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The Dielectric Properties of Liquid Mixtures[1]

BY GERALD OSTER

Introduction

There have been numerous attempts to determine the extent and nature of molecular association in solution from the dielectric polarization of the solutions.[1] The dielectric polarization was calculated from the Clausius–Mosotti equation using the observed dielectric constants of the solution. However, this equation, which is based on the Lorentz "local field," does not lead to correct dipole moments of polar molecules in non-polar solvents except for extremely dilute solutions of the polar molecules. For all but very dilute solutions of polar molecules the polarization as calculated from the Clausius–Mosotti equation is in disagreement with the polarization calculated according to the Debye theory[1a] using the dipole moments of the molecules determined in the gaseous state. The discrepancy between the polarization calculated from the dielectric constant and that from the dipole moment of the gaseous molecules was attributed to molecular association in the liquid state. It was necessary to devise rather artificial molecular models to account for the change in polarization as a function of concentration. Furthermore, the polarization for solutions calculated from the Clausius–Mosotti equation appears to have no relation to the thermodynamic properties of these solutions.

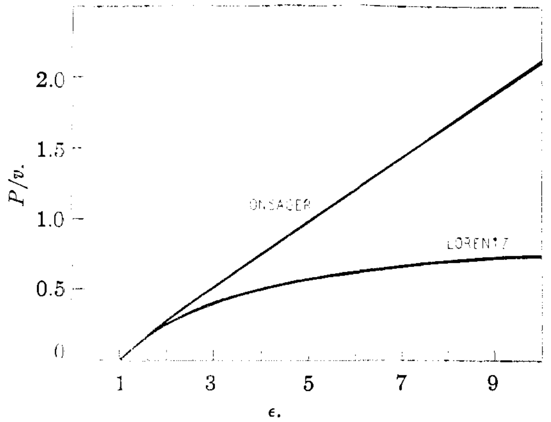

Fig. 1.—Polarization per unit volume as a function of dielectric constant according to Lorentz and to Onsager.

Onsager[2] in 1936 pointed out that the essential difficulty of the Clausius–Mosotti equation is in the choice of the inner or local field due to Lorentz.[3] The derivation of the Lorentz local field is an artificial procedure[4] and for polar liquids does not lead to agreement with experimental results. Onsager determined the local field on a molecule in a liquid by regarding the molecule as a real cavity imbedded in a medium with a homogeneous dielectric constant right up to the surface of the molecule. The polarization per unit volume in the Onsager case is equal to $(\epsilon - 1)(2\epsilon + 1)/9\epsilon$ and differs considerably from the Clausius–Mosotti equation $(\epsilon - 1)/(\epsilon + 2)$ except for very low dielectric constants. The polarizations per unit volume as a function of dielectric constant, ϵ, for the two cases are illustrated in Fig. 1. There is close agreement only for dielectric constants below two, the region corresponding to dielectric constants of extremely dilute solutions of polar molecules in non-polar solvents. In addition Onsager considers the field of the dipole in the cavity which induces polarization on its surroundings and which in turn reacts upon the dipole to enhance its moment. The Onsager theory predicts the dielectric constants for so-called "unassociated" or "normal" liquids such as ethyl bromide or chloroform from the known dipole moments of the molecules.[5] However, the theory fails to give even approximate agreement for the so-called "thermodynamically abnormal" liquids such as water, the aliphatic alcohols, etc.

Kirkwood[6] has generalized the Onsager theory to take into account the dielectric inhomogeneity of the medium in the vicinity of a molecule due to the hindering of rotation of its neighbors by the molecule. He derives for the dielectric polarization

$$\frac{(\epsilon - 1)(2\epsilon + 1)}{9\epsilon}v = P_e + P_a + \frac{4\pi}{3}N\frac{\mu^2 g}{3kT} \quad (1)$$

where v is the molal volume, P_e and P_a are the electronic and atomic polarizations,[7] N is Avogadro's number, k is Boltzmann's constant, T is the absolute temperature, μ is the dipole moment of the molecule in the liquid (μ is slightly larger than μ_0, the moment in the gaseous state, because of the Onsager reaction field), and g is a parameter whose value differing from unity is a measure of the hindering effect of a molecule on its neighbors. Kirkwood showed by statistical mechanics

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[1] Paper presented before the Division of Physical and Inorganic Chemistry at the 109th meeting of the American Chemical Society, Atlantic City, New Jersey, April 11, 1946.

