A Theory of Surface Tension of Debye-Hückel Electrolyte.

By Kyozo ARIYAMA.

(Received June 1st, 1936.)

The present writer has recently proposed a comprehensible theory of adsorption of Debye-Hückel electrolyte.(1) It was found that a similar theory could be advanced to calculate the surface tension of Debye-Hückel electrolyte. Wagner's very elaborate mathematical theory of surface tension(2) which was later simplified by Onsager and Samaras(3) uses the theory of images near the boundary between water and air. Aside from a great mathematical difficulty, the use of theory of images in the atomic realm without justification is rather objectionable. Oka(4) recently formulated a very reasonable theory of surface tension of dilute solution of strong electrolyte and obtained an explicit expression for the change of surface tension with concentration of the solution in the liquid. The present paper(5) gives a very simple yet a quite reasonable methed of calculating the surface tension. The explicit formula is derived and compared with experiment quite satisfactory. The difference between Oka's value and the value that is given here is that Oka's value is exactly twice as large as that of the present author.

Consider a liquid which is in thermodynamic equilibrium with a vapor. We shall apply the thermographic principle to this system, then we obtain

$$dU = Td\eta + \sigma ds - pdV, \tag{1}$$

where U is the internal energy, η the entropy of the total system, σ the surface tension, and T, S, V and p stand for the usual meanings. Since U, the internal energy, is a function of T the temperature, V the volume, and S the surface of the liquid, we obtain

$$Td\eta = \frac{\partial U}{\partial T}dT + \left(\frac{\partial U}{\partial S} - \sigma\right)dS + \left(\frac{\partial U}{\partial V} + p\right)dV.$$

---

(1) This Bulletin, **11** (1936), 687.

(2) *Phys. Z.*, **25** (1924), 474.

(3) Onsager and Samaras, *J. Chem. Physics*, **2** (1934), 529.

(4) S. Oka, *Proc. Phys.-Math. Soc. Japan*, [3], **14** (1932), 649.

(5) The author was unaware of the Oka's paper at the time when he proposed a theory of adsorption of Debye-Hückel electrolyte. Oka's theory contains an integral which seems only approximately estimated, so it may change the result by a factor 2 or 3 if rigorously calculated.

The condition that $d\eta$ is an exact differential gives

$$\frac{\partial}{\partial S}\left(\frac{1}{T}\frac{\partial U}{\partial T}\right)=\frac{\partial}{\partial T}\left[\frac{1}{T}\left(\frac{\partial U}{\partial S}-\sigma\right)\right]$$

or
$$U_s=\sigma-T\frac{d\sigma}{dT},\tag{2}$$

where
$$U_s=\frac{\partial U}{\partial S},$$

If we consider a solution of strong electrolyte, we obtain for small change in the surface energy U_s the following equation

$$\Delta U_s=\Delta\sigma-T\frac{d}{dT}\Delta\sigma,\tag{3}$$

where $\Delta\sigma$ is corresponding small change in the surface tension. Solving equation (3) for $\Delta\sigma$, we get

$$\Delta\sigma=-T\int_{\infty}^{T}\frac{\Delta U_s}{T^2}dT.\tag{4}$$

Here the intergration constant is determined so as to make $\Delta\sigma/T$ vanish at $T=\infty$.

We shall now apply the kinetic theory for the calculation of ΔU_s. If we consider a special case, that is, a dilute solution of univalent ions, the average number of ions in cm.^{3} at a distance between r and $r+dr$ from the free surface of the liquid is given by

$$C_r=C_\infty e^{-\frac{\epsilon^2}{2DkTa}\left(1-\frac{r}{a}\right)}dr\tag{5}$$

as it was shown in the previous paper.(1) In equation (5) $m=\frac{1}{a}=\sqrt{\frac{8\pi C_\infty\epsilon^2}{DkT}}$, where C_∞ is the average number of ions in cm.^{3} at a distance sufficiently far away from the surface, D the dielectric constant of the solution, k the Boltzmann constant, ϵ the charge of the ions.

