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Influence of Dipole Fields between Solute Molecules. II. On Molecular Polarization

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I. Introduction

In the first paper of this series,[2] it was shown that, in the limiting case of low concentrations, the osmotic deviations of dipole solutes were proportional to concentration. The coefficient of proportionality was calculated in first approximation for solutions in which

$$y = \mu^2/\lambda^3a^3DkT >> 1 \qquad (1)$$

where μ is the dipole moment of the solute molecule, assumed to be an ellipsoid of rotation with axes a and $b = \lambda a$ and where D is the dielectric constant of the solvent medium at the temperature T. This condition is fulfilled by solutions of many electrolytes in solvents of low dielectric constant, where the moments of the ion pairs[3] are of the order of 10–20 Debye units.[4]

It is the purpose of this article to calculate the limiting law for the molecular polarization of a dilute dipole solution, using the same model and assumptions as in the previous paper. We make the further restrictions that the field strength used in measuring the dielectric constant is weak, and that the period of the impressed field is large compared to the time of relaxation of a dipole molecule.[5]

The result is that the molecular polarization P for low concentration is given by

$$P = P_0(1 - cG(y,\lambda)) \qquad (2)$$

where c is concentration, P_0 is the molecular polarization of the *solute* extrapolated to zero concentration and G is a function of the parameters y and λ. For the cases considered here, $\lambda < 2^{-1/3}$ and P decreases with increasing concentration. (For $\lambda = 2^{-1/3}$, the limiting tangent on a $P - c$ plot is parallel to the axis of concentration and for $\lambda > 2^{-1/3}$, P increases[6] as c increases.)

II. The Polarization Formula

1. General Method.—In a solution containing dipole molecules, we expect to find a mutual orientation of two given dipoles in each other's field, which will increase as the molecules come closer together. When we measure the polarization through the dielectric constant of the solution, the mutual orientation is superimposed on the orientation produced by the external field. Since the mean distance of separation of molecules depends on concentration, the mutual polarization will also be a function of concentration. In order to calculate the effect, we compute the net moment of a given pair of dipoles, multiply by the appropriate Boltzmann factors, and sum over all possible configurations of molecules present. This procedure avoids the assumption that associated molecules containing two dipoles are formed; for the case of $y >> 1$, however, the main contribution to the final result will arise from configurations in which two dipoles are in contact in their position of lowest potential energy, so that empirically we have the equivalent of an association to quadrupoles produced by electrostatic fields of the dipoles.[7]

Let the solution contain N dipole molecules in a total volume V, and let the concentration in number of molecules per unit volume be $n = N/V$. We use the same device as before to calculate the interaction of the dipoles. Each molecule is surrounded by a sphere of radius R, so chosen that the potential energy of two molecules is negligible compared to kT when r, their distance apart, is greater than R. This condition can be fulfilled because the potential energy of two dipoles is proportional to r^{-3}, *i. e.*, falls off rather rapidly with increasing distance of separation. Configurations in which two spheres of radius R intersect will be called a *dipole pair;* if the sphere around a given dipole does not intersect another sphere, we shall consider the dipole *free.* Configurations in which three or more spheres intersect simultaneously can be made negligibly rare by choosing a sufficiently small concentration. We then roughly specify the condition of the N molecules when we state that there are present N_1 free dipoles and N_2 dipole pairs, where

$$N = N_1 + 2N_2 \qquad (3)$$

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[2] Fuoss, THIS JOURNAL, **56**, 1027 (1934); in later footnotes, designated as I.

[3] Ref. 2, Footnotes 2 and 3.

[4] Kraus and Hooper, *Proc. Nat. Acad. Sci.*, **19**, 939 (1933).

[5] Debye, "Polar Molecules," Chemical Catalog Co., New York, 1929, Chaps. V, VI.

[6] Debye ["Handbuch der Radiologie" (Marx), Leipzig, 1925, p. 636 ff.] has calculated the molecular polarization for the case where $\lambda = 1$, *i. e.*, for spherical molecules.

[7] The situation is similar to the description of certain properties of electrolytes by means of ion-pairs; *cf.* Ref. 1, footnotes 1 and 2.

