their solutions

1. *The structure of different types of surface active agents*

Surface active agents, as defined in Chap. 2, are compounds which, when present in very small amounts (≤ 0.01 M), reduce the surface tension of water by a significant amount (≥ 30 mN/m). Surface activity also exists in non-aqueous media, but the extent of surface tension reduction is generally much less. The discussion that follows concerns aqueous systems. A brief aside on nomenclature is useful at this point. The term "surface active agent" was shortened by Langmuir to "surfactant," and is synonymous with it. Surfactants are also referred to inter-changeably as "amphiphiles" (which reflects the nature of their structure). The term "lipid" refers to long chain aliphatic hydrocarbons, or fats, and derivatives originating in living cells. Only some, such as fatty acids, are also surfactants, although the term is often used as synonymous with "surfactant." The word "soap" refers to salts of fatty acids, although it too is often used more broadly. A "detergent"

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[24] Lucassen-Reynders, E. H., *J. Phys. Chem.*,**70**, 1777 (1966).

[25] Frumkin, A., *Z. Phys. Chem.*, **116**, 466 (1925).

generally refers to a synthetic surfactant such as a fatty sulfate, sulfonate, or long chain quaternary ammonium salts, or it may reference a commercial cleaning mixture containing detergents as well as other compounds, such as "builders," bleaches, enzymes, fragrances, *etc*.

An enormous array of different substances may be surface active in aqueous media, but all such materials have certain features in common. Their molecules are composed of at least two portions *segregated* from one another, one being hydrophilic (such as a highly polar or ionized functional group) and the other hydrophobic, such as a medium-to-long aliphatic chain (usually in the range of C_6 – C_{20}). Surfactants thus generally present themselves as homologous series' of compounds. The hydrophilic portion is referred to as the *head group*, while the hydrophobic portion is called the *tail*. In addition to straight aliphatic chains, the hydrophobes may consist of branched chains, chains with double or triple bonds, or with aromatic groups, dual chains (such as in the dipalmitoyl lecithin lung surfactant shown in Fig. 2-6), chains with halogen (particularly fluorine) substitution, siloxane chains,[26] *etc*.

An enormous variety of hydrophilic head groups is available, and a sample is listed in Table 3-3. Each type of head group yields a different family of surfactants. Surfactants seek the surface because there alone can they orient themselves to satisfy the solubility characteristics of both portions of their structure. The adsorption of surfactant from aqueous solution is pictured (very) schematically in Fig. 3-16. In solution, the hydrophobic tail is believed to be surrounded by an "iceberg" of structured water,[27] which, upon adsorption to either the water-air water-solid interface, is released into the solution, accompanied by a large increase in entropy. The free energy of adsorption:

Table 3-3: Some typical surfactant head groups.

-OH	Hydroxyl
-COOH (low pH)	Carboxyl
$-COO^-$ (high pH)	Carboxylate
$-SO_4^-$	Sulfate
$-SO_3^-$	Sulfonate
$-H_2PO_4^-$ (mod. pH)	Phosphate
$-NH_2$ (high pH)	Amino
$-NH_3^+$ (low pH)	Ammonium
$-N(CH_3)_3^+$	Trimethylammonium, or Quaternary ammonium
$-(OCH_2CH_2)OH$	Polyoxyethylene, or polyethylene oxide

$$\Delta G_{\mathrm{ad}} = \Delta H_{\mathrm{ad}} - T\Delta S_{\mathrm{ad}} \tag{3.107}$$

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[26] Hill, R. M. (Ed.), **Silicone Surfactants**, Surf. Sci. Ser. 86, Marcel Dekker, New York, 1999.

[27] Frank, H. S., and Evans, M. W., *J. Chem. Phys*., **13**, 507 (1945).

is large and negative (thus favoring the process) due largely to the entropic term. The enthalpy of adsorption is often small, and may be either positive (due, for example, to electrostatic repulsion between charged head groups) or negative (due, for example, to tail-tail attractive van der Waals interactions). The apparent attraction of hydrophobic moieties in water for surfaces where they may be either expelled or sequestered is referred to as *hydrophobic bonding* or the *hydrophobic effect.*[28] Its primary origin is the entropic effect described above.

The key feature of surfactant molecular structure is the *segregation* of its hydrophobic and hydrophilic moieties. Thus, *e.g.*, glucose is not surface active because its hydrophilic hydroxyl groups are not segregated from the hydrocarbon structure, as seen in Fig. 3-17, and in fact, glucose appears to produce a small *increase* in the surface tension of water, suggesting *negative* adsorption. Surfactants are used in many ways in our everyday lives. The use of soaps and detergents for cleaning things is just one example. Surfactant compounds, like polymers, can often be tailor-made to suit the needs of a variety of specific applications, as listed in Table 3-4. Much more extensive accounts of the applications of the various types of surfactants can be found in Rosen,[29] Myers[30], Molliet, Collie and Black,[31] or in the detailed

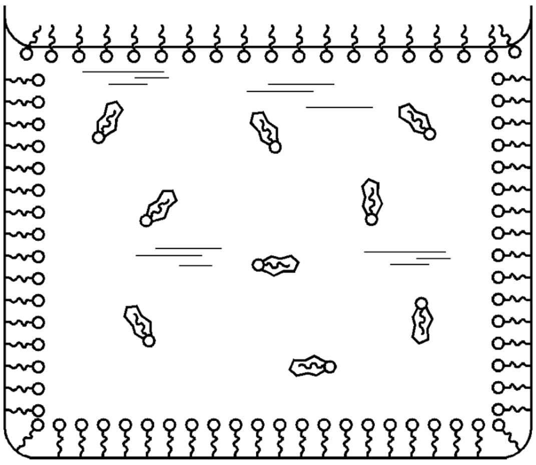

Fig. 3-16: Schematic of surfactant adsorption from aqueous solution, both to the air-water surface and the water-solid interface of the container wall. The “iceberg” of structure water surrounding the hydrophobic tails in solution is depicted.

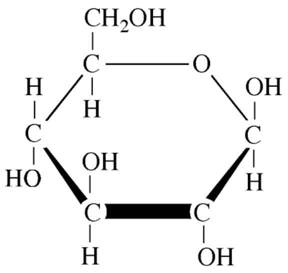

Fig. 3-17: Molecular structure of glucose.

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[28] Tanford, C., **The Hydrophobic Effect: Formation of Micelles and Biological Membranes**, 2nd Ed. , Krieger, Malabar, FL, 1991.

[29] Rosen, M. J., **Surfactants and Interfacial Phenomena**, 2nd Ed., pp. 1-32, Wiley, New York, 1989.

compilations of commercially available surfactants, such as in McCuthcheon's Handbooks.[32] The surfactant properties needed to meet various applications are elucidated as the particular applications are discussed. Some of these have already been mentioned, while others can be appreciated only after getting further into the subject of this text.

Table 3-4: Some uses of surface active agents.

1. Modification of wetting behavior
   - Promotion of wetting (coating, cleaning,,…)
   - Reduction of wetting (waterproofing, soil release, flotation,…)
2. Stabilization of thin films
3. Formation and stabilization of emulsions
4. Solubilization of oil in water
   - Soil removal, detergency
   - Reactions; emulsion polymerization
5. Formation and stabilization of colloidal dispersions
6. Grinding aids
7. Lubrication

Aqueous surfactants are broadly classified into four categories, based on the charge structure of their hydrophilic "head groups," as follows:

1) **Anionic surfactants**:

"Anionics" are ionized salts in which the anion (- charge) possesses the long hydrophobic chain. Examples are:

Sodium stearate	$CH_3(CH_2)_{16}COO^- Na^+$
Sodium dodecyl ("lauryl") sulfate	$CH_3(CH_2)_{11}SO_4^- Na^+$
Sodium dodecyl benzene sulfonate	$CH_3(CH_2)_{11}SO_3^- Na^+$

The first of these, sodium stearate ("Grandma's lye soap") is an example of a "soap," the salt of a fatty acid. Soaps are usually produced by the reaction (saponification) of fatty acids or esters with alkali, usually sodium or potassium hydroxide. The latter two are examples of "detergents," *i.e.*, synthetic fatty sulfates or sulfonates. They are synthesized by the reaction of

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[30] Myers, D., **Surfactant Science and Technology**, VCH Publ., Weinheim, West Germany, 1988.

[31] Molliet, J. L., Collie, B., and Black, W., **Surface Activity**, van Nostrand, Princeton, NJ, 1961.

[32] **McCutcheon's: Vol 1. Emulsifiers and Detergents; Vol. 2. Functional Materials**, published annually by McCutcheon's Division. MC Publishing Co., Glen Rock, NJ.

sulfuric acid with unsaturated fats or fatty alcohols (sulfation or sulfonation). Commercial detergents usually contain traces of the unreacted fats, which may have an important influence on their properties. Sodium dodecyl sulfate (SDS) is a major component of bar soap, while sodium dodecyl benzene sulfonate (SDBS) is a major constituent of laundry detergent. They are fully ionized over the whole practical *pH* range. An important di-tail anionic surfactant is Aerosol OT® (Cytec Industries): the di(ethylhexyl) ester of sulfosuccinic acid. It is an especially effective wetting agent and dispersant. Anionics, primarily the detergents, comprise about 70% of the surfactant market. They are inexpensive and make good wetting agents and cleaning compounds. This is accomplished primarily through a reduction in the surface tension of water and a reduction in the solid-liquid interfacial energy. Recalling Young's Equation, Eq. (3.43), we see that the contact angle, θ, is reduced ($\cos\theta$ is increased) when the liquid surface tension, σ_L, and/or the solid-liquid interfacial energy, σ_{SL}, is reduced. Under water, adsorption of the surfactant leads to reductions in both the substrate-water and the dirt-water interfacial energies and eventually to "roll up" of the dirt from the substrate, as described later in Chap. 4, H.1 under "detergency."

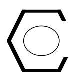
Anionics tend to shun dense adsorption onto solid surfaces from water because these surfaces are often negatively charged (as described in more detail in Chap. 6). Adsorption onto the solid under these conditions generally results in a "tail-down" configuration such that the hydrophilic head groups are exposed to the water, increasing the hydrophilicity of the solid surface. The driving force for such adsorption is *hydrophobic bonding*, *i.e.*, the non-specific desire of the hydrophobic portions of the molecules to "get out" of the water.

2) **Cationic surfactants**:

"Cationics" are ionized salts in which the cation (+ charge) is the surfactant species. The quaternary ammonium compounds are fully ionized over whole practical *pH* range. They have good bactericidal properties and a large number of other special applications, for example as waterproofers and anti-stats, owing to their head-down, tail-out adsorption at most solid-water interfaces, which generally carry a negative charge. Most are nitrogen-containing compounds. Some specific examples include:

Hexadecyl (cetyl) trimethylammonium bromide,

(CTAB), $CH_3(CH_2)_{15}\,N^+(CH_3)_3Br^-$

Dodecyl pyridinium chloride, $CH_3(CH_2)_{11}$  $N^+\,Cl^-$

Dodecyl ammonium hydrochloride, $CH_3(CH_2)_{11}\,NH_3^+\,Cl^-$

Quaternary ammonium compounds are usually synthesized through the reaction of ammonia with fatty alcohols.

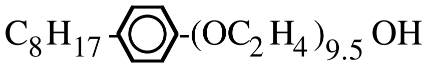
3) **Nonionic surfactants**:

“Nonionics” usually refer to the various alkyl poly(ethylene oxide)’s derived from the condensation of ethylene oxide with fatty acids or alcohols. The simplest example is the Brij® series (ICI Americas):

$$C_nH_{2n+1}O\text{-}(CH_2CH_2O)_mH,$$

where m and n can have different values to produce different properties. The structure of such a surfactant is often abbreviated as: C_nE_m. As the m/n ratio increases, the surfactants become more hydrophilic. Nonionics can be tailor-made for many applications in this way. They are compatible with other types of surfactants, resistant to hard water, generally low foamers, and may be soluble in organic solvents. Because of the method of their synthesis, any given member of the series is polydisperse to a certain, often significant, extent. Some important examples of nonionic surfactant series are:

The Triton X® series (Union Carbide): polyethoxylated alkyl phenols, of which Triton X-100,



is a common wetting agent and dispersant. Other families of nonionics include:

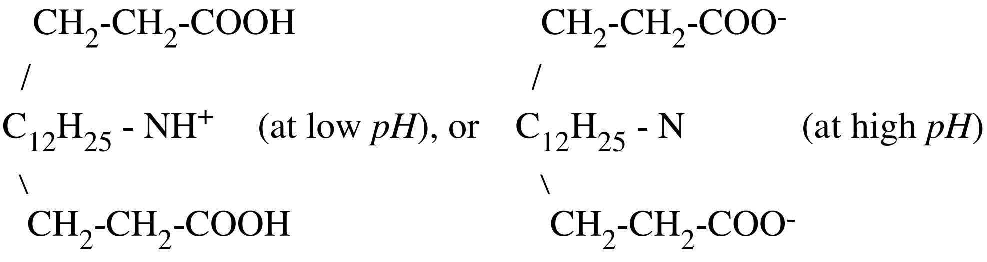
The Tergitol® series (Union Carbide): di-alkyl, di-poly (ethylene oxide)s, useful, for example in formulating injet printing inks.

The Pluronic® series (BASF Corp.): triblock copolymers of poly (ethylene oxide) and poly (propylene oxide), and

The Spans® and Tweens® (ICI Surfactants): various polyoxyethylene-containing sorbitan derivatives. These are important classes of emulsifiers.

4) **Amphoteric surfactants**:

“Amphoterics” can be either anionic or cationic, depending on the *pH* of the solution. Examples include the N-alkylaminoacids, *e.g.*:



$$\begin{array}{llll} & CH_2\text{-}CH_2\text{-}COOH & & CH_2\text{-}CH_2\text{-}COO^- \\ & / & & / \\ C_{12}H_{25}\text{ - }NH^+ & \text{(at low } pH\text{), or} & C_{12}H_{25}\text{ - }N & \text{(at high } pH\text{)} \\ & \backslash & & \backslash \\ & CH_2\text{-}CH_2\text{-}COOH & & CH_2\text{-}CH_2\text{-}COO^- \end{array}$$

Many proteins and other natural surfactants are of this nature.

5) **Zwitterionic surfactants**:

The ionic head group in “zwitterionics” contains both positive and negative charges in close proximity. The phosphoryl choline group of dipalmitoyl lecithin (shown in Fig. 2-6) is an example. An interesting type of di-chain, zwitterionic surfactant is formed from the mixture of anionic and cationic surfactants, which combine in aqueous solution[33] to produce *catanionic* surfactants.

Other, more exotic, types of structures have also been identified,[34] such as *gemini* surfactants, consisting of two single-tail surfactants whose heads are connected by a spacer chain which may be either hydrophilic or hydrophobic.[35] Another example is the *telechelic surfactant*, in which two hydrophobic groups are connected by a hydrophilic chain.[36] *Boloform* surfactants, on the other hand, are hydrophobic chains with hydrophilic groups on each end.

Amphoteric surfactants and nonionics with PEO hydrophilic head groups are example of "function-changing surfactants." Their character as surfactants can be made to change with changes in controllable external variables such as *pH* or temperature. Such changes can lead to wetting transitions, as discussed in Chap. 4, or to the inversion or breaking of emulsions, as discussed in Chap. 9. Another example of function-changing is the conversion of an anionic surfactant with the addition of divalent cations, such as Ca^{+2} or Mg^{+2} to the solution. These will each associate with a pair of surfactant anions to produce an undissociated, hydrophobic di-tail surfactant. Another important class of compounds is that of *cleavable surfactants*.[37] These are intentionally designed with a weak linkage, usually between the hydrophilic and hydrophobic portions of the molecule, that is susceptible to cleavage under high *pH* conditions (*e.g.*, normal esters or carbonates) or low *pH* conditions (*e.g.*, ortho esters or ketals). Ester, amide and carbonate linkages have been investigated with respect to enzymatic hydrolysis, and at least one type of surfactant based on the incorporation of Diels-Alder adducts is found to cleave upon increasing the temperature to approximately 60°C. Cleavability is motivated in part by the desire to achieve biodegradability, but also as an aid to the removal of surfactants from a system once they have performed their function.

Many of the surfactants described above can be produced in polymeric form, with the monomer surfactants as repeat units in the polymers. Some are nonionic, like polyvinyl alcohol or polyethylene oxides, while others are polyelectrolytes (polyanions or polycations). In addition, there are a number of naturally occurring macromolecules that often act as polymeric

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[33] Kaler, E. W., Murthy, A. K., Rodriguez, B. E., and Zasadzinski, J. A. N., *Science*, **245**, 1371 (1989).

[34] Holmberg, K. (Ed.), **Novel Surfactants**, Surf. Sci. Ser. 74, Marcel Dekker, New York, 1998.

[35] Zana, R., Talmon, Y., *Nature*, **362**, 228 (1993).

[36] Semenov, A. N., Joanny, J. F., Khokhlov, A. R., *Macromolecules*, **28**, 1066 (1995).

[37] Stjerndahl, M., Lundberg, D., and Holmberg, K., "Cleavable surfactants," pp. 317-45, in : **Novel Surfactants**, 2nd Ed. (K. Holmberg, Ed.) Marcel Dekker, New York, 2003; Tehran—Bagha, A., and Holmberg, K., *Curr. Opinion Colloid Interface Sci.,* **12**, 81 (2007).

surfactants. These would include polypeptides (proteins), which chains of amino acid groups folded into tertiary structures, as well as nucleic acids and polysaccharides.

The discussion above pertains to aqueous interfaces. Surface activity in non-aqueous systems refers to the ability of a solute or an insoluble monolayer to reduce the surface tension of a non-aqueous liquid, but as mentioned earlier, such reductions are much less than in aqueous media. They are brought about principally by various fluorocarbons or silicones.

A large and growing literature on surfactants and their applications, in addition to the references cited earlier, is provided by Marcel Dekker's *Surfactant Science Series*,[38] beginning in 1967 with Vol. 1: **Nonionic Surfactants**, and up to Vol. 142 in 2008.

2. *Solutions of non-electrolyte surfactants*

Dilute aqueous solutions of surfactants, whether they are electrolytes or non-electrolytes, show remarkably similar surface tension behavior. They all, of course, show linear behavior at great enough dilution, and many of show agreement with the Szyszkowski Equation over the whole range for which surface tension changes significantly with concentration. Their surface tension behavior is thus often expressible as:

$$\sigma_0 - \sigma \equiv \pi = RTB\ln\left(1 + \frac{C_2}{a}\right). \tag{3.108}$$

Over much of the concentration range of interest, $C_2/a >> 1$, so that (in this range):

$$\sigma_0 - \sigma \equiv \pi = RTB\ln\left(\frac{C_2}{a}\right). \tag{3.109}$$

It is useful to plot surface pressure (or surface tension) against the logarithm of C_2, or to use semi-log coordinates, as shown in Fig. 3-18.

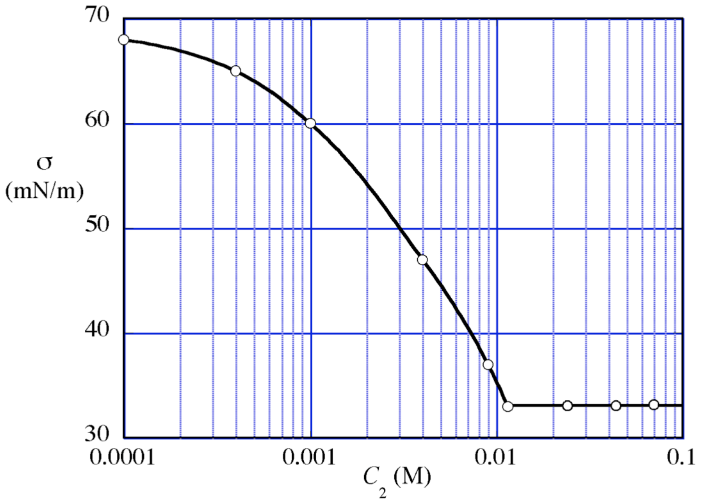

Fig. 3-18: Schematic of surface tension behavior of aqueous surfactant solutions.

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[38] A listing of volume titles through 2006 is given at: http://liv.ed.ynu.ac.jp/senmon/book02.html

"Linear" Szyszkowski behavior, as given by Eq. (3.109) results in a straight line, often observed over one-to-two decades of C_2. The surface tension decrease with concentration comes to an abrupt end, either when the solubility limit of the surfactant is reached, or when further increases in bulk concentration lead to no further changes. The latter behavior is discussed further below.

Szyszkowski behavior in a homologous series of non-electrolyte compounds, *e.g.*, the normal alcohols, is shown in Fig. 3-19. Note that the convenient composition variable, pC_2, defined analogously to the pH, has been introduced. There are two important features to be noticed in Fig. 3-19. The first is that all curves have about the same slope, *i.e.*, $d\pi/d(pC_2) \approx$ constant ($\approx$ the same for each compound). This can be interpreted with the Gibbs Adsorption Equation:

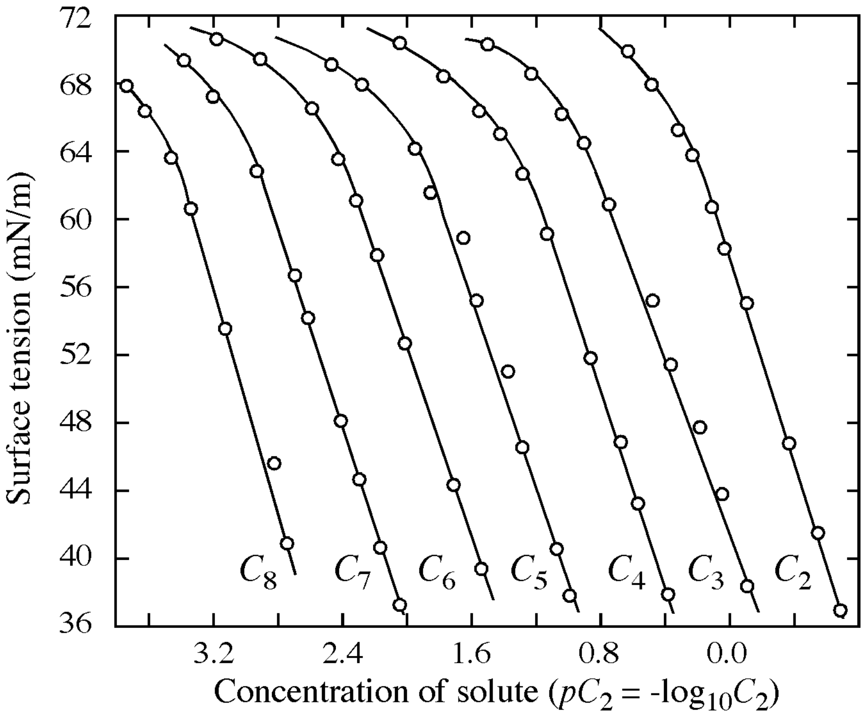

Fig. 3-19: Surface tension dependence on concentration for aqueous solutions of the normal alcohols ($C_2 - C_8$) at 25°C. Data from [Posner, A.M., Anderson, J.R. and Alexander, A.E., *J. Colloid Sci.*, **7**, 623 (1952).]

$$\Gamma_{2,1} = \frac{C_2}{RT}\frac{d\pi}{dC_2} \text{ ; or } \frac{d\pi}{d(pC_2)} = -2.303..RT\Gamma_{2,1} = \text{const.} \qquad (3.110)$$

Equation (3.110) implies that in this region, $\Gamma_{2,1}$ is a constant, or that the surface has been saturated. Such a surface is referred to as a "Gibbs monolayer." We note that the slope, hence $\Gamma_{2,1}$, is the same regardless of chain length (just occurring in different concentration ranges), and furthermore, from the magnitude of that slope, the molecular area turns out to be 30 - 35 Å^2/molecule. Putting this information together implies that the molecules are forming a more-or-less compact monolayer of approximately vertically oriented molecules, the value of $a_{2,1} = 1/\Gamma_{2,1}$ being only about 25-

30 percent higher than the known cross-sectional area of a hydrocarbon chain. The slope gives one the constant "*B*," which is characteristic of the homologous series, while "*a*" is characteristic of the particular member of the series. This has been shown for a number of series' of aliphatic surfactants.

A second observation is that the curves are approximately equally spaced from one another, about 0.5 pC_2 units in this diagram. Thus the concentration required to produce a given surface tension reduction π is less, as the chain length increases, by a constant factor, *viz.*, for a given π:

$$\log(C_2)_\mathrm{n} \approx \log(C_2)_\mathrm{n+1} + 0.5, \tag{3.111}$$

where n = number of carbon atoms. Thus:

$$(C_2)_\mathrm{n} / (C_2)_\mathrm{n+1} \approx 10^{0.5} \approx 3. \tag{3.112}$$

This result stated in words is: For dilute solutions of a homologous series of straight chain aliphatic (nonionic) surfactants, the concentration at which a given surface pressure is obtained diminishes by a factor of three for each additional -CH_2- group in the chain. This is known as *Traube's Rule*, first proposed in 1891[39] and still a useful rule of thumb for extrapolating data within homologous series' of surfactants. The thermodynamic basis for Traube's Rule is readily understood in terms of the hydrophobic effect described earlier. Each -CH_2- addition to the hydrophobic chain of the surfactant would be expected to add a given number of water molecules to the "iceberg" surrounding the hydrophobic chain in the water, producing a given increase in entropy upon their release.

A useful measure of the *efficiency* of a surfactant in reducing the surface tension is the pC-value at which it gives $\pi = 20$ mN/m, denoted pC_{20}. From Fig. 3-19, one can deduce, for example, that pC_{20} for octanol ≈ 3.1. For most soluble surfactants (ionic or nonionic), pC_{20} is between 2 and 6, but there are some higher. Traube's Rule suggests that pC_{20} should increase by ≈ 0.5 for each additional -CH_2- group, and for nonionic surfactants, this is generally the case. Thus, the longer the hydrocarbon chain length, the more *efficient* the surfactant. However, pC_{20} may not be attainable because of limited solubility or if a "break" in the curve of σ *vs.* C_2 occurs (as shown in Fig. 3-18) before $\pi = 20$ is reached. A few *surfactant efficiencies*, so defined, are listed in Table 3-5. Similar surface tension behavior (Traube's Rule, *etc.*) holds for ionic surfactants as well as nonionics. For these cases, at constant ionic strength, the spacing is approximately 0.3 for each additional -CH_2- group, rather than the 0.5-value observed for nonionics, suggesting that the concentration at which a given surface pressure is obtained is diminished by a factor of approximately two for each additional -CH_2- group in the chain.

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[39] Traube, I., *Annalen*, **265**, 27 (1891).

Table 3-5: Some values of surfactant efficiencies. From [Rosen, M.J., **Surfactants and Interfacial Phenomena**, 2nd Ed., pp. 70 ff, Wiley, New York, 1989.]

