molecular weight are obtained. As was discussed in connection with Fig. 1, they can be accurately calculated only if an exact knowledge of all the admixtures and impurities present is available.

Summary

Diffusion through porous membranes of constant properties is one of the simplest, quickest and most accurate methods of determining particle size or molecular weight of molecules larger than sucrose that are approximately spherical.[30] Only at the isoelectric point or, with less certainty, in the presence of buffers is the true molecular weight obtained. For egg albumin 34,000 was found. At other values of P_H or with insufficient or unsuitable buffering widely divergent values result from the phenomena of the mutual acceleration and retardation of ions and charged particles. Thus charged colloids may be found to diffuse faster than ordinary molecules.

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[30] Compare the calculation as to the probability of a spherical shape for palmitic acid in aqueous solution by Langmuir ["Colloid Chemistry, Theoretical and Applied," edited by J. Alexander, The Chemical Catalog Co., Inc., New York, 1926, Vol. 1, p. 538]. Protein molecules are not inherently spherical, but as far therefrom as possible in aqueous or mercury surfaces, spreading out to enormous sheets only a few Å. in thickness [for collected references see N. K. Adam, "The Physics and Chemistry of Surfaces," The Clarendon Press, Oxford, 1930, pp. 79–82]; nevertheless, according to sedimentation velocity and our diffusion measurements, egg albumin is spherical in solution at the isoelectric point.

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Influence of Dipole Fields between Solute Molecules. I. On Osmotic Properties

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I. Introduction

If we consider electrolytic solutions in solvents of various dielectric constant, we first find, as the dielectric constant decreases, an increasing tendency for the formation[2] of ion pairs.[3] As the dielectric constant of the solvent is further decreased (or as concentration is increased), we next find it necessary to take into account configurations in which three[4] specific ions are involved. The next step is the consideration of the interaction of four ions.[5] This case becomes important at even moderate concentrations in solvents of low dielectric constant, where the minimum in equivalent conductance appears at concentrations well below 0.001 *N*. (In such solvents, the minimum indicates the concentration at which the triple ion interaction is equally as important as the ion–ion interaction.)

It is the purpose of this article to calculate in first approximation the osmotic properties of electrolytes in solvents of low dielectric constant. In such solvents, the constants K and k_3 describing the equilibria between ions, ion pairs and ion triples are of the order of 10^{-18} and 10^{-4}, respectively (Ref. 5, Table VII). At a total concentration of 10^{-4} mole per liter, for example, the fraction γ of total solute existing as free ions is 10^{-7} and the fraction γ_3 existing as triple ions is 10^{-6}, if we use the above round values for the constants, so that $(1-\gamma-3\gamma_3)$, the fraction of solute existing as ions pairs, is practically unity. As concentration increases, γ decreases and γ_3 increases, but the relative change in $(1-\gamma-3\gamma_3)$ is negligible. For simplicity, therefore, we shall neglect at present all effects due to unpaired charges, and consider the properties of a solution of ion pairs. Except for the fact that an ion pair can dissociate into free ions under suitable conditions, an ion pair resembles a dipole molecule with a fairly large moment. We shall make the further simplification that the ion pairs are assumed to be rigid dipoles; the energy of dissociation of quaternary ammonium salts in benzene, for example, is of the order of 20,000 calories, which is about 30 times RT. We have thus re-

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[2] "Formation of ion pairs" is a convenient and short way of expressing the fact that, when the potential energy ϵ^2/aD of two oppositely charged ions at contact becomes large compared to the thermal energy kT, we find more and more configurations of ions in which two such ions spend a relatively large fraction of their existence very near to each other. The phrase does not imply the formation of chemically neutral molecules. There are cases where, after Coulomb forces have brought two ions into contact, the electrons in the two ions redistribute themselves in accordance with quantum restrictions, to form a homopolar bond. Then in these cases the formation of the final neutral molecules cannot be described simply by means of Coulomb's law.