The surface energy ΔU_s per unit area of the surface of the liquid, therefore, will be given by

$$\varDelta U_s = \int_0^a C_r \frac{\epsilon^2}{2aD}\left(1-\frac{r}{a}\right)dr$$

$$= \int_0^a C_\infty \frac{\epsilon^2}{2Da}\left(1-\frac{r}{a}\right)e^{-\frac{\varepsilon^2}{2DakT}\left(1-\frac{r}{a}\right)}dr. \tag{6}$$

If we let $y=\left(1-\frac{r}{a}\right)$, $b=\frac{\epsilon^2}{2DakT}$, the above integral becomes $\frac{C_\infty\epsilon^2}{2D}\int_0^1 ye^{-by}dy$.

Since by the fundamental assumption of Debye-Hückel theory $b<1$, we can calculate the above integral and obtain

$$\varDelta U_s = \frac{\epsilon^2 C_\infty}{4D}\left(1-\frac{2b}{3}\right). \tag{7}$$

Since b is small compared with 1 for very dilute solutions, we shall neglect it entirely, and write

$$\varDelta U_s = \frac{\epsilon^2 C_\infty}{4D}.$$

Substituting this in equation (4), we get

$$\varDelta\sigma = -\frac{\epsilon^2 C_\infty}{4D}T\int_\infty^T \frac{dT}{T^2} = \frac{\epsilon^2 C_\infty}{4D}. \tag{8}$$

If we use molar concentration c per c.c. instead of number of ions in cm.^{3} we get

$$\varDelta\sigma = \frac{\epsilon^2 cN}{2D} \tag{9}$$

where N is the Avogadro's number. This agrees except a factor 1/2 with the value found by Oka by a more elaborate yet possibly not much more rigorous calculations. The detailed comparison between the value of $\varDelta\sigma / c$ found by experiments and the theoretical value of $\epsilon^2 N / 2D$ was made in the previous theory of the present author(1). There the agreement between the theory and the experiment was shown to be satisfactory.

Now according to the theory of Debye and Hückel for concentrated solutions of strong electrolyte, the potential energy of an ion due to its ion atmosphere is given by $-\frac{\epsilon^2 m}{D(1+md)}$ where d is the diameter of ions. Therefore the equation (7) is accordingly modified, and given in the first approximation by

$$\Delta U_s = \frac{\epsilon^2 C_\infty}{4D(1+md)}\left(1+\frac{2b'}{3}\right), \tag{10}$$

where $$b' = -\frac{\epsilon^2}{2aDkT(1+md)}.$$

Corresponding to equation (9), we get for the increase in surface tension

$$\frac{\Delta\sigma}{c} = \frac{\epsilon^2 N}{2D(1+md)}\left(1+\frac{2b'}{3}\right). \tag{11}$$

More general case. It is easy to extend the above theory to a more general case in which kinds of ions are homogeneously distributed in the solution. Let us suppose that the charges for S kinds of ions are represented by $z_1\epsilon, z_2\epsilon, \ldots, z_i\epsilon, \ldots, z_s\epsilon$ and the concentrations (no. in cm.^{3}) by $C_1, C_2, \ldots C_i, \ldots, C_s$ respectively. The potential energy of the i th ion species due to its ion atmosphere is $-(z_i\epsilon)^2\frac{m}{D}$, where

$$m^2 = \frac{4\pi\epsilon^2}{DkT}\sum_{i=1}^{s} C_i z_i^2 .$$

Therefore the increase in the surface tension is given by

$$\Delta\sigma = \frac{\epsilon^2}{4D}\sum_{i=1}^{s} C_i z_i^2 .$$

Therefore if we had solutions of the same molar concentration of, for example, KCl and Na_2SO_4, the change of surface tension should be in the ratio 2 to 6. If we take 1/2 molar concentration for solutions of binary mixture of uni- and bi-valent ions, and the molar concentration for solutions of univalent ions, the ratio of change of surface tension is 6 to 4 respectively. Table 1 gives data for a few solutions of dilute concentrations taken from Heydweiller's paper. As we see in the table, the theoretical prediction is satisfied approximately in the case of K_2SO_4, $SrCl_2$, and $BaCl_2$, however, for $MgCl_2$ and Na_2SO_4 the ratio is about 4 to 4. Considering the experimental difficulty in obtaining accurate result, the agreement here obtained may be considered quite satisfactory.

