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## On the Statistical "Interaction Between Ions and Molecules" in Media of Small Dielectric Constant

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In this paper the general theory of the interaction between ions and molecules in solution is discussed with particular reference to the theory of Debye on the salting-out effect. Formulae are developed for the free energy of the interaction between ions and dipoles. The formulae are applied to the dissociation equilibrium of an electrolyte in a medium of low dielectric constant.

### I. INTRODUCTION. COMPARISON WITH A THEORY OF DEBYE

AS is well known, the solubility of neutral molecules is very frequently changed by the presence of ions (salting-out effect). Debye<sup>1</sup> was the first to ascribe this phenomenon to the local changes in the average dielectric constant of the medium produced by the different attractions exerted upon the molecules of different types in the nonhomogeneous electric fields of the ions. From macroscopic electrostatics we learn that substances of high dielectric constant (high dipole moment) accumulate in regions of a higher field of force, while substances of lower dielectric constant are expelled therefrom. In perfect analogy, the molecules of higher dipole moment will accumulate in the neighborhood of the ions, while those of smaller dipole moment will mostly be found in more distant parts. Since the dipole moments of most solute substances are smaller than that of water these molecules will be repelled by the ions, or in other words the volume accessible to them will become diminished by the presence of charges. This explains qualitatively the reduction of solubility of most solutes in water. Inversely, solutes having a dipole moment larger than that of water show an increase in solubility in the presence of charges, as we can predict by the simple picture, and as has been verified experimentally.<sup>2</sup> (Salting-in effect.)

Debye has succeeded in expressing this picture in the form of a quantitative scheme. For this purpose he considered the influence of the various ions as being independent, and determined the free energy of a mixture the dielectric constant of which varies with the distance from the ion which is assumed as being at the center. In statistical equilibrium, the gradient of the osmotic pressure which is produced by the variable concentrations must be just balanced by the electric forces produced by the ion. He thus derives as a function of the distance from the ion the law of distribution into which the ionic diameter, the dielectric constants of the components, the charge of the ion and the absolute temperature enter as parameters. For practical evaluation some assumptions have to be made as to the variation of the dielectric constant with the relative concentrations of the molecules.

There can be no doubt that the principle of Debye's views is valid and leads to a correct understanding of the phenomena observed. On the other hand, some of the assumptions made for the purpose of calculation do not seem to fit all cases of importance. In aqueous solutions the effect generally is so small that we have to take ionic concentrations which are comparatively high (0.1 N and higher). In such solutions the average distance between the ions becomes so small that we can no longer assume the effect of each ion to be independent of the presence of the

<sup>1</sup> P. Debye and I. McAulay, *Phys. Zeits.* **26**, 23 (1925); P. Debye, *Zeits. f. physik. Chemie* **130**, 56 (1927).

<sup>2</sup> Gross and Schwarz, *Monatshefte f. Chemie* **55**, 287

(1930); Sitzber. Ak. Wien. IIb **139**, 179 (1930); Gross and Iser, *ibid.* **55**, 329 (1930); IIb **139**, 221 (1930).

others.<sup>3</sup> Furthermore, it is an essential assumption on which Debye's theory is based that we shall have at every point in the mixture a composition corresponding to the equilibrium distribution. This assumption is the more dangerous since the volume elements with which we are concerned are of a molecular order of magnitude, so that fluctuations will invariably play an important part and will influence the free energy of the composition decisively. The following calculations will show that this point is of paramount importance, and it could have been suspected to play a decisive part on *a priori* grounds. In fact, it changes completely the quantitative form of the result for the case of a "salting-in" effect to which the formulae given below can be directly applied.

Without any calculations it is easy to understand the qualitative difference between Debye's treatment and that which we are going to propose, by considering the following example: The energy density of an ion carrying the charge  $\epsilon$  in a medium of a dielectric constant  $D$  in the distance  $r$  from the ion is given by the expression

$$\epsilon^2/(8\pi Dr^4).$$

The maximum change which can be reached by the presence of molecules of higher dipole moment is precisely equal to the value given above. This maximum change would correspond to an infinite dielectric constant. On the other hand, let us take a molecule with a dipole  $\mu$  and put it at a distance  $r$  from the ion. The work gained by carrying the molecule from infinity to  $r$  will increase with the dipole moment. The difference in the results is due to the fact that, in statistical equilibrium for the case of an ideally homogeneous complete mixture, the various dipoles influence each other, and in this way reduce the work which could be gained by the attraction of one single dipole.

