A Note on the Osmotic Coefficient and the Activity Coefficient at the Surface.

By Kyozo ARIYAMA.

(Received June 20th, 1936.)

The exact theoretical calculation of the negative adsorption of Debye-Hückel electrolyte requires the knowledge of activity coefficient of the solute at the surface of the solution. The surface tension of the solution is given by the Gibbs thermodynamic equation.

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

where σ is the surface tension of the solution, c the molar concentration of solute, Γ the negative adsorption, f the activity coefficient of the solute at the surface of the solution. If a non-electrolyte is added to the system, the above simple equation does not apply, but become if the concentration of non-electrolyte is kept constant.

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

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

$$\sigma-\sigma_0 = KC_1\,, \tag{3}$$

where σ_0 is the surface tension of water, K a constant.

In order to calculate the change of negative adsorption due to the addition of non-electrolyte, Belton(1) assumed the relation $\frac{\partial \log f}{\partial c} = \left(\frac{\partial \log f_1}{\partial c_1}\right)_{c_2}$ at the surface and $\left(\frac{\partial \log f_2}{\partial c_1}\right)_{c_2}$ is the same at the surface of the solution as in the interior of the solution.

Then by equations (1), (2), and (3) we get

$$\left(\frac{\partial\sigma_{12}}{\partial c_1}\right)_{c_2} = K_1\frac{\Gamma_1}{{}_0\Gamma_1}-RT\Gamma_2\left(\frac{\partial \log f_2}{\partial c_1}\right)_{c_2}. \tag{4}$$

---

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

Therefore we can calculate the value of $\Gamma_1/{}_0\Gamma_1$ knowing all the other factors in the equation. The present author wishes to prove theoretically by taking a specific example that the above two assumptions that Belton made is justified.

Osmotic coefficient of ions at the surface.⁽²⁾ We shall first consider the total mutual potential energy of the ions with respect to their ionic atmospheres, considering mono-mono-valent electrolyte first for the sake of simplicity. The potetial energy of one ion of charge $+\epsilon$ as well as $-\epsilon$ is equal to $-\frac{\epsilon^2 m}{D}$, where $m^2=\frac{8\pi C_\infty \epsilon^2}{DkT}$, D is dielectric constant of the solution, C_∞, the average number of ions in cm.^{3} If we have altogether $2N$ ions, the total potential energy is therefore $-\frac{N\epsilon^2 m}{D}$ since if we have a number of charges e_i at points where the potentials are ψ_i, the total potential energy is given by

$$U=\frac{1}{2}\sum e_i\psi_i .$$

As is shown in the previous paper, the potential energy of an ion near the surface is greater than the potential energy of an ion sufficiently far away from the surface. The ion which is situated at a distance $r<\frac{1}{m}$ from the surface of the solution has potential energy $-\frac{\epsilon^2 m}{2Da}\left(1-\frac{r}{a}\right)$, where $a=1/m$. Since N is the average concentration of the positive ions in the solution, the total lack of potential energy for the unit surface of depth a is given by

$$\varDelta U=\frac{\epsilon^2 N}{4D}.$$

Therefore the average total potential energy per cm^3 at the surface is given by

$$U=-\left(\frac{N\epsilon^2}{aD}-\frac{N\epsilon^2}{4Da}\right)=-\frac{3}{4}\frac{N\epsilon^2}{aD}.$$

This result can easily be generalized for an electrolyte containing $N_1,\ldots,N_i,\ldots,N_s$ ions of valencies $z_1,\ldots,z_i,\ldots,z_s$. In this case the potential energy of the central ion with respect to its ionic atmosphere is given by $\frac{z_i^2\epsilon^2 m}{D}$ and the potential energy of the solution is then given by

$$U_e=-\sum_i\frac{3}{8}\frac{N_i z_i^2\epsilon^2 m}{D},\quad \text{where}\quad m^2=\frac{4\pi\epsilon^2}{DkT}\sum_i N_i z_i^2 .$$

---

(2) The argument presented in the following follows closely the Debye's theory presented by Falkenhagen in "Electrolyte."

The total electric work w necessary to discharge and recharge the ions at the surface becomes correspondingly

$$W = -\sum \frac{1}{3}\,\frac{3}{4}\,\frac{N_i\epsilon^2 z_i^2 m}{D}$$

$$= -\sum \frac{1}{4}\,\frac{N_i\epsilon^2 z_i^2 m}{D}.$$

In order to calculate the osmotic pressure, we must differentiate the electrical work with respect to the volume V. It must be noted that the expression for m contains V implicitly since $n_i = N_i/V$, $e_i = \epsilon z_i$ we have $\frac{\partial w}{\partial V} = \frac{\partial w}{\partial m}$. $\frac{\partial m}{\partial V} = -\Sigma \frac{N_i e_i^2}{4D} \cdot \frac{\partial m}{\partial V}$ since $\frac{\partial m}{\partial V} = -\frac{m}{2V}$, we get

$$\frac{\partial W}{\partial V} = \sum \frac{n_i e_i^2 m}{8D}.$$

The osmotic pressure of real solution is given by

$$P = \sum n_i kT - \sum \frac{n_i e_i^2 m}{8D}$$

$$= \sum \left(1 - \frac{e_i^2}{8DkT}\right) n_i kT = \sum g_i n_i kT, \tag{5}$$

where $g_i = 1 - \frac{e_i^2}{8DkT}$ is called osmotic coefficient of the ions. The osmotic coefficient of the ions in the interior of the solution is given by

$$G_i = 1 - \frac{e_i^2}{6DkT}.$$

We see that the osmotic coefficient of the ions is slightly greater at the surface than in the interior of the solution.