Compound (T, in °C)	pC_{20}
$C_{10}H_{21}SO_4^-Na^+$ (27)	1.89
$C_{12}H_{25}SO_4^-Na^+$ (25)	2.57
$C_{12}H_{25}SO_4^-Na^+$ (60)	2.24
$C_{16}H_{33}SO_4^-Na^+$ (25)	3.70
$C_{16}H_{33}SO_4^-Na^+$ (25) (0.01 N NaCl)	5.24
p- $C_{12}H_{25}C_6H_4SO_3^-Na^+$ (70)	3.10
$C_{12}H_{25}N(CH_3)_3^+Cl^-$ (25) (0.10 N NaCl)	3.68
$C_{16}H_{35}N(CH_3)_3^+Cl^-$ (25) (0.10 N NaCl)	5.00
$C_{16}H_{33}(C_2H_4O)_6$ (25)	6.80

3. *Solutions of electrolyte surfactants*

The use of the Gibbs Adsorption Equation in the form of Eq. (3.91) applies only to non-electrolyte systems. The treatment of ionic surfactant solutions involves additional complications. Consider a situation in which the surfactant solute is fully ionized, *e.g.*, a solution of sodium dodecyl sulfate (SDS): $CH_3(CH_2)_{11}SO_4^-Na^+ = DS^- + Na^+$, in which the adsorbed surfactant species is the DS^- ion. Electrical neutrality in the surface layer requires that an equal adsorption of Na^+ *counterions* be present in the surface layer, so that

$$\Gamma_{\mathrm{Na}^+} = \Gamma_{\mathrm{D}S^-}. \tag{3.113}$$

Both species must be considered in using of the Gibbs Adsorption Equation:

$$d\sigma = -RT\Gamma_{\mathrm{Na}^+} d\ln[\mathrm{Na}^+] - RT\Gamma_{\mathrm{DS}^-} d\ln[\mathrm{DS}^-], \tag{3.114}$$

where $[Na^+]$ and $[DS^-]$ refer to the concentrations of the respective ions, both equal to the *nominal* concentration of the SDS, [NaDS]. Similarly, Γ_{Na^+} and $\Gamma_{\mathrm{D}S^-}$ are *each* equal to the nominal adsorption of SDS, Γ_{NaDS}. Thus:

$$d\sigma = -2RT\Gamma_{\mathrm{NaDS}} d\ln[\mathrm{NaDS}], \text{ and} \tag{3.115}$$

$$\Gamma_{\mathrm{NaDS}} = -\frac{[\mathrm{NaDS}]}{2RT}\frac{d\sigma}{d[\mathrm{NaDS}]}. \tag{3.116}$$

A factor of 2 thus appears in the denominator of the Gibbs Adsorption Equation.

If a salt containing a common ion with the surfactant, say NaCl, is present in excess, then $d\ln[\mathrm{Na}^+]$ will be essentially zero with (the relatively small) changes in [NaDS], and one returns to the original form of the Gibbs Adsorption Equation (*i.e.*, without the factor of 2):

$$\Gamma_{\mathrm{NaDS}} = -\frac{[\mathrm{NaDS}]}{RT}\frac{d\sigma}{d[\mathrm{NaDS}]} \quad \text{(excess Na}^+\text{ ion).} \tag{3.117}$$

When the additional (common ion) salt is present, but *not* in excess, the factor in the denominator becomes[40]

$$1+\frac{[\mathrm{NaDS}]}{[\mathrm{NaDS}]+[\mathrm{NaCl}]}. \tag{3.118}$$

Other problems with the Gibbs Adsorption Equation arise if the ionic dissociation is not complete. In these cases, the undissociated surfactants must be considered as a separate species from the dissociated species in the Gibbs equation. When the undissociated and the dissociated electrolyte surfactants are present in the same solution, the undissociated form is almost always the more surface active, and will be preferentially adsorbed. Thus, even if only a small fraction of the surfactant is undissociated in the bulk solution, a large proportion of the adsorbed layer may be of the undissociated form. As such, the surface properties of partially dissociated surfactants may be strongly sensitive to small *pH* changes or the presence of common electrolyte ions, since the extent of association (and hydrolysis) is strongly sensitive to these changes. There are other difficulties as well associated with the use of the Gibbs equations for ionic, as well as many nonionic, surfactants due to the formation of aggregates in solution, as described below.

Another difference in dealing with electrolyte solutions is that the degree of dilution required to yield Henry's Law behavior in the bulk solution is often orders of magnitude greater than that required for non-electrolyte solutes. (This is a consequence of the long-range Coulombic interactions between ions.) One should in principle, therefore, work with *activities* instead of concentrations.[41] Fortunately for the most important cases with no added salt or excess added salt, the concentration terms in the Gibbs Adsorption Equation for the relative adsorption appear in both the numerator and denominator so that the effects of solution non-ideality effectively cancel out.

H. Self-assembly of surfactant monomers in solution

1. *Formation of micelles: critical micelle concentration (CMC)*

As the concentration of most of the strongly surface active solutes is increased, a point is reached beyond which surface tension shows essentially no further decrease, producing the sharp change in slope seen in Fig. 3-18.

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[40] Matijevic, E., and Pethica, B. A., *Trans. Faraday Soc.*, **54**, 1382 (1958).

[41] Prausnitz, J. M., Lichtenthaler, R. N., and Gomez de Azevado, E., **Molecular Thermodynamics of Fluid-Phase Equilibria**, 3rd Ed., Chap. 9, Prentice Hall, Upper Saddle River, NJ, 1999.

At about the same concentration, many other properties of the solution also show sharp breaks in slope, as shown schematically in Fig. 3-20. These sudden changes are attributable to the formation of aggregates of the surfactant in solution, termed *micelles*, pictured in Fig. 3-21. The spontaneous formation of micelles is an illustration of a general phenomenon associated with amphiphiles, termed *self-assembly*. The ordered arrays of molecules produced in adsorbed surfactant monolayers are also examples of such a process. The precise size and shape of the micellar aggregates differ from case to case, but quite often they are spherical and contain a few tens to hundreds of monomer units each. They form "back-to-back" so as to shield the hydrophobic moiety from the aqueous medium. The tendency to form micelles is a manifestation of the same hydrophobic effect that leads to their adsorption at interfaces. Figure 3-21 also suggests that equilibria exist between the monomers, micelles and adlayers at both the water-air and water-solid interfaces. As the concentration of the surfactant is increased, the formation of micelles begins to occur rather suddenly, or at least in a very narrow concentration range. The concentration at which they begin to form is termed the "critical micelle concentration" (*CMC*) and is characteristic of the particular surfactant and the thermodynamic state, *i.e.*, (T, p, $C_{\text{additional solutes}}$). The micelle size (aggregation number) is also characteristic, and the distribution of micelle sizes for a given case may be quite narrow. The subject of micelle formation is treated in more detail in Tanford,[42] Israelachvili,[43] Rosen,[44] Moroi,[45] and elsewhere.

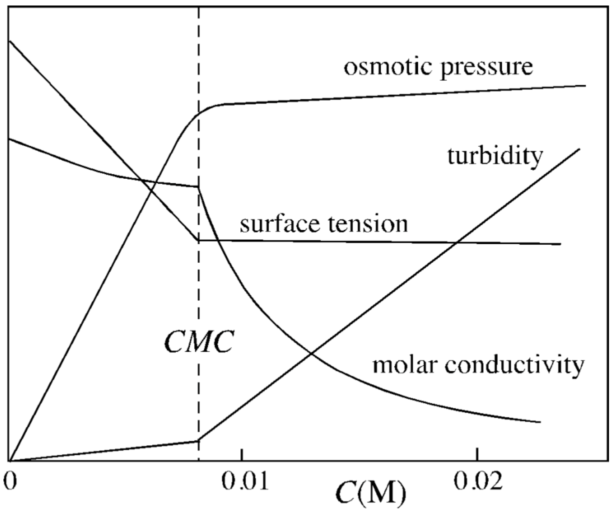

Fig. 3-20: Schematic diagram of physical property changes of aqueous solutions of sodium dodecyl sulfate at 25°C as a function of concentration.

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[42] Tanford, C., **The Hydrophobic Effect: Formation of Micelles and Biological Membranes**, 2nd Ed., Krieger, Malabar, FL, 1991.

[43] Israelachvili, J. N., **Intermolecular and Surface Forces**, 2nd Ed., pp. 341ff, Academic Press, New York, 1992.

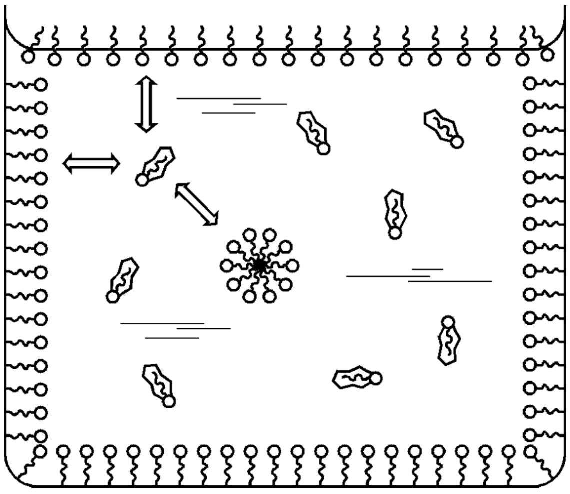

Fig. 3-21: Micelle formation in a surfactant solution.

The formation of micelles can be described using a mass-action model, and the examination of the consequences of such a model illuminates the nature of the process of micellization. Micelles of an electrically neutral species A may be formed in accord with:

$$\mathrm{N}\,A_1 = A_\mathrm{N}\,, \tag{3.119}$$

where N is the aggregation number; A_1 refers to the isolated monomer, and A_N is the aggregate. Actually, a family of such "reactions" occurs for N = 2, 3, ... If equilibrium exists for the formation of N-mers from monomers, and Henry's Law holds for all species in solution, we may write for each N:

$$K_\mathrm{N} = \frac{\left(\frac{x_\mathrm{N}}{\mathrm{N}}\right)}{x_1^\mathrm{N}}\,, \tag{3.120}$$

where K_N is the equilibrium constant for the formation of N-mers; x_1 is the mole fraction of the surfactant as free monomer, while x_N is the mole fraction of the monomers which find themselves in N-mers. (x_N/N) is thus the mole fraction of N-mers themselves. (We may just as well have used molar concentrations to express the system composition; at the degrees of dilution of interest, the quantities are proportional.) With knowledge of K_N as a function of N (for all N), one may complete the description of the system by noting that the sum of the mole fractions of the surfactant in *all* of the aggregates must equal the nominal mole fraction of monomer in the solution, x_0:

$$x_0 = x_1 + x_2 + x_3 + \ldots \tag{3.121}$$

x_0 is a known quantity, and if K_N (N) is known, one may compute the distribution of aggregates to be expected for any given value of x_0.

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[44] Rosen, M. J., **Surfactants and Interfacial Phenomena**, 2nd Ed. Chaps. 3-4, Wiley, New York, 1989.

[45] Moroi, Y., **Micelles: Theoretical and Applied Aspects**, Plenum, New York, 1992.

It may be assumed, on an *ad hoc* basis for now, that aggregates of only a *single* size n can form in significant amounts. This of course does not assume that the micelles are formed via an n-body interaction, but rather that it occurs through the formation of a sequence of multimers, all of which at equilibrium are present in vanishingly small amounts, except for the preferred n-mer. For this case, one has: $x_{i\neq 1,n} \approx 0$, and therefore $x_0 = x_1 + x_n = (1-\beta)x_0 + \beta x_0$, where β is the fraction of the solute monomers that are present in the aggregates. β may be computed as a function of the nominal surfactant mole fraction, x_o, using the equilibrium expression:

$$K = \frac{\left(\dfrac{x_n}{n}\right)}{x_1^n} = \frac{\left(\dfrac{\beta x_0}{n}\right)}{\left[(1-\beta)x_o\right]^n}. \tag{3.122}$$

The abruptness of micelle formation as x_0 is increased is demonstrated with the above expression. A typical aggregation number n would be 100. Thus, due to the smallness of x_0, the expected value for *K* would be enormous. In fact, a reasonable value may be 10^{200}! Using these values produces the results shown in Fig. 3-22, in which the sharpness of the transition to micelles is evident. The *CMC* in this case is in the vicinity of x_0 = 0.0085. Presumably, when the concentration is made to exceed the *CMC*, more micelles of the same size and shape are formed, and the monomer concentration remains essentially constant at the *CMC*. Thus, as the *total* concentration increases, only the concentration of the micelles increases.

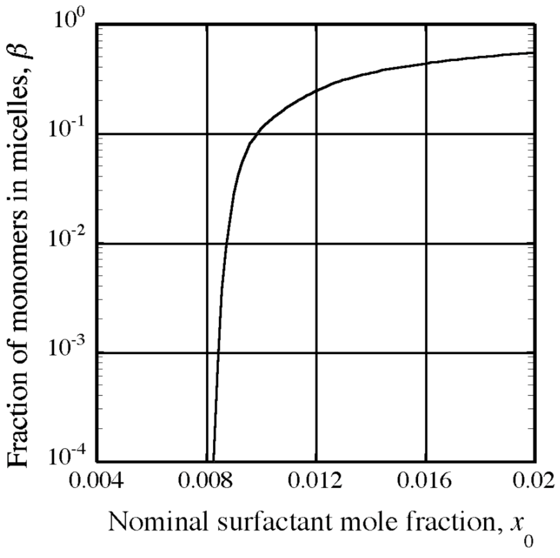

Fig. 3-22: Results of a mass-action model for micellization showing the fraction of the total surfactant monomers in micelles as a function of the nominal surfactant mole fraction.

If the micelles are formed from ionic surfactant, the effective "reaction" by which they are formed might be written as (assuming they are anions):

$$nA_1^- + ynC^+ = A_nC_{yn}^{-(1-y)n}, \tag{3.123}$$

where C^+ refers to a (monovalent) counterion, and *y* is the fraction of anionic surfactant monomers in the micelles to which such a counterion is *bound.*

The binding of counterions to some of the monomers in the micelles, effecting their partial neutralization, always occurs to some extent. The value of y may typically be between 0.3 and 0.8. The extent of counterion binding is only weakly dependent on the electrolyte concentration, but increases sharply with counterion valence. Often polyvalent counterions will bind to the free monomers, causing their precipitation. The micelle which is formed when there is monovalent counterion binding thus carries a "valence" of $-(1-y)\mathrm{n}$. When the surfactant is fully ionized and is the only source of cations (counterions), and the solution continues to obey Henry's Law (a more suspect assumption than in the case of solutions of neutral surfactants), one may set the activity of the counterions equal to the nominal mole fraction of the surfactant: $x_\mathrm{c} = x_0$, and the equilibrium equation becomes:

$$K = \frac{\left(\dfrac{x_\mathrm{n}}{\mathrm{n}}\right)}{x_1^\mathrm{n} x_\mathrm{c}^{y\mathrm{n}}} = \frac{\left(\dfrac{x_\mathrm{n}}{\mathrm{n}}\right)}{\mathrm{x}_1^\mathrm{n} \mathrm{x}_0^{y\mathrm{n}}} = \frac{\left(\dfrac{\beta x_0}{\mathrm{n}}\right)}{(1-\beta)^\mathrm{n} x_\mathrm{o}^{\mathrm{n}(1+y)}}. \tag{3.124}$$

The sharpness of the transition to micelles in this case is even greater than that shown for neutral surfactants.

The narrowness of the micelle size distribution around the value n may be anticipated by a thermodynamic analysis of the micellization process, *i.e.*, the process of the association of one mole of monomers into aggregates of size n. For this case, the standard (Gibbs) free energy of micellization is given by:

$$\Delta G^\Theta_\mathrm{mic} = -\frac{RT}{\mathrm{n}} \ln K. \tag{3.125}$$

The value of N = n to be expected is the one for which $K(\mathrm{N})$ takes on the largest value; hence $\Delta G^\Theta_\mathrm{mic}$ takes on the largest negative value. The aggregation of monomers is a *cooperative* process (*i.e.*, its tendency to occur depends in part on how much it has already occurred). When the first N-mers start to form, the larger they are, the greater the resulting drop in the system free energy when an *additional* monomer is added, since the hydrophobes are more effectively able to shield themselves from the water. This effect does not continue indefinitely, however, or even level off (as would be the case for bulk phase change) because as more monomers are added, the head groups become more crowded at the surface of the aggregate. This crowding is especially acute if the head groups are ionized, and the like-charged entities are obliged to reside next to one another. These opposing effects come into balance at a particular value of N that yields the largest negative $\Delta G^\Theta_\mathrm{mic}$. It has been shown (for the case in which the micelles are spherical in shape)[46] that even when $-\Delta G^{\Theta}_{\text{mic}}$ goes through a rather shallow maximum with N, the resulting micellar size distribution is narrow.

The effect that reaching the *CMC* has on many of the solution properties were known for some time before McBain first explained them (in 1911)[47] in terms of micelle formation. Consider the properties of surface tension, specific electrical conductivity, turbidity and osmotic pressure (and other colligative properties). All show dramatic slope changes in the vicinity of the *CMC* that can be explained by the formation of micelles, and all of these changes serve as methods for detecting the *CMC* in the laboratory. Surface tension halts its decrease with concentration as additional surfactant goes into the formation of additional micelles rather than increasing the bulk concentration of monomers or increasing the packing of surfactant into the surface (which is full). Surface tension measurement is the most common method for locating the *CMC*. Specific (molar) electrical conductivity (for ionic surfactants) decreases sharply with micellization primarily due to the binding of counterions to the micelle "interface," thus neutralizing a portion of the electrolyte present. Conductivity measurement thus provides a useful method for the determination of the *CMC* of ionic surfactants. Turbidity increases sharply beyond the *CMC* because micelles (diameter ≥ 20 Å) scatter light much more strongly than the monomers (see Chap. 5). The *CMC* may thus be detected using a turbidimeter or spectrophotometer. Osmotic pressure, Π_{OS} (and other colligative properties) depend directly on the number of particles in a unit volume of solution, which increases much more slowly with total surfactant concentration when additional surfactant molecules aggregate into micelles (which count only as one particle each). At least roughly, the slope of the Π_{OS} *vs*. x_0 curve should decrease by a factor of n (the micellar aggregation number) when the *CMC* is exceeded, so that osmotic pressure measurements may be used not only to locate the *CMC*, but also to determine the aggregation number. Although noting the extent of the change in colligative properties of the solution can give information about the size of the micelles, light scattering is probably the commonest method used for this. Other properties are similarly affected, and many of them also serve as methods for locating the *CMC* experimentally.

A large tabulation of *CMC*-values, together with a discussion of the various experimental methods used for obtaining them, is given in Mukerjee and Mysels.[48] Some typical values (together with aggregation numbers) are shown in Table 3-6. These are taken from the text by Rosen, which provides a rich source of property data for surfactants and their solutions.

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[46] Mukerjee, P., in **Physical Chemistry, Enriching Topics from Colloid and Surface Science**, H. van Olphen and K. Mysels, Eds., Chap. 9, Theorex, La Jolla, CA, 1975.

[47] McBain, J. W., **Frontiers in Colloid Chemistry**, Interscience, New York, 1949.

[48] Mukerjee, P. and Mysels, K. J., **Critical Micelle Concentrations of Aqueous Surfactant Systems**, Nat. Bur. Stds., NSRDS-NBS 36, U.S. Govt. Printing Office, Washington, DC, 1971.

Table 3-6: Some values for *CMC* and aggregation number. From [From Rosen, M. J., **Surfactants and Interfacial Phenomena**, 2nd Ed., pp. 108ff, Wiley, New York, 1989.]

Surfactant	Medium	*T*(°C)	*CMC* (mM)	Agg. No., *n*
$C_{10}H_{21}SO_4^-Na^+$	H_2O	40	33	$40_{30°C}$
$C_{12}H_{25}SO_4^-Na^+$	H_2O	40	8.6	54
$C_{14}H_{29}SO_4^-Na^+$	H_2O	40	2.2	
$C_{12}H_{25}SO_4^-Na^+$	H_2O	25	8.2	
$C_{12}H_{25}SO_4^-Na^+$	0.01 M NaCl	21	5.6	
$C_{12}H_{25}SO_4^-Na^+$	0.03 M NaCl	21	3.2	
$C_{12}H_{25}SO_4^-Na^+$	0.10 M NaCl	21	1.5	$90_{20°C}$
$C_{14}H_{29}SO_4^-Na^+$	0.01 M NaCl	23		138
$C_{12}H_{25}SO_4^-Na^+$	3M urea	25	9.0	
$C_{12}H_{25}N(CH_3)_3^+Br^-$	H_2O	25	1.6	$50_{23°C}$
$n\text{-}C_{12}H_{25}(C_2H_4O)_7OH$	H_2O	25	0.05	
$n\text{-}C_{12}H_{25}(C_2H_4O)_6OH$	H_2O	25	0.05	
$n\text{-}C_{12}H_{25}(C_2H_4O)_{14}OH$	H_2O	25	0.055	
$C_{16}H_{33}(C_2H_4O)_6OH$	H_2O	25		2,430
$C_{16}H_{33}(C_2H_4O)_6OH$	H_2O	34		16,600

The *CMC* is of course one of the most important properties of surfactant solutions, and the large database that exists for it lets us examine how its magnitude depends on system properties. It is possible to make some useful generalizations about the magnitude of the *CMC* and its trends with various factors, and some results are summarized below[49]. Many of the trends for the *CMC* can be rationalized using a simple thermodynamic analysis, as follows. Substitution of the expressions for K into the expression given above for $\Delta G^{\ominus}_{\text{mic}}$, *i.e.* Eq. (3.125), gives

for nonionic micelle formers:

$$\Delta G^{\ominus}_{\text{mic}} = -\frac{RT}{\text{n}}\ln\left(\frac{\beta x_0}{\text{n}}\right) + RT\ln\left[x_0(1-\beta)\right], \tag{3.126}$$

and for ionic micelle formers:

$$\Delta G^{\ominus}_{\text{mic}} = -\frac{RT}{\text{n}}\ln\left(\frac{\beta x_0}{\text{n}}\right) + RT\ln\left[x_0(1-\beta)\right] + yRT\ln(x_0). \tag{3.127}$$

Right at the *CMC*, β (the fraction of the monomers in micelles) ≈ 0, and $x_0 \approx$ *CMC* (expressed as mole fraction). Thus

$$\Delta G^{\ominus}_{\text{mic}}\Big|_{\text{nonionic}} = RT\ln(CMC), \text{ or} \tag{3.128}$$

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[49] Osipow, L. I., **Surface Chemistry**, pp. 168 ff, ACS Monograph Series, No. 153, Reinhold, New York, 1962.

$$\Delta G^{\Theta}_{\text{mic}}\big|_{\text{ionic}} = (1+y)RT\ln(CMC), \tag{3.129}$$

so that for either nonionic or ionic micelles, $\ln(CMC) \propto \Delta G^{\Theta}_{\text{mic}}/RT$. $\Delta G^{\Theta}_{\text{mic}}$ must of course be negative, and the more negative it is, the more favorable the conditions for aggregation and the *lower* the *CMC*. $\Delta G^{\Theta}_{\text{mic}}$ may be broken down into contributions from the hydrophobic chain and hydrophilic head group:

$$\Delta G^{\Theta}_{\text{mic}} = \Delta G^{\Theta}_{\text{mic}}(\text{hc}) + \Delta G^{\Theta}_{\text{mic}}(\text{head}) \tag{3.130}$$

The contribution of the hydrophobic group is negative (due to the entropic hydrophobic effect described earlier), and for straight-chain hydrocarbons may be further broken down:

$$\Delta G^{\Theta}_{\text{mic}}(\text{hc}) = \Delta G^{\Theta}_{\text{mic}}(\text{CH}_3) + (n_{\text{c}} - 1)\Delta G^{\Theta}_{\text{mic}}(-\text{CH}_2-). \tag{3.131}$$

One would expect $\Delta G^{\Theta}_{\text{mic}}(-\text{CH}_2-)$ to be constant for any surfactant (*i.e.*, head group) type, leading to a systematic decrease of *CMC* with chain length, *i.e.*, Traube's Rule. The contribution of the head group $\Delta G^{\Theta}_{\text{mic}}(\text{head})$, on the other hand, is positive, and results from the steric and electrostatic repulsion encountered in bringing the head group into the micelle "interface." It depends inversely on the effective head group area, a_0, in the micelle. For ionic surfactants, the electrostatic contribution to the effective head group area should be proportional to the radius of the "ionic atmosphere" around an ion as given by the Debye-Hückel theory.[50] This in turn is inversely proportional to the total molar concentration of the counterions in the solution. It should be independent of the hydrophobe and only weakly dependent on temperature. Some of the important trends observed experimentally are as follows:

1) Increasing the hydrophobic chain length, n_{C} (of aliphatic surfactants) decreases the *CMC* in a regular manner. For a given homologous series of ionic surfactants (usually up to $n_{\text{C}} \approx 18$), adding a single -CH$_2$- group approximately *halves* the *CMC*. For nonionics (of the polyethylene oxide type), the *CMC* is dropped by closer to a factor of 3 for each -CH$_2$- addition to the chain. It is found that for many types of micelle-formers, this dependence can be accurately expressed by the equation suggested by Klevens[51] (for straight chain surfactants):

$$\log(CMC) = A - Bn_{\text{C}}. \tag{3.132}$$

(CMC) [=] mole/liter; n_{C} = number of carbon atoms in the chain. Table 3-7 shows "Klevens constants" for various ionic surfactants. Such relationships,

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[50] Lewis, G. N., Randall, M., Pitzer, K. S., and Brewer, L., **Thermodynamics**, 2nd Ed., pp. 332-243, McGraw-Hill, New York, 1961.

[51] Klevens, H. B., *J. Phys. Colloid Chem.*, **54**, 283 (1950).

Table 3-7: Klevens constants for various surfactant types. From [Rosen, M., **Surfactants and Interfacial Phenomena**, 2nd Ed., p. 136, Wiley, New York, 1989.]

Surfactant series	*T* (°C)	*A*	*B*
Na carboxylates (soaps)	20	1.8_5	0.30
K carboxylates (soaps)	25	1.9_2	0.29
Na (K) *n*-alkyl 1-sulfates or -sulfonates	25	1.5_1	0.30
Na *n*-alkane-1-sulfonates	40	1.5_9	0.29
Na *n*-alkane-1-sulfonates	55	1.1_5	0.26
Na *n*-alkane-1-sulfonates	60	1.4_2	0.28
Na *n*-alkane-1-sulfates	45	1.4_2	0.30
Na *n*-alkane-1-sulfates	60	1.3_5	0.28
Na *n*-alkane-2-sulfates	55	1.2_8	0.27
Na *p*-*n*-alkylbenzenesulfonates	55	1.6_8	0.29
Na *p*-*n*-alkylbenzenesulfonates	70	1.3_3	0.27
n-Alkylammonium chlorides	25	1.2_5	0.27
n-Alkylammonium chlorides	45	1.7_9	0.30
n-Alkyltrimethylammonium bromides	25	1.7_2	0.30
n-Alkyltrimethylammonium chlorides (in 0.1 M NaCl)	25	1.2_3	0.33
n-Alkyltrimethylammonium bromides	60	1.7_7	0.29
n-Alklpyridinium bromides	30	1.7_2	0.31
n-$C_nH_{2n+1}(OC_2H_4)_6OH$	25	1.8_2	0.49

which are another manifestation of Traube's Rule, are of great practical value in extrapolating and interpolating experimental data on *CMC*'s. The *B*-value of ≈ 0.3 suggests a molar free energy contribution of ≈ $0.7RT$ for each -CH_2- group. For nonionics (at least of the PEO type), the *B*-value of ≈ 0.5 (see bottom entry of Table 3-7) yields a free energy contribution of ≈ $1.2RT$ for each -CH_2- group, suggesting in this case a more nearly complete transfer of the hydrophobe from the water into the micelle. This is consistent with the idea that the greater spacing required between the head groups of ionic surfactants (due to electrostatic repulsion) permits greater contact of the hydrophobes in the micelle with water in that case. The nature of $\Delta G^{\Theta}_{\text{mic}}(\text{hc})$ is further understood by considering the weak temperature dependence of the *CMC* for ionic surfactants. Applying Gibbs-Helmholtz analysis:

$$\frac{d\ln(CMC)}{dT} = \frac{d\left(\dfrac{\Delta G^{\Theta}_{\text{mic}}}{RT}\right)}{dT} = -\frac{\Delta H^{\Theta}_{\text{mic}}}{RT^2} = \text{small}, \qquad (3.133)$$

it is seen that the enthalpy of micellization is small, a fact confirmed by independent calorimetric studies of the process. Thus, in view of the general relationship

$$\Delta G^{\Theta}_{\mathrm{mic}} = \Delta H^{\Theta}_{\mathrm{mic}} - T\Delta S^{\Theta}_{\mathrm{mic}}, \tag{3.134}$$

it is seen again that the principal driving force for micellization is *entropic*. This may at first be counter-intuitive, because the monomers would be expected to suffer an entropy *decrease* upon confinement to micelles, but this is far outweighed by the entropy increase of the water.

