

## A Theory of Surface Tension of Ternary Solutions.

By Kyozeo ARIYAMA.

(Received June 20th, 1936.)

Since Heydweiller and his co-workers<sup>(1)</sup> discovered that the surface tension of the solution of inorganic salts in water increases as the solute is increased, various attempts have been made to explain the phenomenon. The theories so far advanced may be divided into two main groups; one which is based on the assumption of the existence of the 'image force' near the boundary between water and air, and the other based on the calculation of surface energy caused by the electrostatic force of the ions. Theories of Wagner,<sup>(2)</sup> Shiba,<sup>(3)</sup> and Oneager and Samaras<sup>(4)</sup> belong to the former, while theories of Oka<sup>(5)</sup> and Ariyama<sup>(6)</sup> (present author) belong to the latter category. Aside from a great mathematical difficulty involved in the theories of the former category, the use of the theory of images in the atomic realm without justification was rather objectionable. However, until very recently there was not any experimental evidence to decide which theory is right. It seems that the experiment of Belton<sup>(7)</sup> conclusively favours the theories of latter category. The present author intends to show a reason for it in the following discussions.

The amount of ions negatively adsorbed at the surface of the solution of an aqueous salt is given by the Gibbs equation

$$-\frac{1}{2RT}\left(\frac{\partial\sigma}{\partial c}\right) = {}_0\Gamma\left(\frac{1}{c} + \frac{\partial \log f}{\partial c}\right). \quad (1)$$

Where  $f$  is the activity coefficient of the salt and  ${}_0\Gamma$  its negative adsorption. When a non-electrolyte is added to the system this simple relation does not apply, but becomes, when the surface concentration of one of the components is put equal to zero,

$$\begin{aligned} d\sigma &= -\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2 \\ &= -\Gamma_1 2RT d \log f_1 C_1 - \Gamma_2 RT d \log f_2 C_2, \end{aligned}$$

---

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

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

(3) Shiba, *Bull. Inst. Phys. Chem. Research*, (Tokyo), **13** (1934), 190.

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

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

(6) Ariyama, this Bulletin, **11** (1936), 687.

(7) Belton, *Trans. Faraday Soc.*, **31** (1935), 1420.

where  $\mu_1$  and  $\mu_2$  are the chemical potentials,  $f_1$  and  $f_2$  the activity coefficients of electrolyte and non-electrolyte respectively.  $\Gamma_1$  and  $\Gamma_2$  are their corresponding adsorption and  $C_1$  and  $C_2$  are their molal concentrations. If the concentration of the non-electrolyte is kept constant, this may be written

$$-\left(\frac{\partial \sigma_{12}}{\partial c_1}\right)_{c_2} = 2RT\Gamma_1\left[\frac{1}{c_1} + \left(\frac{\partial \log f_1}{\partial c_1}\right)_{c_2}\right] + RT\Gamma_2\left(\frac{\partial \log f_2}{\partial c_1}\right)_{c_2}. \quad (2)$$

Now for dilute solution of Debye-Hückel electrolyte the surface tension was experimentally found to be given by

$$\rho - \sigma_0 = K_1 C_1, \quad (3)$$

where  $\sigma_0$  is the surface tension of water,  $K_1$  a constant,  $C_1$  the molal concentration of the salt.

If the change of activity of the salt is unaffected by the non-electrolyte,<sup>(8)</sup> (1), (2), and (3) may be combined to give

$$\left(\frac{\partial \sigma}{\partial c_1}\right)_{c_2} = K \frac{\Gamma_1}{\Gamma_1} - RT\Gamma_2\left(\frac{\partial \log f_2}{\partial c_1}\right)_{c_2}. \quad (4)$$

Since  $\log f_2$  is given by Debye-McAulay,<sup>(9)</sup> it is possible to calculate  $\Gamma_1/\Gamma_1$  if we determine  $(\partial \sigma / \partial c_1)_{c_2}$  experimentally. Such an experiment was carried out by Belton<sup>(10)</sup> for systems of ethyl alcohol-water salt and acetic acid-water-salt. He discovered that 2% of ethyl-alcohol mixed in water lowers the surface tension of the solution when the concentration of salt is increased, and that acetic acid-water-salt system increases the surface tension of the solution as the concentration of salt is increased. The calculated values of  $\Gamma_1/\Gamma_0$  showed values always less than one for salts like KBr,  $K_2SO_4$ ,  $KClO_2$ , and  $KNO_3$ . For  $NH_4Cl$  the value was about 1.2 for dilute concentration.