Activity coefficient of ions at the surface. With the parallel argument with that of Debye, the thermodynamic potential of the real solution Φ is given by

$$\Phi = \sum_0^s N_i\left(\Phi_i + kT \log y_i - \frac{e_i^2 m}{4D}\right),$$

where Φ_i's depend only on the pressure and temperature, and y_i is the mol fraction of the solute.

The change of thermodynamic potential with changing temperature and pressure being kept constant is given by

$$\delta\Phi = \sum_{i=0} \delta N_i \left[\Phi_i + k \log y_i - \frac{e_i^2 m}{4D} - \sum_{j=0}^{s} \frac{e_i^2}{4D} N_i \frac{\partial m}{\partial N_i} \right].$$

If the index i refers to the dissolved particles, i.e., one of the values $i = 1, 2, \ldots, s$ we have

$$\sum_{j=0}^{s} \frac{e_j^2}{4D} N_j \frac{\partial m}{\partial N_i} = \frac{e_i^2 m}{8D} \quad \text{for} \quad i = 1, \ldots, s\,.$$

If on the other hand, $i = 0$ i.e. we are dealing with variations in the solvent, we may proceed as follows. We can write the total volume of the solution V in the linear form

$$V = V_0 N_0 + \sum^{s} N_i v_i\,,$$

where v_0 and v_i represent the changes in the total volume caused by adding respectively a molecule of the solvent or a particle of the sort the solution. We then have

$$\frac{\partial m}{\partial N_i} = \frac{\partial m}{\partial V} \frac{\partial V}{\partial N_0} = V_0 \frac{\partial m}{\partial V} = -\frac{V_0}{2V} m$$

and hence

$$\sum_{j} \frac{e_j^2}{4D} N_j \frac{\partial m}{\partial N_0} = -V_0 \frac{n_j e_i^2}{8D}.$$

The total variation in thermodynamic potential is thus

$$\delta\Phi = \delta N_0 \left[\Phi_0 + kT \log y_0 + v_0 \sum \frac{n_j e_j^2 m}{8D} \right]$$

$$+ \sum_{1} \delta N_i \left[\Phi_i + kT \log y_i - \frac{3}{8} \frac{e_i^2 m}{D} \right].$$

The coefficient of δN_i is termed the chemical potential. In the case of ideal dilute solution, the chemical potential is given by

$$\xi_i = \Phi_i + kT \log y_i$$

The chemical potential of the real solution is obtained by replacing the concentration y_i by the activity $f_i\, y_i$ for dilute solutions, where f_i being the activity coefficient. We then have

$$\xi_i = \Phi_i + kT\log(f_i y_i).$$

Thus $\log f_i = -\dfrac{3}{8}\dfrac{e_i^2 m}{DkT}.$ (6)

The activity of the solvent is also affected by the dissolved ions, the activity coefficient being given by

$$\log f_0 = v_0 \sum_j \frac{n_j e_j^2 m}{8DkT}. \tag{7}$$

Thus the decrease in the activity coefficient of the ions at the surface is smaller than that of the interior. The increase in the activity coefficient of the solvent at the surface is also smaller than that of the interior.

The limiting law for the activity coefficients of binary salts in water at the surface is given by

$$0°\text{C.}\quad \log f = -0.839\sqrt{J},$$

$$15°\text{C.}\quad \log f = -0.860\sqrt{J},$$

$$20°\text{C.}\quad \log f = -0.872\sqrt{J},$$

where J is the ionic strength defined by

$$J = \frac{1}{2}\sum \gamma_i z_i^2$$

and γ_i is expressed in moles per litre.

Thus we get for

$$\frac{\partial \log f}{\partial J} = -0.419\frac{1}{\sqrt{J}}.$$

Therefore for concentration $J = 0.01$, the absolute magnitude of $\dfrac{d\log f}{dJ}$ is about 4.2 % of the value of $\dfrac{1}{J}$. Therefore for very dilute solutions this term can be neglected in rough calculations.