2) Nonionic surfactants (of the PEO type) have lower *CMC's* (for the same hydrophobic chain length and temperature) than ionic ones. This is due primarily to the absence of electrostatic repulsion between adjacent head groups at the micelle "interface." In fact, nonionics have *CMC's* usually an order of magnitude less than ionics with the same hydrophobe. For example (in contrast to the C_{12} ionic surfactants above, which under low salt conditions give *CMC* ≈ 8 mM) a C_{12} nonionic surfactant with a head group consisting of six ethylene oxide units, *i.e.*, $C_{12}E_6$, has a *CMC* of 0.087 mM. As the polyethylene oxide chain length is increased for a given hydrophobe, the *CMC* is increased in a regular fashion, in accord with

$$\log(CMC) = A' + B'm_{\mathrm{E}}, \tag{3.135}$$

where m_{E} is the number of ethylene oxide units. Some values for the constants are listed in Table 3-8.

Table 3-8. Klevens constants for nonionic (PEO) surfactants. From [Rosen, M. J., **Surfactants and Interfacial Phenomena**, 1st ed., p. 103, Wiley-Interscience, New York, 1978.]

Surfactant series	T (°C)	A'	B'
n-$C_{12}H_{25}(OC_2H_4)_x OH$	23	-4.4	+0.046
n-$C_{12}H_{25}(OC_2H_4)_x OH$	55	-4.8	+0.013
p-t-$C_8H_{17}C_6H_4(OC_2H_4)_x OH$	25	-3.8	+0.029
$C_9H_{19}C_6H_4(OC_2H_4)_x OH$	25	-4.3	+0.020
n-$C_{16}H_{33}(OC_2H_4)_x OH$	25	-5.9	+0.024

3) For ionic micelle-formers, anything tending to reduce the electrostatic repulsion between head groups decreases the *CMC*. This may be accomplished by the addition of non-surfactant electrolyte, which has a *screening effect* due to an increased concentration of counterions, as discussed above. For a given compound, the *CMC* depends directly on the total concentration of counterions in accord with

$$\log(CMC) = -a\log(C_C) - b, \qquad (3.136)$$

where C_C is the total molar concentration of counterions (both from the surfactant itself and any additional electrolyte present), and "*a*" and "*b*" are characteristic constants. A couple of examples given by Osipow [52] are:

K dodecanoate: $\log(CMC) = -0.570 \log C_C^+ - 2.617$, and (3.137)

Na dodecyl sulfate: $\log(CMC) = -0.458 \log C_C^+ - 3.248$, (3.138)

where the $^+$ is a reminder that the counterions are the cations in these cases. Under swamping electrolyte conditions, the *CMC*-values approach those associated with nonionic surfactants. Electrolytes can also affect the *CMC* for nonionics and zwitterionics, but not in the same way and to the same degree as stated above. In this case, the influence of added electrolyte may be to alter the monomer solubility, *i.e.*, to "salt in" or "salt out" the hydrophobic portion of the monomer. Salting out is more common, and refers to a decreasing of the monomer solubility and hence the *CMC*. It usually requires a higher level of salt concentration than that needed to affect the *CMC* of ionic surfactants.

4) Temperature effects on the *CMC* can be quite complex, as suggested by Fig. 3-23. For ionic micelles, the dependence may be fairly weak over significant ranges, as stated earlier, but for nonionics (*i.e.*, polyethoxylates), increasing temperature always decreases the *CMC* sharply due to the progressive dehydration of the PEO groups.

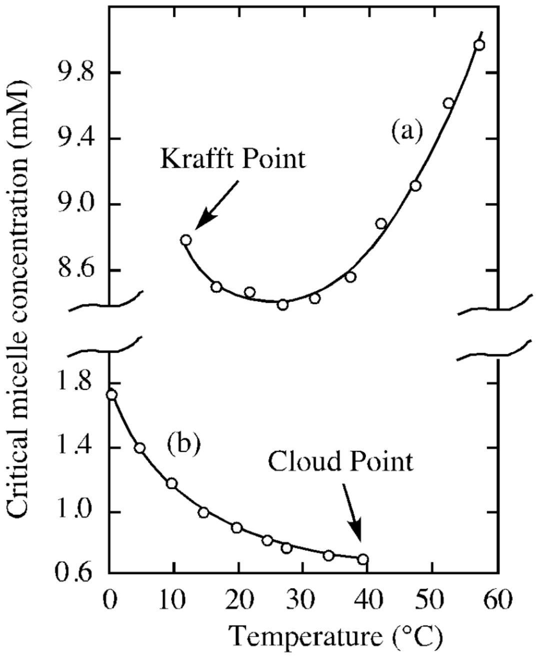

Fig. 3-23: Variation of *CMC* with temperature for:
(a) sodium dodecyl sulfate;
(b) $CH_3(CH_2)_9(C_2H_4O_5)OH$
After [Elworthy, P. H., Florence, A. T., and Macfarlane, C. B., **Solubilization by Surface Active Agents**, Chapman and Hall, London, 1968.]

There are two important benchmark temperatures for surfactant solutions, one for ionic surfactants and one for PEO type nonionics: the *Krafft point* and the *cloud point*, respectively.

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[52] Osipow, L. I., **Surface Chemistry**, ACS Monograph Series, No. 153, p. 168, Reinhold, New York, 1962.

Most ionic surfactants can form micelles if the hydrophobic portion is large enough that there is a significant decrease in free energy when they form. Below that, some loose association, “incipient micelle formation,” occurs, *i.e.*, dimerization, *etc.* The hydrophobic portion must not be *too* large, however, so that the monomer itself has insufficient solubility. The total solubility of a typical ionic surfactant as a function of T gives the results shown in Fig. 3-24, which shows the definition of the *Krafft Point* as the temperature where the solubility equals the *CMC*, and solubility undergoes a sudden increase. Nonionic surfactants (in particular, the PEO type) have more complex solubility behavior. A monomer solution or solution of micelles of ordinary size may exist at a given temperature, but as temperature is raised, the PEO chains are progressively dehydrated until a point is reached where very large aggregates are formed, producing visible turbidity. The temperature at which this occurs is quite sharp for a given surfactant and is termed its *cloud point*. The transition occurring as the cloud point is traversed is usually regarded as a macroscopic phase change. Some cloud point data for dodecyl ether surfactants are shown as a function of the PEO chain length x in Fig. 3-25.

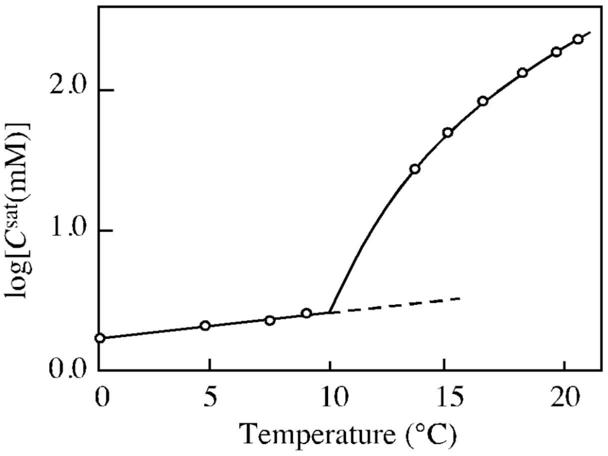

Fig. 3-24: Logarithm of the solubility of sodium dodecyl sulfate as a function of temperature. The dashed line represents the expected behavior in the absence of micelle formation. After [McBain, M.E.L. and Hutchinson, E., **Solubilization and Related Phenomena**, Academic Press, New York, 1955.]

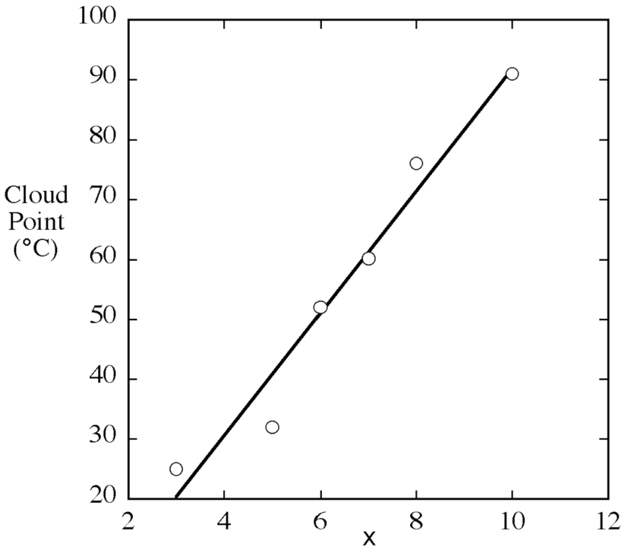

Fig. 3-25: Cloud points for dodecyl ether nonionic surfactants:

$n\text{-}C_{12}H_{25}(OC_2H_4)_x$

Data from [Karabinos, J.V., Hazdra, J.J., and Kapella, G.E., *Soap and Chemical Specialties*, **7**, April (1955).]

5) Organic additives may have a strong effect on the *CMC*. Large amounts of such materials may associate themselves with the micelles in the phenomenon termed *solubilization*, discussed below. This may greatly change the size and structure of the micelles, and reduces the *CMC*. Another class of additives is that of solutes whose presence in the solution affects the solubility of the monomer. They are thought of as “structure breakers” or “structure makers.” Urea and formamide are examples of structure breakers, which disrupt the water structure and hence the interaction of water with the hydrophobes. Their presence increases the *CMC*. Xylose and fructose are examples of structure makers, which decrease the *CMC*.

6) Most factors that tend to *decrease* the *CMC* also tend to *increase* micelle size, or aggregation number. These are often in the range of 30-300 for ionic micelle-formers and 200-20,000 for nonionic (PEO) surfactant, the latter strongly dependent on temperature.

2. *Solubilization*

One of the most important consequences of the micellization phenomenon is the fact that micelles provide a hydrocarbon, or more generally an *apolar*, environment within an aqueous medium. Not only does the formation of micelles greatly enhance the solubility of the surfactant itself beyond what it would be if micelles did not form, but the solubility of *other* sparingly soluble organic materials is greatly enhanced as well.

Apolar materials are incorporated into the interior of the micelle as shown in Fig. 3-26, while long-chain, and/or polar molecules may penetrate the outer shell of the micelle (called the palisade layer) in an oriented fashion, possibly to form *co-micelles*. Finally, other ionic or highly polar materials may adsorb on the outside of the micelles. Regardless of which mechanism is responsible for the enhanced solubility (by factors of 10^3-10^4 or higher are typical) it is termed *solubilization*.

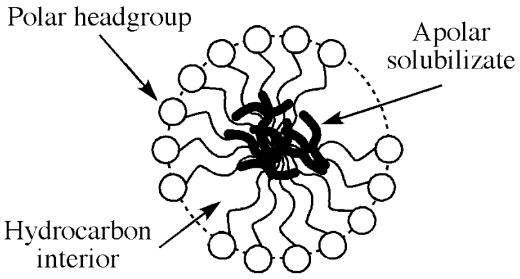

Fig. 3-26: Solubilization of apolar material into the interior of a micelle.

The cleansing action of soaps and detergents is due in part to solubilization of oily dirt so that it may be swept away. Detergency is a combination of enhanced wetting, detachment of dirt from the substrate surface (termed “roll up”) and solubilization. Dry cleaning depends in part on the solubilization of hydrophilic soils into inverted micelles, discussed below.

Solubilization leads to an easy way to detect the *CMC*, by solubilizing a dye.[53] In dilute aqueous solution, the dye would be nearly invisible, but when micelles are formed, most of it would be solubilized, thus concentrated into micelles, and would show visible color. Thus, *CMC*'s could be determined very quickly by titration. It should be noted, however, that the solubilization of the dye itself will at least slightly decrease the *CMC*.

A similar phenomenon explains an anomaly that puzzled surface chemists for many years. When studying the surface tension behavior of many anionic surfactants, there was a *minimum* in the surface tension, as shown in Fig. 3-27, for solutions of sodium dodecyl sulfonic acid and other detergents. The Gibbs Adsorption Equation would seem to dictate that the relative adsorption of the surfactant be zero at any minimum in such a curve, and *negative* just beyond it. Such behavior seemed unlikely, but McBain and coworkers documented a number of examples of the apparent paradox. His microtome measurements on a number of these systems,[54] was motivated to check the validity of the Gibbs Adsorption Equation, but revealed $\Gamma_{2,1}$ to have significant positive values throughout the region. The explanation was given finally by Crisp,[55] as sketched in Fig. 3-28(a)-(c). The dodecyl sulfonic acid used (as an example) contained a very small impurity of dodecyl (lauryl) alcohol (the material from which the surfactant was synthesized) (component 3), a non-ionized compound with significantly greater surface activity than the main component. It was this impurity that

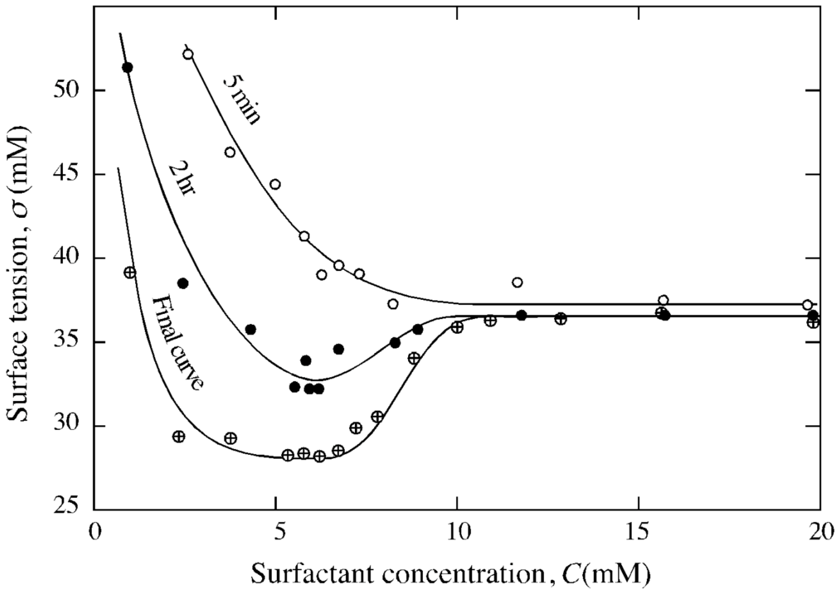

Fig. 3-27: Surface tension behavior of dodecyl sulfonic acid solutions as a function of concentration, measured at different rates. After [McBain, J. W., Vinograd, J. R., and Wilson, D. A., *J. Amer. Chem. Soc.*, **62**, 244 (1940).]

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[53] Corrin, M. C., and Harkins, W. D., *J. Amer. Chem. Soc.*, **69**, 679 (1947).

[54] McBain, J. W., and Wood, L. A., *Proc. Roy. Soc. A*, **174**, 286 (1940).

[55] Crisp, D. J., *Trans. Faraday Soc.*, **43**, 815 (1947).

predominated at the surface at low overall concentrations, given enough time to get there, and was primarily responsible for the observed surface tension reduction. Thus, as C_2 was increased, more of component 3 (the alcohol) adsorbed, until finally the *CMC* of the dodecyl sulfonic acid was reached. Then the lauryl alcohol was drawn into the micelles, even away from the surface, leaving behind SDS. This produced an increase in the surface tension. In terms of the Gibbs Adsorption Equation for a *ternary* system:

$$\frac{d\sigma}{dC_2} = -\Gamma_{2,1}\left(\frac{\partial \mu_2}{\partial C_2}\right) - \Gamma_{3,1}\left(\frac{\partial \mu_3}{\partial C_2}\right). \tag{3.139}$$

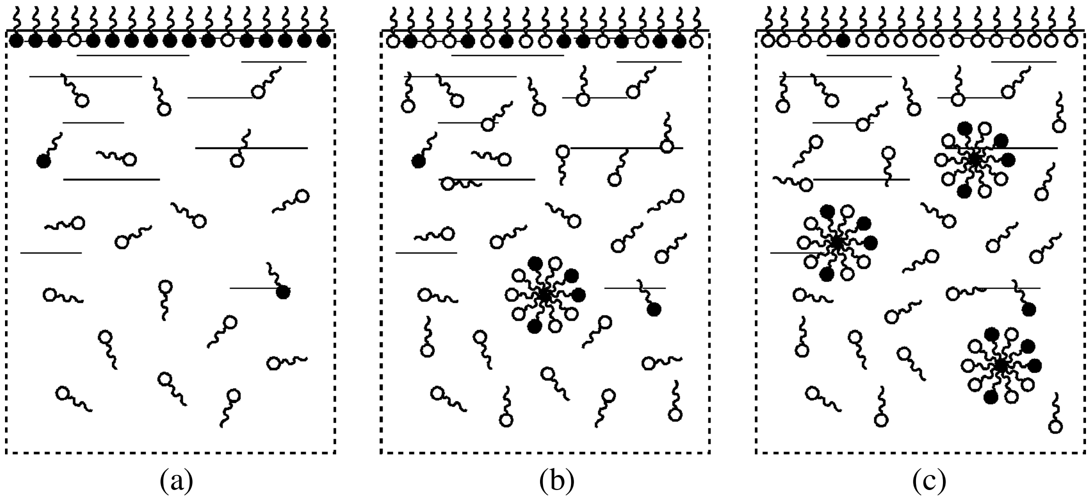


Fig. 3-28: Explanation of surface tension with concentration. Dark head groups represent fatty alcohols, and light head groups represent sulfate anions.

Above the *CMC* of component 2, $(\partial\mu_2/\partial C_2) \approx 0$ (but *not* $\Gamma_{2,1}$) and $(\partial\mu_3/\partial C_2)$ is *negative*, since as C_2 increases, there are more micelles which *attract* the alcohol, decreasing its monomer concentration and hence its chemical potential. Thus:

$$\left(\frac{\partial \mu_2}{\partial C_2}\right) = \frac{RTd\ln(C_2)_{\text{mono}}}{d(C_2)_{\text{total}}} \approx 0, \text{ and} \tag{3.140}$$

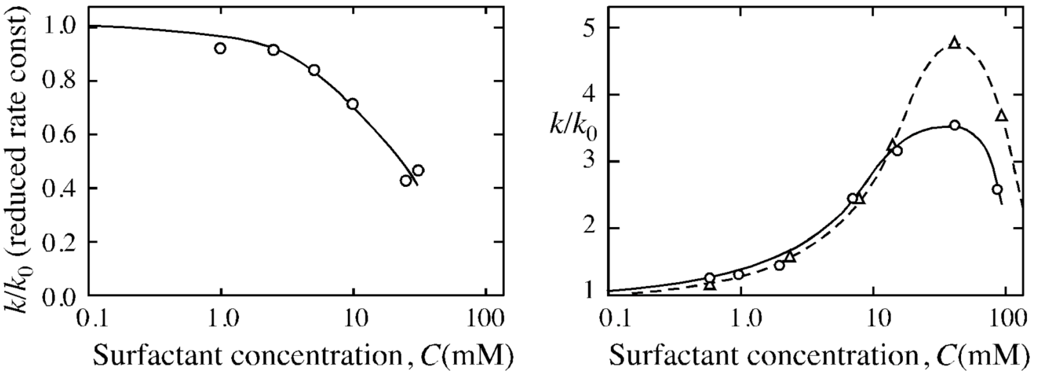
$$\left(\frac{\partial \mu_3}{\partial C_2}\right) = \frac{RTd\ln(C_3)_{\text{mono}}}{d(C_2)_{\text{total}}} < 0. \tag{3.141}$$

When carefully purified surfactant was used, there was no minimum in the surface tension, and conversely, when small (0.1%) amounts of contaminants like lauryl alcohol were added, the minimum reappeared. A practical implication of the above is that when *CMC* determinations are to be made by surface tension measurements for ionic surfactants containing traces of nonionic precursor surfactants (such as fatty alcohols), the measurements should be made quickly enough to avoid the effects of these contaminants.

Solubilization has a great potential for application in chemical reactions, such as in emulsion polymerization, discussed briefly in Chap. 5.C.3. Reactions which occur between (or involve) both water-soluble and water-*insoluble* components (as acid- or base-catalyzed hydrolysis) could have their rates drastically increased by incorporating the water-insoluble ester into micelles in acidic or basic aqueous solutions. Enhancing such a reaction by solubilization of one of the reactants into micelles is termed "secondary valence catalysis" or "micellar catalysis."[56] An example is provided by the Cannizzaro reaction in which benzaldehyde decomposes in the presence of a strong base to benzyl alcohol and the salt of the corresponding carboxylic acid, *viz.*:

$$2\,C_6H_5CHO + KOH \rightarrow C_6H_5CH_2OH + C_6H_5CHOO^-K^+,$$

The alkali is insoluble in the water-immiscible benzaldehyde, dooming the reaction to the water-oil interface. Incorporation of the benzaldehyde into cationic micelles, however, greatly enhances the rate of the reaction as the hydroxyl ions are attracted to the vicinity of the micellar "interface," whereas the use of anionic micelles effectively shuts the reaction off, as pictured in Fig. 3-29. In the latter case the hydroxyl ions are repelled from the micelle "interface." A summary tabulation of reactions mediated by secondary valence catalysis has been given by Fendler.[57]



(a) (b)

Fig. 3-29: Secondary valence catalysis: (a) the effect of an anionic surfactant (potassium palmitate) on the rate of the Cannizzaro reaction; (b) the effect of cationic surfactants (Δ eicosanyltroimethylammonium bromide, O octadecyl trimethylammonium bromide) on the rate of the same reaction. After [Cramer, L.R., and Berg, J.C., *J. Phys. Chem.*, **72**, 3686 (1968).]

The ultimate amount of solubilizate that can be incorporated in a given case, known as the maximum additive concentration (*MAC*) is limited by the size of the original micelle, and the incorporation of the solubilizate may change the nature and the shape of the micelles. Under certain

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[56] Fendler, J., and Fendler, E., **Catalysis in Micellar and Macromolecular Systems**, Academic Press, New York, 1975.

[57] Fendler, J. H., **Membrane Mimetic Chemistry**, pp. 341-409, John Wiley & Sons, New York, 1882.

circumstances, micelles can be swollen by solubilization to hundreds of times their original size (diameters up to 100 nm or more), and such structures are termed *microemulsions*.[58] This high degree of swellability is often facilitated by the addition of medium-chain-length alcohols or other amphiphiles (termed co-surfactants), as shown in Fig. 3-30. Microemulsion droplets are considered to be dissolved species and as such, form thermodynamically stable systems. Microemulsions, and the situations leading to their spontaneous formation, are discussed in more detail in Chap. 9.D in the context of the treatment of emulsions in general. They are finding applications that parallel the exploitation of solubilization with ordinary micelles, but their requirement for large amounts of (expensive) surfactant to some extent limits their practical use.

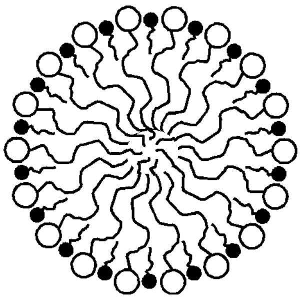

Fig. 3-30: Schematic of a highly swollen micelle formed by a mixture of surfactant and co-surfactant capable of imbibing a large amount of solubilizate to form a microemulsion "droplet."

I. Micelle morphology, other self-assembled structures, and concentrated surfactant solutions

1. *Micellar shape and the Critical Packing Parameter (CPP)*

Up to this point it has been tacitly assumed that micelles are spherical in shape. This is often not the case. Figure 3-31 suggests that in order for surfactant monomers to be able to form a space-filling sphere, there are

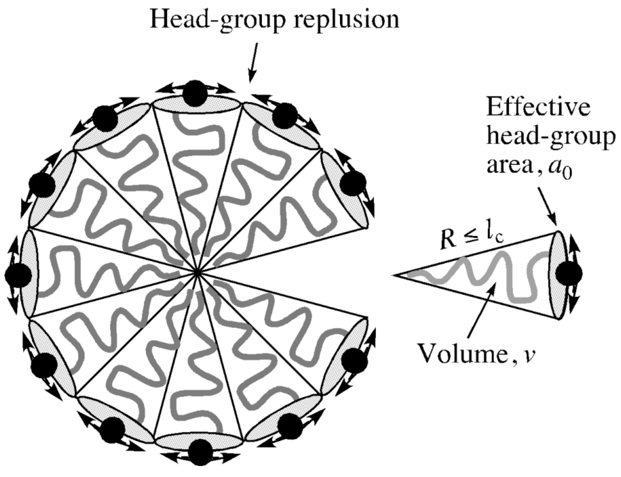

Fig. 3-31: Micelles as shape-filling structures, depend upon the size and shape characteristics of the monomer.

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[58] Bourrel, M., and Schechter, R. S., Eds., **Microemulsions and Related Systems**, Dekker, New York, 483 pp., 1988.

geometric constraints on their hydrophilic "heads" and hydrophobic "tails." It may also be evident that only a narrow range of aggregation numbers will be able to satisfy these requirements for a given monomer. The head groups occupy an effective surface area "a_0" (per molecule) at the aggregate-solution "interface," while the hydrophobic tails have a volume v and a maximum length l_C (the contour length). l_C is the largest chain extension possible while maintaining liquid-like properties. For a spherical micelle of radius R, the aggregation number n may be expressed either in terms of the micelle area occupied by the monomer head groups, or the micelle volume, assumed to consist of the hydrophobic tails:

$$n = \frac{4\pi R^2}{a_0} = \frac{4/3\pi R^3}{v}, \text{ so that: } R = \frac{3v}{a_0} \tag{3.142}$$

Since R must be $\leq l_C$, spherical micelles can form only when $3v/a_0 < l_C$, or when

$$\left[\frac{v}{a_0 l_C}\right] \leq \frac{1}{3}. \tag{3.143}$$

The quantity in brackets above is called the "critical packing parameter" (*CPP*), or the "surfactant number,"[59] and its value determines the expected shapes of the aggregates that form[60], as discussed below. For spherical micelles to form, the monomer is envisioned to have a conical morphology. While the packing parameter may be less than 1/3 for spherical micelles, if we assume the material of the aggregate to be incompressible, it is clear that it cannot be *much* less than 1/3 or there would be an unfilled region in the core. Estimates of v and l_C may be obtained for aliphatic chains with n_C carbon atoms as[61]

$$\begin{aligned} v &\approx (27.4 + 26.9 n_c) \times 10^{-3} \text{ [=] nm}^3\text{, and} \\ l_c &\approx l_{\max} \approx 0.15 + 0.1265 n_c \text{ [=] nm} \end{aligned} \tag{3.144}$$

The effective head group area a_0 is not generally calculable *a priori* and depends not only on the physical size of the head group, but also on its state of hydration, ionization, ionic environment, *etc.* The common single-tail detergents, such as SDS or CTAB, form spherical micelles under low salt conditions.

When the head group area is too small relative to the bulk of the hydrophobe to allow formation of spheres, the monomer morphology more closely resembles that of a truncated cone, and the self-assembled structures

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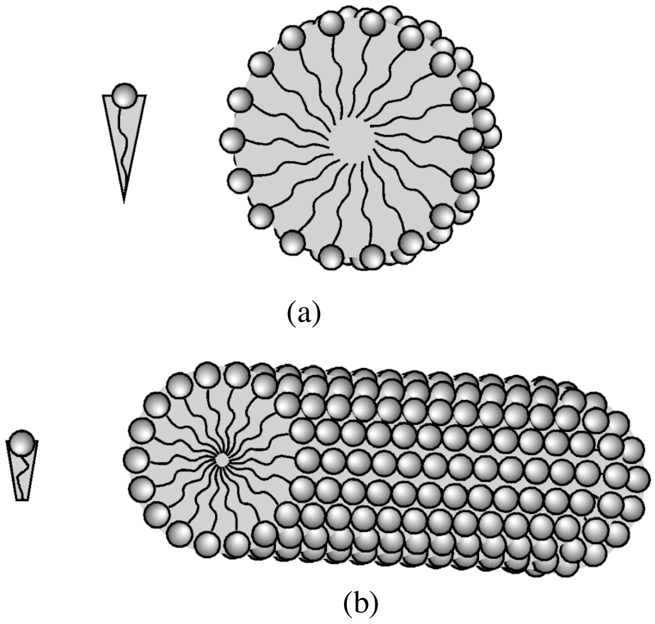
[59] Evans, D.F., Wennerström, H., **The Colloidal Domain**, pp. 12ff, VCH, New York (1994).

