

Adsorption at Fluid–Fluid Interfaces: Part II

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4.2.1 Surface pressure isotherm

- ◆ If the solubility of the monolayer is negligible in the subphase, it can be regarded as a separate phase with thermodynamic properties analogous to those of the three dimensional systems. The compression of the monolayer by the barrier is similar to the piston used for compression in a three dimensional system.
- ◆ If the properties of the subphase are held constant, there is an exact correspondence between the equation of state for a pure monolayer, $\pi_s = \pi_s(A_m, T)$, and that for a one-component three-dimensional system, $p = p(V, T)$. The determination of π_s versus A_m isotherm is the most common measurement that is performed on a Langmuir monolayer.
- ◆ A schematic of the Langmuir monolayer isotherm is shown in Fig. 4.2.1.

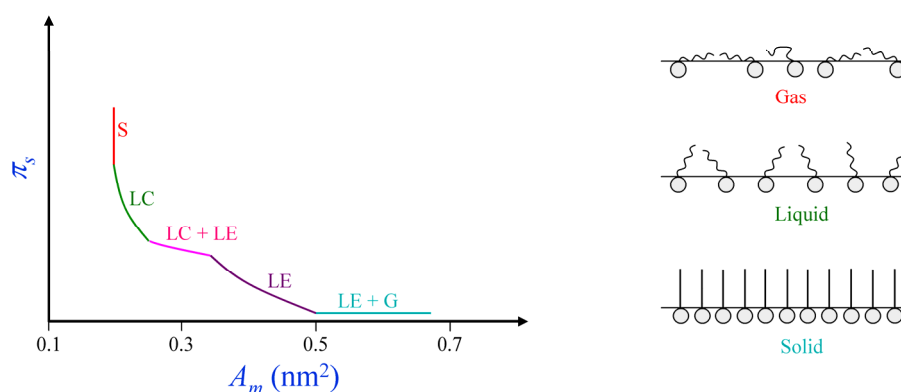


Fig. 4.2.1 Schematic of Langmuir monolayer isotherm and the orientation of the molecules in different phases.

- ◆ The monolayer is gaseous (represented by 'G') where the area per molecule is large compared to the molecular dimensions (e.g., $A_m > 4 \text{ nm}^2$). In the gaseous phase the hydrocarbon portions of the molecules make significant contact with the surface.
- ◆ As the monolayer is compressed, a long plateau arises, which is associated with the transition to a liquid phase. This is often called *liquid expanded* (LE) phase. The plateau is predicted by the phase rule, which for the insoluble monolayers is similar to the three dimensional systems. When two phases are present, a pure monolayer has a single degree of freedom. Therefore, if we fix the temperature,

the surface pressure is fixed. In the LE phase, the hydrocarbon chains stand upon the surface in a disordered manner.

- ◆ When the monolayer is compressed further, the *liquid condensed* (LC) phase is formed. This phase, however, is not a liquid. The degree of alignment of the chains is higher than that in the LE phase. There is long-range order in this phase. The plateau is not horizontal, which indicates that the LE→LC transition is not first order.
- ◆ At even higher compressions ($A_m \approx 0.2 \text{ nm}^2$), the LC phase is transformed to a phase which is similar to an ordered two dimensional solid phase. The area per molecule corresponds closely to the packing of the chains found in the three dimensional crystals of the surfactant.
- ◆ Knobler (1990) used fluorescence microscopy to study the morphology of Langmuir monolayers. Some of his results for pentadecanoic acid monolayers are presented in Fig. 4.2.2.