Osmotic pressure and activities in dilute mixture of electrolyte and non-electrolyte. In order to find the additional free energy caused by the pressence of the ionic charges, we shall proceed in the same way as before. We imagine the ions discharged in an infinitely dilute solution, and recharged in a solution of finite concentration. If the solution contains $N_1, \ldots, N_i, \ldots,$

N_s ions of the species $1, \ldots, i, \ldots, s$ having charges $e_1, \ldots, e_i, \ldots, e_s$ the work necessary to carry out this process W is given by

$$W = -\sum \frac{N_i e_i^2}{2D_0 b_i} + \sum \frac{N_i e_i^2}{2D_m b_i} - \sum \frac{N_i e_i^2 m}{4D_m}. \tag{8}$$

For the sake of simplicity, an ion of the i th sort is considered as a sphere of radius b_i which is charged in pure water of dielectric constant D_0, and subsequently in the solution of given concentration D_m at the surface of the solution. m is the reciprocal thickness of the ionic atmosphere. Since we are dealing only with a first approximation, we can represent the dielectric constant of the mixture D_m by the linear interpolation formula.

$$D_m = D_0(1 - \alpha n - \beta n'), \tag{9}$$

where n and n' represent the number of molecules of non-electrolyte and electrolyte respectively per c.c., and α and β are two constants which may be determined from experiment.

We introduce (9) in (8) and expand $1/D_m$ in the 2nd term in powers of n and n', retaining only the 1st term of the expansion, and write D_0 for D_m in the third term. We then have

$$W = \alpha n \sum \frac{N_i e_i^2}{2D_0 b_i} + \beta n' \sum \frac{N_i e_i^2}{2D_0 b_i} - \sum \frac{N_i e_i^2 m}{4D_0}.$$

Thus we get

$$-\frac{\partial W}{\partial V} = \alpha n \sum \frac{n_i e_i^2}{2D_0 b_i} + \beta n' \sum \frac{n_i e_i^2}{2b_i D_0} - \sum \frac{n_i e_i^2 m}{8D_0},$$

where $n = N/V,\ n' = N'/V.$

If one molecule of the electrolyte dissociate into ν_i of the species $1, \ldots, \nu_s$ of the species s, having valencies $z_1, \ldots, z_i \ldots, z_s$, we have $n_i = \nu_i n'$, $e_i = z_i \epsilon$. Introducing abreviations

$$\nu = \sum \nu_i$$

$$P_N = nkT$$

$$P_E = \nu n' kT\left(1 - \frac{n_0 \epsilon^2}{8D_0 kT} \frac{\sum \nu_i z_i^2}{\nu}\right)$$

$$p = \alpha \frac{n \nu n' \epsilon^2}{2D_0 \nu} \sum \frac{\nu_i z_i^2}{b_i}$$

we can write for the osmotic pressure

$$P = P_N + P_E + p. \tag{10}$$

Thus the effect of surface on the osmotic pressure appears only in osmotic pressure P_E which would be exerted by the $n'\nu$ ions of electrolyte if present alone in the surface phase.

The effect of surface is to increase the osmotic pressure P_E slightly.

We shall now calculate the effect of the electrolyte on the activity of the non-electrolyte at the surface of the solution. If we write the electrical energy contribution W in the form $W = \Sigma N_i \bar{\omega}_i$, where $\bar{\omega}_i = \omega_i / N$ the activity potential h_i is defined by

$$\log h_i = \frac{\bar{\omega}_i}{kT} = \frac{\alpha n e_i^2}{2D_0 b_i kT} + \beta \frac{n' e_i^2}{2D_0 b_i kT} - \frac{e_i^2 m}{4D_0 kT}.$$

The activity potential of the non-electrolyte is unity, and only the activity potential of the ions differs from unity. Activity coefficient f_i of any component i is

$$\log f_i = \log h_i + \sum_j N_j \frac{\partial \log h_i}{\partial N_i}.$$

Since $h = 1$, $\log h = 0$. Activity coefficient of non-electrolyte is given by

$$\log f = \alpha \sum \frac{n_j e_j^2}{2D_0 b_i kT}. \tag{11}$$

Thus the activity coefficient of non-electrolyte at the surface of the solution is the same as the activity coefficient in the bulk of the solution in the first approximation.

The activity coefficient of ions at the surface is calculated by means of

$$\sum_j N_j \frac{\partial \log h_i}{\partial N_i} = -\frac{1}{8} \frac{e_i^2 m}{D_0 kT}.$$

The second term of $\log h_i$ can be neglected for solution of dilute concentration. Then

$$\log f_i = \frac{\alpha n e_i^2}{2D_0 b_i kT} - \frac{3}{8} \frac{e_i^2 m}{D_0 kT}. \tag{12}$$

Since n is the concentration of non-electrolyte,

$$\left(\frac{\partial \log f_i}{\partial c_1}\right)_{c_2} = \frac{\partial \log f_i}{\partial c_1}.$$

This is what we wanted to prove. From the above discussion it may be apparent that the above relation will hold for the case in which a more general form of energy is assumed than the one discussed in the paper.

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

Summary.

The osmotic pressures and the activity coefficients for strong electrolyte solution and for solutions of mixture of electrolyte and non-electrolyte at the surface are calculated on the basis of Debye-Hückel theory. Some relations between the activity coefficients for two cases are given.

Physics Department, University of Minnesota,
Minneapolis, Minn., U.S.A.