To sum up: Debye's treatment would be rigorous if we were dealing with infinitely small molecules carrying infinitely small dipoles so that there is always a complete mixture even in

molecular dimensions according to the laws of thermodynamics. We shall on the other hand neglect the "competition for space around an ion" which the different molecules are making each other. The formulas derived in the following paragraph therefore apply directly only to the case of a solute of very low concentration in a medium, the dielectric constant of which is negligibly small compared to the dielectric constant of the solute molecule. This permits us to consider the "fluctuation-terms" which are of decisive importance for dissociation—equilibria.

## II. STATISTICAL CALCULATION OF THE FREE ENERGY

Let us consider the dilute solution of an electrolyte in a solvent of the small dielectric constant  $D$ . The electrolyte shall be partially dissociated, the concentrations expressed in mols per liter of the ions, and the undissociated molecules shall be denoted respectively by  $c_i$  and  $c_M$ . The charge of the ion, which shall be characterized by the index  $i$ , shall be  $\epsilon_i$ . The total volume of the solution shall be  $V$ , so that the volume which can be ascribed on the average to each ion will be equal to

$$v_i = 4\pi R^3/3 = 1000/N\sum c_i,$$

where  $N$ =Loschmidts number. The minimum distance between the molecules and the ion  $i$  shall be  $a \ll R$ . We shall assume for the purpose of calculation that the value of the dielectric constant  $D$  shall be constant up to the surface of the ion, an assumption to be discussed in detail in due course. We now can divide the total volume into  $N\sum c_i$  cells each containing one ion; and it shall furthermore be assumed that on the boundary of this volume the force exerted by the ion shall have become vanishingly small. Each volume  $v$  will contain  $Nc_M v/1000$  undissociated molecules. The excess free energy  $\psi_M$  of each molecule *due to the interaction between ion and molecules* is then given by the following equation

$$ve^{-\psi_M/kT} = 2\pi \int_a^R r^2 dr \int_0^\pi \sin \vartheta d\vartheta e^{\epsilon\mu \cos \vartheta / DkTr^2}. \quad (1)$$

<sup>3</sup> Gross, Monatshefte f. Chemie 53 and 54, 445 (1929).

To evaluate this integral we expand the exponential function in a power series, and first carry out the integration over  $\vartheta$ . We thus arrive at the following expression:

$$\begin{aligned} v e^{-\psi_M/kT} &= 4\pi \int_a^R r^2 dr \left\{ 1 - \frac{1}{2} \sum_n \left( \frac{\epsilon\mu}{DkTr^2} \right)^n \frac{\cos \vartheta^{n+1}}{(n+1)!} \right\} \\ &= 4\pi \int_a^R r^2 dr \left\{ 1 + \sum_n \left( \frac{\epsilon\mu}{DkTr^2} \right)^{2n} \frac{1}{(2n+1)!} \right\}. \quad (2) \end{aligned}$$

This series can be integrated term by term, with the result

$$\begin{aligned} v e^{-\psi_M/kT} &= \left\{ \frac{4\pi r^3}{3} - 4\pi \sum_n \frac{1}{(2n+1)!} \frac{1}{(4n-1)} \left( \frac{\epsilon\mu}{DkT} \right)^{2n} r^{-4n+1} \right\} \Big|_a^R \\ &= \left\{ \frac{4\pi r^3}{3} - 2\pi \sum_n \frac{r^3}{(2n+2)!(1-7/2(2n+2))} \left( \frac{\epsilon\mu}{DkTr^2} \right)^{2n+2} \cdot \left( \frac{DkTr^2}{\epsilon\mu} \right)^2 \right\} \Big|_a^R. \quad (3) \end{aligned}$$

We will now discuss the value of the integrated power series separately for the two boundaries. For  $r=R$  the first term gives  $(4\pi/3)R^3=v$  while all following are smaller by a factor of the order of  $(\epsilon\mu/DkTR^2)^2$ . It is therefore sufficient to limit ourselves to the first term.

The lower boundary necessitates a more elaborate treatment. For practical reasons we are mostly interested in such values of the dipole moment and ionic diameter for which  $\epsilon\mu/DkTa^2$  becomes large compared to 1, since only then can an appreciable effect be expected. If we now rewrite the expression for our power series at the lower boundary in the following form

$$\frac{2\pi a^3}{\sigma^2} \sum_n \frac{\sigma^{2n+2}}{(2n+2)!(1-7/2(2n+2))} \quad (\sigma = \epsilon\mu/DkTa^2)$$