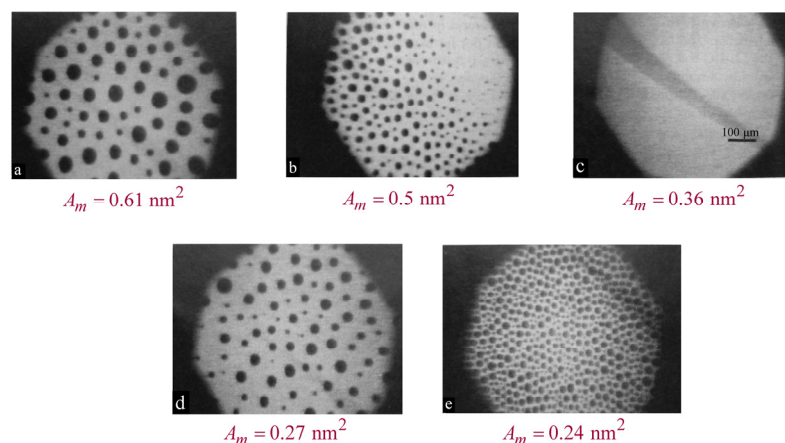


Fig. 4.2.2 Fluorescence microscope images of pentadecanoic acid monolayers at 298 K (Knobler, 1990) [reproduced by permission from The American Association for the Advancement of Science and Professor Charles M. Knobler © 1990].

- ◆ The pentadecanoic acid contained 1% 4-(hexadecylamino)-7-nitrobenz-2-oxa-1,3-diazole, which acted as the probe. The fluorescent probe was excited with laser and the images of the monolayer were detected with a high-sensitivity

camera and recorded on a videotape. Fig. 4.2.2 (a) corresponds to the LE + G two phase region. The image contains dark circular bubbles of gas in the white field representing the LE phase. The contrast between the two phases is due to the difference in density.

- ◆ The amount of gas decreases when the monolayer is compressed, as shown in Fig. 4.2.2 (b). At a sharply defined area ($A_m = 0.36 \text{ nm}^2$), a completely white field appears [Fig. 4.2.2 (c)], which indicates that all of the monolayer is in the LE phase.
- ◆ This one-phase region persists as A_m is decreased further until dark circular domains of the LC phase appear abruptly [Fig. 4.2.2 (d)]. The difference in contrast reflects the low solubility of the probe in the LC phase. The fraction of the LC phase grows with increasing density as shown in Fig. 4.2.2 (e). If the concentration of the probe is low, the termination of LE + LC coexistence can be detected by the complete loss of the bright LE regions.

4.2.2 Model of gas phase monolayer

- ◆ When the monolayer is in the gaseous (G) phase, the number of molecules surfactant in the monolayer is small. In the limit of low film pressure, the two-dimensional equivalent of the ideal gas law applies, which is given by,

$$\pi_s A_m = kT \quad (4.2.1)$$

where k is the Boltzmann constant and T is temperature. In the gaseous phase, the hydrocarbon tails lie almost flat on the surface. If the temperature and chain length are known, the surface pressure can be calculated from Eq. (4.2.1).

- ◆ At higher surface pressures, deviations from Eq. (4.2.1) similar to that for a real gas are observed. An equation similar to the van der Waals equation of state for real gases has been proposed to account for the excluded volume and intermolecular attractions (Hiemenz and Rajagopalan, 1997).

$$\left(\pi_s + \frac{a}{A_m^2} \right) (A_m - b) = kT \quad (4.2.2)$$

The parameters a and b are analogous to the van der Waals constants for real gases. This equation can connect the gaseous and liquid-expanded states in the monolayers. The transition between the two phases is equivalent to the *critical point*.

Example 4.2.1: Calculate the surface pressure in the gaseous phase at 300 K if the length of the hydrocarbon chain of the surfactant molecule is 1.5 nm.