Let dN_2 designate the number of dipole pairs satisfying the conditions that the distance apart of the constituent dipoles is in dr at r, ($r < R$), that the axis of the first dipole μ' is in the (element of) solid angle $d\Omega'$, that the axis of the second dipole μ'' is in $d\Omega''$, and that r lies in the solid angle $d\Omega$. Then by a slight generalization of a formula previously derived[8] we have

$$dN_2 = \frac{N^2}{32\pi^2 V} e^{-u/kT}\, r^2 dr\, d\Omega\, d\Omega'\, d\Omega'' \qquad (4)$$

where u is the total potential energy of the dipole pair. Equation (4) will be the starting point for the calculation of the effect of dipole interaction on molecular polarization.

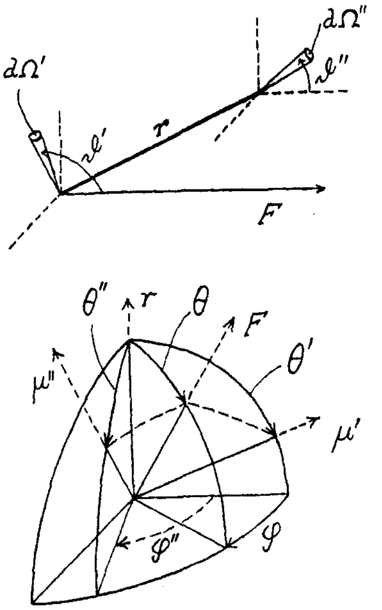

Fig. 1.—Definition of angles.

2. Total Moment.—The total electrical moment of the solution[9] due to orientation of permanent moments by the external field and by the fields of neighboring molecules is given by the sum

$$\Sigma N\mu = \left(N - 2\int dN_2\right) m + \int m_2\, dN_2 \qquad (5a)$$

$$= Nm + \int (m_2 - 2m)\, dN_2 \qquad (5)$$

where m is the average moment of a single dipole and m_2 that of a dipole pair. The first term on the right in (5a) represents the contributions due to free dipoles (*i. e.*, those with no other molecule within a distance R) and the second term includes all configurations of dipole pairs, as is implied by the integral sign.

As Debye[10] has shown

$$m = \mu^2 F/3kT \qquad (6)$$

where F is the external field. The dipole pairs have components of moment parallel to the field given by

$$m_2 = \mu \cos\vartheta' + \mu \cos\vartheta'' \qquad (7)$$

if ϑ' and ϑ'' are the angles the two single moments make with the external field. If we substitute (4) in (5), we obtain

$$\Sigma N\mu = Nm + \frac{N^2}{32\pi^2 V}\int \cdots \int e^{-u/kT} (m_2 - 2m)\, dV\, d\Omega'\, d\Omega'' \qquad (8)$$

The integral in (8) must now be evaluated.

3. Integration over Field Angles.—In calculating the integral in (8), it is necessary to average over all orientations of the dipole pairs with respect to the external field. It is indifferent, as far as the result is concerned, whether we keep the field direction fixed and allow r to take all orientations, or whether we keep r fixed and give the field F all orientations. The latter method is, however, much simpler when we use the angles defined in Fig. 1. The total energy u is made up of the mutual energy of the two dipoles in the pair, plus their potential energies in the external field

$$u = u_m + u_F$$
$$u_F = \mu F (\cos\vartheta' + \cos\vartheta'')$$

Since the mutual energy is independent of ϑ' and ϑ'', the integration over the angles in $dV = r^2 dr \sin\Theta\, d\Theta\, d\varphi$ may be carried out quite simply. We write

$$e^{-u/kT} = e^{-u_m/kT}\, e^{-u_F/kT}$$

and expand the second factor in its power series. Since the field is assumed to be weak, we drop terms of order F^2 and higher, leaving to evaluate

$$I(\Theta,\varphi) = \int_0^{\pi} \sin\Theta\, d\Theta \int_0^{2\pi} d\varphi\, \{\mu(\cos\vartheta' + \cos\vartheta'') - 2m\} \left\{1 + \frac{\mu F}{kT}(\cos\vartheta' + \cos\vartheta'')\right\}$$

From the trigonometrical relationships on the unit sphere, we have

$$\cos\vartheta' = \cos\Theta \cos\Theta' + \sin\Theta \sin\Theta' \cos\varphi$$
$$\cos\vartheta'' = \cos\Theta \cos\Theta'' + \sin\Theta \sin\Theta'' \cos\varphi'' \cos\varphi + \sin\Theta \sin\Theta'' \sin\varphi'' \sin\varphi$$

Substituting these equations and (6), and carrying out the integration, we obtain

$$I(\Theta,\varphi) = \frac{8\pi}{3}\frac{\mu^2 F}{kT}\left[\cos\Theta' \cos\Theta'' + \sin\Theta' \sin\Theta'' \cos\varphi''\right]$$

as the result of the integration over the field

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[8] Fuoss, *Physik. Z.*, **35**, 59 (1934).