[60] Israelachvili, J. N., Mitchell, D. J., and Ninham, B, W., *J. Chem. Soc. Faraday Trans.*, **72**, 1525 (1976).

[61] Tanford, C., **The Hydrophobi Effect: Formation of Micelles and Biological Membranes**, 2nd Ed., p. 52, Krieger, Malabar, FL, 1991.

observed are *cylindrical* micelles, pictured in Fig. 3-32(b), shown in comparison with spherical micelles. Cylindrical micelles are expected in the range 1/3 < *CPP* < 1/2. The head group area for ionic surfactants may be reduced by simply increasing the salt concentration of the medium, reducing the degree of head-to-head electrostatic repulsion, so that the common detergents like SDS or CTAB produce cylindrical micelles under high salt conditions. Single hydrophobic chain nonionics with small head groups also produce cylindrical micelles. Near the lower end of the above *CPP* range, presumably intermediate structures such as short cylinders with hemispherical caps, form, while higher *CPP* values produce longer cylinders that are polydisperse with respect to their length, with their average length dependent upon the total surfactant concentration. At higher concentrations, they may become very long (> 1 μm), *i.e.*, "wormlike," resembling linear polymers in solution. They are dynamical structures that are able to break and re-form reversibly upon shearing, and have become common model systems for rheological studies.[62]


(a)

(b)

Fig. 3-32: (a) Spherical micelles: *CPP* ≤ 1/3; (b) Cylindrical micelles: 1/3 < *CPP* < 1/2.

2. *Beyond micelles: other self-assembled structures*

When the critical packing parameter becomes still larger, an array of other structures may be formed (self-assembled) from surfactant monomers in solution.[63] When the monomer has a double rather than a single hydrophobic tail, the ratio of hydrophobe volume to head group area becomes quite large so that the monomer shape is still that of a truncated cone, but with a smaller aspect ratio. Such molecules are exemplified by a

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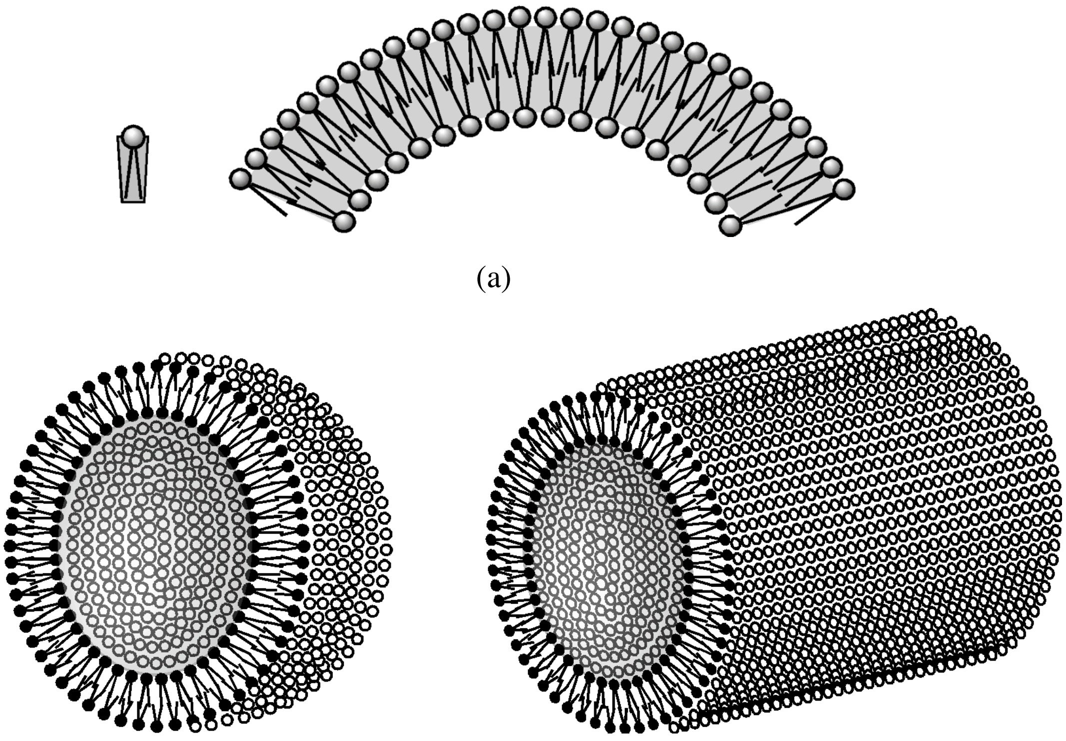
[62] Keller, S. L., Boltenhagen, P., Pine, D. J., and Zasadzinski1, J. A., *Phys. Rev. Lett.*, **80**, 2725 (1998).

[63] Israelachvili, J. N., **Intermolecular and Surface Forces**, 2nd Ed., pp. 381, Academic Press, New York, 1992.

variety of naturally occurring phospholipids, including the dipalmitoyl lecithin (lung surfactant) pictured in Fig. 2-6, as well as synthetic di-tail surfactants such as Aerosol OT®. With *CPP*-values between 1/2 and 1, such monomers tend to form curved bilayer structures, as pictured in Fig. 3-33(a). These may produce bilayer spheres, termed *vesicles* (or *liposomes*), and under some conditions, bilayer tubules, as shown in Fig. 3-33(b), or even toroids (doughnuts).[64] The structures may be unilamellar or multilamellar.



(a)

(b)

Fig. 3-33: (a) Curved bilayers structures: ½ < *CPP* < 1; (b) Unilamellar vesicle and tubule.

Unilamellar vesicles of dipalmitoyl lecithin (lung surfactant) as small as approximately 30 nm diameter may be formed, while multi-lamellar vesicle structures as large as one micrometer or greater in diameter are commonly produced from egg lecithin. The formation of vesicles appears in some cases to require some energy input (stirring, sonication), but in most cases is effectively spontaneous. For example, a polydisperse vesicular dispersion may be formed by gently stirring a mixture of egg lecithin and water at room temperature. The mixture may be fractionated into various sizes by sieving or dialysis through membranes. Vesicles currently show promise as controlled-release drug delivery devices[65,66] or in the synthesis of highly uniform-sized mineral particles with applications in catalysis, or in

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[64] Mutz, M., and Bensimon, D, *Phys. Rev. A*, 43(8), 4525 (1991);
Fourcade, B., Mutz, M., and Bensimon, D. *Phys. Rev. Lett.*, 68(16), 2551 (1992).

[65] Uster, P. S., "Liposome-Based Vehicles for Topical Delivery," in **Topical Drug Delivery Formulations**, Drugs and the Pharmaceutical Sciences, Vol. 42, Marcel Dekker, New York (1990).

[66] Virden, J. W., and Berg, J. C., *J. Colloid Interface Sci.*, **153**, 411 (1992).

the production of magnetic or electronic devices[67]. The unilamellar form of these and other bilayer structures have much in common with natural membranes, and their study has been termed “membrane mimetic chemistry.”[68] When the *CPP* rises to ≈ 1, the monomer morphology is near that of a cylinder, and lamellar micelles, bilayer fragments or even bicontinuous structures may be formed, as shown in Fig. 3-34. The bilayers sheets in any case are of effectively zero mean curvature. The may occur as single wall or multi-wall structures. The monomers are most often di-tail surfactants with small head groups, but may also be single-tail compounds if they contain multiple double bonds or double bonds near the center of the chain (such as oleates). Video enhanced microscopy suggests many other structures can form as well, such as bilayer chains, filaments, and multilayer sandwiches.

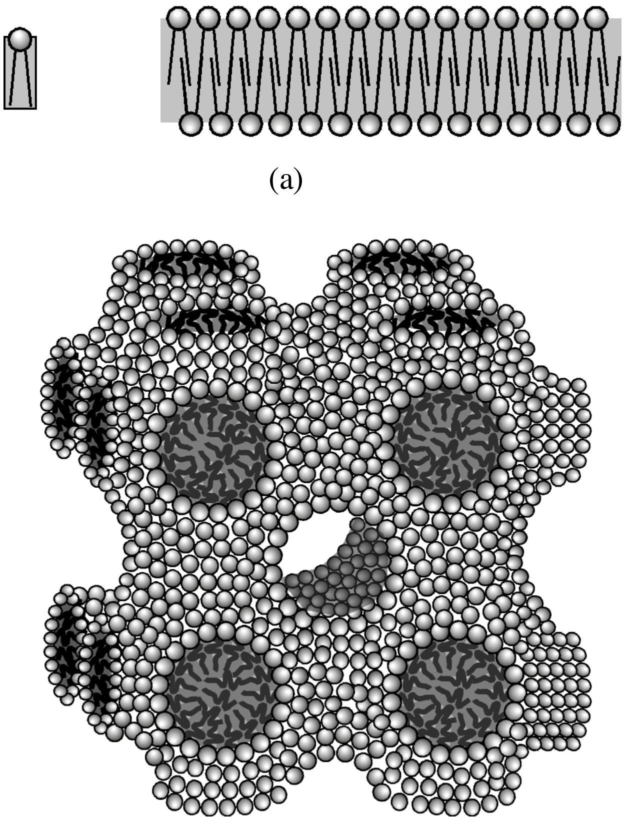

Fig. 3-34: (a) Flat bilayer fragment: *CPP* ≈ 1; (b) Bicontinuous structure of zero mean curvature.

Values of the critical packing parameter in excess of unity imply the formation of *inverse*, or *reverse* micelles, *i.e.*, aggregates of surfactant molecules in *non*-aqueous media, with the head groups together in the core of the micelle and the hydrophobes extended.[69] These in fact do form under

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[67] Mann, S., and Hannington, J. P., *J. Colloid Interface Sci.*, **122**, 326 (1988).

[68] Fendler, J. H., **Membrane Mimetic Chemistry**, John Wiley & Sons, New York (1982).

[69] Luisi, P. L., and Straub, B. E., Eds., **Reverse Micelles**, Plenum, New York, 1984;

the right conditions. The hydrophobic effect contributes little or nothing to the driving force for their formation, but instead it is largely attractive interactions (dipolar, hydrogen bonding, or more general acid-base effects) between the head groups that are responsible for micelle formation. Their formation is believed to be facilitated by or even to require the presence of small (almost undetectable) amounts of water in the organic medium.[70] Water, which acts as both an acid and a base, clearly facilitates donor-acceptor interactions. Reverse micelles are often but not always spherical and more often than not smaller than ordinary micelles, sometimes with aggregation numbers less than ten. One of the most commonly used reverse micelle formers is Aerosol OT®, which has been shown to form trimers in hydrocarbon solutions above a critical concentration (*CMC*).[71] Reverse micelles are swollen through the solubilization of water, and may evolve from spherical shapes to cylinders, and in some circumstances reverse microemulsions are formed. Many of the compounds found to form reverse micelles in low dielectric media are ionic surfactants in aqueous media, but with sufficient oil solubility. They have found application as solubilizing vehicles important in dry cleaning and as agents for secondary valence catalysis in apolar media.[72] Their widest use arises from their ability to stabilize electric charges in apolar media. They may thus be used to confer sufficient electrical conductivity to liquid fuels to prevent the dangerous buildup of static charges. They also provide a mechanism for charging surfaces, such as those of colloidal particles, in contact with low dielectric media, as discussed further in Chap. 6. This in turn provides a contribution to their stabilization against aggregation, as occurs in the buildup of carbon sludges in motor oil. Charged colloids in apolar media are also the basis for the rapidly developing technology of electrophoretic inks for electronic displays.[73] In addition to micelles, reverse vesicles[74] and toroidal reverse vesicles[75] have also been reported.

In summary, it must be noted that while the use of the critical packing parameter of a surfactant monomer as a predictor of self-assembled structures in solution appears to be very powerful, its use is hampered by the fact that one seldom knows the appropriate value for the head group area, a_0. It is often the *post hoc* observation of structure that gives clues to the appropriate value for this parameter.

Morrison, I. D., *Colloids Surfaces A*, **71**, 1 (1993).

[70] Nelson, S. M., and Pink, R. C., *J. Chem. Soc.*, **1952**, 1744 (1952).

[71] Denal, A., Gosse, B., and Gosse, J. P., *Rev. Phys. Appl.*, **16**, 673 (1981).

[72] Kitihara, A., *Adv. Colloid Interface Sci.*, **12**, 109 (1980).

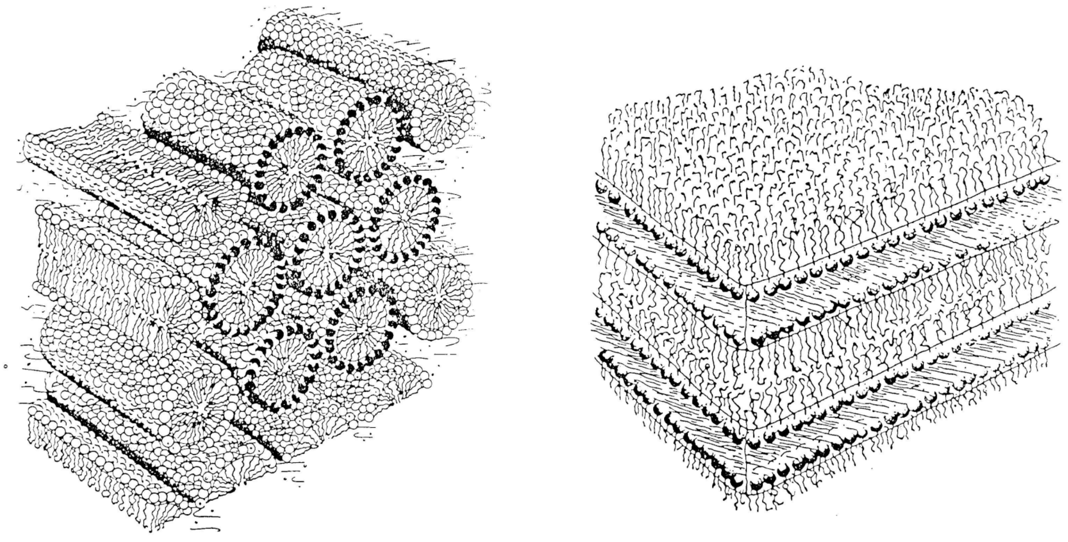
[73] Cominsky, B., Albert, J. D., Yoshizawa, H., and Jacobson, J., *Nature*, **394**, 253 (1998).

[74] Kunieda, H., Shigeta, K., Nakamura, K., and Imae, T., *Progr. Colloid Polym. Sci.,* **100**, 1 (1996).

[75] Murdan, S., Gregoriadis, G., and Florence, A. T., *Intl. J. Pharmaceutics,* **183** [1], 47 (1999).

3. *Concentrated surfactant solutions; liquid crystalline mesophases*

When the concentration of surfactant in aqueous solution is made to exceed about 10% by weight, micelle-micelle interactions become significant, and the spherical or finite cylindrical structures generally undergo conversion to long cylinders or multi-bilayers, as pictured in Fig. 3-35. The cylinders usually form first (as concentration is increased) and pack themselves into hexagonal arrays yielding a liquid crystalline mesophase called the "normal hexagonal phase" or the "middle phase." This is a nematic liquid crystalline phase, and it exhibits optical birefringence (opalescence). Further concentration often produces the multilayer structure known as the "lamellar" or "neat" phase, an example of a smectic liquid crystal. Other liquid crystalline phases may also occur, and in general, the phase behavior of concentrated surfactant solutions is quite complex. It is well described in the monograph by Laughlin.[76]



(a) (b)

Fig. 3-35: Structures forming in concentrated surfactant solutions: (a) normal hexagonal (or "middle") phase; (b) lamellar (or "neat") phase. Other structures also can form in these solutions under different conditions. From [Bourrel, M., and Schechter, R. S., **Microemulsions and Related Systems**, Surf. Sci. Ser. 30, pp. 100 and 102, Marcel Dekker, New York, 1988.]

The reason for the occurrence of the above structural changes with concentration is the long-range repulsive forces that exist between the aggregates. They consist chiefly of electrostatic and hydration forces (solvent structuring around the hydrophilic groups). These can be ignored in the dilute systems (as we have done), but not in more concentrated solutions. The micelle surfaces try to get as far apart as possible, but their ability to do so is limited. Converting to a structure of quasi-infinite cylinders increases the average inter-surface distance, and subsequent conversion to lamellae increases the distance still further.

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[76] Laughlin, R. G., **The Aqueous Phase Behavior of Surfactants**, Academic Press, London (1994).

One of the important recent applications of the various fluid micro- and nano-structures that can be created from the spontaneous assembly of surfactants in solution is their use as templates for mineralization via inorganic precursors to produce micro- or nano-structured solids (monoliths). The latter are examples of "nanocomposites."[77] A virtually inexhaustible array of new materials including high-performance coatings and catalysts, as well as electronic, photonic, magnetic and bio-active materials, have either been produced in this way, or are contemplated.

4. *Kinetics of micellization and other self-assembly processes*

It has been tacitly assumed to this point that surfactant solutions are in instantaneous equilibrium with respect to micelle or other structure formation when changes in conditions (degree of dilution, temperature, salt addition, *etc.*) are made. Indeed it has been shown that relaxation times for the exchange of single monomers in solution with simple micelles is generally of the order of microseconds, while the time required for complete breakdown and reformation of a micelle if of the order of one millisecond.[78] The latter should correspond to the time required for solubilizate to distribute itself amongst the micelles in a solution, provided it is well mixed. The times required for the formation or disruption of the equilibrium phase structure in concentrated surfactant solutions are often much greater.[79] For example, the dissolution of sufficient sodium dodecyl sulfate (SDS) in water to form the birefringent hexagonal phase described earlier may require several days. The kinetics of annealing in such systems of long-range order could benefit from further study.

J. Dynamic surface tension of surfactant solutions

1. *Diffusion-controlled adsorption*

We must return to consideration of the surface tension of surfactant solutions and recognize that in many, perhaps even most, of the situations of practical interest, the system is not in a state of adsorption equilibrium. While pure liquids do not show a surface tension time-dependence in any measurable time range, dilute surfactant solutions show equilibration times ranging from less than 1 ms (the shortest that can currently be measured) to several minutes or even hours.[80] In spray coating operations of various kinds, surfactants are added to the liquid in part to assist in spreading as the drops impact the target surface. This is accomplished only if sufficient

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[77] Dagami, R., *Chem. & Eng. News*, **77** [23], 25 (1999).

[78] Aniansson, E. A. G., Wall, S. N., Almgren, M., Hoffmann, H., Kielmann, I., Ulbricht, W., Zana, R., Lang, J., and Tondre, C., *J. Phys. Chem.*, **80**, 905 (1976).

[79] Zana, R., **Dynamics of Surfactant Self-Assemblies: Micelles, Microemulsions, Vesicles and Lyotropic Phases**, Surf. Sci. Ser. 125, Marcel Dekker, New York, 2005.

[80] Dukhin, S. S., Kretzschmer, G., Miller, R., **Dynamics of Adsorption at Liquid Interfaces**, Elsevier, Amsterdam (1995).

adsorption has occurred over the lifetime of the spray droplets, which in the case of inkjet printing is less than one millisecond. It is thus important to be able to calculate the time course of adsorption and surface tension, as well as to be able to measure dynamic surface tension, as discussed in Chap. 2. The maximum bubble pressure technique (Fig. 2-46) can now be used[81] for surface ages in the millisecond and sub-millisecond range, supplanting the more difficult oscillating jet method (Fig. 2-48).[82]

In the simplest case, the time effect is controlled by the rate of surfactant diffusion to the surface, as pictured in Fig. 3-36. For some cases, there may be a kinetic barrier to adsorption, or surface re-orientation of the adsorbate molecules, but if the solution is sufficiently dilute, one would expect the time effect to be due to diffusion alone. In that case, transport of the monomers through the solution is described by the diffusion equation:

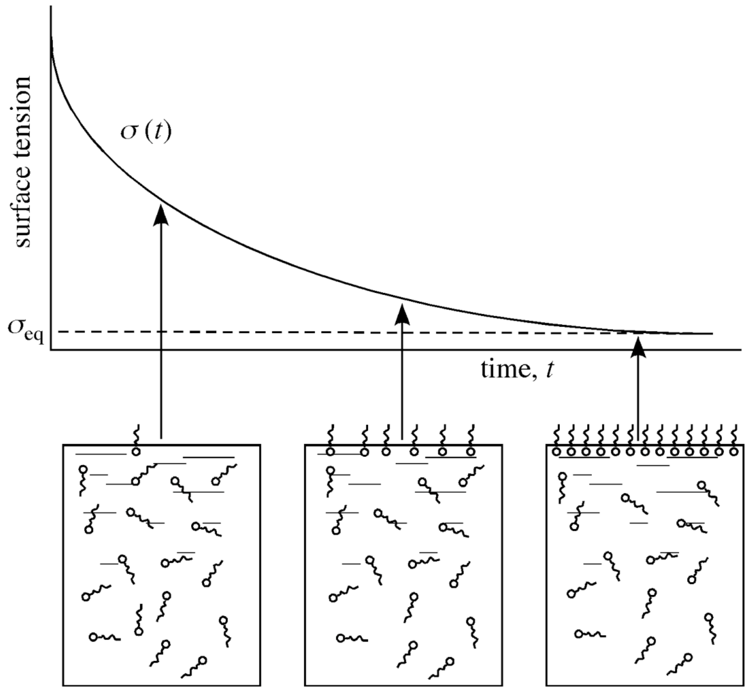

Fig. 3-36: Dynamic surface tension. For dilute solutions (particularly of surface active agents) the surface tension decreases with surface age as the solute diffuses to the surface and adsorbs.

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2}, \tag{3.145}$$

where C is the concentration of surfactant, D is its diffusivity, and z is the distance measured *away* from the surface (hence the positive sign on the right hand side). Before the surface is formed, the surfactant is at the uniform concentration C_∞. The adsorption Γ is a function of time as the

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[81] Miller, R., Fainerman, V. B., Schano, K.-H., Hoffmann. A., Heyer, W., *Tenside Surf. Det.*, **34** [5], 357 (1997).

[82] Defay, R., and Pétré, G., "Dynamic Surface Tension," in **Surface and Colloid Science**, Vol. 3, pp. 27-81, E. Matijevic, Ed., Wiley-Interscience, New York (1970).

surface "fills," and during the course of filling is assumed to be in local equilibrium with the sublayer immediately beneath it, where $C = C_s$. The initial conditions are:

$$\begin{aligned} &t = 0(-);\;\; C = C_\infty(\text{all } z) \\ &t = 0(+);\;\; C_s = 0 \\ &t = 0;\;\; \Gamma = 0 \end{aligned} \quad , \tag{3.146}$$

and the boundary conditions are:

$$z \to \infty;\;\; C \to C_\infty \text{ and} \tag{3.147}$$

$$z = 0;\;\; C = C_s(\Gamma), \text{ the adsorption isotherm.} \tag{3.148}$$

Then the time course of the adsorption, $\Gamma(t)$ is given by

$$\frac{d\Gamma}{dt} = D\left(\frac{\partial C}{\partial z}\right)_{z=0}. \tag{3.149}$$

The solution for $\Gamma(t)$, obtained first by Ward and Tordai[83], takes the form of the integral equation:

$$\Gamma(t) = 2\sqrt{\frac{D}{\pi}}\left[C_\infty\sqrt{t} - \int_0^{\sqrt{t}} C_s(t-\tau)d(\sqrt{\tau})\right], \tag{3.150}$$

where τ is a delay time. The first term on the right reflects the rate of diffusion of solute toward the surface, while the second term expresses the rate of back-diffusion from the surface as it fills. As is evident, the solution to this equation requires knowledge of the adsorption isotherm, which relates C_s to Γ at equilibrium, and the diffusivity D. The surface tension $\sigma(t)$ is then given by the surface equation of state. For many cases, the Langmuir isotherm and the corresponding Frumkin equation of state are adequate. These involve only two parameters, which together with the diffusion coefficient, suffice to predict the dynamic surface tension. The predicted behavior of solutions of the nonionic surfactant Triton X-100 obtained on this basis is shown in Fig. 3-37, and it is found to agree reasonably well with experimental data obtained by the pendant bubble technique for this case. Solutions to the Ward and Tordai equation must in general be obtained numerically, although analytical solutions exist for very short times (when back diffusion can be neglected, and Henry's Law adsorption may be assumed)[84] or very long times, as equilibrium is approached.[85]

The Ward and Tordai analysis using Langmuir-Frumkin equilibrium can be nondimensionalized using a characteristic length h, the "adsorption

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[83] Ward, A. F. H., and Tordai, L., *J. Chem. Phys.*, **14**, 453 (1946).

[84] Hansen, R. S., *J. Colloid Sci.*, **16**, 549 (1961).

[85] Daniel, R., and Berg, J. C., *J. Colloid Interface Sci.*, **237**, 294 (2001).

depth," and a characteristic time τ_D. The adsorption depth is defined as the depth of solution of concentration C_∞ needed to supply a unit area of surface with its equilibrium inventory of surfactant, $\Gamma(C_\infty)$. It is thus expressible in terms of the adsorption equilibrium parameters, *viz*.

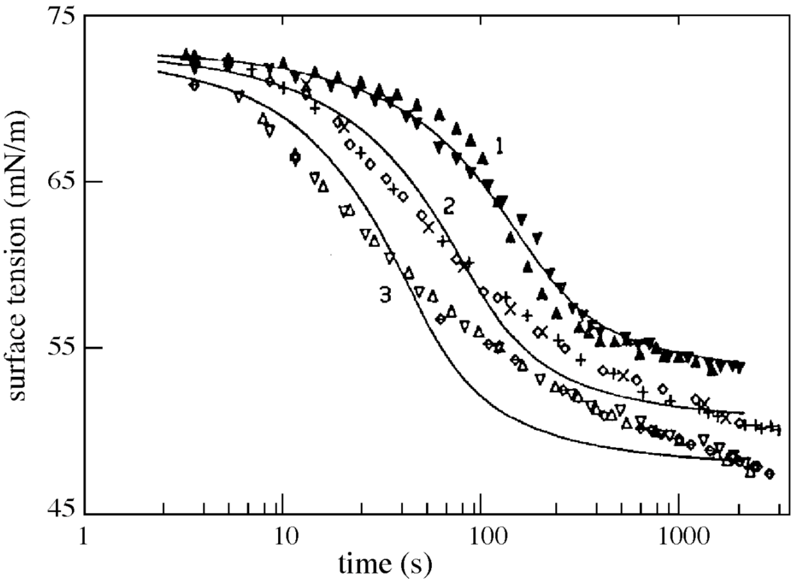

Fig. 3-37: Dynamic surface tension of aqueous solutions of Triton X-100 calculated using Ward and Tordai analysis with $D = 2.6 \times 10^{-6}$ cm^2/s. Data are shown for C_∞ = (1) 9.89, (2) 15.5, and (3) 23.2 mM. From [Lin, S.-Y., McKeigue, K., and Malderelli, C., *AIChE J.*, **36**, 1785 (1990).]

$$h = \frac{\Gamma(C_\infty)}{C_\infty} = \frac{B}{a + C_\infty}, \qquad (3.151)$$

where B and a are the Szyszkowski-Langmuir parameters defined earlier. The characteristic diffusion time is then defined as[86]

$$\tau_D = \frac{h^2}{D}. \qquad (3.152)$$

When the surface tension is nondimensionalized as

$$\Theta = \frac{\sigma(t) - \sigma_{eq}}{\sigma_0 - \sigma_{eq}}, \qquad (3.153)$$

where σ_{eq} is the final equilibrium surface tension (at C_∞), and σ_0 is the surface tension of pure water. When plotted against (t/τ_D), a family of curves is obtained for varying values of the parameter $k = C_\infty/a$. $\Theta(t/\tau_D)$ drops from 1 to 0 as the system equilibrates, but for all values of k, falls to ½ at $(t/\tau_D) = 1$. τ_D is thus the characteristic diffusion time for the system. The time

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[86] Ferri, J. K., Stebe, K. J., *Adv. Colloid Interface Sci.*, **85**, 61 (2000).

required, in terms of t/τ_D, for, say 90% equilibration, depends on k, being longer for low-k (low concentration) systems. Even for k as low as 0.1, however, 90% equilibration is achieved at a time of approximately $10\tau_D$. The diffusivities of ordinary monomeric surfactants in water are mostly in the range of 1.0 –10.0×10^{-6} cm^2/s, so if the equilibrium adsorption parameters are known for a given surfactant, the diffusion time can readily be estimated for a solution of given concentration. For example, for Triton X-100, the Szyszkowski-Langmuir parameters are: B = 2.91×10^{-10} mol/cm^2; a = 0.662×10^{-9} mol/cm^3, and the diffusivity is 2.6×10^{-6} cm^2/s. For a solution of C_∞ = 9.89 μM (= 9.89×10^{-9} mol/cm^3), we may compute: h = 0.0276 cm, and τ_D = 293 s, which may be compared with the result shown in Fig. 3-37. At the *CMC* for Triton X-100, 2.3×10^{-7}mol/cm^3, the characteristic diffusion time is computed to be τ_D = 0.70 s. As another example, for sodium dodecyl sulfate (SDS) at 10^{-4}M, one may compute $\tau_D \approx 0.5$ ms.