we notice that it differs from the power series for the exponential function  $e^\sigma$  for three reasons. The first four terms are missing, the factorials in the denominator have the additional factor  $1-7/2(2n+2)$  and every second term has dropped out. If now  $\sigma$  is a large number compared to 1, as assumed, the value of the exponential function is almost exclusively determined by those terms in its power series the index of which is almost equal to  $\sigma$ . In this case the first few missing terms do not contribute anything appreciable, and the

additional factor in the denominator can be replaced by a constant factor  $1-7/2(2\sigma+2)$ . (It will appear later on that it is without influence in any case.) For the missing terms we can account by introducing the factor  $\frac{1}{2}$ . Keeping this in mind we can sum the power series for the lower boundary also, and thus arrive at the final expression

$$v e^{-\psi_M/kT} = v + \frac{\pi a^3 e^\sigma}{\sigma^2(1-7/2(2\sigma+2))}. \quad (4a)$$

$$\psi_M = -kT \log \left\{ 1 + \frac{\pi a^3 e^\sigma}{v \sigma^2(1-7/2(2\sigma+2))} \right\}. \quad (4b)$$

Since

$$v = 1000/N \sum c_i$$

we arrive at the following expression for the additional free energy of each molecule

$$\psi_M = -kT \log \left\{ 1 + \frac{N \pi a^3 \sum c_i e^\sigma}{1000 \sigma^2(1-7/2(2\sigma+2))} \right\}. \quad (5)$$

For sufficiently low ionic concentrations we can expand the logarithm, and we thus obtain the following expression for the additional free energy of the total solution:

$$\Psi_1 = N c_M \psi_M = - \frac{\pi a^3 k T N^2 c_M \sum c_i e^\sigma}{1000 \sigma^2(1-7/2(2\sigma+2))}. \quad (6)$$

## III. REMARKS AND APPLICATIONS

The most objectionable point in our derivation seems to be the use of the microscopic dielectric constant of the solvent up to the surface of the ion. For all practical applications where ionic diameter and the dipole of the molecule will be constants which must be determined empirically we have to keep in mind that the values thus obtained are not strictly correct, but might be considerably influenced by the probably wrong assumption as to the value of the dielectric constant. At the present stage we do not think that matters can be improved in this respect.

The application to the change of solubility is quite obvious. The equilibrium condition for the molecule in solution can be simply obtained by differentiating  $\Psi_1$  with respect to  $N_{c_M}$  and adding the resulting expression  $\psi_M$  to the free energy of the solute. The dissolved molecules have an activity coefficient  $e^{\psi_M/kT}$  the logarithm of which is proportional to the concentration of the ions, and which depends in a very sensitive way on the dielectric constant of the solvent.

A more important application, for which our treatment would seem to be particularly appropriate, is the dissociation equilibrium, and its dependence on concentration. In media of low dielectric constant the effect calculated above will be of great importance, and might account, as we have anticipated, for a number of observed anomalies. The equilibrium condition between ions and non-dissociated molecules can be written in the form

$$f_i^2 c_i^2 / f_M c_M = K \quad (7)$$

$f_M$  stands for the activity coefficient of the molecule,  $f_i$  for that of the ion.  $f_i$  is due to the interionic effects as well as to the interaction between ions and molecules. We shall here omit the interionic contribution to the activity coefficient, since it can always be inserted easily,

provided that the theory of ionic interaction has been developed for the solvent under consideration. The contribution to the activity coefficient resulting from the ion-molecule interaction is obtained by differentiating  $\Psi_1$  with respect to  $N_{c_M}$  and  $N_{c_i}$ . Inserting these expressions into (7), we arrive at the following equilibrium condition

$$\log \frac{c_i^2}{c_M} = \log K + \frac{kT\pi a^3 M e^\sigma}{1000\sigma^2(1-7/2(2\sigma+2))} (c_M - \sum c_i). \quad (8)$$

In the special case of slight dissociation (8) simplifies to

$$\log \alpha^2 c = A + Bc \quad (9)$$

( $\alpha$  = degree of dissociation and  $c$  = analytic concentration of solute).

This equilibrium condition shows interesting features, insofar as the dissociation sometimes increases with increasing concentration, because of the presence of the term  $Bc$  on the right-hand side. The concentration for which the dissociation does not change with concentration is given by the relation

$$d\alpha/dc = 0,$$

which can be written in the form

$$1/c_{\min.} = B. \quad (10)$$

If we substitute this expression for  $B$  in (9) we notice that the change of dissociation with concentration is very unsymmetrical on both sides of the point  $c_{\min.}$ , and that more particularly the dissociation increases very rapidly if we pass  $c_{\min.}$

We shall make use of the formulae here derived in the following paper, to explain conductivity phenomena in media of low dielectric constant.