Solution: Since the monolayer is in gaseous phase,

$$A_m \approx \pi l^2 = \pi (1.5 \times 10^{-9})^2 = 7.07 \times 10^{-18} \text{ m}^2$$

$$\pi_s = \frac{kT}{A_m} = \frac{1.381 \times 10^{-23} \times 300}{7.07 \times 10^{-18}} = 5.86 \times 10^{-4} \text{ N/m}$$

4.2.3 Surface potential

- ♦ The surface potential is a very important parameter of the charged monolayers. The usual practice is to measure it along with the surface pressure isotherm. The technique involves the measurement of the potential between the surface of the liquid and that of a metal probe. A popular technique is the vibrating-plate capacitor method (e.g., KSV-SPOT1 surface potential meter). The Helmholtz formula for the potential difference between two conducting plates separated by a distance d and a charge density σ is given by,

$$\Delta V = \frac{\sigma d}{\epsilon \epsilon_0} \quad (4.2.3)$$

where ϵ is the dielectric constant and ϵ_0 is the permittivity of the free space.

ΔV is proportional to the surface concentration, and the proportionality constant is a quantity characteristic of the film.

- ♦ The measured value of ΔV can be used as an alternative means for determining the concentration of molecules in a film and to ascertain whether a film is

homogeneous or not. Fluctuation in the value of ΔV with position across the film may occur if two phases are present (Adamson and Gast, 1997).

- ◆ For weakly-ionized monolayers, the surface potential can be calculated by using the Grahame equation (see Lecture 3 or Module 3). If the surface is considered as a uniformly-charged homogeneous plane with charge density σ and the double layer ions are assumed to be single point charges, the Grahame equation gives,

$$\psi = \left(\frac{2kT}{e} \right) \sinh^{-1} \left[\frac{\sigma \alpha}{(8RT \epsilon \epsilon_0 c^\infty)^{1/2}} \right] \quad (4.2.4)$$

where k is Boltzmann's constant, T is temperature, e is electronic charge, α is the degree of dissociation in the monolayer and c^∞ is the concentration of electrolyte in the subphase.

Example 4.2.2: Derive the simplified form of Eq. (4.2.4) for a partially ionized monolayer in water at 293 K.

Solution: From Eq. (4.2.4) we have,

$$\psi = \left(\frac{2kT}{e} \right) \sinh^{-1} \left[\frac{\sigma}{(8RT \epsilon \epsilon_0 c^\infty)^{1/2}} \right]$$

$$\epsilon = 78.5, \epsilon_0 = 8.854 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}, k = 1.381 \times 10^{-23} \text{ J/K}$$

$$e = 1.602 \times 10^{-19} \text{ C}, R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}, T = 293 \text{ K}$$

$$\frac{2kT}{e} = \frac{2 \times 1.381 \times 10^{-23} \times 293}{1.602 \times 10^{-19}} = 0.05$$

$$\sigma = \frac{1.602 \times 10^{-19} \alpha}{A_m \times (1 \times 10^{-9})^2} = \frac{0.16 \alpha}{A_m}$$

$$(8RT \epsilon \epsilon_0 c^\infty)^{1/2} = (8 \times 8.314 \times 293 \times 78.5 \times 8.854 \times 10^{-12} \times c^\infty)^{1/2} = 0.00368 \sqrt{c^\infty}$$

Therefore,
$$\frac{\sigma}{\left(8RT\epsilon\epsilon_0c^\infty\right)^{1/2}} = \frac{0.16\alpha/A_m}{0.00368\sqrt{c^\infty}} = \frac{43.5\alpha}{A_m\sqrt{c^\infty}}$$

