

THE SURFACE TENSION OF STRONG ELECTROLYTES

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The surface tension of any interface must be interpreted first with respect to the Gibbs adsorption equation which, in the general case, is

$$d\gamma = -\sum_i \Gamma_i d\mu_i \quad (1)$$

For a simple binary system containing water and one solute, (1) can be written

$$d\gamma = -\Gamma d\mu \quad (2)$$

where Γ is the adsorption of the solute at the interface, and μ is the chemical potential of the solute. The adsorption is defined by the equation

$$\Gamma = (C_s - C_i) \frac{t}{1000}, \quad (3)$$

C_s and C_i being the concentrations in moles per liter in the surface layer and the interior of the solution, respectively,

and t the thickness of the surface layer. The adsorption is expressed, therefore, in units of moles per sq. cm. of surface.

The chemical potential of the solute, μ , is defined by the equation

$$\mu = \mu_0 + RT \ln C_0 \cdot f, \quad (4)$$

f being the activity coefficient and μ_0 a constant. Equation (2) follows from (1) by measuring the surface layer from a point such that

$$\Gamma_{\text{H}_2\text{O}} = 0 \quad (5)$$

In more familiar terms (2) can be written as

$$\frac{d\gamma}{d(C, f)} = -\Gamma \frac{RT}{C_i f} \quad (6)$$

Equation (6) tells us that if the solute

accumulates at the surface, Γ positive, the surface tension will fall with rising concentration, as is the case with solutions of the fatty acids such as acetic, propionic, etc. On the other hand if Γ is negative as it will be when the solute is repelled from the surface toward the interior of the solution, equation (6) predicts that the surface tension will rise with rising concentration.

When equilibrium has been attained, we may write the law of mass action equation, letting A represent the solute $A(\text{solution}) \rightleftharpoons A(\text{interfacial layer})$, (7) or

$$\frac{C_s^A}{C_i^A} = K \quad (8)$$

where K is the equilibrium constant of (7). From the principles of thermodynamics it also follows that

$$\frac{C_s^A}{C_i^A} = e^{-\frac{\Delta G^\circ}{RT}} \quad (9)$$

where ΔG° is the free energy increase of (7) for the reactants and products in their standard states. (The surface standard state is thus seen to be different from the standard state in the interior of the liquid). Omitting the unnecessary superscript A , and combining (9) and (3) we see that

$$\Gamma = C_i \left(e^{-\frac{\Delta G^\circ}{RT}} - 1 \right) \frac{t}{3000} \quad (10)$$

If the work required to bring the solute to the surface is large, ΔG° positive and large, Γ will be negative and the surface tension will rise with rising concentration as it does in the case of sucrose solutions; conversely a negative value for ΔG means free energy evolved on adsorption, Γ will be positive and the surface tension should fall with rising concentration, as it does for most solutions of organic substances.

What may we expect the surface tension of ionic solutions to be? Consider an ion suspended in the vapor phase over a flat surface of water. It will be strongly attracted to the water because of the ion-dipole forces; in fact estimates show that the energy evolved when one mole of an ion passes from a vacuum to the interior of water is relatively enormous, from 50 to 100 kilocalories per gram ion. Most

of the energy has probably been liberated by the time the ion has reached the surface layer, but there is still enough ion-dipole attraction to pull the ion toward the interior of the solution. For a point size ion, the attractive force is readily shown to be given by the equation

$$\frac{q^2}{4\pi^2 D} \left[\frac{D-1}{D+1} \right] \quad (11)$$

where q is the charge on the ion and x is the distance from the interface. Equation (11) tells us that only when x becomes infinite, does the force on the ion pulling it toward the interior become equal to zero; however, this can be shown to be an absurd conclusion because it means that all the ions in a solution would be repelled an infinite distance from the interface with a consequent infinite value to the slope of the surface tension concentration curve. Actually, ions are not repelled an infinite distance from the interface and the surface tension does not rise infinitely greatly as the concentration increases.