2. *Finite adsorption-desorption kinetics*

With the exception of some pure nonionic surfactants at very low concentrations, and certain alcohols, many surfactants show slower adsorption (in any case, slower surface tension decrease) than that predicted by the diffusion-control model, suggesting the importance of adsorption barriers for many cases,[87] so that calculated diffusion times represent upper limits for the rate of surface tension relaxation.

The very long-time dependence of surface tension that is sometimes observed is usually associated with the presence of small traces of impurity more surface active than the main component, as encountered when a minimum in the surface tension curves is observed, as in Fig. 3-27. Such behavior is often used as an indicator of the presence of such impurities. For solutions well above the *CMC*, time effects are shorter, since the micelles provide a large reservoir of monomers near the surface, and a simplified analysis of adsorption kinetics for this situation has been suggested.[88] The kinetic model consistent with Langmuir adsorption, *cf.* Eq. (3.104) is

$$\frac{d\Gamma}{dt} = k_1 C_\infty (B - \Gamma) - k_{-1}\Gamma, \tag{3.154}$$

where k_1 and k_{-1} are the adsorption and desorption rate constants. At $t \to \infty$, $d\Gamma/dt = 0$, from which it may be seen that k_{-1}/k_1 = the adsorption parameter a. Solution to the rate equation gives

$$\Gamma = \Gamma_{\text{eq}}\left[1 - e^{-k_1 a(1+k)t}\right], \tag{3.155}$$

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[87] Eastoe, J., Dalton, J. S., *Adv. Colloid Interface Sci.*, **85**, 103 (2000).

[88] Daniel, R. C., and Berg, J. C., *J. Colloid Interface Sci.*, **260**, 244 (2003).

where it is to be recalled that $k = C_\infty/a$. $\sigma(t)$ is then given by the Frumkin equation. While adjustment of the rate parameter k_1 can sometimes produce better fits to the shape of the $\sigma(t)$ curve than adjustment of the diffusivity in the Ward and Tordai model, *a priori* or independent determination of k_1 is in general not possible.

K. Insoluble (Langmuir) monolayers

1. *Formation of monolayers by spontaneous spreading*

Insoluble monomolecular films are formed at the air-water interface by water-insoluble compounds that spontaneously spread, *i.e.*, have a positive spreading coefficient,[89] as defined in Chap. 2:

$$S_{o/w} = \sigma_w - (\sigma_o + \sigma_{o/w}) > 0. \tag{3.156}$$

The spreading coefficient for any liquid at any fluid-fluid or fluid-solid interface may be computed in the same way. It is thus possible to predict "immiscible displacement" at a solid-liquid interface, if the solid-vapor interfacial energy is known. If $S_{o/w}$ is positive, spreading should occur, and if negative, it should not. When spreading *does* occur, it proceeds until the entire available surface is covered with monolayer, with the excess material existing as unspread bulk lenses or solid particles. Under such conditions, the surface tension reduction achieved is the equilibrium spreading pressure, π, of the material at the given interface.

When mineral oil (*e.g.*, Marcol-70) is deposited at the water/air interface, one may compute the spreading coefficient from the following data: $\sigma_w = 72.8$, $\sigma_o = 31.0$, and $\sigma_{o/w} = 50.0$ mN/m, respectively, yielding: $S_{o/w} = 72.8 - (31.0 + 50.0) = -8.2$ mN/m. Thus one would not expect spreading, and such behavior is typical of all the higher hydrocarbons at the water/air interface. A lower hydrocarbon, such as benzene, is an interesting case to examine. For this case, $S_{b/w} = 72.8 - (28.9 + 35.0) = +8.9$ mN/m, a positive value, suggesting that spreading should occur. A demonstration, using talc particles at the surface to render the spreading visible, shows that spreading does indeed occur, but once the film is formed, it quickly retreats backward into lenses. The explanation for such behavior, typical of the light hydrocarbons at the water/air interface, is that when the oil and water equilibrate, there is a slight amount of oil dissolved in the upper layer of water in contact with the oil, and a small amount of water dissolved in the oil. The former effect in particular, changes the equilibrium tensions involved. At equilibrium between benzene and water, $\sigma_{w(b)} = 62.2$ mN/m and $\sigma_{b(w)} = 28.8$ mN/m. The interfacial tension in this case remains unchanged. The final *equilibrium* spreading coefficient is thus $62.2 - (28.8 + 35.0) = -1.6$ mN/m. We thus distinguish between *initial* and *final* spreading coefficients,

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[89] Gaines, G. L., Jr., **Insoluble Monolayers at Liquid-Gas Interfaces**, pp. 136ff, Interscience, New York, 1966.

and while a number of materials may have positive initial spreading coefficients at the water/air interface, only those we have recognized as surface active agents have positive *final* spreading coefficients. For example, the data for oleic acid yield $S_{o/w}$ = 72.8 - (32.5 + 15.7) = 24.6 mN/m.

Solids as well as liquids may be observed to spread at interfaces. Camphor, for example, is surface active due the carbonyl group in its structure, as shown in Fig. 3-38. It is a crystalline material with slightly different values of the spreading coefficient from the different crystal faces. The particles are thus observed to spin while spreading, leading to the well-known "camphor dance."[90] The average spreading coefficient for camphor is 16 mN/m. Thus when oleic acid is added to a surface upon which camphor is spreading, its larger spreading coefficient suppresses the spreading, and brings the "dance" to a halt.

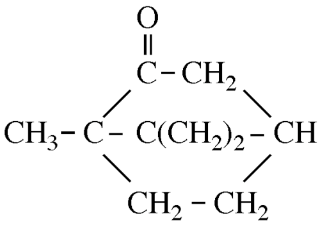

Fig. 3-38: Molecular structure of camphor.

The kinetics of spreading of *liquid* surfactants is governed primarily by the viscous drag of the water,[91] and the hydrodynamics of the event is quite complex.[92] Spreading from solids may be governed, however, by a much slower rate process at the solid-fluid interline. Stearic acid at room temperature, for example, has a large positive spreading pressure at the water/air interface, but shows little spreading over a period of several days.

2. *Hydrodynamic consequences of monolayers: Gibbs elasticity*

The presence of an insoluble surfactant monolayer at a fluid interface has a profound influence on the properties of that interface. Many of the changes are hydrodynamic in nature and are dealt with in more detail in Chap. 10. Simple laboratory demonstrations reveal that a clean water/air interface is quite fragile with respect to mechanical, thermal or chemical disruption. Gently blowing on a talc-covered surface shows that the particles may be moved around quite easily in this way. When a monolayer is present, however, the particles are rigidly held in place. Similarly, if a clean surface is heated locally, the surface is seen to dilate itself at that point, and if an adsorbing vapor such as acetone (decreasing surface tension) is brought near the surface, it is also seen to dilate. The presence of a monolayer suppresses such dilation in both cases. The interface with an insoluble monolayer acts

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[90] Lord Rayleigh (J. W. Strutt), *Proc. Roy. Soc.*, **47**, 364 (1890).

[91] Di Pietro, N. D., Huh, C., and Cox, R. G., *J. Fluid Mech.*, **84**, 529 (1978); Foda, M. A., and Cox, R. G., *J. Fluid Mech.*, **101**, 33 (1980).

[92] Camp, D. W., and Berg, J. C., *J. Fluid Mech.*, **184**, 445 (1987).

like an elastic membrane resisting distortion, and the mechanism for such action is shown in Fig. 3-39. A local dilation sweeps away surfactant leading to a strong gradient in surface tension tending to resist the dilation. This is the phenomenon of *Gibbs elasticity* to be described in more detail in Chap. 10. It is responsible for the legendary ability of oil "to calm troubled waters," as mentioned in ancient times in the writings of Roman historians Pliny the Elder and Plutarch,[93] and exemplified in the photograph of the mirror-like surface of Loch Laggan in Fig. 1-4. It was also the subject of a report by Benjamin Franklin to the Royal Society in 1774 documenting experiments in which he deposited a teaspoon of olive on the pond at Clapham Common in London, and observed it "spread amazingly…making perhaps half an acre as smooth as a looking glass."[94] A schematic of the mechanism for the damping of capillary waves is shown in Fig. 3-40.[95]

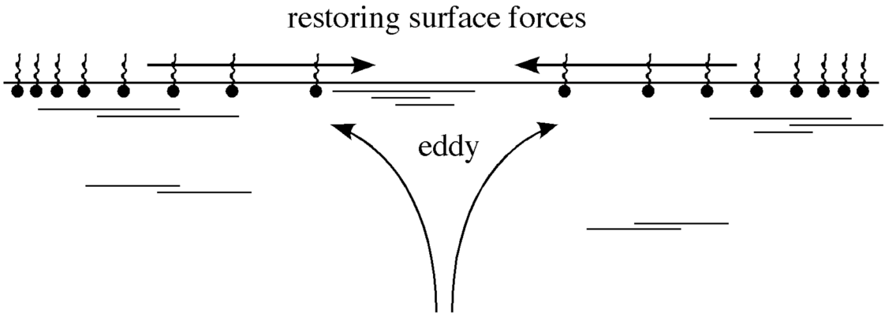

Fig. 3-39: The mechanism of Gibbs elasticity.

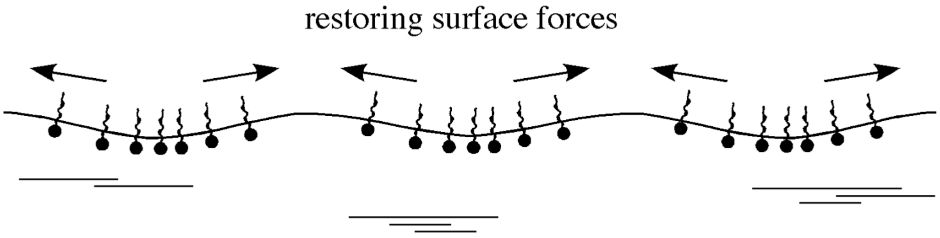

Fig.3-40: Damping of capillary waves by surface active agents.

3. *π-A isotherms of insoluble monolayers*

Insoluble monolayers are studied using Langmuir troughs, as shown in Fig. 2-42 or Langmuir-Wilhelmy troughs, in Fig. 2-43. The films are generally deposited by means of a micrometer syringe in carefully measured amounts using dilute solutions of the surfactant in a volatile *spreading solvent*. The latter quickly evaporates leaving the monolayer behind. The

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[93] Gaines, G. L., Jr., **Insoluble Monolayers at Liquid-Gas Interfaces**, p. 1, Interscience, New York, 1966.

[94] **The Complete Works of Benjamin Franklin**, Vol. V, p. 253, J. Bigelow (Ed.), G. P. Putnam's Sons, New York, 1887.

[95] Levich, V. G., **Physicochemical Hydrodynamics**, pp. 609 ff, Prentice-hall, Englewood Cliffs, NJ, 1962.

film is then manipulated (compressed or expanded) by means of movable barriers that form a leak-proof seal between the film-covered and clean portions of the surface. Results of compression-expansion experiments are generally reported as plots of surface pressure, π (surface tension reduction) *vs*. specific area of the surfactant, A, *i.e.*, area/molecule. An example of π-A behavior (on a highly nonlinear set of axes) is shown schematically in Fig. 3-41. This is a plot of the surface equation of state for the monolayer. The features of the π-A curve (or a family of such curves for different temperatures) for a given surfactant reveal a wealth of information concerning the size, shape and molecular interactions between the molecules that constitute the monolayer. These were broadly exploited by Langmuir and coworkers,[96] and played an important role in Langmuir's attainment of the 1932 Nobel Prize for Chemistry.

Imagine an experiment in which an initially sparsely populated monolayer is gradually compressed. At the highest degrees of expansion, a two-dimensional ideal gas equation is observed:

$$\pi A = kT, \tag{3.157}$$

where A is the specific area (usually expressed in Å^2/molecule). This has some practical utility in providing a method for determining the molecular weight of proteins, which spread as monolayers at the water/air interface and exhibit an accessible range of 2-d ideal gas behavior. Compression to about 1000 Å^2/molecule leads to a first-order phase change, producing islands of a two-dimensional "liquid" within the gaseous film. This occurs at a surface pressure of the order of one mN/m, a two-dimensional "vapor pressure," π^s.

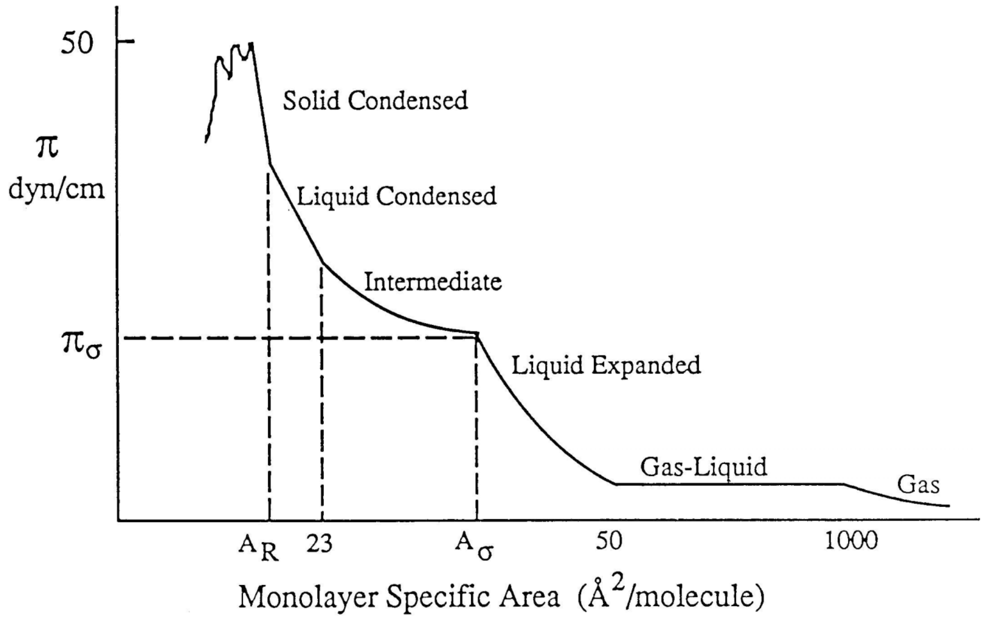

Fig. 3-41: Schematic of a π-A curve at constant temperature. Both axes are greatly expanded near the origin to reveal the phase behavior occurring there.

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[96] **The Collected Works of Irving Langmuir**, C. G. Suits and H. E. Way, Eds., Vol. 9: Surface Phenomena, Part 2: Monomolecular Films, Pergamon, New York, 1961.

The temperature dependence of π^s, which requires very accurate data, can be subjected to analysis using the Clausius-Clapeyron equation, to give the enthalpy of surface vaporization:

$$\Delta h^{\text{s-vap}} = RT^2\left(\frac{d\pi^{\text{s-vap}}}{dT}\right), \tag{3.158}$$

and the latter yields information on the energetics of tail-tail interactions in the surface liquid phase. The surface pressure remains at π^s until a specific area of approximately 50 Å^2/molecule is reached, when it begins to rise sharply (called "liftoff"). At this point, the monolayer is single-phase and liquid-like, but of greater compressibility than a corresponding three-dimensional liquid and is referred to as a "liquid expanded" phase. Further compression often (but not always) leads to a second-order phase transition corresponding to the onset of the formation of surface aggregates ("surface micelles") of greater density, and noticeable in the π–A trace as a characteristic "knee." The surface micelles become more numerous through what is called the "intermediate phase," until the entire film is comprised of such aggregates, leading to the "liquid condensed" phase. Further compression leads to a two-dimensional solid phase as the last lateral water of hydration is squeezed out of the film, producing a highly ordered structure. Eventually, the film collapses (fractures) in a macroscopic failure, sometimes visible in what Langmuir called "crumple patterns." In reality, a more subtle form of collapse generally begins at a slow rate at a much lower degree of compression. This collapse is in the form of the nucleation and growth of bulk phase nuclei of the surfactant.[97] Frozen surface biopsies of Langmuir monolayers have been examined by "cryo-electron microscopy."[98] The foregoing sequence of monolayer structures and phase states as surface pressure is increased was postulated by Langmuir but later buttressed by independent measurements. For example, the use of an air-ionizing electrode in combination with a reference electrode in the subphase measured surface electrical potential, which in turn could be related to the orientation of the molecular dipoles, and thus the closeness of the head group packing. Some techniques that have been employed to detect the orientation of hydrocarbon tails, two-dimensional phase structures and the coexistence of different surface phases include ellipsometry,[99] Brewster angle microscopy (BAM),[100] and fluorescence microscopy.[101] In ellipsometry, a beam of plane-polarized, monochromatic laser light is shone on the surface, producing a reflected beam that is elliptically polarized, *i.e.*,

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[97] Smith, R. D., and Berg, J. C., *J. Colloid Interface Sci.*, **74**, 273 (1980).

[98] Berg, J. C., *Proc. Work. Interfacial Phen.*, Seattle, pp. 89-107, NSF/RA-790442, PB80-201551 (1979).

[99] Thompkins, H. G., **A User's Guide to Ellipsometry**, Academic Press, Boston, 1993.

[100] Vollhardt, D., *Adv. Colloid Interface Sci.*, **64**, 143 (1996).

[101] Knobler, C. M., *Science*, **249**, 870 (1990).

has both horizontal and vertical components of polarization. For a given angle of incidence, the state of polarization of the reflected beam depends on the both the refractive index and the effective thickness of the film. It is thus possible to distinguish clean surface area (which produces no ellipticity) from both sparsely covered surfaces and densely packed monolayers. In Brewster angle microscopy the beam is aimed at precisely Brewster's angle (≈ 53°), producing very high contrast in the polarization between regions of condensed and expanded monolayer and therefore yields detailed images of the domain structure. In fluorescence microscopy a small amount of a fluorescent tag, miscible with the monolayer, is incorporated into the film, providing contrast between condensed and expanded regions.

A family of π-A curves for different temperatures shows remarkable similarity to three-dimensional phase behavior, as shown schematically in Fig. 3-42. For example, two-dimensional critical points may be identified for many insoluble monolayers. This figure makes it evident that not all of the phase states pictured in Fig. 3-41 are observed for all Langmuir monolayers. In particular for the fatty acids, the intermediate phase state and the liquid expanded phase eventually disappear as the chain length is increased or the temperature is decreased. In these cases, the surface pressure "lifts off" directly to the liquid condensed state upon compression. On the other hand, when the temperature is raised to a sufficient level, the film is in the gaseous (supercritical) state all the way to collapse.

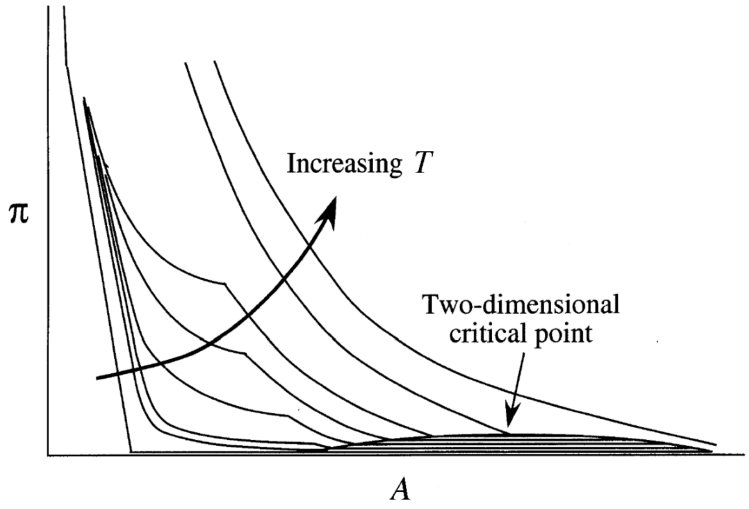


Fig. 3-42: Schematic of π-A isotherms for fatty acid monolayers over a range of temperatures.

One application of insoluble surfactant monolayers is illustrated in Fig. 3-43. When compressed to the point where the molecules are tightly packed together, the measured specific area may be used to determine the size of the molecule by extrapolating the solid-condensed branch of the curve to zero surface pressure. Langmuir used such measurements on straight-chain aliphatic surfactants to obtain the cross-sectional area of a

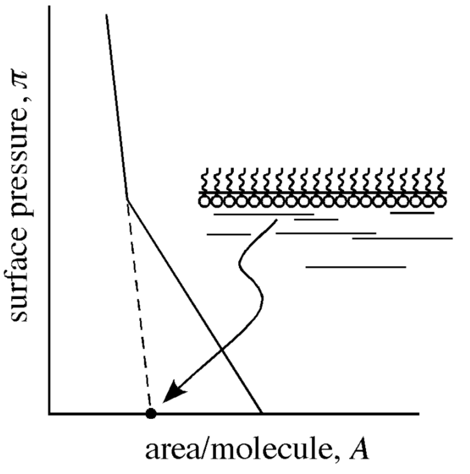
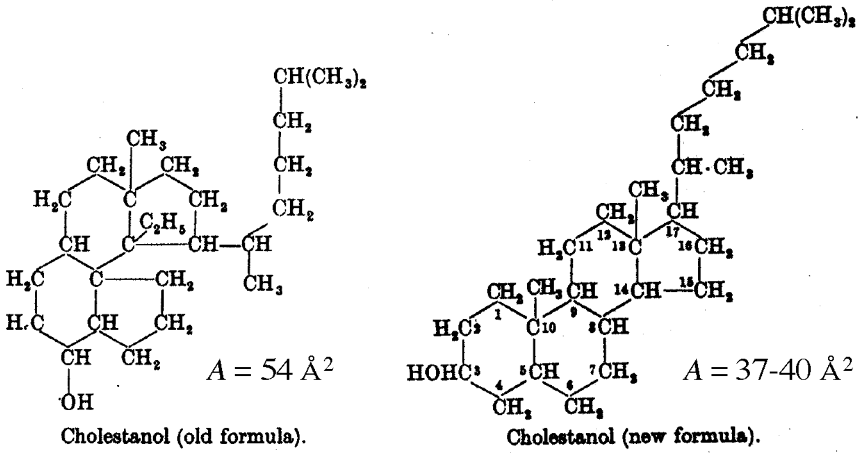


Fig. 3-43: Determination of molecular cross-sectional area from π-A measurements.

hydrocarbon chain.[102] His results were within 15% of the results obtained years later using X-ray diffraction. In the 1920's and 30's, such measurements were used to settle disputes concerning the structure of a variety of molecules, as illustrated in Fig. 3-44. Two suggestions for the structure of cholestanol had been proposed, each with a different implication for the molecular area. Langmuir trough measurements led unambiguously to a decision in favor of the second structure shown.



Cholestanol (old formula). Cholestanol (new formula).

Fig. 3-44: Two competing formulas for cholestanol, each implying a different specific area. Molecular diagrams from [Adam, N. K., **The Physics and Chemistry of Surfaces**, pp. 79-80, Dover, New York (1968).]

4. *Langmuir-Blodgett films*

Another important method for studying insoluble monolayers was pioneered by Langmuir, in collaboration with his coworker, Katherine Blodgett.[103] It is shown in Fig. 3-45 and consists of transferring the monolayer in a highly compressed two-dimensional phase state from the liquid surface to the surface of a solid. This is referred to as the Langmuir-

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[102] Langmuir, I., *J. Amer. Chem. Soc.*, **39**, 1848 (1917).

[103] Langmuir, I., and Blodgett, K. B., *Phys. Rev.*, **51**, 964 (1937).

Blodgett (or LB) technique, and by repeated dippings may be used to produce films of up to a thousand monolayers or more. The successive layers may be built up in different ways, producing multilayers of different properties. In what is called an X-type multilayer, the original deposition and all subsequent depositions are in the tail-down configuration. In a Y-type multilayer, all monolayers are alternately head-down and tail down, and in the Z-type, the monolayers all in the head-down configuration. While a primary motivation of its inventors was the production of anti-reflective coatings (since the thickness could be so carefully controlled), it later proved invaluable for studying monolayer structure. Monolayers on a *solid* substrate may be treated and examined in the electron microscope. An example, showing a two-phase region of the stearic acid monolayer, is shown in Fig. 3-46. (Note that the condensed-phase islands are perfect circles, suggesting the existence of an "edge tension.") LB films are also amenable to examination by an array of different scanning probe microscopy (SPM) techniques, described in more detail in Chap. 4. The use of the LB technique has aroused interest as a means for producing new materials with unique optical properties (*e.g.*, secondary harmonic generators) that may lead to the development of new types of optical sensors or switches.[104] The most common monolayers used for LB deposition are those of fatty acids and their salts, and a review of these systems, including methods for their preparation and characterization has been given by Peng, *et al.*[105]

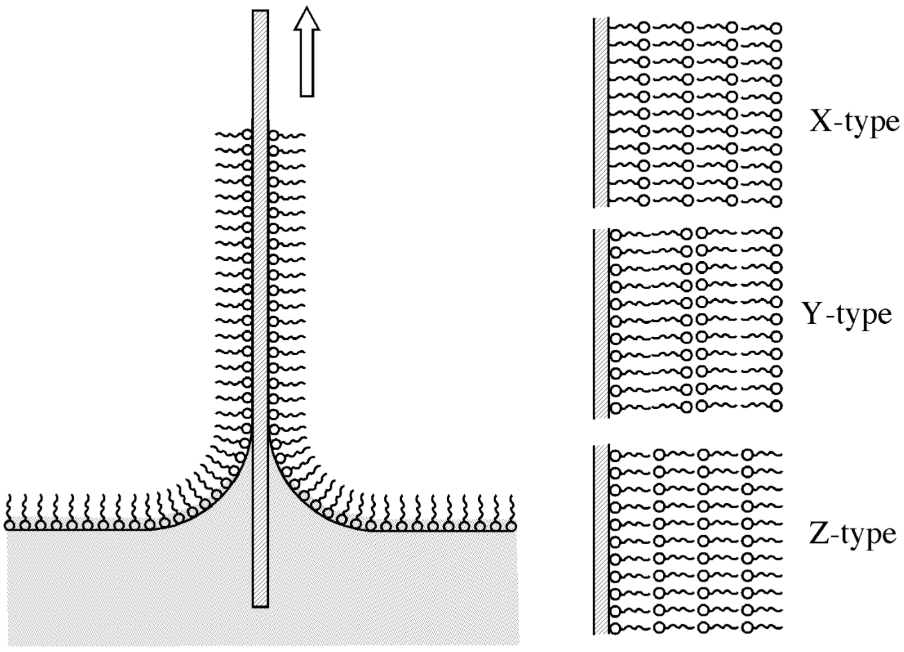

Fig. 3-45: The Langmuir-Blodgett technique. Different types of multiple layers may be produced by successive immersion and emersion of the plate.