Thus, the simplified form of Eq. (4.2.4) is given by,

$$\psi = 0.05 \sinh^{-1} \left[\frac{43.5\alpha}{A_m\sqrt{c^\infty}} \right]$$

4.2.4 Monolayers at liquid–liquid interfaces

- ◆ Most studies have been made at the air–water interface due to the simplicity involved in the experiments. However, biological systems are approximated in a better way by the oil–water interface. Therefore, the films of proteins, lipids and steroids have been studied at oil–water interfaces.
- ◆ The protein layers are more expanded at water–oil interfaces than at the air–water interface. Davies (1954) has studied the monolayers of hemoglobin, serum albumin, gliadin and synthetic polypeptide polymers at water–petroleum ether interface. He observed that the molecules forming the monolayer were forced into the oil phase upon compression.
- ◆ Brooks and Pethica (1964) have developed a technique for compressing the monolayer at water–oil interface. They have used a hydrophobic Wilhelmy plate for measuring the interfacial tension.
- ◆ Barton *et al.* (1988) have studied stearic acid monolayers at water–mercury interface. They used grazing incidence X-ray diffraction method to study the monolayer.
- ◆ A modified design of the KSV Langmuir trough for studying monolayers at liquid–liquid interface has been presented by Galet *et al.* (1999).

4.2.5 Langmuir and Frumkin adsorption isotherms for fluid–fluid interfaces

- ◆ The Langmuir adsorption isotherm is one of the simplest adsorption isotherms, developed by Irving Langmuir. It is a two-parameter equation relating the surface excess (Γ) to the bulk surfactant concentration (c).
- ◆ According to this model, the adsorbed layer of surfactant is no more than a single molecule in thickness. The effect of charge on adsorption and surface tension is ignored. The adsorbed surfactant monolayer may be viewed as a simple two dimensional lattice. The total number of sites represents the maximum number of surfactant molecules which can fit on the surface. All such sites are of equal area.
- ◆ Therefore, it is possible to obtain indirect information on the packing arrangement at the surface. The experimentally measured value of surfactant density at the surface is unlikely to reach the maximum value, which is represented by Γ_{∞} . The minimum surface area occupied by a surfactant molecule ($A_{\min}$) is given by,

$$A_{\min} = \frac{1}{\Gamma_{\infty} N_A} \quad (4.2.5)$$

where N_A is Avogadro's number. Typical value of Γ_{∞} is 6×10^{-6} mol/m².

- ◆ The Langmuir isotherm can be derived by either kinetic or thermodynamic approaches. The kinetic derivation is presented here. A detailed thermodynamic derivation has been presented by Prosser and Franses (2001).
- ◆ In the kinetic approach, adsorption is considered as a dynamic equilibrium between adsorption to and desorption from the surface lattice. The rate of surfactant adsorption is taken to be proportional to the concentration of the surfactant in the bulk solution, and the fraction of the surface lattice unoccupied by the surfactant.
- ◆ Let us represent the fraction of surface occupied by the surfactant as θ . Therefore, the rate of adsorption, r_a , is given by,

$$r_a = k_a (1 - \theta) c \quad (4.2.6)$$

- ◆ The rate of desorption of surfactant is taken to be proportional to θ , i.e.,

$$r_d = k_d \theta \quad (4.2.7)$$

- ◆ When dynamic equilibrium is established, we can write,

$$k_a (1 - \theta) c = k_d \theta \quad (4.2.8)$$

where k_a and k_d are the rate constants for adsorption and desorption, respectively.

- ◆ If we represent the equilibrium constant as $K_L (= k_a/k_d)$ and $\theta = \Gamma/\Gamma_\infty$, we can write the Langmuir equation as,

$$\frac{\Gamma}{\Gamma_\infty} = \frac{K_L c}{1 + K_L c} \quad (4.2.9)$$

The two limiting cases are low and high surfactant concentrations. In the first case, $K_L c \ll 1$ and Γ/Γ_∞ is proportional to the surfactant concentration. In the second case, $K_L c \gg 1$ and $\Gamma/\Gamma_\infty \rightarrow 1$.