[3] Fuoss and Kraus, THIS JOURNAL, **55**, 476, 1019 (1933); Fuoss, *Physik. Z.*, **35**, 59 (1934).

[4] Fuoss and Kraus, THIS JOURNAL, **55**, 2387 (1933). A more rigorous treatment, which will eliminate the arbitrary limit in the integration, is proposed by Fuoss, Ref. 3.

[5] Fuoss and Kraus, THIS JOURNAL, **55**, 3614 (1933).

duced the problem to the calculation of the effect on osmotic properties due to dipole fields between solute particles. Debye[6] has discussed this problem[7] for the case of molecules which may be represented by *spheres* containing point dipoles, but as Debye himself and others[8] have pointed out, this model is not sufficiently general to account for all experimentally observed cases of dipole solutes. Due to the fact that the interaction of dipole molecules at short distances depends on the geometry of the structure, it is necessary to introduce at least two molecular parameters.

For this discussion, we shall replace the real physical system by an idealized system in which the solvent is a homogeneous medium of dielectric constant D at a temperature T, and where the solute particles are replaced by ellipsoids of rotation containing dipoles of strength μ at the center with axes parallel to the major axes of the ellipsoids.[9] Let a and b be the major and minor axes of the ellipsoids, and let $\lambda = b/a$. By evaluating the phase integral for a system containing N such particles in a total volume V, and thus determining the free energy, we are in a position to calculate the osmotic pressure for low concentrations. The result is

$$p = p_i\,(1 - (N/V)\,F(\lambda, x)) \qquad (1)$$

where $p_i = NkT/V$ is the osmotic pressure of an ideal solution and $x = \mu^2/DkTa^3$. The function F depends in a rather complicated way on its arguments, but for large values of the parameter x compared to unity and for $\lambda^2 < {}^1/_2$, an asymptotic expansion in x is readily obtained. For solutions of quaternary ammonium salts in benzene at 25°, for example, x is considerably greater than 10.

There are two arbitrary constants, x and λ, to be determined by experiment, which require two equations for their evaluation; for example, determinations at two different temperatures. In the next paper, the influence of intermolecular dipole fields on molecular polarization P will be investigated, and it will be shown that, as a limiting law for low concentrations

$$P = P_i\left(1 + \frac{N}{V}\,G(\lambda, x)\right) \qquad (2)$$

so that a and λ may be determined by measuring an osmotic property and the molecular polarization as a function of concentration. (The function G is positive or negative, according to the value of λ; F is, of course, always positive.)

II. The Osmotic Properties

In order to obtain the osmotic properties of the solution, we must first calculate the free energy ψ of the solution by evaluating the phase integral

$$e^{-\psi/kT} = \int \ldots \int e^{-E/kT}\, dq_{11} \ldots\ldots dp_{3N}$$

Here, E is the total energy of the N solute particles to be averaged over all coördinates q_{ij} and conjugate momenta p_{ij} ($i = 1, 2, 3$; $j = 1, 2, \ldots, N$). We may integrate at once over the momenta and obtain

$$e^{-\psi/kT} = f(T) \int \ldots\ldots \int e^{-U/kT}\, dq_{11} \ldots dq_{3N} \qquad (3)$$

where U is the total potential energy of the system due to dipole forces, to be averaged over all space configurations. The mutual energy u of two dipoles at a distance r is proportional to $1/r^3$, and hence decreases quite rapidly with increasing distance. We therefore apply the device used in the calculation of Van der Waals forces:[10] each molecule is surrounded by a sphere of radius $R > a$, so chosen that the potential energy of two molecules is negligible compared to kT when their distance of separation is greater than R. The solution is assumed so dilute that we may neglect configurations in which more than two molecules are within a sphere of radius R. The integral in (3) may then be calculated as a power series in concentration N/V by well-known methods.[11] To first approximation in concentration, the result is