These results are difficult to be accounted for by the theories of surface tension based on the theory of images, but are easily accounted for by the theories of Oka<sup>(5)</sup> and Ariyama.<sup>(6)</sup>

It is well known that non-electrolyte are positively adsorbed at the free surface of the solution. Therefore let us assume, for simplicity of discussion, that the adsorption layer has thickness  $d$ , and the dielectric constant of this layer is  $D'_a$ . The dielectric constant of electrolyte solution is represented by  $D$ , and the dielectric constant of mixture of electrolyte and non-electrolyte solution sufficiently far away from the surface is represented by  $D'$ .

(8) Theoretical proof of this assumption will be given in this Bulletin shortly by the present author.

(9) Debye and McAulay, *Physik. Z.*, **26** (1925), 22.

(10) See (7).

Then the repulsive force acting on the ions of charge  $+\epsilon$  at a distance  $r$  from the surface of the electrolyte solution is given by  $j\epsilon^2/4r^2D$  if we assume the image force at the boundary of water and air. In the above expression  $j = D-1/D+1$ . If non-electrolyte like ethyl-alcohol, which has much smaller dielectric constant than water, is added,  $D'$  will be in general smaller than  $D$ . The repulsive force for the ion in the mixture becomes  $j'\epsilon^2/4r^2D'$ . Now  $j' = D'-1/D'+1$  will be smaller than  $j$  but  $D'$  in the denominator becomes smaller in the same order, the repulsive force outside of the adsorption layer remains almost unchanged. This can be seen very clearly if we take a specific example, and calculate each quantity specifically. Now in the adsorption layer  $D'_a$  will be very small compared with  $D$  for alcohol. Therefore  $j'_a\epsilon^2/4r^2D'_a$  becomes larger than  $j\epsilon^2/4r^2D$  since increase in  $1/D'_a$  outweighs the decrease in  $j'_a$ . Therefore it is apparent that the addition of non-electrolyte tends to increase the negative adsorption of ions: or in any case will not decrease the negative adsorption except for those substances which have higher dielectric constants than water. This entirely contradicts the experimental fact that  $\Gamma_1/\Gamma_1^0$  is much smaller than unity. Therefore the theory of surface tension based on 'image force' seems incompatible with the experimental data.

Next let us consider the question of how Oka's theory will be applied in this case. Let us consider an ion of charge  $+\epsilon$  situated at a distance  $x$  from the surface. We shall take a cylindrical coordinate origin at this point, choosing  $z$  axis normal to the surface. Then for  $x < d$ , the dielectric constant is  $D'_a$ , and for  $x > d$ , the dielectric constant is  $D'$ . For simplicity of notation let us write these as  $D'_a = D$ , and  $D' = D_2$ . The surface of the solution is taken as  $x = 0$ . We set up Debye-Hückel equations

$$\begin{aligned}\Delta\psi_1 &= k_1^2\psi_1 \\ \Delta\psi_2 &= k_2^2\psi_2 \\ \Delta\psi' &= 0,\end{aligned}\tag{5}$$

where  $\psi_1$  is a potential at  $(r, z)$  in the adsorption layer  $d$ ,  $\psi_2$  is a potential at  $(r, z)$  in the bulk of the solution, and  $\psi'$  is the potential at any point in the air.  $k_1$  and  $k_2$  are given by

$$k_1^2 = \frac{8\pi n\epsilon^2}{D_1kT}, \quad k_2^2 = \frac{8\pi n\epsilon^2}{D_2kT},$$

where  $n$  is the average number of ions in c.c.

