A THEORY OF THE NEGATIVE ADSORPTION OF DEBYE-HÜCKEL ELECTROLYTE.

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I. **Introduction.** Since Heydweiller and his coworkers(1) 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 phenomena. Wagner(2), for example, developed a very elaborate mathematical theory of surface tension, and attributed the effect to the 'image force' near the boundary between two dielectrics, e.g., water and air. Recently Onsager and Samaras(3) tried to simplify the mathematical difficulty of Wagner's theory by introducing new simplifying assumptions. However, the mathematics involved is still very difficult. The present author derives an explicit formula for the negative adsorption by a very simple calculation assuming fundamentally nothing more than those assumed by the previous workers.

II. **Special case.** In order to simplify the discussion, let us consider a special case, that is, very dilute binary solutions of univalent ions. In accordance with the theory of Debye-Hückel for the dilute solution of strong electrolyte, we consider that each ion is surrounded by the ion atmosphere of the opposite charge in the statistical average. The potential energy of a positive ion of charge E due to the negative ion atmosphere surrounding it may be shown to be $-\dfrac{E^2 m}{D}$ where $m^2 = \dfrac{8\pi C_\infty E^2}{DkT}$. In the expression for m, C_∞ is the average concentration of the solution, and D the dielectric constant of the solution, T the absolute temperature. If we suppose that the charge $-E$ is distributed uniformly on the surface of the sphere of radius $1/m$, the potential at its center is given by $-Em/D$. Therefore as long as we are concerned with the potential energy of an ion due to its ion atmosphere, we shall be able to replace the ion atmosphere by a sphere of $1/m$ on whose surface the opposite charge is uniformly distributed. This simplifies the mathematics of our arguments a great deal without serious loss in accuracy. Then, a positive ion of charge E situated at a distance $r > \dfrac{1}{m} = a$ from the

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

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

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

free surface of the solution will be completely surrounded by the negative ion atmosphere. However, if we consider an ion of $+E$ situated at a distance $r < \frac{1}{m}$ from the surface, the sphere that carries charge $-E$ surrounding the $+E$ ion will be cut by the free surface of the solution. The area of the sphere that lies above the surface of the solution will be equal to $2\pi a(a-r)$. The contribution of the potential energy by this area of the sphere on the positive ion at its center will be equal to $\frac{-E^2}{2Da}\left(1-\frac{r}{a}\right)$. Since the positive ion at a distance $r < a$ has the potential energy much smaller than the positive ions at a distance $r > a$, it appears that this ion ($r < a$) is acted upon by a force directing into the solution from the surface. The potential energy of this force is given by $\frac{E^2}{2Da}\left(1-\frac{r}{a}\right)$. We have so far considered the case for positive ions, but it is easy to see that each negative ion of charge E situated at a distance $r < a$ is acted upon by a force directing into the solution, and that the potential energy of this force is also equal to $\frac{E^2}{2Da}\left(1-\frac{r}{a}\right)$.

According to the Maxwell-Boltzmann Statistics, the probability that an ion lies at a distance between r and $r+dr$ will be proportional to $e^{\frac{-E^2}{2aDkT}\left(1-\frac{r}{a}\right)}dr$. If C_∞ is the average number of ions in 1 c.c. at a distance sufficiently far away from the surface, the number of ions C at a distance between r and $r + dr$ will be given by

$$C = C_\infty e^{\frac{-E^2}{2aDkT}\left(1-\frac{r}{a}\right)}dr\,. \tag{1}$$

Therefore the number of ions adsorbed at the surface, α, will be given by

$$\alpha = \int_0^a (C-C_\infty)\,dr = -C_\infty\int_0^a\left[1-e^{\frac{-E^2}{2aDkT}\left(1-\frac{r}{a}\right)}\right]dr$$

$$= -C_\infty a\left[1-\frac{2akTD}{E^2}\left(1-e^{\frac{-E^2}{2aDkT}}\right)\right] \tag{2}$$

$$\doteqdot -\frac{C_\infty}{kT}\frac{E^2}{4D}\,. \tag{3}$$

If we compare this equation with Gibbs's adsorption equation,

$$a_1 = -\frac{C_\infty}{RT}\left(\frac{\partial \sigma}{\partial C}\right)_T , \qquad (4)$$

where σ is the surface tension, we can immediately recognize that the equation (3) is essentially correct in form. In order that the equation (3) and (4) should be identical, the following equation should hold:

$$\left(\frac{\partial \sigma}{\partial C}\right)_T = \frac{E^2 N}{4D} . \qquad (N: \text{ Avogadro's number}) \qquad (5)$$

Now the equation (5) can be subjected to experimental test. The equation (5) means that for a given concentration the increase in surface tension is the same for all univalent binary electrolytes, and that the change of the surface tension of the univalent binary electrolyte with the concentration of the solution is constant as long as the solution is sufficiently dilute. These theoretical conclusions were conclusively shown to hold in Schwenker's experiment.(4)

Table 1. Surface Tension for KCl Solution.