- ◆ The Frumkin adsorption isotherm is a three-parameter model. According to this model, the bulk solution is ideal but the adsorbed monolayer is not ideal. It allows for the interactions between the adsorbed surfactant molecules. The interactions occur only between the neighbor adsorbed surfactant molecules in the monolayer in a pair-wise manner. The Frumkin equation is given by,

$$\theta = \frac{\Gamma}{\Gamma_\infty} = \frac{K_F c \exp(-\alpha \theta)}{1 + K_F c \exp(-\alpha \theta)} \quad (4.2.10)$$

- ◆ The kinetic derivation of the Frumkin adsorption isotherm is similar to that of the Langmuir isotherm [see Prosser and Franses (2001)]. The equilibrium constant is K_F and the interaction parameter is α . The interaction parameter represents a measure of the interaction energy of the adsorbed surfactant molecules. If α is positive, it reflects net repulsive interaction which may occur between the charged surfactant head-groups. On the other hand, if α is negative, it reflects attractive interactions between the chains, which are stronger than the repulsive interactions among the head-groups. In the case where $\alpha = 0$, there is no

interaction between the surfactant molecules, and the Frumkin isotherm becomes identical with the Langmuir isotherm.

4.2.6 Surface equation of state (EOS)

- ◆ We can derive a surface equation of state as follows. From Gibbs adsorption equation, we have,

$$\Gamma = -\frac{1}{\nu RT} \frac{d\gamma}{d \ln c} \quad (4.2.11)$$

where the quantity, ν , represents the number of species produced by surfactant in the solution. For a nonionic surfactant (e.g., Tween 20) $\nu = 1$, and for an ionic surfactant that produces two ions in solutions (e.g., sodium dodecyl sulfate or cetyltrimethylammonium bromide), $\nu = 2$.

- ◆ From Eq. (4.2.9) and (4.2.11) we get,

$$\frac{d\gamma}{d \ln c} = -\frac{\nu RT \Gamma_{\infty} K_L c}{1 + K_L c} \quad (4.2.12)$$

Equation (4.2.12) can be written as,

$$d\gamma = -\nu RT \Gamma_{\infty} \left(\frac{K_L c}{1 + K_L c} \right) d \ln c \quad (4.2.13)$$

The surface tension of the solution is equal to the surface tension of the pure solvent (γ_0) when the concentration of surfactant is zero.

- ◆ Using this condition, Eq. (4.2.13) can be integrated to give,

$$\gamma = \gamma_0 - \nu RT \Gamma_{\infty} \ln(1 + K_L c) \quad (4.2.14)$$

- ◆ Equation (4.2.14) is known as *Szyszkowski equation*. This is the simplest surface EOS that can be used to describe the variation of surface (or interfacial) tension with the concentration of surfactant in the solution. The parameters, Γ_{∞} and K_L , are obtained by fitting the experimental γ versus c curves. The difference between the surface tension of the pure liquid and the surfactant solution, i.e., $\gamma_0 - \gamma$, is the surface pressure.

- ◆ The surface EOS described by Eq. (4.2.14) is simple. However, it may not be accurate for the adsorption of ionic surfactants. When the ionic surfactant molecules adsorb at the interface, a potential is developed. The Langmuir model does not account for this potential.
- ◆ Furthermore, when the charged surfactant head-groups are adsorbed on the interface, a diffuse layer of counterions lies in very close proximity. It is likely that these ions will have interactions with the adsorbed ions, and in the extreme case, they may bind on the surfactant ions adsorbed at the interface. The Langmuir model, which corresponds to an ideal interface, does not account for these interactions.
- ◆ The following example demonstrates the application of Eq. (4.2.14).

Example 4.2.3: The interfacial tension data for the water–toluene system in presence of sodium dodecyl benzene sulfonate (SDBS) are given below (Mitra and Ghosh, 2007).

Concentration of SDBS (mol/m ³)	Interfacial Tension (mN/m)
0.029	27.3
0.057	23.7
0.086	20.6
0.115	18.5
0.143	17.2

Fit the Szyszkowski equation to these data and obtain the EOS parameters. Given: interfacial tension in absence of SDBS is 35.8 mN/m.