It is interesting to note that the Debye-Hückel theory of solutions provides us with the explanation of this apparent anomaly. As the solution becomes more concentrated, an ionic atmosphere is set up about each ion which in effect tends to screen the ion from the dipole attractions. The dipole attraction can be considered as a repulsion from the interface; the repulsion being between the ion in question and its "mirror image" in the vacuum at an equal distance above the water surface. The ionic atmosphere about the ion limits the thickness of the surface layer, the layer in which the ion concentration is depleted, to a distance of the same order of magnitude of the thickness of the ionic atmosphere, $1/K$ where K is the well known parameter of the Debye equation.

Making use of the Boltzmann distribution law, of Equations (11) and (10) and of the general equations of the Debye theory, Onsager and Samaras¹ have been able to compute the course of the surface tension concentration curve for symmetrical strong electrolytes. For univalent electrolytes the equation is

$$\frac{\gamma}{\gamma_0} = 1 + \frac{79.517}{D \gamma_0} \frac{1.143 \times 10^{-23} (DT)^{3/2}}{C} \log \frac{C}{C} \quad (12)$$

As the logarithm term of Equation (12) is positive in the concentration range of

validity of the equation, the Onsager theory means a rise in the surface tension as the concentration increases. The first experimental measurements of surface tension in very dilute solutions were those of Jones and Ray² who found, most surprisingly, a decrease in surface tension as a function of the concentration up to a concentration of 0.001 N; above this concentration the surface tension rose in a manner suggestive of Equation (12). The significance of Jones and Ray's data in the light of the fundamental Gibbs equation was discussed at length by Dole³ who developed a statistical theory of surface tension leading to the equation

$$\frac{\gamma}{\gamma_0} = 1 + \frac{RT}{\gamma_0} \frac{t \cdot C}{1000} - \frac{RT}{a \gamma_0} \ln \left[1 + \frac{C \cdot t / 1000}{W / RT} \right] \quad (13)$$

where a is the number of surface locations per sq. cm. available for adsorption, and W is the adsorption potential. If the adsorption potential is high and positive, Equation (13) reduces to

$$\frac{\gamma}{\gamma_0} = 1 + \frac{RT}{\gamma_0} \frac{t \cdot C}{1000} \quad (14)$$

an equation which satisfactorily reproduces Jones and Ray's data for sucrose solutions. If W is negative, the logarithm term (at low concentrations) may far outweigh the second term of Equation (13) yielding the equation

$$\frac{\gamma}{\gamma_0} = - \frac{aRT}{\gamma_0} \ln \left[1 + \frac{C \cdot t / 1000}{W / RT} \right] \quad (15)$$

valid for solutions of fatty acids.

By proper choice of the parameters a and W , Equation (13) can be fitted nicely to Jones and Ray's data, but the treatment seems unreasonable for the following reasons: First, the value for a , the

number of adsorption positions per sq. cm., is only 1/100,000 the number of water molecules on the surface. There is no good reason to believe that the water surface would become saturated with ions with so few adsorbed on the surface. Second, there is no known mechanism to account for any attractive force.

Langmuir⁴ has attempted to explain Jones and Ray's data on the basis of a water film held to the quartz surface of the capillimeter by ϕ -potential forces, the thickness of the film as a function of height being given by the equation

$$t = \left(\frac{kT}{\epsilon} \right) \left(\frac{\Pi D}{8\rho gh} \right)^{1/2} \quad (16)$$

When salts are added to the pure water, the film disappears producing an effective increase in the radius of the capillary tube with a corresponding drop in the height of rise and an apparent fall in the surface tension. Langmuir's explanation was held to be doubtful by Dole and Swartout⁵ who confirmed Jones and Ray's results using a differential twirling surface tensiometer. In this case there is, apparently, no vertical film of the type postulated by Langmuir.

However, we cannot yet assume that Jones and Ray's observations and the observations of Dole and Swartout represent true surface tension values. This is particularly true in as much as Long and coworkers⁶ at Cornell University find that the surface tension of potassium chloride solutions as measured by a differential maximum-bubble pressure method follows along the Onsager and Samaras curve without the minimum of the Jones-Ray effect.

REFERENCES

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