$$-\psi = NkT \ln V + N^2kT\,I/2V + F(T)$$

where $F(T)$ is independent of volume and I is an abbreviation for the integral

$$I = \int (e^{-u/kT} - 1)\, dv \qquad (4)$$

The integral I is extended over a sphere of radius R and u is the mutual potential energy of two molecules inside such a sphere. (By assumption, $u/kT \approx 0$ for $r > R$.) The osmotic pressure is obtained at once, by means of the thermodynamic relationship

$$p = -(\partial\psi/\partial V)_{T,N}$$

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(6) Debye, "Handbuch der Radiologie" (Marx), Leipzig, 1925, p. 636 ff.

(7) A closely related problem, the equation of state of a gas whose molecules contain permanent dipoles, has been treated by Keesom, *Physik. Z.*, **22**, 129 (1921).

(8) Smyth, "Dielectric Constant and Molecular Structure," Chemical Catalog Co., New York, 1931, p. 176.

(9) We prefer this choice for location of the dipole axis, because in ion pairs (−) (+) the electrical axis is presumably the long axis of the molecule in most cases.

(10) Herzfeld, Müller-Pouillet's Handbuch, Vol. III, p. 167.

(11) Herzfeld, *loc. cit.*; Keyes, *Chem. Rev.*, **6**, 175 (1929).

which gives

$$p = \frac{NkT}{V}\left(1 - \frac{NI}{2V}\right) \qquad (5)$$

Since the osmotic pressure p_i of a force-free solute is NkT/V, (5) may be written

$$\frac{p_i - p}{p_i} = \frac{N}{V}\frac{I}{2} \qquad (6)$$

The integral in (6) is independent of concentration, so that we already see that in the limit of low concentrations, the osmotic deviations of the osmotic properties of a dipole solute from those of an ideal solute are proportional to concentration. There remains the task of evaluating the function on the right of (6) from the known force law between the particles.

The integral I was defined by (4), where the integration represents an averaging over all possible relative positions of two dipoles μ' and μ'' within a sphere of radius, R. If we use polar coordinates with the origin at the first dipole, the integral becomes

$$I = \frac{1}{16\pi^2}\int\ldots\int (e^{-u/kT} - 1)\, r^2 dr\, d\Omega\, d\Omega'\, d\Omega''$$

where $d\Omega$, $d\Omega'$ and $d\Omega''$ are the elements of solid angle which contain, respectively, the line r joining μ' with μ'', the axis of μ' and the axis of μ''. With this definition of angles, the potential energy of two dipoles[12] is, by Coulomb's law

$$u = \frac{\mu^2}{Dr^3}(\sin\Theta' \sin\Theta'' \cos\varphi'' - 2\cos\Theta' \cos\Theta'') \qquad (7)$$

We may integrate at once over $\int d\Omega = 4\,\pi$ and $\int d\varphi' = 2\,\pi$, since these angles do not appear in the exponent, giving

$$I = \frac{1}{2}\int\ldots\int (e^{u/kT} - 1)\, r^2 dr \sin\Theta'\, d\Theta' \sin\Theta''\, d\Theta''\, d\varphi'' \qquad (8)$$

In its present form the integral is a function of the upper limit for distance $r = R$. If we substitute a new variable of integration for one of the angles, defined by

$$\xi = +\sqrt{3\cos^2\Theta' + 1}$$

we may carry out explicit integration over two variables, which gives the integral

$$I = \frac{2\pi}{\sqrt{3}}\int_1^2 \frac{\xi\, d\xi}{\sqrt{\xi^2 - 1}}\int_\rho^R r^2 dr\left(\frac{e^{Z\xi} - e^{-Z\xi}}{Z\xi} - 2\right)$$

where $Z = \mu^2/DkTr^3$ and ρ, the lower limit for r, corresponds to contact of the molecules in some orientation defined by the angles. In this form, we can investigate conveniently the influence of the upper limit. If we expand the integrand as a power series in r, we note that the first term is proportional to r^{-4}, which integrates to r^{-3}. The lower limit ρ is of the order of molecular dimensions, a, so that, on substituting limits of integration, we obtain a term roughly proportional to $(R^{-3} - a^{-3})$. By choosing R large, we can make its contribution to the result negligible, and the same argument applies to all succeeding terms. For practical purposes, therefore, we may replace the upper limit by $r = \infty$, leaving our result independent of the choice of R.