Solution: For SDBS, $\nu = 2$, and the surface EoS becomes,

$$\gamma = \gamma_0 - 2RT\Gamma_\infty \ln(1 + K_L c), \quad \gamma_0 = 35.8 \text{ mN/m}$$

The interfacial tension data and the fit of the EOS are plotted in Fig. 4.2.3.

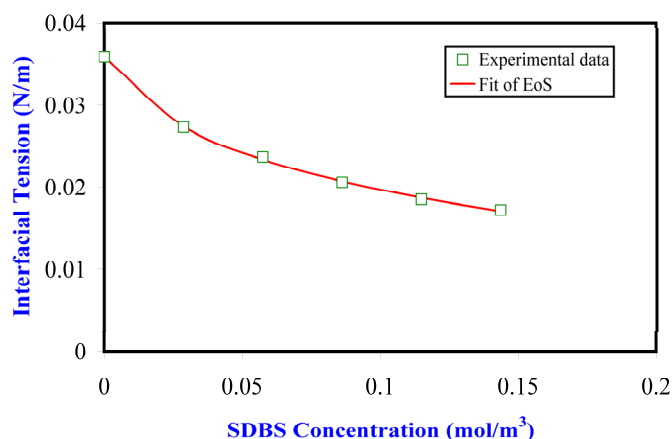


Fig. 4.2.3 Variation of interfacial tension with surfactant concentration. The line depicts fit of the Szyszkowski equation.

The EOS parameters, Γ_{∞} and K_L , were obtained by using the ‘Solver’ of Microsoft Excel, minimizing the error between the experimental data and the prediction of the EOS. The optimum values of these parameters are, $\Gamma_{\infty} = 1.64 \times 10^{-6} \text{ mol/m}^2$ and $K_L = 63.2 \text{ m}^3/\text{mol}$.

4.2.7 Effect of salt on the adsorption of surfactants

- ◆ In many applications of surfactants such as minerals processing, food stabilization and oil recovery, inorganic salts are present in the medium along with the surfactant. These salts strongly influence the adsorption characteristics of ionic surfactants.
- ◆ The nonionic surfactants are not significantly affected by the salts. However, the repulsion between the charged head-groups of ionic surfactants reduces in presence of salt due to the enhanced electrostatic screening (Gurkov *et al.*, 2005). This encourages further adsorption of the surfactant molecules at the interface. Many such examples are available for air–water (Adamczyk *et al.*, 1999) as well as water–hydrocarbon interfaces (Kumar *et al.*, 2006).
- ◆ Fig. 4.2.4 depicts how the adsorption of sodium dodecyl sulfate (SDS) at air–water interface is influenced by the presence of magnesium chloride at various concentrations.

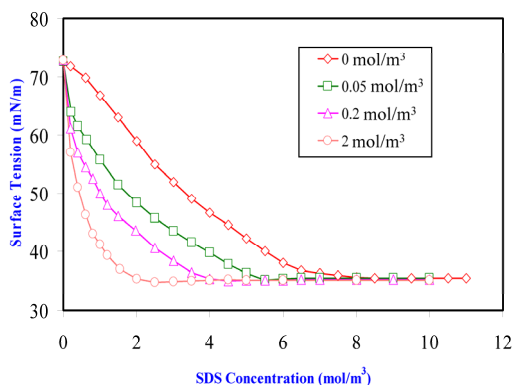


Fig. 4.2.4 The effect of MgCl_2 on the surface tension of aqueous solutions of sodium dodecyl sulfate (Giribabu *et al.*, 2008) (adapted by permission from Taylor and Francis Ltd. © 2008).