We want to determine  $\psi_1$  and  $\psi_2$  under the following boundary conditions

$$\psi_{1z=0} = \psi'_{z=0}$$

$$\begin{aligned}
 D_1\left(\frac{\partial\psi_1}{\partial z}\right)_{z=x} &= \left(\frac{\partial\psi'}{\partial z}\right)_{z=x} \\
 \psi_{1z-x_1'-x-d} &= \psi_{2z-x_1} \\
 D_2\left(\frac{\partial\psi_2}{\partial z}\right)_{z=x_1} &= D_1\left(\frac{\partial\psi_1}{\partial z}\right)_{z=x_1}
 \end{aligned} \tag{6}$$

Suppose we obtained solutions for  $\psi_1$  and  $\psi_2$  satisfying these conditions. Then the negative adsorption is given by

$$\Gamma = -n \int_0^d \left(1 - e^{-\frac{\varphi_1(x)}{kT}}\right) dx - n \int_d^\infty \left(1 - e^{-\frac{\varphi_2(x)}{kT}}\right) dx \tag{7}$$

where  $\varphi_1(x) = \varphi_{1+}(x) = \varphi_{1-}(x) = \epsilon\psi_{1+} = -\epsilon\psi_{1-}$   
 and  $\varphi_2(x) = \varphi_{2+}(x) = \varphi_{2-}(x) = +\epsilon\psi_{2+}(x) - \epsilon\psi_{2+}(\infty)$   
 $= -\epsilon\psi_{2-}(x) + \epsilon\psi_{2-}(\infty)$

So let  $\varphi_2 = \psi(x) - \psi(\infty)$

If we write eq. (5) in full, we get

$$\frac{\partial^2\psi_1}{\partial r^2} + \frac{1}{r} \frac{\partial\psi_1}{\partial r} + \frac{\partial^2\psi_1}{\partial z^2} = k_1^2\psi_1, \text{ etc.}$$

We shall let the solutions take the following form

$$\begin{aligned}
 \psi_1 &= \int_0^\infty \left[ A(a)e^{\sqrt{\alpha^2+k_1^2}z} + B(a)e^{-\alpha z} \right] J_0(ar) da \\
 \psi_2 &= \int_0^\infty \left[ D(a)e^{\sqrt{\alpha^2+k_2^2}z} + \frac{\alpha}{D_1\sqrt{\alpha^2+k_2^2}} e^{-\sqrt{\alpha^2+k_2^2}z} \right] \delta_0(ar) dr \\
 \psi' &= \int_0^\infty C(a)e^{-\alpha z} J_0(ar) da,
 \end{aligned}$$

where  $A(a)$ ,  $B(a)$ ,  $C(a)$ , and  $D(a)$  are the coefficients that have to be determined by 4 boundary conditions.  $J_0(ar)$  is the Bessel functions of zero order.

It is easy to obtain these coefficients, and they are given by

$$A(a) = \frac{-2\alpha(1-D_1a)e^{-\alpha x - \sqrt{\alpha^2+k_2^2}x_1}}{P}$$

$$B(\alpha) = \frac{+2a(\alpha + D_1\sqrt{\alpha^2 + k_1^2})e^{\sqrt{\alpha^2 + k_1^2}x - \sqrt{\alpha^2 + k_2^2}x_1}}{P},$$

$$\text{where } P = (\alpha - D_1\sqrt{\alpha^2 + k_1^2})(D_2\sqrt{\alpha^2 + k_2^2} + D_1)e^{\sqrt{\alpha^2 + k_2^2}x - \alpha_1} \\ - (D_1\sqrt{\alpha^2 + k_1^2} - D_2\sqrt{\alpha^2 + k_2^2})(1 - D_1\alpha)e^{\sqrt{\alpha^2 + k_1^2}x_1 - \alpha x}$$

and  $C(\alpha)$  and  $D(\alpha)$  are obtained from the following boundary equations :

$$A(\alpha)e^{\sqrt{\alpha^2 + k_1^2}x} + B(\alpha)e^{-\alpha x} = C(\alpha)e^{-\alpha x}$$

$$\text{and } A(\alpha)e^{\sqrt{\alpha^2 + k_1^2}x_1} + B(\alpha)e^{-\alpha x_1} = D(\alpha)e^{\sqrt{\alpha^2 + k_2^2}x_1} + \frac{\alpha}{D_2\sqrt{\alpha^2 + k_2^2}}e^{\sqrt{\alpha^2 + k_2^2}x_1}$$