We see, then, that we are able to express the integral (8) in the form of a (convergent) infinite integral. This integral represents contributions from all possible configurations of dipole pairs; but of these, the ones corresponding to small values of the distance r will be the most important, due to the appearance of $1/r^3$ in the *exponential* function of the integrand. Of these configurations, in turn, the most important will be those in which the dipoles are in and near the position of lowest mutual potential energy at contact. When $\lambda = 1$, *i. e.*, in the case of spherical molecules, the stable position, where the two dipoles are parallel and in the same line according to (7), corresponds to $u = -2xkT$. When $\lambda = 1/\sqrt[3]{2}$, the potential energy in the above parallel position is the same as that for the dipoles antiparallel and the ellipsoids in contact at the ends of their minor axes; these two configurations are then equally probable. When $\lambda < 2^{-1/3}$, the antiparallel position is the stable (and most probable), with $u = -\lambda^{-3}xkT$. Here $r = \lambda a = b$, $\Theta' = \pi/2$, $\Theta'' = \pi/2$ and $\varphi'' = \pi$. We shall limit our discussion to the case where the antiparallel position is the stable position and consider cases where $\lambda < 2^{-1/2}$ (*i. e.*, $< 2^{-1/3}$). We may visualize the integral as the (hyper-) volume under a (hyper-) surface in r, Θ', Θ'', φ'' 4-space; in view of the fact that the numerically large parameter x appears in the exponent, we see that the integrand has a very high peak over the point $(b, \pi/2, \pi/2, \pi)$ from which it falls off rapidly in all directions integrably to zero. The main contribution to the integrand then is in the neighborhood of this

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(12) The energy (7) is, of course, the energy for two *point* dipoles. In the case of ion pairs, the two charges are separated by a finite distance, and a rigorous treatment demands that we retain the further terms of the expansion of the potential in spherical harmonics. These terms involve higher powers of $(1/r)$ than the cube and correspond to quadrupole and higher interactions, and are neglected here. The ion–ion interaction involves an energy proportional to $1/r$ and the ion triple equilibrium an energy proportional to $1/r^2$. In (7), we are therefore taking into account the next term of the formal series which can be set up to describe the mutual interaction of ions in solution, and higher terms are for the present not taken into account.

peak, which suggests that we look for the asymptotic expansion of the integral in terms of x. This asymptotic expansion will have the conventional form

$$F(x)\left(1 + \frac{a_1}{x} + \frac{a_2}{x^2} + \ldots\right)$$

where $F(x)$ takes into account the rapid variation of the function with changing argument, and the quantity in parentheses is the semi-convergent series, whose total value changes only slowly with x where x is large. We shall retain only the first term of the series, and consistently drop all terms of order x^{-1} or smaller as compared to unity.

In order to obtain the desired expansion, equation (8) furnishes the most convenient starting point. In the region of the peak of the integrand, we set

$$\varphi'' = \pi + \epsilon, \qquad \cos\varphi'' = -1 + \frac{\epsilon^2}{2} - \,..$$

$$\Theta' = \frac{\pi}{2} + \epsilon_1, \qquad \Theta'' = \frac{\pi}{2} + \epsilon_2,$$

$$r = b\left(1 + \frac{1-\lambda^2}{2\lambda^2}\epsilon_1^2 + \,..\right)\left(1 + \frac{\delta}{b}\right)$$