---

(6) Heydweiller, *Ann. Physik*, (4), **33** (1910), 145.

Table 1.* Increase of Surface Tension of Strong Electrolyte.

σ: the surface tension of solution; σ_0: the surface tension of pure water;
c: the molar concentration; $\Delta = 100\ \frac{\sigma - \sigma_0}{c\sigma_0}$

NaCl	
c	Δ
0.020	2.61
0.059	2.33
0.093	2.30
0.123	2.30
0.251	2.13
0.290	2.11

KCl	
c	Δ
0.025	2.55
0.090	2.38
0.114	2.34
0.225	2.26

1/2 $MgCl_2$	
c	Δ
0.269	2.00
0.336	1.97
0.539	1.84
0.808	1.74

1/2 Na_2SO_4	
c	Δ
0.210	2.46
0.321	2.16
0.330	2.37
0.428	2.16

1/2 K_2SO_4	
c	Δ
0.031	2.39
0.052	2.38
0.093	2.37
0.124	2.16
0.150	2.13
0.208	2.08
0.217	2.11

1/2 $SrCl_2$	
c	Δ
0.036	3.16
0.071	2.99
0.107	2.89
0.132	2.88
0.192	2.78
0.203	2.71

1/2 $BaCl_2$	
c	Δ
0.103	2.68
0.131	2.49
0.247	2.28
0.306	2.24
0.353	2.25

* Data taken from Heydweiller's paper, *loc. cit.*

Interfacial tension. The interfacial tension between two liquids is affected, in general, more or less by a third component which is added to this system. In the system of water and hydro-carbon oil each component has actually no mutual solubility and the added inorganic salt is only soluble in the water phase. Therefore, the change of the interfacial tension caused by the concentration change of the salt solution should run parallel to that of the surface tension of the salt solution.

But an unexpected result was obtained in the experiment of McLewis(7) on the interfacial tension of hydro-carbon oil against aqueous solution of metallic salt, namely, the lowering of the interfacial tension occurred by the addition of $CuCl_2$, $AgNO_3$, KCl. Since each of these substances raises the

---

(7) McLewis, *Phil. Mag.*, (6), **17** (1909), 466.

surface tension of water against air, and does not influence that of organic liquid, so that the interfacial tension might be expected to be raised. Mc-Lewis used a dynamical method for the measurement of interfacial tension. M. Kidokoro(8) recently repeated the experiment using both dynamical and statical method, and found that the interfacial tension is raised by the addition of inorganic salt in the water phase. The increase in the interfacial tension between normal hexane from petroleum and water by the addition of inorganic salt run parallel to that of the surface tension of the salt solution, as is expected from the theoretical anticipation. However, the magnitude of rise in the interfacial tension was about 2/3 of the rise in the surface tension of the salt solution for the same concentration.

The decrease in the rise of interfacial tension between hexane and water from that of water and air would possibly be accounted for by the consideration that there exists an electric force acting on the layer of hexane molecules due to the incomplete neutralization of the charge of any ion by the ion atmosphere of opposite charge at the vicinity of the surface. The molecules of hydro-carbon oil may orient themselves in such a way as to decrease the interfacial tension between the two phases. To attempt quantitative account for this effect will be too speculative since we have not yet any experimental evidence of molecular reorientation of hexane at the interface when inorganic salt is added.

In conclusion, the author wishes to express his thanks to Professor H. Erikson for his kind encouragement.

Summary.

A very comprehensible theory of surface tension of Debye-Hückel electrolyte is proposed. An explicit formula for surface tension is derived and compared with experiment very satisfactorily. A qualitative explanation of Heydweiller effect is given. Interfacial tension is also discussed very briefly.

---

(8) This Bulletin, **7** (1932), 280.