Concentration (mol/litre)	Diff. of surface tension of water and solution $\sigma-\sigma_0$ (mg./mm.)	$\frac{\sigma-\sigma_0}{C}\times 10^{-2}$ (σ in dyn./cm.)
0.015	0.0034	11.11
0.030	0.0066	10.91
0.050	0.0108	10.59
0.075	0.0156	10.20
0.100	0.0202	9.91
0.130	0.0245	9.24
0.160	0.0272	8.34

To show that the equation (5) holds quantitatively, we shall take, as an example, the case for KCl solutions given in Schwenker's paper. In Table 1 the experimental values for the increase of the surface tension with the concentration is shown in the third column. The values for $\frac{\sigma-\sigma_0}{C}$ decreases slightly as the concentration is increased, so that the constancy of the quantity demanded by our theory does not hold strictly. However, the theoretical

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(4) Schwenker, *Ann. Physik*, (5), **11** (1931), 525.

account for this slight variation of the value for $\frac{\sigma-\sigma_0}{C}$ will be discussed later.

Now taking $E=4.8\times10^{-10}$ e.s.u., and $D=80$ for the solution, we get

$$\frac{E^2N}{4D}=4.36\times10^2\,.$$

This value agrees with the experimental value in the order of magnitude. But for very dilute solutions discrepancy with the experimental value becomes quite large. However, generally speaking the agreement may be considered very satisfactory for such a simple theory as this one.

III. **Effect of concentration.** It may be possible that some force other than the one we have considered above may be acting upon the ions at the vicinity of the free surface. Therefore, taking into account of all possible effects there may be at the surface we may write the equation (5) as

$$\left(\frac{\partial\sigma}{\partial C}\right)_T=\gamma\frac{E^2N}{4D}=\frac{E^2N}{4D'}\,. \tag{6}$$

Where γ is a constant and D' takes this correction factor into account in D. Calculating D' for the most dilute concentration we get $D'=31.5$.

Now according to the theory of Debye and Hückel⁽⁵⁾ for concentrated solutions of strong electrolyte, the potential energy of an ion due to its ion atmosphere is given by $-E^2m/D\,(1+md)$ where d is the diameter of ions. Therefore, the adsorption α is accordingly modified, and is given in the first approximation by

$$\alpha=-\frac{C_\infty}{kT}\frac{E^2}{4D(1+md)}\,. \tag{7}$$

Taking into consideration of the equation (6) gives

$$\left(\frac{\partial\sigma}{\partial C}\right)_T=\frac{E^2N}{4D'(1+md)}\,. \tag{8}$$

The value of d for KCl is 3.76×10^{-8} cm. Using the value $D'=31.5$, and calculating the values of the right hand side of the equation (8) for concentrations given in Table 1, we get the values that agrees quite well with the values in the table. This seems to support strongly the view that the decrease of $\partial\sigma/\partial C$ from the constant value as the concentration is increased is due to the relative decrease in the activity coefficient of the solution.

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(5) See for example Falkenhagen, "Electrolyte," p. 250.

IV. **General case.** It is easy to extend the above theory to a more general case in which S kinds of ions are homogeneously distributed in the solution. Let us suppose that the valences for S kinds of ions are represented by Z_1E, Z_2E, ..., Z_sE, and the concentrations by C_1, C_2, ..., C_s respectively. The potential energy of an i th ion species due to its ion atmosphere is $-(Z_iE)^2m/D$ where

$$m^2 = \frac{4\pi E^2}{DkT}\sum_{i=1}^{s} C_iZ_i^2$$

Therefore the adsorption α is expressed as

$$\alpha = \frac{-1}{4kTD}\sum_{i=1}^{s} C_i(Z_iE)^2 . \tag{9}$$

In the case of binary solutions of univalent ions the adsorption layer is electrically neutral since there are as many positive ions as there are negative ions. In general, however, there will be a resultant electric charge in the adsorption layer because the number of adsorbed ions for the ions of the species is proportional to the square of the charge of the ions. The total net electric charge in the adsorption layer is given by

$$\begin{aligned}\text{total charge} &= -\frac{1}{4kTD}\sum_{i=1}^{s}(Z_iE)^2C_i(Z_iE)\\ &= -\frac{1}{4kTD}\sum_{i=1}^{s}C_i(Z_iE)^3 .\end{aligned} \tag{10}$$

For an example, the adsorption layer of the solution of Na_2SO_4 should be charged positively. Such electric unbalance will tend to retard the negative adsorption. It is extremely important to find out whether such an electric unbalance in the adsorption layer for solutions like Na_2SO_4 exists or not.

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