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[104] Möbius, D., Ed., **Langmuir-Blodgett Films 3**, Vols. 1 and 2, Elsevier, London, 1988.

[105] Peng, J. B., Barnes, G. T., and Gentle, I. R., *Adv. Colloid Interface Sci.*, **91**, 163 (2001).

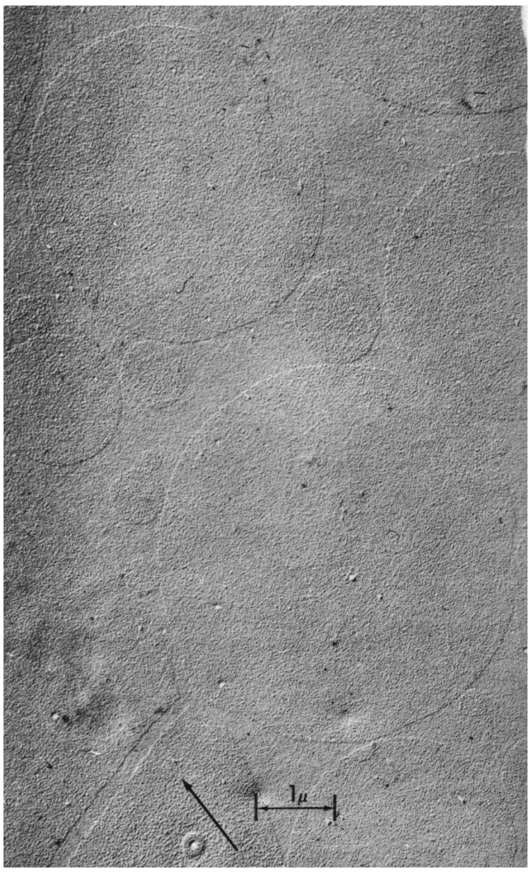

Fig. 3-46: Circular islands of condensed phase, one monolayer thick, in a sea of the uncondensed monolayer phase. Electron micrograph of a Langmuir-Blodgett monolayer of stearic acid at 10 mN/m, originally spread on water. From [Ries, H. E., Jr., and Kimball, W. A., *Nature*, **181**, 901 (1958).]

5. *Transport properties of monolayers*

One of the early applications of Langmuir monolayers was to the suppression of evaporation.[106] Close-packed monolayers of hexadecanol or mixtures of hexadecanol and octadecanol have produced as much as a 90% reduction in the rate of water evaporation in the laboratory and as high as 50% in the field. While a number of practical problems must be overcome, such as the need for continuing repair of damage caused by wind and wave action, the use of these materials is seen as a viable strategy for water conservation. The reduction in evaporation rate is attributed to the sieving effect of the film, *i.e.*, the resistance of the close-packed hydrocarbon layer of the surfactant to penetration by water molecules. Thus there was found a direct relationship between the hydrophobic chain length and the evaporation resistance. Anything leading to a more open structure, such as branching, double bonds or halogen substitution in the chains, destroys the evaporation resistance. A breakthrough in laboratory studies of the phenomenon occurred when it was realized that certain compounds (in particular benzene) used as spreading solvents were retained in the films to a sufficient extent to produce "holes" that allowed for escape of evaporating water.

The intrinsic surface rheology of monolayers may be envisioned in terms of surface constitutive equations relating bending, dilational and shear

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[106] La Mer, V. K. (Ed.), **Retardation of Evaporation by Monolayers**, Academic Press, New York, 1962.

deformations of the surface to the stresses that induce them. Dilational properties, such as surface dilational viscosity and elasticity, are difficult to separate from the effects of surface compositional changes that inevitably accompany such dilations (or contractions) leading to Gibbs elasticity. Analysis of both transverse and compressional waves produced in Langmuir monolayers, however, has yielded values for their complex surface moduli.[107] The simplest surface rheological parameter to envision is the surface viscosity, μ_s, which may be defined for a one-dimensional surface shear using a two-dimensional form of Newton's Law of viscosity:

$$\tau_{yx}^{\sigma} = -\mu_s \frac{dv_x^{\sigma}}{dy}, \qquad (3.159)$$

where x and y are coordinates drawn in the surface, v_x^{σ} is the velocity in the surface in the x-direction (a function of y), and τ_{yx}^{σ} is the tangential force per unit length on a line in the surface perpendicular to the y-axis. It is evident that the units of μ_s will be mass/time (compared with bulk viscosity units of mass/length·time). Attempts to measure the surface viscosity are generally confounded with the need to separate out the effect of the underlying subphase, to which the monolayer is attached by virtue of the hydrodynamic no-slip condition. A successful device, however, is the deep channel viscometer of Burton and Mannheimer,[108] in which an annular surface is produced by dipping a pair of concentric circular cylindrical surfaces into a circular dish that is rotated while the annular walls are held stationary. A parabolic flow is established in the channel, as shown in Fig. 3-47. The measurement consists of tracking the circuit time for a small Teflon particle deposited at the center of the channel. A slight concave-upward shape to the meniscus guarantees that the particle stays in the center. The circuit time measured when a monolayer is present is compared to that obtained when the surface is clean, and the ratio permits deduction of the surface viscosity. Values obtained for close-packed monolayers are in the range of 10^{-3}–1

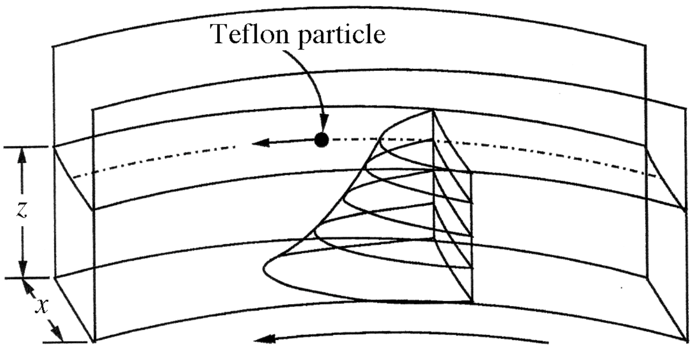

Fig. 3-47: Flow produced in the Burton-Mannheimer deep channel surface viscometer.

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[107] Lucassen, J., and van den Tempel, M., *Adv. Colloid Interface Sci.*, **41**, 491 (1972).

[108] Burton, R. A., and Mannheimer, R. J., **Adv. Chem. Ser. 3**, p. 315, 1967.

surface Poise (g/s). To obtain the same result with a bulk layer of thickness ≈ 1 nm (typical for a surfactant monolayer) would require a viscosity of 10^4–10^7 Poise, approximately the viscosity of butter at room temperature.

Surface diffusion in monolayers has been measured using radioactive tracers.[109] The surface of a Langmuir trough was divided by a flexible Teflon thread into two parts, one supporting a monolayer of myristic acid, and the other a monolayer of the same compound, but containing a proportion of ^{14}C-tagged material. The surface pressure on the pure monolayer side was adjusted until the disposition of the flexible dividing thread became slightly S-shaped, indicating that it was the same on both sides. The thread was then removed, allowing surface inter-diffusion. The time evolution of the surface concentration profile of the tagged surfactant was monitored with a Geiger-Mueller tube, and the results analyzed using a two-dimensional form of Fick's Law modified to account for dissolution and diffusion in the underlying bulk phase, *viz.*,

$$\frac{\partial\Gamma}{\partial t} = D_s\frac{\partial^2\Gamma}{\partial x^2} - k_{-1}\Gamma + k_1(hC), \qquad (3.160)$$

where D_s is the surface diffusivity, k_1 and k_{-1} are the rate constants for adsorption and desorption of the surfactant, h is the depth of the liquid and C is the bulk concentration of surfactant. Independent measurements provided values for k_1 and k_{-1}, and the above equation was solved simultaneously with the corresponding equation for bulk transport. Values for the surface diffusivity in the intermediate surface phase state were found comparable to those for bulk liquids, but in the liquid-expanded state, about an order of magnitude larger.

L. The thermodynamics of fluid-solid interfacial systems revisited

1. *The concept of interfacial energy and its measurement in fluid-solid systems*

It is useful first to attempt to define an appropriate surface or interfacial energy to be associated with a given interfacial system for purposes of comparing different systems to one another and for formulating expressions for the driving forces for various processes involving interfacial systems. Thus the definition and experimental determination of the interfacial energy of various interfacial systems is one of the major goals of the thermodynamic analysis of such systems. It is evident that more than one "interfacial energy" may be defined. First, it is generally assumed that the

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[109] Sakata, E. K., and Berg, J. C., *Ind. & Eng. Chem. Fund.*, **8**, 570 (1969); Chung, S. T., and Berg, J. C., *J. Kor. Chem. Eng.*, **10**, 189, 231 (1972).

terminology refers to interfacial *free* energy, as opposed to interfacial internal energy or enthalpy. One measure of interfacial energy, particularly relevant to capillary systems, is the boundary tension, σ, defining the Helmholtz free energy change associated with unit interfacial area extension under conditions of constant temperature and total volume, and internal equilibrium. For capillary systems, the boundary tension is readily measured, but the "boundary tensions" of solid-fluid interfaces are not so easily accessible by direct measurement. It is important first to recognize that σ is a surface free energy *derivative* rather than the surface energy itself. A surface free energy (per unit area) may be defined with reference to the Gibbs dividing surface as a surface excess quantity, *viz.*

$$\left(\frac{F^\sigma}{A}\right) \equiv f^\sigma = \frac{1}{A}\left[F - F' - F''\right]. \tag{3.161}$$

The above expression can be given for an arbitrary location of the dividing surface in terms of the component adsorptions and chemical potentials, *viz.*[110]:

$$f^\sigma = \sigma + \sum_i \Gamma_i \mu_i . \tag{3.162}$$

f^σ is clearly a property of the dividing surface, but if it is computed for the dividing surface location such that the adsorption of the solvent 1 is zero, one obtains the *relative* surface free energy:

$$f_1^\sigma = \sigma_0^1 + \sum_{i=2} \Gamma_{i,1} \mu_i , \tag{3.163}$$

which is independent of dividing surface location, but of course dependent on the standard state values chosen for evaluating the component chemical potentials. It is clear that the relative surface free energy is equal to the boundary tension for a pure-solvent (component 1) system or for a system in which solute adsorption is zero, designated as σ_0^1, but not otherwise. If the component standard states are chosen appropriately, one may identify f_1^σ with σ, so that for capillary systems, the interfacial free energy is identifiable with the measurable boundary tension. The same identification can be made for fluid-solid systems, but determination of the "interfacial tension" for fluid-solid interfacial systems is more challenging, as discussed below.

In examining the various approaches to determining fluid-solid interfacial energies, it is first assumed that the system is immiscible, and it is useful to distinguish three types of fluid-solid interfacial systems:

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[110] Defay, R., Prigogine, I., Bellemans, A., and Everett, D. H., **Surface Tension and Adsorption**, p. 288, Longmans, London, 1966.

1) *Pristine* surface systems refer to surfaces formed and kept *in vacuo* (or if the solid has a finite volatility, in contact with the equilibrium vapor). The surface energy for pristine systems is designated as:

$$\left(f^{\sigma}\right)_{\text{prist}} = \sigma_0. \tag{3.164}$$

2) *Clean* surface systems are those in which the surface is formed and kept in a pure "solvent medium", which may be a pure gas or a pure liquid, designated as component 1. One may distinguish two types of "clean" surfaces, *viz.* "pure" and "modified" surfaces. In the case of pure clean systems, component 1 is capable of only physical interaction (*i.e.*, physical adsorption) with the solid. The surface energy for a pure clean system in the presence of fluid 1 is designated as $\sigma_0{}^1$, and is related to the pristine surface energy by

$$\left(f^{\sigma}\right)_{\text{clean}} = \sigma_0^1 = \sigma_0 - \pi_{\text{eq}}^1, \tag{3.165}$$

where π_{eq}^1 is the "equilibrium spreading pressure" of pure liquid 1 physisorbed on the solid surface. It may be obtained by integrating the gas-phase adsorption isotherm for the physical adsorption of component 1 from zero to its saturation concentration (or partial pressure), in accord with the Gibbs Adsorption Equation, *i.e.*,

$$\pi_{\text{eq}}^1 = \int_0^{C_1^{\text{sat}}} \Gamma_1(C_1')d\ln C_1', \ \text{(or} \int_0^{p_1^{\text{sat}}} \Gamma_1(p_1')d\ln p_1'). \tag{3.166}$$

In the case of modified clean surface systems, some of component 1 is capable of *chemisorbing* to the solid surface, changing its surface chemistry and hence energy. Most high-energy surfaces sustain such chemisorption. For example, most metal surfaces chemisorb oxygen to form an oxide layer, and most mineral oxide surfaces chemisorb water to form a layer of hydroxyl groups. If the pristine surface is modified by chemisorption either from the adjoining fluid phase 1 (or from some previous contact with a chemisorbing component), one may write:

$$\left(f^{\sigma}\right)_{\text{mod. clean}} = \sigma_0^1 = \sigma_0^{\text{mod}} - \pi_{\text{eq}}^1 = (\sigma_0 - \pi_{\text{chem}}) - \pi_{\text{eq}}^1, \tag{3.167}$$

where $\sigma_0{}^{\text{mod}}$ is the energy of the surface modified by chemisorption, and π_{chem} is the surface energy reduction caused by the chemisorption. This reduction is often a significant fraction of the original pristine surface energy. The modified clean surface is then capable of sustaining subsequent physical adsorption of component 1, as indicated above.

3) Finally, *practical* surface systems refer to the case where the solid is or has been in contact with "practical," *i.e.*, dirty, multicomponent fluid environments such as gas mixtures or solutions containing physically adsorbable components. The surface free energy for practical surface

systems in which the fluid-phase portion consists of a diluent gas or solvent component 1 and one or more adsorbable components is given by:

$$\left(f^{\sigma}\right)_{\text{pract}} \equiv \sigma_{\text{pract}} = \sigma_0^1 - \pi = \sigma_0^1 - \sum_{i=2} \int_0^{C_i} \Gamma_{i,1} \mathrm{d}\ln C_i', \tag{3.168}$$

where π represents the surface pressure resulting from the combined adsorption of all of the solute species.

Pristine surface energies can be measured if fresh solid surface can be created *in vacuo* without surface stretching. This has been accomplished in two ways, as pictured schematically Fig. 3-48. The first, shown in Fig. 3-48(a), is that of cleaving a brittle solid and measuring the total reversible work required to open a unit area of the crack. Subtracting from this the elastic strain energy yields the energy involved in creating new surface. The pristine surface energy is given by:

$$\sigma_0 = \frac{1}{2}\left[\frac{\text{total work}}{\text{crack area}} - \frac{\text{strain energy}}{\text{crack area}}\right]. \tag{3.169}$$

This method has been applied to ionic and covalent crystalline materials, particularly at cryogenic temperatures at which any ductility in the solid specimen is frozen out. It has also been applied to so-called van der Waals solids under these conditions. These are solids formed of simple molecules held together only by van der Waals forces. For ductile materials, like metals and polymers, a second technique, pictured in Fig. 3-48(b), and known as the "zero-creep" method has been developed. A series of wires of fixed radius r are hung with a range of different weights and brought to a temperature just below the melting point. Those with weights too large will become distended, while those with the smallest weights will contract

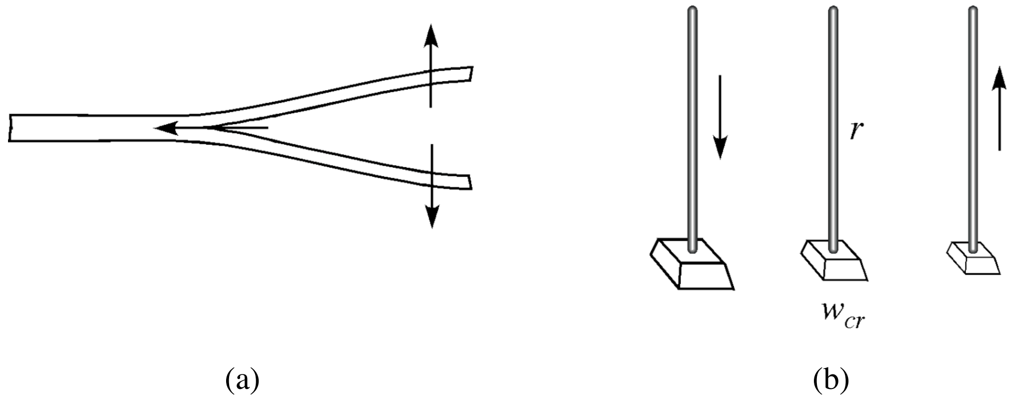

Fig. 3-48: Methods for measuring the surface free energy of solids. (a) The fracture method for brittle solids. (b) The zero-creep method for ductile solids.

upward due to the effect of surface tension forces. For a particular critical weight, w_{cr}, there will be zero creep, and this is used to determine the surface tension in accord with[111]:

$$\sigma_0 = \frac{w_{\mathrm{cr}}}{\pi r}. \tag{3.170}$$

Since at "zero creep" one is not stretching the surface, it is the surface free energy that is being measured rather than the "stretching tension" discussed earlier. Clean surface energies may also be obtained by the cleavage and zero-creep methods when the processes are carried out in either a pure gas or liquid. Some qualitative ranges of results of measurements of this type are summarized in Table 3-9. It is reassuring that the numbers for the pristine surfaces are in reasonably good accord with theoretical calculations for these surface energies.[112] Such calculations are easier to carry out than the experiments. The large differences in surface energy between those formed *in vacuo* and those formed in air are due to surface modification by chemisorption, particularly of oxygen, onto the surface and only negligibly by subsequent physical adsorption. Another method for the determination of a clean surface energy σ_{SL} of a sparingly soluble solid S in a liquid L is afforded by the Kelvin effect. If the solubility in the form of particles of known radius a is compared with its solubility in macroscopic form, the Kelvin equation (analogous to that for vapor pressure in Chap. 2, and discussed further with regard to the solubility of solids in Chap. 5) yields:

Table 3-9: Comparison of ranges of surface energy values for "pristine" surfaces (formed and kept *in vacuo*) and "clean" surfaces (formed and kept in air) for various types of materials.

Solid type	Surface energy range (mJ/m^2)	
	In vacuo (σ_0)	In air (σ_0^1)
Van der Waals	20-60	20-60
Polymers	20-60	20-60
Ionic crystals	100-1000	60-300
Metals	500-2000	60-300
Covalent crystals	3000-9000	300-600

$$\sigma_{\mathrm{SL}} = \frac{aRT}{2v_{\mathrm{S}}} \ln \frac{(C_{\mathrm{S}})_a^{\mathrm{sat}}}{(C_{\mathrm{S}})_\infty^{\mathrm{sat}}}, \tag{3.171}$$

where a is the radius of the solid particle and v_{s} is its molar volume.

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[111] Tabor, D., **Gases, Liquids and Solids and other States of Matter**, 3rd Ed., p. 418, Cambridge Univ. Press, Cambridge, UK, 1996.

[112] Tabor, D., *ibid.*, p. 164.

Calorimetric measurement of the net heat absorbed when particles initially in gas G are dissolved into liquid L yield the difference between the actual heat of solution and the heat evolved due to the destruction of the SG interface. If a mass *m* of solid of specific area Σ is dissolved, the measured amount of heat absorbed is given by

$$Q_{\text{net}} = m\hat{\lambda}_{\text{soln}} - m\Sigma u_{\text{SG}}, \tag{3.172}$$

where $\hat{\lambda}_{\text{soln}}$ is the heat of solution per unit mass, and u_{SG} is the internal energy (per unit area) of the solid-gas interface. It may be related to the free energy by recalling that for an isothermal, constant-volume process

$$u_{\text{SL}} \equiv \left(\frac{\partial U_{\text{SL}}}{\partial A_{\text{SL}}}\right)_{\text{T,V}} = \left[\sigma_{\text{SL}} - T\left(\frac{d\sigma_{\text{SL}}}{dT}\right)\right], \text{ so that} \tag{3.173}$$

$$Q_{\text{net}} = m\hat{\lambda}_{\text{soln}} - m\Sigma \mathrm{u}_{\text{SG}} = m\hat{\lambda}_{\text{soln}} - m\Sigma\left[\sigma_{\text{SL}} - T\left(\frac{d\sigma_{\text{SL}}}{dT}\right)\right]. \tag{3.174}$$

Calorimetric measurement of the heat evolved when an immiscible solid is immersed in a liquid yields information on the difference between the energy of the SG interface destroyed and the SL interface created:

$$\frac{Q_{\text{imm}}}{m\Sigma} = u_{\text{imm}} = u_{\text{SL}} - u_{\text{SG}} = (\sigma_{\text{SL}} - \sigma_{\text{SG}}) - T\frac{d(\sigma_{\text{SL}} - \sigma_{\text{SG}})}{dT}. \tag{3.175}$$

The above are statements of the Gibbs-Helmholtz Law relating energy quantities to the corresponding free energies and their temperature derivatives.

The other common methods for determining surface or interfacial energies are based on wetting, adhesion or wicking measurements, or vapor adsorption measurements, as discussed in Chap. 4. They generally yield information concerning "clean" interfaces (if pure fluids are used and care is taken) or "practical" interfaces.

2. Adsorption of non-polymeric molecules at the solid-liquid interface

Adsorption at the solid-liquid interface differs in fundamental ways from adsorption at a fluid-fluid or a gas-solid interface, and its description is frequently effected in different ways.[113-114] As discussed earlier in the context of describing the direct measurability of such adsorption, it is usually reasonable to assume an *immiscible interfacial system*, *i.e.*, that there is no mutual solubility between the solid substrate and the components of the

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[113] Parfitt, G.D., and Rochester, C.H. (Eds.), **Adsorption from Solution at the Solid/Liquid Interface**, Academic Press, London (1983).

[114] Kipling, J. J., **Adsorption from Solutions of Non-Electrolytes**, Academic Press, London, 1965.

liquid solution. For such systems, the dividing surface location is not ambiguous and may be taken as *precisely* at the outer boundary of the solid, *i.e.*, to separate the atoms of the solid lattice from the liquid. The dividing surface located in this way leads to finite values for both Γ_1 and Γ_2 for a binary solution of solute 2 (*adsorbate*) in solvent 1, and the total occupancy of the surface is constant. For example, if the area occupied by one mole of solute is n times that occupied by a mole of solvent molecules, one would have:

$$\Gamma_2 + n\Gamma_1 = \Gamma_\infty, \tag{3.176}$$

where Γ_∞ is the total number of (moles of) "sites"/area for adsorption on the adsorbent surface.

The relative adsorption is computed as

$$\Gamma_{2,1} = \Gamma_2 - \Gamma_1\left(\frac{C_2}{C_1}\right), \tag{3.177}$$

and if interest is limited to sufficiently dilute solutions (as is often the case), the relative adsorption reduces to Γ_2. It is clear that in general adsorption at the solid-liquid interface is *competitive* between the solute and solvent for the available adsorbent surface area. (This situation contrasts with the case of adsorption at the gas-solid interface, where adsorbate molecules are assumed to occupy otherwise empty space at the surface.) The competition involved in such adsorption is more complex than that of the solute and solvent for the adsorbent area, as suggested by Fig. 3-49. The adsorbent and solvent may also be thought of as competing for the solute, and the solute and the adsorbent are competing for solvent. The nature of the adsorption that occurs depends on the result of this three-way competition. Considering adsorption is the process whereby a molecule of adsorbate (A) replaces a molecule (or n molecules) of solvent (B) from the adsorbent surface (S), it may be represented in terms of the pseudo chemical reaction:

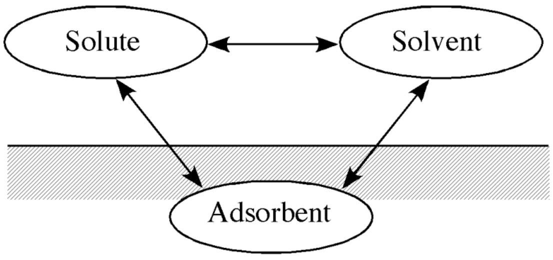
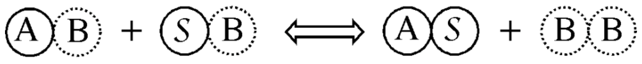


Fig. 3-49: Competition in adsorption at the solid-liquid interface.



$$\text{AB} + \text{SB} \Longleftrightarrow \text{AS} + \text{BB} \tag{3.178}$$

The energy change associated with the process is

$$\Delta\Phi_{\text{ads}} = \Phi_{\text{AS}} + \Phi_{\text{BB}} - \Phi_{\text{AB}} - \Phi_{\text{SB}} \propto -B_{\text{AS}} - B_{\text{BB}} + B_{\text{AB}} + B_{\text{SB}}, \tag{3.179}$$

where B_{AS}, *etc.* refer to the intermolecular interaction coefficients, *cf.* Eq. (2.7). If the interactions are of the dispersion (apolar) type only, these are proportional to the products of the molecular polarizabilities, so that

$$\Delta\Phi_{ads} \propto -\alpha_A\alpha_S - \alpha_B\alpha_B + \alpha_A\alpha_B + \alpha_S\alpha_B = (\alpha_A - \alpha_B)(\alpha_B - \alpha_S). \qquad (3.180)$$

Thus if the relative values of the molecular polarizabilities are such that either

$$\alpha_B < \alpha_A < \alpha_S \text{ or } \alpha_B > \alpha_A > \alpha_S, \qquad (3.181)$$

i.e., the polarizability of the solute A is intermediate to that of the solvent B and the substrate S, $\Delta\Phi_{ads}$ is guaranteed to be negative, and adsorption is thermodynamically favored. Since molecular polarizability is directly proportional to dielectric constant ε (and to the square of the refractive index) the above leads to the useful rule of thumb that adsorption of a solute should occur when the dielectric constant (or the refractive index) of the solute is intermediate to that of the solvent and the adsorbent, an axiom known in the older literature as *Rehbinder's Rule*. The rule applies only when van der Waals forces are dominant, and definitely not when electrostatic effects or acid-base interactions (*e.g.*, H-bonding) are at play. Thus, for example, an acidic solute (like chloroform) in a neutral solvent (like heptane) will adsorb strongly onto a basic adsorbent surface (like calcium carbonate), but not so strongly from a basic solvent like benzene.

If one examines adsorption from a binary solution of miscible components over the whole composition range, as shown in Fig. 3-50, three types of isotherms are observed.[115] In Type I, the solute is positively adsorbed over the whole composition range, while in Type II, the solvent is favored (the solute is negatively adsorbed). In Type III, the adsorption changes sign over the composition range. Another type of isotherm, as shown in Fig. 3-51, may be observed for the case in which the adsorbate is a liquid with finite solubility in the solvent. The adsorption often increases sharply as the solubility limit is approached. Another effect may give rise to such behavior when the adsorbent surface is porous. In this case, the steep

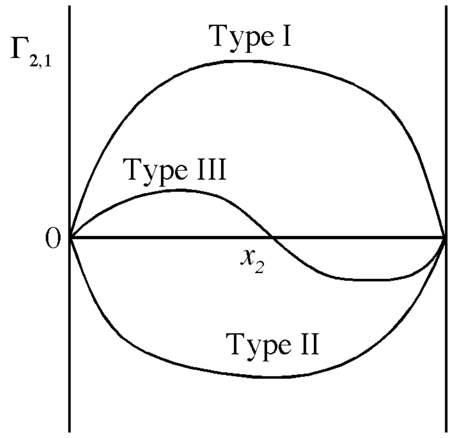


Fig. 3-50: Types of adsorption at the solid-liquid interface.

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[115] Voyutsky, S., **Colloid Chemistry**, p. 156, Mir Publ., Moscow, 1978.

increase in apparent adsorption as the solubility limit is approached may be capillary condensation of the adsorbate liquid into the pores of the adsorbent, as described in Chap. 2.