- ◆ As the concentration of MgCl_2 is increased, the surface tension reduces considerably. In fact, it has been found that the salts containing divalent counterions (e.g., MgCl_2) are more effective than the salts containing monovalent counterions (e.g., NaCl) in reducing the surface tension. The salts containing trivalent ions (e.g., AlCl_3) are even more effective.
- ◆ The critical micelle concentration (CMC) is reduced considerably in presence of salt. This can be observed from the surface tension profiles shown in the figure. The CMC of aqueous solution of sodium dodecyl sulfate is $\sim 7 \text{ mol/m}^3$. However, with increase in concentration of the salt, the CMC is lowered. When the concentration of MgCl_2 is 2 mol/m^3 , the CMC is $\sim 2 \text{ mol/m}^3$.
- ◆ The surface EOS is modified when a salt is present. Let us assume that both the surfactant and the salt are completely dissociated. The salt is assumed to be indifferent, i.e., it does not adsorb on the interface, and it produces the same counterion as the surfactant. An example of such a surfactant–salt combination is sodium dodecyl sulfate and sodium bromide (or cetyltrimethylammonium bromide and sodium bromide).
- ◆ Let us consider the adsorption of sodium dodecyl sulfate in presence of NaBr . Let us represent the adsorbing organic ion as R^- . The common counterion in this case is Na^+ . It is represented as A^+ . The bromide ion is represented as X^- . The

adsorption of X^- is negligible in comparison with R^- . Since the ions are completely dissociated in solution, we have,



- ◆ The Gibbs adsorption equation gives the following relation between the change in equilibrium surface tension and the change in composition of the solution.

$$d\gamma = -RT \sum \Gamma_i \ln c_i \quad (4.2.16)$$

The summation is over all ionic species in the solution. The solution has been assumed to be ideal. Therefore, the activity coefficients are unity. We represent the ion concentrations in terms of the bulk concentration as follows.

$$c_{R^-} = c \quad \text{and} \quad c_{X^-} = c_s \quad (4.2.17)$$

- ◆ At the interface,

$$\Gamma_{R^-} = \Gamma \quad \text{and} \quad \Gamma_{X^-} = 0 \quad (4.2.18)$$

- ◆ The requirement of electroneutrality gives, at bulk,

$$c_{A^+} = c_{R^-} + c_{X^-} \quad (4.2.19)$$

and at the interface,

$$\Gamma_{A^+} = \Gamma_{R^-} + \Gamma_{X^-} \quad (4.2.20)$$

- ◆ Therefore, from Eq. (4.2.16), we obtain,

$$d\gamma = -RT \left[\Gamma_{A^+} d \ln c_{A^+} + \Gamma_{R^-} d \ln c_{R^-} + \Gamma_{X^-} d \ln c_{X^-} \right] \quad (4.2.21)$$

- ◆ Substituting Γ_{A^+} from Eq. (4.2.20), c_{A^+} from Eq. (4.2.19), Γ_{R^-} and Γ_{X^-} from Eq. (4.2.18), and c_{R^-} and c_{X^-} from Eq. (4.2.17) into Eq. (4.2.21), we obtain,

$$d\gamma = -RT \Gamma \left[d \ln (c + c_s) + d \ln c \right] \quad (4.2.22)$$

- ◆ Substituting $\Gamma = \frac{\Gamma_\infty K_L c}{1 + K_L c}$ from Eq. (4.2.9) into Eq. (4.2.22) we obtain,

$$d\gamma = -RT \Gamma_\infty \left(\frac{K_L c}{1 + K_L c} \right) \left[d \ln (c + c_s) + d \ln c \right] \quad (4.2.23)$$

- ◆ Integrating Eq. (4.2.23), we obtain the following surface equation of state.

$$\gamma = \gamma_0 - \left(\frac{RT\Gamma_\infty}{K_L c_s - 1} \right) \left[(K_L c_s - 2) \ln(1 + K_L c) + K_L c_s \ln \left(\frac{c + c_s}{c_s} \right) \right] \quad (4.2.24)$$

where γ_0 is the surface tension of the pure solvent.