[9] The molecules of the solvent medium are assumed to have no permanent dipole moments.

[10] Debye, "Polar Molecules," p. 29.

angles. Substitution in (8) gives for the total electric moment

$$\Sigma N\mu = \frac{N\mu^2 F}{3kT}\left\{1 + \frac{N}{4\pi V}\int \cdot\cdot \int e^{-u_m/kT} r^2 dr\, d\Omega'\, d\Omega''\,[\ ]\right\} \tag{9}$$

If we divide the above equation by the total volume V, we obtain the electrical moment per unit volume, and this divided by the field strength F gives the polarization $n\alpha$ per unit volume due to the presence of permanent dipoles in the solute molecules

$$\Sigma N\mu/FV = n\alpha$$

so that

$$\alpha = \frac{\mu^2}{3kT}\left(1 + \frac{n}{4\pi}J\right)$$

where J replaces the integral in (9). Differentiating with respect to concentration, we finally obtain

$$\frac{\partial\alpha}{\partial n} = \frac{\mu^2}{3kT}\frac{1}{4\pi}J \tag{10}$$

After evaluation of the integral J and conversion to practical units (polarization in cc. and concentration as mole fraction), (10) will give the limiting slope on a plot of molecular polarization of solute (usually written P_2) against mole fraction.

4. **Asymptotic Expansion of the Integral.**—As in the calculation of osmotic properties, we can show that the integral J becomes independent of the upper limit R for r when we choose $R >> a$, where a represents the length of the major axis of the ellipsoidal molecule. We therefore write $r = \infty$ as the upper limit. Furthermore, we are assuming that $y >> 1$, so that the principal value of the integral arises from values of the variables near $r = b$, $\Theta' = \pi/2$, $\Theta'' = \pi/2$, $\varphi'' = \pi$, due to the peak of the exponential integrand in the vicinity of this point. By the means of the approximate method illustrated in the treatment of the osmotic properties, we obtain

$$I \sim -4\pi\left(\frac{\pi}{3}\right)^{3/2}\frac{\mu^2}{DkT}\frac{ze^y}{y^{7/2}} \tag{11}$$

Substituting this result in (10) gives

$$\frac{\partial\alpha}{\partial n} = -\left(\frac{\pi}{3}\right)^{3/2}\frac{\mu^2}{DkT}\frac{\mu^2}{3kT}\frac{ze^y}{y^{7/2}} \tag{12}$$

The molecular polarization P is defined by

$$P = 4\pi N\alpha/3 \tag{13}$$

where N is now Avogadro's number. For f, the mole fraction of solute, we have for low concentrations

$$f = n/(n + n_0) \approx n/n_0 = (M/d_0N)n \tag{14}$$

where n_0 is the number of solvent molecules per unit volume and M is the molecular weight and d_0 the density of the solvent. Combining equations (12), (13) and (14), we obtain the final result

$$\left.\frac{\partial P}{\partial f}\right|_{f=0} = -\frac{4\pi^{5/2}}{3^{3/2}}\left(\frac{N\mu^2}{3kT}\right)^2\frac{d_0}{MD}\frac{ze^y}{y^{7/2}} \tag{15}$$

where y is defined in (1) and z is given by

$$z = \left(\frac{1}{2\lambda^2} - 1\right)^{-1/2} \tag{16}$$

According to (15), the molecular polarization is a linear function of the mole fraction at low concentrations. The coefficient of proportionality is determined by the electrical and geometrical properties of the model used to represent the solute molecules and by the constants describing the solvent medium. By differentiating (15) with respect to temperature, we may obtain in first approximation the temperature coefficient of the limiting slope on a P–f plot.

The writer takes this opportunity to thank Professor P. Debye for many valuable suggestions regarding the treatment of this problem.

Summary

1. The dielectric properties of a dilute solution of dipole molecules are derived, using an ellipsoidal model to represent the solute particles.

2. An explicit asymptotic expansion, valid for the case of large moments and solvents of low dielectric constant, is calculated in first approximation. This case corresponds to electrolytic solutions in such solvents.

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