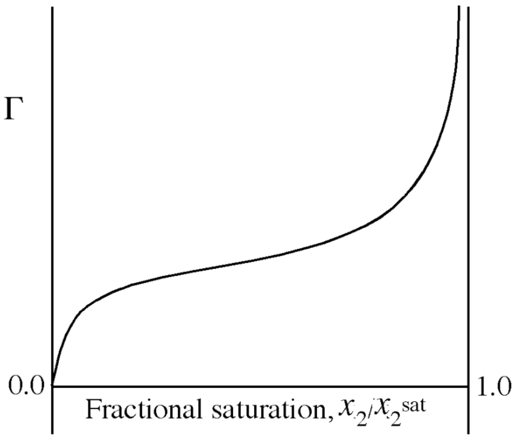

Fig. 3-51: S-shaped adsorption isotherm characteristic of adsorption of a partially miscible adsorbate onto a finely porous adsorbent.

The situations of greatest practical interest are those of positive adsorption from dilute solutions, and are be the focus of the rest of this section. For such cases, particularly with reference to aqueous surfactant solutions, it is useful to classify adsorption at the solid-liquid interface in another way, *viz.*, in terms of the two general mechanisms responsible for it. When adsorption occurs *primarily* because the adsorbing solute (or part of its functionality) would like to escape the solvent (such as a hydrocarbon surfactant seeking to escape water), the driving force is the "hydrophobic effect," and adsorption may be referred to as *amphipathic*. The mechanism of amphipathic adsorption is pictured in Fig. 3-52(a). The hydrophobic (usually hydrocarbon) tails of the surfactant in solution are encased in ice-like water structures. Upon adsorption, these structured water sheaths are released (with the attendant entropy increase), and the hydrophobic moieties of the solute are oriented toward the adsorbent surface. The hydrophobic effect is the same driving force that leads to adsorption of surfactants at the water/air interface and to the formation of micelles and other fluid microstructures in aqueous media, as discussed earlier.[116] On the other hand,

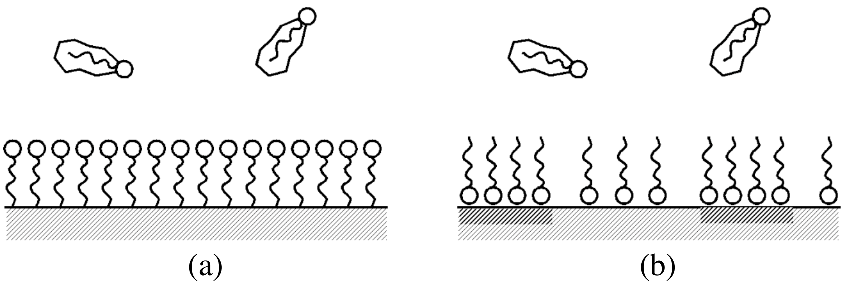

Fig. 3-52: Mechanisms of surfactant adsorption from aqueous solutions. (a) Amphipathic adsorption, (b) amphiphilic adsorption.

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[116] Tanford, C., **The Hydrophobic Effect: Formation of Micelles and Biological Membranes**, 2nd Ed., Krieger Publ., Malabar, FL, 1991.

if adsorption occurs primarily because of an attraction between the solute and the adsorbent surface, it may be referred to as *amphiphilic*. Its mechanism is suggested in Fig. 3-52(b). These specific attractions may be, for example, electrostatic or may be the result of acid-base interactions (including hydrogen bonding) between the head groups of the solute and functional groups on the solid adsorbent surface. These may be distributed unevenly (often characterized in terms of adsorbent surface energetic heterogeneity) and to monolayer adsorption of uneven density. The orientation of the adsorbate is "head down," exposing the hydrophobic groups to the solution. Adsorption of this type should be regarded as a type of *chemisorption*. Both mechanisms are described in greater detail below, and some examples are sketched in Fig. 3-53.

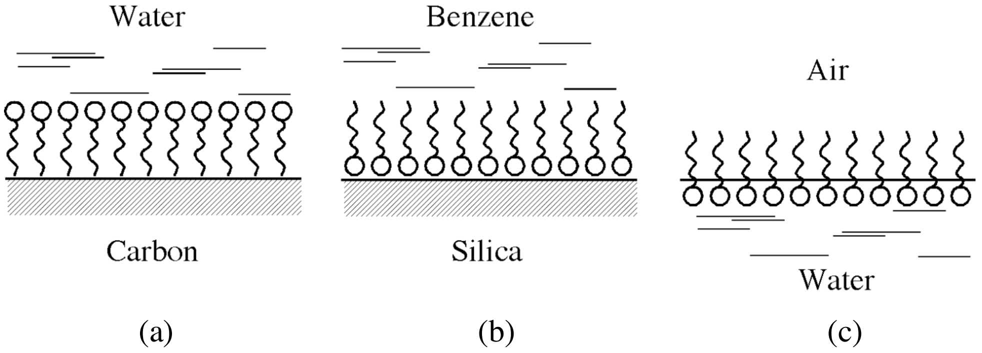


Fig. 3-53: Examples of amphipathic adsorption (a) and (c), and amphiphilic adsorption (b).

Amphipathic adsorption is often well described by the Langmuir adsorption isotherm,

$$\Gamma = \frac{\Gamma_\infty C}{a + C}, \tag{3.182}$$

as shown in Fig. 3-54, which also shows the coordinates used to render such results in the form of a straight line (a "Lineweaver-Burke plot"):

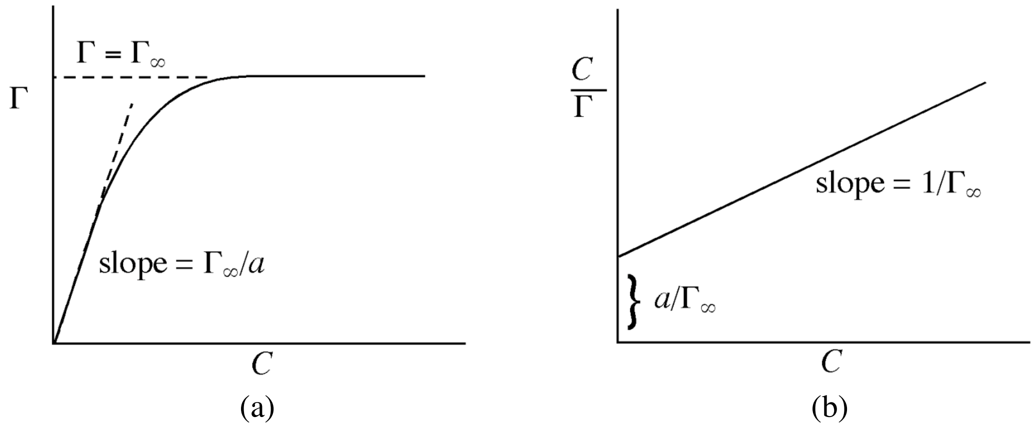


Fig. 3-54: (a) Langmuir adsorption isotherm, characteristic of amphipathic adsorption; (b) Lineweaver-Burke plot.

$$\frac{C}{\Gamma} = \left(\frac{a}{\Gamma_\infty}\right) + \left(\frac{1}{\Gamma_\infty}\right)C, \tag{3.183}$$

for purposes of obtaining the constants from the least squares slope and intercept. Langmuir behavior shows linear adsorption at very low solute concentrations and saturation (assumed to correspond to a close-packed monolayer) as concentration is increased. Once a saturated monolayer is formed, there is little tendency to form a second layer even when solute concentration is increased further. The initial linear slope of the Langmuir isotherm may be interpreted in terms of the standard free energy change of adsorption as follows. For simplicity, assume solute (A) and solvent (B) molecules occupy approximately the same area on the surface. The adsorption process may then be envisioned as a "chemical reaction," in which an A molecule displaces a B molecule from the surface:

$$\mathrm{A}^{\mathrm{bulk}} + \mathrm{B}^{\sigma} \xleftrightarrow{K_{\mathrm{ads}}} \mathrm{A}^{\sigma} + \mathrm{B}^{\mathrm{bulk}}\ . \tag{3.184}$$

Then at equilibrium:

$$K_{\mathrm{ads}} = \frac{a_{\mathrm{A}^\sigma} a_{\mathrm{B}^{\mathrm{bulk}}}}{a_{\mathrm{A}^{\mathrm{bulk}}} a_{\mathrm{B}^\sigma}} = \frac{\gamma_{\mathrm{A}}^{\sigma}\Gamma_{\mathrm{A}}\gamma_{\mathrm{B}}C_{\mathrm{B}}}{\gamma_{\mathrm{A}}C_{\mathrm{A}}\gamma_{\mathrm{B}}^{\sigma}\Gamma_{\mathrm{B}}}, \tag{3.185}$$

where a_i's are species activities and γ_i's activity coefficients. Noting that $\Gamma_A + \Gamma_B = \Gamma_\infty$, and assuming that the system is sufficiently dilute that all the γ's ≈ 1, and $C_B \approx C_B^0$, the pure solvent concentration, [=] mole/m^3:

$$K_{\mathrm{ads}} = \frac{\Gamma_{\mathrm{A}}C_{\mathrm{B}}^{0}}{C_{\mathrm{A}}(\Gamma_\infty - \Gamma_{\mathrm{A}})}, \text{ or} \tag{3.186}$$

$$\Gamma_{\mathrm{A}} = \frac{K_{\mathrm{ads}}\Gamma_\infty C_{\mathrm{A}}}{C_{\mathrm{B}}^{0} + K_{\mathrm{ads}}C_{\mathrm{A}}}, \text{ the Langmuir isotherm.} \tag{3.187}$$

The initial slope ($C_A \to 0$) of the isotherm is:

$$\left(\frac{\Gamma_{\mathrm{A}}}{C_{\mathrm{A}}}\right)_{C_{\mathrm{A}}\to 0} = \left(\frac{\Gamma_\infty}{C_{\mathrm{B}}^{0}}\right)K_{\mathrm{ads}} = \left(\frac{\Gamma_\infty}{C_{\mathrm{B}}^{0}}\right)\exp\left(-\frac{\Delta G_{\mathrm{ads}}^{\Theta}}{RT}\right), \tag{3.188}$$

where $\Delta G_{\mathrm{ads}}^{\Theta}$ is the standard free energy of adsorption. Thus the steeper the initial slope of the isotherm, the stronger the adsorption. The standard states are conveniently chosen as

for B in solution: pure B, at C_{B}^{0} [=] mole/m^3

for adsorbed B: $\Gamma_B = \Gamma_\infty$ [=] mole/m^2

for A in solution: (Henry's Law solution at $C_{\mathrm{A}}^{\Theta} = 1$ mole/m^3)

for adsorbed A: (Henry's Law surface solution at $\Gamma_{\mathrm{A}}^{\Theta} = 1$ mole/m^2)

Amphipathic adsorption is stronger (*i.e.*, the initial slope of the isotherm is steeper) in direct proportion to the hydrocarbon chain length in aliphatic surfactants. Such adsorption thus obeys Traube's Rule, as exemplified in the data of Fig. 3-55 for a homologous series of carboxylic acids onto carbon. For a constant extent of adsorption, Γ, the required bulk concentration decreases by a constant factor (usually between 2 and 3) for each -CH_2- group added to the hydrophobic chain. When the solute may be regarded as a surfactant, amphipathic adsorption is generally expected for nonionics and for ionic surfactants of charge the same as that of the substrate surface. Anionics are usually amphipathically adsorbed, since most solid surfaces in contact with water bear a negative charge. If micelles form, the *CMC* is usually a concentration slightly less than that corresponding to the knee of the isotherm. For surfactants, the isotherm observed may sometimes exhibit a second (or even a third) plateau, as pictured in Fig. 3-56. This behavior is attributed to orientational effects. At low concentrations, the adsorbate molecules are believed to be lying flat on the surface, but as

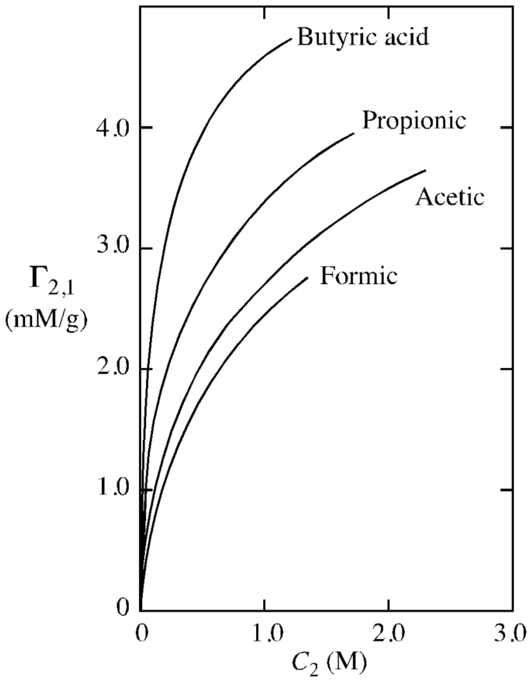


Fig. 3-55: Adsorption of fatty acids onto carbon from aqueous solution, illustrating the applicability of Traube's Rule. For a constant value of Γ, $C(n)/C(n+1) = 2.....3$. Data from [Traube, I., *Annals*, **265**, 27 (1891).]

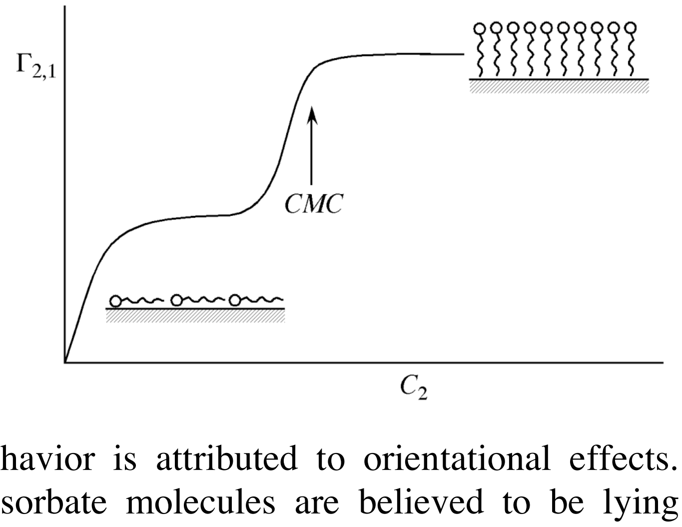


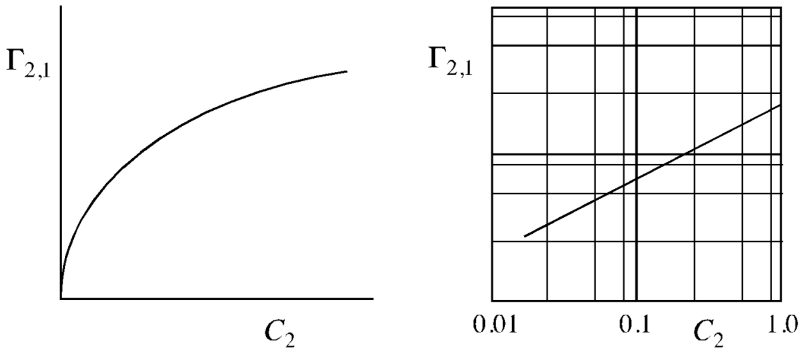
Fig. 3-56: Stepwise isotherm due to adsorbate re-orientation.

concentration increases, and adsorbate-adsorbate interactions arise, the molecules become more nearly vertically oriented.

Amphiphilic adsorption is often described by a Freundlich isotherm,

$$\Gamma_2 = kC_2^{1/n}, \tag{3.189}$$

where k and n are empirical constants, as shown in Fig. 3-57. It may be plotted on logarithmic coordinates to yield a straight line, as shown. This isotherm is associated with an energetically heterogeneous adsorbent surface. It is steepest at lowest concentrations, since the most energetic sites are covered first, *etc*. The Freundlich isotherm is reproduced when the surface is modeled as consisting of energetically homogeneous patches of exponentially varying adsorption energy, *i.e.*, $\Delta G^{\Theta}_{\text{ads}}$, and the adsorption to each "patch" is described by a Langmuir isotherm. Frequently a Freundlich-Langmuir behavior is observed as full monolayer coverage is eventually attained. On the other hand, a second adsorbate layer is often formed (by amphipathic adsorption) on top of the first layer, producing a stepped isotherm similar in shape to that shown in Fig. 3-56, but with a different interpretation. Other and more complex adsorption equilibria may also be observed for amphiphilic adsorption as described below.



(a) (b)

Fig. 3-57: (a) Freundlich adsorption isotherm, characteristic of amphiphilic adsorption; (b) log-log plot of Freundlich isotherm.

Amphiphilic adsorption does not obey Traube's Rule, and in some cases, as shown in Fig. 3-58, may seem to reverse it. This shows data for the adsorption of fatty acids onto silica gel from a toluene solution. In this case the higher members of the series are least adsorbed because the solvent competes more successfully for them. It should be mentioned that this type of adsorption series may also sometimes be observed even for amphipathic adsorption, when the adsorbent is very finely porous. In this case it is the fact that the smaller molecules are able to access the finer pores, and hence more surface area, than the larger molecules.

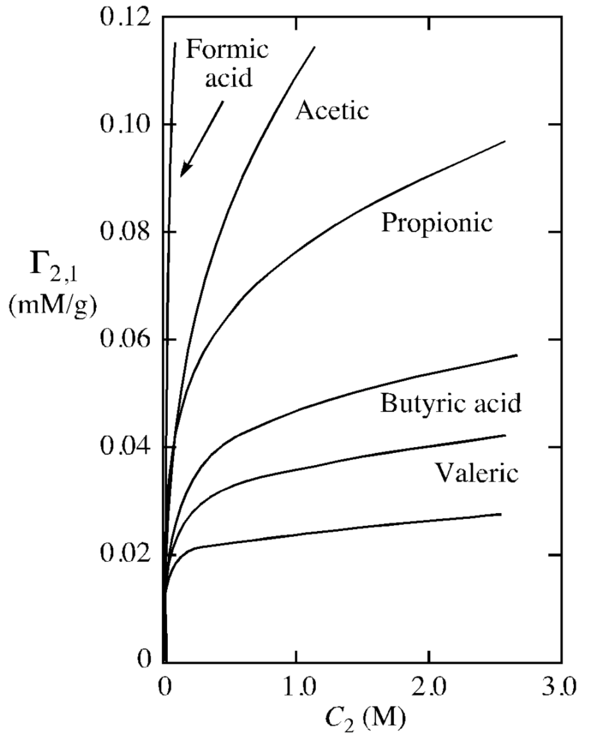


Fig. 3-58: Adsorption of fatty acids onto silica gel from toluene, illustrating what appears to be a "reverse Traube's Rule." Data from [Traube, I., *Annals*, **265**, 27 (1891).]

Amphiphilic adsorption may occur through a variety of mechanisms. Ion pairing and ion exchange are shown in Fig. 3-59. This is the mode of adsorption of cationic surfactants from water onto most solid surfaces (since they are usually negatively charged in contact with water) at low solute concentrations. The adsorption is "head-down" in its orientation and may result in the neutralization (or reversal) of the surface charge. These attributes lead to a number of important applications for cationic surfactants, such as antistats in plastics and textiles, anti-caking agents for powdered or granular materials, flotation agents, boundary lubricants and corrosion inhibitors. All of these applications rely on the adsorption rendering the surface hydrophobic. At increasing bulk concentration, however, as mentioned above, a second layer of adsorption often occurs as shown in Fig. 3-60. This leads eventually back to a hydrophilic surface. The second layer

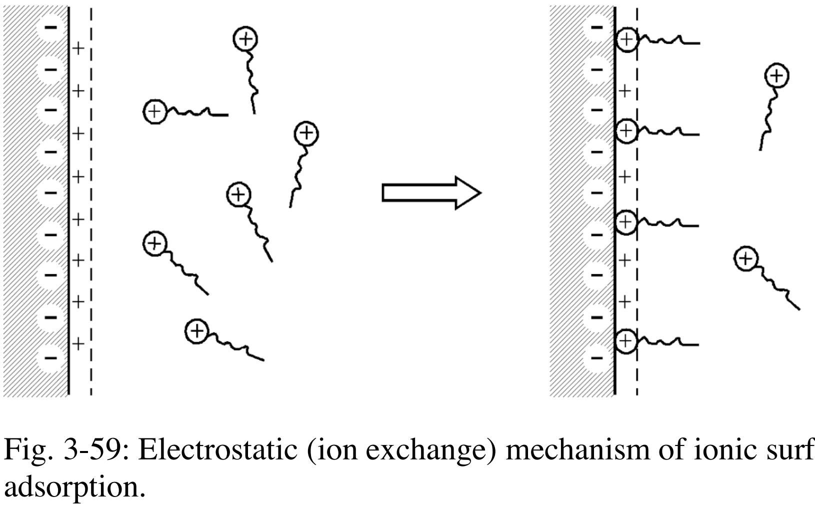


Fig. 3-59: Electrostatic (ion exchange) mechanism of ionic surfactant adsorption.

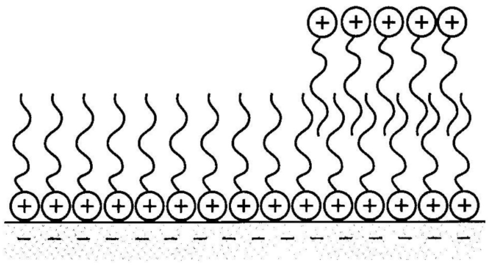


Fig. 3-60: Hemi-micelle formation as second monolayer adsorbs in amphiphilic adsorption.

appears to form in patches, which are sometimes called "hemi-micelles" and may be sites for immobilized solubilization[117] referred to as *adsolubilization.*

Other specific mechanisms for amphiphilic adsorption are of the acid-base type (in either the Brønsted or Lewis senses), as pictured in Fig. 3-61. This is the mode of adsorption of fatty acids onto silica gel from a toluene solution, as shown in Fig. 3-58.

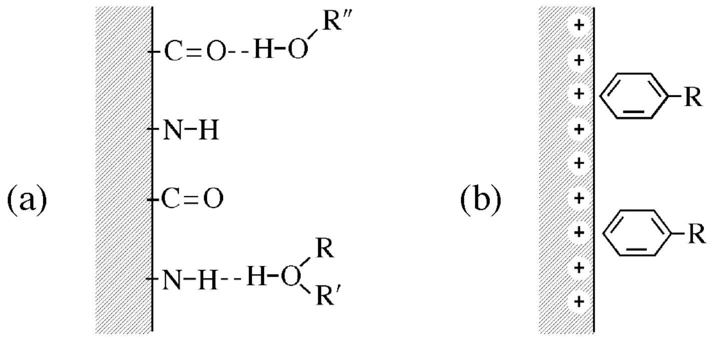


Fig. 3-61: Amphiphilic adsorption by acid-base interactions: (a) hydrogen bonding; (b) polarization of π-electrons.

Another important type of amphiphilic adsorption of surfactants at the solid-liquid interface is that which leads to the formation of "self-assembled monolayers," or SAM's. In fact, all adsorption is a form of self-assembly, but the term SAM refers to highly ordered monolayers that are chemisorbed to the substrate. Their structure resembles that which is attainable through Langmuir-Blodgett (LB) dipping, but they are often more robust than such films. Tri-hydroxy or tri-chloro silane coupling agents (as described in Chap. 4) with long alkane organofunctional groups, chemisorbed to smooth SiO_2 (or other oxide) surfaces provide one example of SAM's. The name has been more commonly associated, however, with adsorbed layers of alkane thiols, $HS(CH_2)_nX$ (with $n \geq 7$) adsorbed to smooth, clean surfaces of various metals, usually gold,[118] but also silver, copper and others ("coinage metals"). The structure is pictured in Fig. 3-62. The sulfur of the thiol coordinates covalently to the metal surface, in accord with

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[117] Sharma, R., Ed., **Surfactant Adsorption and Surface Solubilization**, ACS Symposium Series 615, ACS, Washington DC, 1995.

[118] Bain, C. D., and Whitesides, G. M., *Science*, **240**, 62 (1988).

$$\text{Au} + \text{RSH} = \text{AuSR} + 1/2\,\text{H}_2. \tag{3.190}$$

The -CH_2- chains pack in an all-trans conformation, tilted approximately 30° from the perpendicular to the surface. They are most often prepared by dipping the clean metal surface into an ethanol solution of the desired alkanethiol(s) and allowing a few minutes to a few hours for the chains to anneal into the ordered configuration. The end-group X may be of many different types, or mixtures of types, of functional groups. SAM's thus provide a powerful tool for the study of carefully tailored surface chemistry.

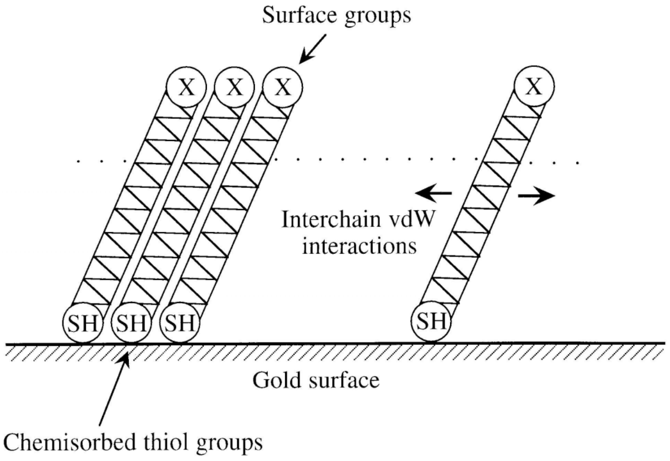

Fig. 3-62: Self-assembled monolayers (SAM's) of long-chain thiols onto a gold surface.

They are well suited to such studies owing not only to their well-ordered and characterizable structure and their ease of preparation, but also to their extraordinary stability. In fact, a terminal =CH_2 group may be functionalized *in situ* under a variety of conditions without disturbing the monolayer. The preparation, properties and experimental characterization of SAM's has been treated in detail by Ulman.[119]

3. *Experimental measurement of small molecule solid-liquid adsorption*

The experimental investigation of adsorption at the solid-liquid interface usually focuses on obtaining the equilibrium adsorption isotherm, and when sufficient solid-liquid interfacial area is available (as is the case when the solid is micro-porous and/or in a finely-divided form), this is conveniently done stoichiometrically by measuring the amount of adsorbate removed (and presumably adsorbed) from a supernatant solution. A variety of analytical techniques may then be used to measure this concentration change. One method for investigating surfactant adsorption from aqueous solutions is that of *soap titration*[120]. A dispersion containing a known amount of dispersoid (with known specific area) is titrated with a "soap

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[119] Ulman, A., **An Introduction to Ultrathin Organic Films: from Langmuir-Blodgett to Self-Assembly**, Academic Press, Boston, 1991;
Ulman, A. (Ed.), **Characterization of Organic Thin Films**, Butterworth-Heinemann, Boston, 1995.

[120] Maron, S. H., *et al.*, *J. Colloid Sci.*, **9**, 89, 104, 263, 382 (1954).

solution," where the "soap" is the desired surfactant adsorbate. The surface tension (or sometimes the conductivity) of the dispersion is monitored during the titration until the *CMC* is reached. A comparison of the amount of soap added to that which would have to be added to an equivalent amount of particle-free solvent yields the amount adsorbed at the *CMC*. Knowledge of the surface tension *vs*. concentration behavior of the solution below the *CMC* and its measurement during the titration permits the amount adsorbed at any bulk concentration to be determined using a material balance. If the adsorbed area-per-molecule is known, and the assumption of a fully close-packed monolayer at the *CMC* is made, the technique may be used as a method for determining the specific area of the particles.

Another convenient technique, especially when the specific area of the solid is not large, is frontal analysis solid-liquid chromatography[121]. Adsorption is measured by noting the "break-through" times for solutions of different concentrations in passing through a chromatographic column packed with the adsorbent. First, the dead volume of the packed column is determined by passing pure solvent (or solvent containing a non-adsorbing tracer) through the column. Then, with solvent being pumped through the system at a steady rate, the inlet is switched from solvent to a solution of known concentration at the same flow rate. With the eventual emergence of the adsorbing solute from the column, a detector monitors the outlet concentration until a new steady-state value (corresponding to adsorption equilibrium) is established. The amount of solute adsorbed may then be computed from a material balance. By repeating the procedure for different inlet concentrations, the adsorption isotherm is built up.