and integrate over the new variables ϵ, ϵ_1, ϵ_2 and δ in the neighborhood of $\epsilon = 0$, $\epsilon_1 = 0$, etc. The method will be illustrated by the integration over φ'' near $\varphi'' = \pi$; in order to save space, the details of the other entirely analogous steps will be omitted. We have from (8)

$$I \sim \frac{1}{2}\left\{\int_{\Theta' \approx \frac{\pi}{2}} \sin\Theta'\, d\Theta' \int_{\Theta'' \approx \frac{\pi}{2}} \sin\Theta''\, d\Theta'' \int_{r \approx b} r^2 dr \exp\left(\frac{2B}{r^3}\cos\Theta'\cos\Theta''\right)\right\} \int_{\varphi'' \approx \pi} \exp\left(\frac{-B}{r^3}\sin\Theta'\sin\Theta''\right) \cos\varphi''\, d\varphi''$$

where $B = \mu^2/DkT$ and unity has been neglected compared to the exponential function in the integrand. Substituting the expansion for φ'' near $\varphi'' = \pi$, we obtain

$$I \sim \frac{1}{2}\left\{\quad\right\} \int_{-\epsilon}^{+\epsilon} \exp\left(\frac{B}{r^3}\sin\Theta'\sin\Theta''\left[1 - \frac{\epsilon^2}{2} + \,..\right]\right) d\epsilon$$

where we integrate over the region of ϵ near zero. Writing $A = B\sin\Theta'\sin\Theta''/r^3$, this becomes

$$I \sim \frac{1}{2}\left\{\quad\right\} e^A \int_{-\epsilon}^{+\epsilon} e^{-A\epsilon^2/2}\, d\epsilon$$

Since A is numerically large (when Θ' and Θ'' are near $\pi/2$), we may replace the above expression by

$$I \sim \frac{1}{2}\left\{\quad\right\} e^A \int_{-\infty}^{+\infty} e^{-A\epsilon^2/2}\, d\epsilon$$

within the permissible error of x^{-1} compared to unity. This integral is known, and gives

$$I \sim \frac{1}{2}\left\{\quad\right\} e^A \sqrt{2\pi/A}$$

In a similar way, we integrate over the other variables, Θ', Θ'' and r near the peak of the integrand, and obtain the result

$$I = \left(\frac{\pi}{3}\right)^{3/2} \frac{\mu^2}{DkT} \frac{ze^y}{y^{7/2}} \left(1 + o\,(x^{-1})\right) \tag{9}$$

where

$$y = \frac{x}{\lambda^3} = \frac{\mu^2}{b^3\, DkT} \tag{10}$$

and

$$z = \left(\frac{1}{2\lambda^2} - 1\right)^{-1/2} \tag{11}$$

Substituting this result in (6), we obtain for the osmotic equation

$$\frac{p_0 - p}{p_0} = \frac{N}{V}\left(\frac{\pi}{3}\right)^{3/2} \frac{\mu^2}{DkT} \frac{z}{2} \frac{e^y}{y^{7/2}} \tag{12}$$

where z, defined by (11), depends on the eccentricity of the ellipsoidal model and y, defined by (10), is a function of the temperature, the dielectric constant of the solvent medium and the minor axis of the ellipsoid (or major axis and λ).

Equation (12) represents the limiting law (valid for low concentrations) for solutes where the dissolved molecules possess dipole fields. The result is subject to the mathematical and physical approximations made in the derivation. The important mathematical approximations depend on the facts that

$$\mu^2/a^3DkT >> 1$$

for electrolytic solutions in solvents of low dielectric constant and that we have assumed a dilute solution of dipole molecules. The physical approximations are that we have neglected effects due to unpaired ions and have replaced the ion pairs by ellipsoids containing point dipoles. The result is therefore subject to the restrictions implied in these assumptions.

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

Summary

1. The osmotic 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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