- ◆ The surface EOS represented by Eq. (4.2.24) does not take into account the electrostatic and intra-monolayer interactions. This causes variations in the parameters of the EOS (i.e., K_L and Γ_∞) with salt concentration.
- ◆ The effects of salt on surface excess concentration (Γ) or critical micelle concentration are often quantified in terms of the *ionic strength* of the solution. The ionic strength of the solution is defined as,

$$I = \frac{\sum z_i^2 c_i}{2} \quad (4.2.25)$$

where the concentration is expressed in mol per unit volume of the solution. The ionic strength is a measure of the effective influence of all the ions present in the solution.

- ◆ The solutions of strong electrolytes are inherently nonideal due to the electrostatic forces. Therefore, the activity coefficients of the electrolyte solutions deviate from unity at high salt concentrations ($> 1 \text{ mol/m}^3$) (Debye and Hückel, 1923).
- ◆ The activity coefficients of electrolytes containing divalent or trivalent ions are considerably less than unity even at low concentrations. This variation in the activity coefficient can be modelled using the Debye–Hückel theory. There are semi-empirical formulae stemming from this theory for correlating the mean activity coefficient with the ionic strength of solution. One such correlation is,

$$\log \phi_{\pm} = - \frac{A |z_+| |z_-| \sqrt{I}}{1 + B d \sqrt{I}} + b I \quad (4.2.26)$$

where $\phi_{\pm}$ is the mean rational activity coefficient, d is the distance of closest approach of the ions, and A , b and B are constants.

- ◆ Experimental values of activity coefficient are extensively tabulated in the literature (Robinson and Stokes, 2002). These data indicate that the activity coefficient varies from one salt to another even though these salts are of the same

type (e.g., 1:1 or 1:2). Therefore, instead of concentration, activities need to be used when the activity coefficient deviates significantly from unity.

Exercise

Exercise 4.2.1: The interfacial tension data for water–toluene system in presence of cetyltrimethylammonium bromide (CTAB) and NaBr (1 mol/m³) at 298 K are given below.

c (mol/m ³)	γ (mN/m)	c (mol/m ³)	γ (mN/m)
0.003	26.5	0.015	16.9
0.004	25.3	0.020	14.7
0.005	24.0	0.030	9.8
0.007	22.4	0.040	7.7
0.010	20.6	0.050	5.8

The interfacial tension between water and toluene in absence of any surfactant and salt is 35.5 mN/m. Fit the surface EOS derived from Gibbs and Langmuir isotherms to these data and calculate the minimum area occupied by a CTAB molecule at the interface. Comment on your results.

Exercise 4.2.2: Consider a monolayer of stearic acid on water. It has been found that 5.25×10^{-8} kg of this acid covers 0.025 m² of the surface. Calculate the cross-sectional area of a stearic acid molecule. Given: molecular weight of stearic acid = 0.284 kg/mol.

Exercise 4.2.3: Calculate the mean rational activity coefficient of a 25 mol/m³ aqueous solution of sodium chloride at room temperature. Given: $A = 0.5115$ (kmol/m³)^{-1/2}, $Bd = 1.316$ (kmol/m³)^{-1/2} and $b = 0.055$ (kmol/m³)⁻¹.

Exercise 4.2.4: Answer the following questions clearly.

- Explain the various parts of a surface pressure isotherm. Explain the terms liquid expanded phase and liquid condensed phase.
- If the surface area occupied by a surfactant molecule is 10 nm², what is the surface pressure?

- (c) Explain how the minimum surface area occupied by a surfactant molecule can be calculated.
- (d) Write the Langmuir and Frumkin adsorption isotherms and explain their difference.
- (e) Explain how the presence of salt affects adsorption and surface tension. How does it affect the critical micelle concentration?
- (f) Define the ionic strength of a solution and explain its significance.

Suggested reading

Textbooks

- ◆ P. C. Hiemenz and R. Rajagopalan, *Principles of Colloid and Surface Chemistry*, Marcel Dekker, New York, 1997, Chapter 7.
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