A technique closely related to the above is that of *serum replacement*[122]. The particulate dispersion (adsorbent) is confined to a stirred cylindrical cell, one end of which is bounded, for example, by a Nuclepore® or other appropriate membrane with pore size sufficiently small to retain all the particles. After adsorption equilibrium is established between the solid particles and a known amount of adsorbate-containing solution ("serum"), pure solvent is used to flush the adsorbate from the cell. The concentration of adsorbate is monitored in the effluent stream, and a material balance equating the total adsorbate to that remaining in the cell plus that which has been flushed out at any instant gives the adsorption isotherm.

4. *Adsorption of polymers at the solid-liquid interface*

The adsorption of polymers differs in fundamental ways from the adsorption of lower molecular weight solutes.[123,124] Thermodynamically,

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[121] Sharma, S. C., and Fort, T., Jr., *J. Colloid Interface Sci*., **43**, 36 (1974).

[122] Ahmed, S. M., El-Aasser, M. S., Pauli, G. H., Poehlein, G. W., and Vanderhoff, J. W., *J. Colloid Interface Sci*., **73**, 388 (1980).

[123] Fleer, G. F., and Lyklema, J., "Adsorption of Polymers," in **Adsorption from Solution at the Solid-Liquid Interface**, Parfitt, G. D., and Rochester, C. H., Eds., Academic Press, New

polymer adsorption occurs when the entropic penalty associated with tethering the polymer to the surface and restricting the number of confirmations it can assume is balanced by a favorable (exothermic) enthalpy of sufficient magnitude associated with establishing segment-surface contact. This is often quite low, *i.e.*, of the order of *kT*. Thus most polymers adsorb to most surfaces to some extent, and assume a variety of configurations. Linear polymers adsorb in a series of loops, tails and trains, as shown in Fig. 3-63. “Train segments” correspond to those groups in the polymer that are in direct contact with the surface, while “loops” and “tails” dangle out into the solution. When even a single segment of the polymer is in direct contact with the solid, the entire molecule is considered to be adsorbed. The trains generally provide multiple contacts so that polymeric adsorption is often effectively irreversible upon simple dilution. Polymers *can* be desorbed, however, by use of a competitive lower molecular weight adsorbate that “zippers off” the polymer segments. When polymer adsorption is established by increasing the bulk concentration, the observed isotherm is often of the “high affinity” type shown in Fig. 3-64, wherein up to a certain adsorbed amount, all dissolved polymer will be scavenged from the solution, after which the isotherm forms a pseudo-plateau. The plateau level is generally of the order of a few mg/m^2, corresponding to 2-5 equivalent segment monolayers. The bulk composition is usually expressed in terms of polymer mass concentration or volume fraction. Polymer adsorption increases with decreasing solvent quality and with polymer molecular weight in a poor solvent. In a good solvent, adsorption is low and indifferent to polymer molecular weight. Polymer adsorption is slower than that of non-polymeric adsorbates, and if the polymer is broadly polydisperse, there is a slow re-conformation process that occurs as the segments from the higher molecular weight portions gradually displace those from the lower molecular weight molecules that got there first. Desorption, if it occurs at all, proceeds in the reverse order.

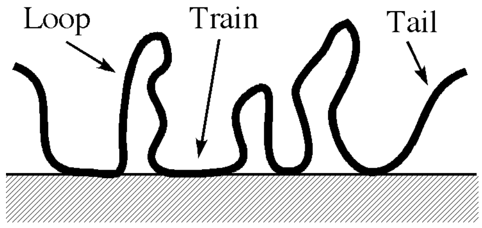

Fig. 3-63: Adsorption of a linear homopolymer to a solid substrate.

For many of the applications in which polymeric adsorption is important (such as steric stabilization of colloids, to be discussed later), one needs to know more than the adsorption isotherm. Structural aspects of the adlayer are also of interest, *e.g.*, the proportion of train segments and the

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York, 1983.

[124] Fleer, G. J., Cohen-Stuart, M., Scheutjens, J. M. H. M., Cosgrove, T., and Vincent, B., **Polymers at Interfaces**, Chapman and Hall, London, 1993.

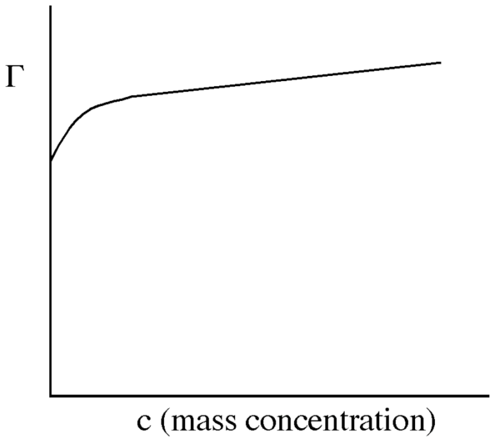

Fig. 3-64: A “high affinity” isotherm, characteristic of polymeric adsorption.

thickness and density of the tails and loops. Of interest in many cases is knowledge of the complete segment density distribution, *i.e.*, the density of segments as a function of distance from the adsorbent surface. Such information may be obtained using small angle neutron scattering (SANS).[125] Many scenarios for adlayer structure are possible, but the most important ones to consider are those of terminally anchored, or grafted, chains and multiply anchored homopolymers or copolymers. For terminally anchored chains at low grafting density, the polymers resemble the Gaussian coils that exist in free solution, with a high segment density near the center dropping to zero density at the edge of the coil. The segment density of the adlayer would rise from a low value at the surface to a maximum at a distance from the surface approximately equal to the radiation of gyration, R_g, of the free coil, and fall off thereafter. As the grafting density is increased, crowding causes the coils to become distended, leading to a more nearly uniform segment density profile. In the extreme case of very high grafting density one obtains a polymer *brush*, consisting entirely of more or less linear tails. Brushes may also be produced by closely spaced side chains on a polymer backbone that adsorbs to the substrate in train segments. Multiply anchored polymers may also produce a fairly uniform segment density, but the segments are a mixture of those occurring in loops and tails. Copolymers consisting blocks that are solvent-incompatible (*anchor blocks*) and solvent-compatible (*buoy blocks*) are very important as steric stabilizers against particle aggregation, to be discussed in Chap. 7. The anchor blocks adsorb as trains separated or terminated by loops or tails, respectively, of buoy blocks. An important simple example is provided by the Pluronic® series of compounds from BASF Wyandotte, which consist of two polyoxyethylene (PEO) chains separated by a block of polyoxypropylene (PPO).[126] The PPO block acts as an anchor in aqueous media, while PEO chains are buoy blocks. An important question for a given adsorbate of this type is what relative proportion (in terms of molar mass) of anchor groups to buoy groups optimizes the adsorbed amount and the adlayer thickness. Both

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[125] Cosgrove, T., Crowly, T. L., and Vincent, B., *ACS Symp. Ser.*, **240**, 147 (1984).

[126] Reverse Pluronics are also available, consisting of two PPO blocks separated by a central PEO block.

simulation calculations and data suggest that this occurs at an anchor fraction between 10 and 20%.[127]

A number of theories for modeling polymer adsorption have been developed. Scaling theories[128] have led to expressions proportional to the segment volume fraction dependence on distance from the surface for terminally attached chains, polymer brushes and homopolymers, and Monte Carlo and molecular dynamic simulations have been applied to a wide variety of situations.[129] A number of lattice models have been proposed, first for isolated polymer molecules and later for the general case. These are described and reviewed by Fleer and Lyklema[130] and Fleer, *et al.*[131] The most versatile (powerful) of them is the approach of Scheutjens and Fleer (SF).[132] Polymer segments (from multiple chains) and solvent molecules are assigned to positions in the lattice layer by layer based on their attachments and on extended Flory-Huggins theory.[133] The latter requires the Flory-Huggins χ-parameter for the solution and a corresponding surface parameter χ_S expressing the strength of interaction between a segment of the polymer and the surface. χ_S must be larger than a certain critical values for adsorption to occur. The partition function is computed for each allowable assignment of lattice occupancies, and the arrangement that maximizes it is determined. The theory yields not only the segment density distribution, but gives also the density of segments in any given layer that are in loops or tails, information not at present accessible to measurement. The overall segment density profiles predicted from SF theory are generally found to be in good agreement with SANS data.

Several experimental methods are available for accessing some of the useful descriptors of polymer adlayers short of a full segment density profile. The amount or proportion of train segments (bound fraction), for example, may be determined by monitoring the amount of small-ion adsorbate (counterions) initially present that are ejected into the solution,[134] by spectroscopic methods such as FTIR, by microcalorimetry or solvent

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[127] As reported by T. Cosgrove in: Cosgrove, T. (Ed.), **Colloid Science**, pp. 136-139, Blackwell, Oxford, 2005.

[128] de Gennes, P.-G., **Scaling Concepts in Polymer Physics**, Cornell Univ. Press, Ithaca, NY, 1979.

[129] Binder, K., **Monte Carlo and Molecular Dynamics Simulations in Polymer Science**, Oxford Univ. Press, Oxford, 1995.

[130] Fleer, G. J., and Lyklema, J., "Adorption of Polymers," in: **Adsorption from Solution at the Solid/Liquid Interface**, G. D. Parfitt and C. H. Rochester, Eds., pp. 153-220, Academic Press, London, 1983.

[131] Fleer, G. J., Cohen Stuart, M. A., Scheutjens, J. M. H. M., Cosgrove, T., and Vincent, B., **Polymers at Interfaces**, Chapman & Hall, London, 1993.

[132] Scheutjens, J. M. H. M., and Fleer, G. J., *J. Phys. Chem.*, **83**, 1619 (1979).

[133] Flory, P. J., **Principles of Polymer Chemistry**, pp. 497ff., Cornell Univ. Press, Ithaca, NY, 1953.

[134] Wågberg, L., Ödberg, L., Lindström, T., and Aksberg, R., *J. Colloid Interface Sci.*, **123**, 287 (1988).

NMR relaxation. The effective polymer adlayer thickness may be obtained from viscometric measurements (*cf.* Chap. 8), from measurements of effective particle diffusivity (as with photon correlation spectroscopy,[135] *cf.* Chap. 5), from sedimentation rates, *etc.*, all dependent on the assumption that the effective particle size includes the adlayer. Another popular technique is ellipsometry[136], mentioned in Chap. 2 and earlier in this chapter, but suitable generally only for adsorption onto flat surfaces. Another technique, suitable for studying adsorption onto the surface of a transparent solid, is that of internal reflection spectroscopy.[137] When a light beam enters a transparent medium at a sufficiently oblique angle, it is reflected internally between the back and front surfaces of the solid many times before it finally exits the material. While the light beam does not cross the surface as it is totally internally reflected, an "evanescent" non-propagating electric field is generated above the outside surface of the solid. Decaying exponentially in amplitude with distance from the surface, it penetrates a distance of the order of 100 nm. The evanescent beam may experience absorption characteristic of the thickness and nature of the layer directly adjacent to the external surface of the solid, absorption that is evident in the characteristics of the light beam exiting the solid. Such absorption may thus reveal information on the chemistry, refractive index, thickness, *etc.* of the adsorption layer present.

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[135] Baker, J. A., and Berg, J. C., *Langmuir*, **4**, 1055 (1988).

[136] Takahashi, A., Kawaguchi, M., and Kato, T., **Adhesion and Adsorption of Polymers**, p. 729, Plenum, New York, 1980.

[137] Harrick, N. J., **Internal Reflection Spectroscopy**, Interscience Publ., New York, 1967.

Some fun things to do: Experiments and demonstrations for Chapter 3

1. *The work of surface area extension*

The thermodynamic work of area extension at constant temperature and composition is given by $\sigma\Delta A$. While this is usually very small, it can be demonstrated by noting the need to apply a force to extend the area of a soap film. The soap film has two sides, so the work of extending the film is $2\sigma\Delta A$.

Materials:

- Open wire frame measuring about 2×3×2 inches, with a handle fashioned from a kink in the wire as shown in Fig. E3-1. 16 AWG (≈ 1.3 mm diam.) bailing wire is about right. Tie a flexible string (dental floss is good) about 4 in. in length to each end of the wire. Tie a second string, about 2 in. in length to the center.
- Petri dish large enough to accommodate the wire frame
- Soap solution (50/50 v/v mixture of water and dishwashing liquid) to fill Petri dish

Procedure:

1) Dip the wire frame with string attached into the soap filled dish and withdraw, to produce the film of minimum area shown in Fig. E3-1(b). Then pull down on the string to increase the film area (c), and release to see the minimum area return.

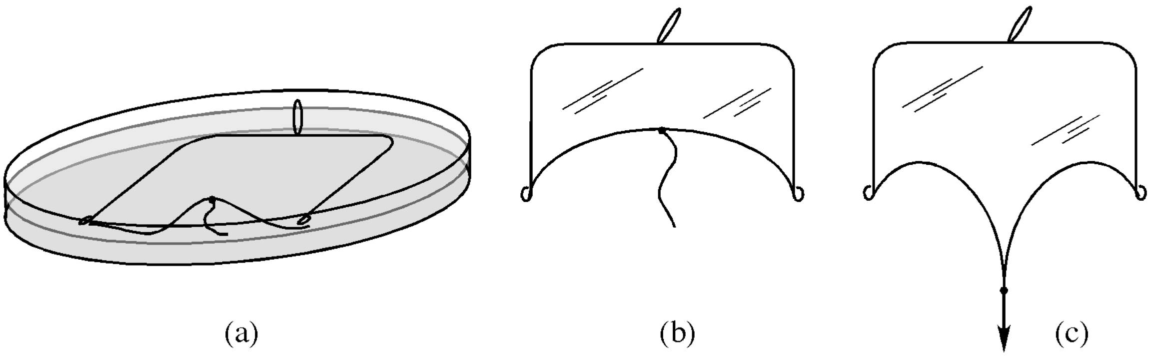

Fig. E3-1: Demonstrating the work of area extension with a soap film on a wire frame. (a) Dip the frame in a soap solution, (b) withdraw the frame and note that the thread deforms to minimize the area, and (c) when force is applied, the area of the film may be expanded, but as soon as it is removed, the configuration of minimum area returns.

2. *Surface tension reduction with surfactant*

Surfactants, by definition, drop the surface tension of water from a value of ≈ 70 to ≈ 25 mN/m at low concentrations (usually < 10mM). One way to demonstrate the effect is to "float" a paper clip on water, and then cause it to sink by injecting surfactant into the water beneath it. The paper clip is about eight times as dense as water, but is held up by buoyancy and surface tension forces acting upward around its perimeter. While the exact solution to the problem is rather complex, one can make a *rough* estimate of the surface tension required to maintain the paperclip at the surface as follows. The paperclip may be modeled as a rod of circular cross-section of diameter d against which the water has a contact angle of $\theta \approx 90°$. The metastable equilibrium that exists just before it sinks is shown in Fig. E3.2. The rod is essentially completely submerged, so the buoyancy force/length is: $1/4\pi d^2\rho_{\mathrm{w}}g$. The upward component of the surface tension force/length is $2\sigma\cos 45° \approx 1.41\sigma$. These forces must balance the weight/length of the rod, $1/4\pi d^2\rho_{\mathrm{rod}}g$, so that for the rod to "float,"

$$\sigma \geq \frac{\pi d^2}{8\cos 45°}(\rho_{\mathrm{rod}} - \rho_{\mathrm{w}})g.$$

For the paperclip floating on water described above, this works out to $\sigma \geq 38.5$ mN/m.

Materials:

- 100-mL beaker, filled to the brim with clean water
- Paperclip and forceps
- Disposable 1 mL polyethylene pipette, filled with soap solution (*e.g.*, Joy® dishwashing detergent)

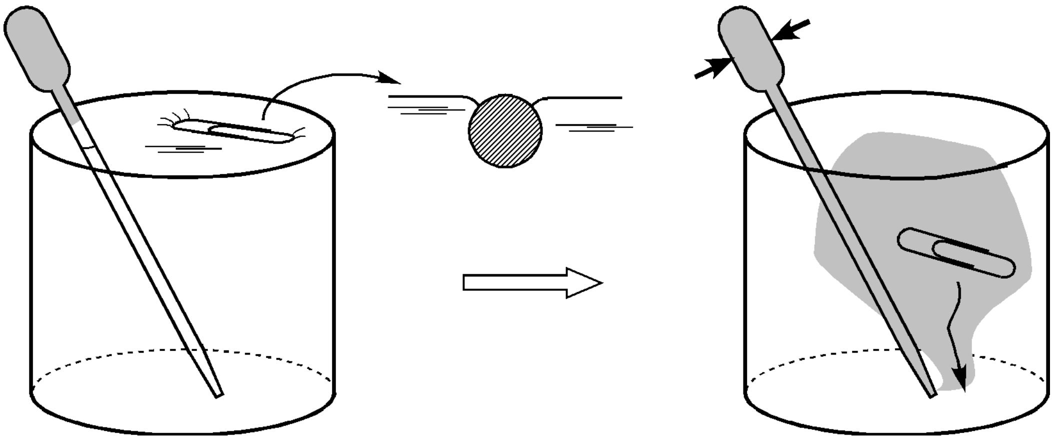

Fig. E3-2: "Floating" a paper clip on water, and sinking it by injection of surfactant from beneath.

Procedure:

1) Use forceps to gently place paperclip on top of the water in the beaker, in which the soap-filled pipette is placed.

2) Squeeze the pipette, injecting the soap into thereby lowering the surface tension and causing the paperclip to sink.

3. *CMC determination by dye titration*

A rough, but quick and easy, way to determine the critical micelle concentration of a surfactant is the method of dye titration, in which a concentrated surfactant solution (assumed to be above its *CMC*) containing a solubilized dye is progressively diluted until it exhibits a fairly abrupt drop in color intensity (optical absorbance), signaling the loss of micelles. Since the dye itself may participate in the micelle formation, the *CMC* value obtained is likely to be somewhat lower than that for the surfactant by itself. In the experiment described below, the *CMC* of sodium dodecyl sulfate (SDS) is determined using the dye pinacyanol chloride.

Materials:

- 200 mL Erlenmeyer flask
- Magnetic stirrer and stir bar
- Sodium dodecyl sulfate (MW 288.38)
- Pinacyanol chloride (or quinaldine blue) (MW 388.94)
- Spectrophotometer, set for measurement at 615 nm
- 1. 5- and 20-mL pipettes

Procedure:

1) Prepare 100 mL of stock solution containing SDS at 0.0175M (0.505g) and 1L stock solution of pinacyanol chloride at 7.3×10^{-5}M (28.4 mg). Prepare a second dye stock solution by adding 100 mL of the original solution to a 1L volumetric flask and fill to the line with de-ionized water.

2) Pipette 40 mL of the SDS solution, 5 mL of the dye solution and 5 mL of pure water into the 200mL flask placed on the magnetic stirrer.

3) Withdraw a sufficient volume to fill the spectrophotomer cuvette and measure the absorbance, and return the liquid to the mixing flask.

4) Add a succession of aliquots of the diluted dye stock solution according to the following schedule:

Data Pt.	Dye Soln Added	Total Vol.	Conc. of Soln
1	0 mL	50 mL	14.0mM
2	5	55	12.7
3	5	60	11.7
4	5	65	10.8
5	5	70	10.0
6	10	80	8.75
7	10	90	7.77
8	10	100	7.00
9	20	120	5.83
10	20	140	5.00
11	20	160	4.38
12	20	180	3.89

5) Plot the absorbance for each data point, resulting in a graph as shown in Fig. E3-3.

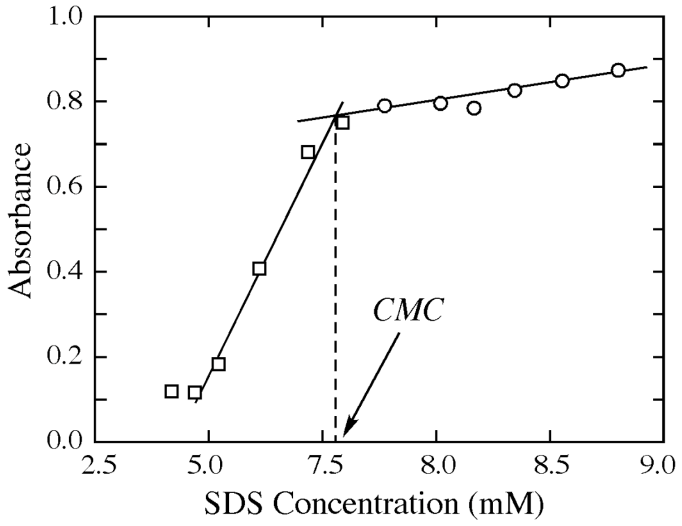

Fig. E3-3: Absorbance data for determination of the *CMC* of SDS by dye titration. (Data from a student lab report)

6) Fit the absorbance data to least squares straight lines, and take the intersection as the location of the *CMC*. For the data shown, the *CMC* is approximately 7.6 mM, slightly lower than the handbook value of 8.0 mM, as expected.

* If desired, the procedure above may be repeated for various salt concentrations to determine the effect of electrolyte on the *CMC* of this ionic surfactant.

3. *Insoluble monolayers*

Insoluble (or Langmuir) monolayers are formed from the direct spontaneous spreading of an insoluble "oil" from a lens or crystal at the surface. This requires that the spreading coefficient be positive, as expressed by Eq. (3.156):

$$S_{o/w} = \sigma_w - (\sigma_o + \sigma_{o/w}) > 0.$$

where the subscripts "w" and "o" refer to water and "oil" (the candidate spreader), respectively. Mineral oil, with a surface tension of 31.0 mN/m and an interfacial tension against water of 50 mN/m, gives (with the surface tension of water equal to 72.8 mN/m) a spreading coefficient of $S_{o/w}$ = - 8.2 mN/m at 20°C, and is therefore not expected to form a monolayer. This behavior is typical of most insoluble liquids and solids on water. Those that do spread are materials that have been identified as surface active agents. Oleic acid, for example, has a spreading coefficient on water of 24.6 mN/m. Solid surfactants, such as stearic acid will also spread, but often so slowly that if one wishes to form a monolayer, a spreading solvent is required. Other surfactant solids may spread quickly. Camphor is an interesting example because it is crystalline and has slightly different spreading coefficients from its different crystal faces. This gives the spreading particles a torque that causes them to spin during spreading in what is termed the "camphor dance," shown in Fig. E3-4. Its average spreading coefficient is about 16 mN/m. When a material of higher spreading coefficient is put on a water surface that already has a monolayer of lower spreading coefficient it will displace the original monolayer. All of these spreading phenomena are easily demonstrated in a *clean* Petri dish of *clean* water on which talc particles have been sprinkled, placed on an overhead projector.

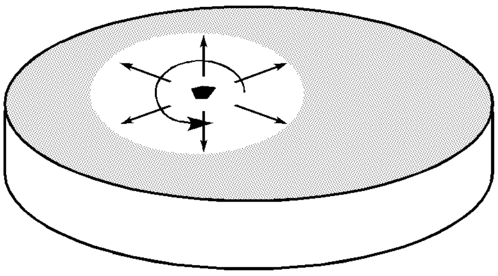

Fig. E3-4: The camphor dance.

When an insoluble monolayer is present, it confers some remarkable properties on the surface. Whereas clean water surfaces are quite fragile to mechanical disturbances, such as air drafts, or temperature variations, or the presence of vapors of a solvent lower surface tension than water, monolayer-covered surfaces are nearly impervious to all these insults, as a direct result of Gibbs elasticity.

Materials:

- 250 mL of *clean* (preferably distilled) water in a plastic squeeze bottle.
- Six clean disposable plastic Petri dishes (10 cm diameter)
- Talc stick (also called "Tailor's chalk")
- Small penknife
- Tweezers
- About 5 g of white mineral oil

- About 5 g of natural camphor (the synthetic variety will not work)
- About 5 g of oleic acid
- About 5 g of acetone (in a tightly capped vial)
- Matches
- Two or three cotton swabs
- Five or six 1-mL disposable PE pipettes
- Large beaker or container for disposal
- Paper towels

Procedure:

1) Show that mineral oil does not spread. Put one of the Petri dishes on the overhead projector and fill it half full with water from the squeeze bottle. Use the penknife to scrape particles from the talc bar and sprinkle them lightly on the surface. Then deposit a small drop of mineral oil on the surface with one of the disposable pipettes and notice that no spreading occurs. Dispose of the Petri dish and contents in the waste container.

2) Demonstrate the camphor dance. Place a clean Petri dish on the overhead projector, half fill it with water, and sprinkle talc particles on the surface. With the tweezers, extract three or four small (≈ 1 – 3 mm) pieces of camphor and place on the surface. Observe the particles spinning and the displacement of the talc particles as the camphor spreads.

3) Demonstrate the displacement of one monolayer by another. After the camphor dance has gone on for one or two minutes, place a small drop of oleic acid at the center of water surface. Notice that the oleic acid instantly spreads to the edge of the dish, displacing the camphor film and bringing the “dance” to a halt. Set this Petri dish aside being careful not to let the oleic acid contaminate anything.

4) Demonstrate the fragility of a clean surface *vs*. the rigidity of a monolayer-covered surface by putting another Petri dish on the overhead projector (next to dish with the oleic acid-covered surface) and fill as close to the top as possible without spilling any water. Sprinkle talc particles on the surfaces in both dishes. Gently blow on the clean surface, showing that the talc particles are easily moved around, while on the oleic acid surface it is very difficult to move them. Re-apply particles to the clean surface, and then light a match and hold it close to (but don’t touch) the center of the dish, noticing how the particles move away. Do the same thing to the surfactant-covered surface and notice that the particles do not move. Again, re-apply particles to the clean surface if needed. Then dip a cotton sway into the acetone, recap the vial, and bring the swab near (but do not touch) the center of clean surface. Notice how the particles rush away

from where the acetone vapors fall upon the surface. In contrast, the surfactant-covered surface shows no response to the presence of the acetone vapors.

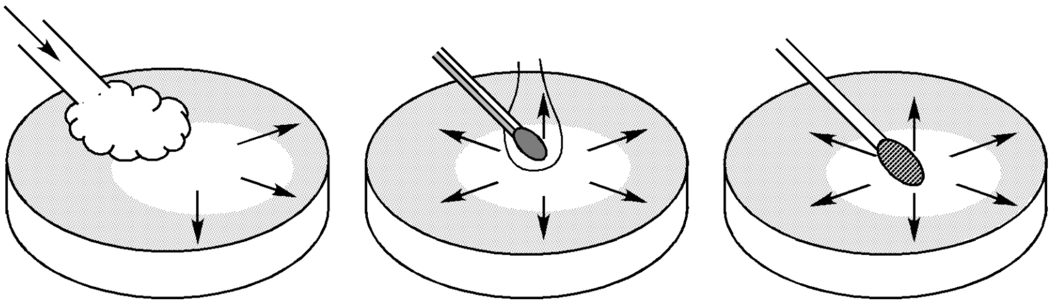
(a) (b) (c)

Fig. E3-5: Fragility of clean water surfaces to (a) mechanical disturbances, as being blown upon, (b) heat, as when a lit match is brought near, or (c) chemical disturbances, as when a swab with acetone releases acetone vapor on the surface.

5. *Adsorption from solution by activated carbon*

Activated carbon or charcoal is one of the most commonly used materials for the removal of contaminants from water or other liquid streams, owing to its enormous adsorptive capacity. It typically has a specific area from several hundred to more than one thousand m^2/g. This is easily demonstrated by observing its removal of a dye from a water sample.

Materials:

- 5–10 g activated carbon, coarse-grained (4-8 mesh) or pelletized
- Two or three tea bags
- 250-mL beaker
- Food coloring

Procedure:

1) Sacrifice a tea bag by carefully removing the staple and emptying out the tea, replacing it with about 5 g of activated carbon and re-stapling it together.

2) Add one drop of food coloring to water in the 250-mL beaker, so that it is brightly colored.

3) Hang the tea bag of carbon particles in the solution, and in about 30 min the color will disappear.