$$\text{Thus}^{(11)} \quad \varphi_1(x) / \epsilon^2 = \int_0^\infty A(\alpha) d\alpha + \int_0^\infty B(\alpha) d\alpha \quad (8)$$

$$\text{and } \varphi_2(x) / \epsilon^2 = \int_0^\infty D(\alpha) d\alpha.$$

Therefore the formal solution of the problem is obtained. But since expressions for  $\varphi_1(x)$  and  $\varphi_2(x)$  are so complicated, that it is not possible to evaluate the negative adsorption  $\Gamma$  unless some method of simplification is discovered. However, it may be possible that this sort of theory might reproduce a result which is demanded by the experimental fact that  $\Gamma_1 / \Gamma_0$  is smaller than unity.

Now we shall discuss the application of the theory<sup>(6)</sup> that the present author has proposed recently. If we consider an adsorption layer of thickness  $d$  at the surface, the potential energy of inward force for ions is accordingly modified. Let the dielectric constant in  $d$  be  $D'$  and the dielectric constant of the bulk of the solution be  $D$ . The thickness of the ion atmosphere in  $d$  be represented by  $a'$ , and in the solution by  $a$ . Then in the first approximation, the potential energy of inward force on an ion situated at a distance  $r(a+d)$  from the surface is given by

$$E = \frac{\epsilon^2}{2Da} \left[ 1 - \left( \frac{r-d}{a} \right) \right] - \frac{\epsilon^2}{2D'a'} \left[ 1 - \frac{(r-d)}{a'} \right] + \frac{\epsilon^2}{2D'a'} \left( 1 - \frac{r}{a'} \right) \\ = \frac{\epsilon^2}{2Da} \left( 1 - \frac{r}{a} \right) + \frac{\epsilon^2}{2Da} \left( \frac{d}{a} \right) - \frac{\epsilon^2}{2D'a'} \left( \frac{d}{a'} \right).$$

---

(11) See Oka's paper in this connection.

According to the Maxwell-Boltzmann statistics, the probability that an ion lies at a distance  $r$  and  $r+dr$  will be proportional to  $e^{-\frac{E}{kT}}dr$ . Therefore if  $C$  is the average number of ions in  $\text{cm}^3$  the number of ions at a distance between  $r$  and  $r+dr$  will be given by

$$C_r = Ce^{-\frac{E}{kT}}dr.$$

Therefore the negative adsorption is given by

$$\Gamma = -C \int_0^{a+d} \left(1 - e^{-\frac{E}{kT}}\right) dr.$$

Substituting the value of  $E$  in the above equation, and carrying out the integration, we obtain after simplification

$$\Gamma = -\frac{c}{kT} \left[ \frac{\epsilon^2}{4D} + \frac{\epsilon^2}{4D} \left( \frac{d^2 + 2da}{a} \right) - \frac{\epsilon^2}{2D'} - \left( \frac{da + d^2}{a'^2} \right) \right]. \quad (9)$$

The first term represents the amount of adsorption which would result if the adsorption layer  $d$  of dielectric constant  $D'$  were not present. Since in general  $D > D'$  and  $a > a'$ , the third term is much larger than the second term. In other words the negative adsorption decreases as the adsorption layer  $d$  increases.

Since for mixture of alcohol-water-salt solutions in Belton's experiment the dielectric constant of the system is not appreciably different from that of aqueous solutions, the decrease in negative adsorption must be attributed to the effect we have discussed above.

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

### Summary.

The theories of surface tension of Debye-Hückel electrolyte can be divided into two main groups; one which is based on the assumption of the existence of the 'image force' near the boundary between water and air, and the other based on the calculation of surface free energy caused by the electrostatic force of ions. On the basis of experimental evidence on the surface tension of ternary solution, the theories of former category are shown to be unacceptable. Theories of Oka and also of Ariyama which belong to the latter category are applied to explain the surface tension of ternary solutions. Agreement with experiment is satisfactory.

---