[1a] C. P. Smyth, "Dielectric Constant and Molecular Structure," New York, 1931, Chapter IX; P. Debye and H. Sack, "Handbuch der Radiologie," Band VI, 2 Auflage, Leipzig, 1934, Chapter II, Section 12. These authors cite numerous references to earlier work.

[2] L. Onsager, THIS JOURNAL, **58**, 1486 (1936).

[3] H. A. Lorentz, "Theory of Electrons," Leipzig, 1909, p. 303.

[4] For a critique of Lorentz's theory, see J. A. van Vleck, *Ann. N. Y. Acad. Sci.*, **60**, 293 (1940).

[5] J. N. Wilson, *Chem. Rev.*, **25**, 377 (1939); S. R. Phadke, S. D. Gokhale, W. L. Phalnikar and B. V. Bhide, *J. Indian Chem. Soc.*, **22**, 235 (1945).

[6] J. G. Kirkwood, *J. Chem. Phys.*, **7**, 911 (1939). See also A. J. Anselm, *Acta Physicochimica U. R. S. S.*, **18**, 499 (1943).

[7] See, for example, J. van Vleck, "Electronic and Magnetic Susceptibilities," Oxford, 1932, Chapter III.

how g can be calculated from a knowledge of the structure of the liquid in the vicinity of any molecule. From X-ray data on the structure of water and alcohols Oster and Kirkwood[8] have calculated values for g which give good agreement with values determined from the observed dielectric constants of these liquids.

The Onsager–Kirkwood theory has been applied by Kirkwood[9] to dilute aqueous solutions of dipolar ions and by Oster[10] to solutions of dipolar ions in mixed solvents. In the latter case electrostatic sorting of the higher dielectric constant component of the solvent by the dipolar ions results in a rather special type of molecular association with a consequent electrostatic shielding of the dipolar ion.

In the present paper the dielectric properties of polar molecules in non-polar and in polar solvents will be considered in the light of the Onsager–Kirkwood theory. Attempts will be made to explain the dielectric properties of these systems as a function of concentration and of temperature by intermolecular association; the molecular models chosen are reasonable and generally applicable.

Application of the Onsager–Kirkwood Theory to Solutions

In the simpler case of polar molecules in a non-polar solvent we shall assume that the properties of the non-polar component are independent of the concentration. An obvious extension of Eq. (1) is then

$$\frac{(\epsilon - 1)(2\epsilon + 1)}{9\epsilon} \frac{M_1x_1 + M_2x_2}{d_{12}} = x_1P_1 + x_2P_2 \qquad (2)$$

$$P_2 = P_{e2} + P_{a2} + \frac{4\pi}{3} N \frac{\mu^2 g}{3kT}$$

1 and 2 refer to the non-polar and polar components, respectively, ϵ and d_{12} are the dielectric constant and density of the mixture at mole fraction x_2 of the polar constituent. P_1 is the polarization of the non-polar solvent as determined from the index of refraction of that constituent. μ is the dipole moment of the polar molecules in solution. According to Onsager,[2] for a spherical molecule

$$\mu = \frac{2\epsilon + 1}{2\epsilon + n_2^2} \frac{n_2^2 + 2}{3} \mu_0 \qquad (3)$$

where n_2 is the index of refraction of the polar component and μ_0 is the dipole moment in the gaseous state. Although the formula can be generalized for an elliptical molecule, such a correction is so small for most molecules that Eq. (3) is used throughout this paper. If it is assumed that a molecule in a liquid hinders the rotation of only its first shell of neighbors then the hindering or correlation parameter, g, becomes, according to Kirkwood[6]

$$g = 1 + z(\cos \gamma)\, av \qquad (4)$$

$$(\cos \gamma) av = \int\int \cos \gamma e^{-W_0/kT} d\omega_1\, d\omega_2$$

where γ is the angle between the dipole moment of a molecule and its neighbor and the integration extends over all relative orientations of the pair. W_0 is the potential of average torque on a pair of nearest neighbors. z is the number of nearest neighbors beyond which the local dielectric constant is considered effectively equal to the macroscopic dielectric constant. Oster and Kirkwood[8] found that even for the highly coördinated liquid, water, only the first shell of neighbors need be considered. The amount g differs from unity is a measure of the divergence from the Onsager theory, *i.e.*, it is a measure of the influence of a molecule on the rotation of molecules in its vicinity. This parameter which depends only on the number of neighbors of a molecule and their relative configuration is a more explicit measure of the extent and nature of molecular association than is the polarization. For example, in the case of dimer association g nearly zero indicates strong antiparallel association, g nearly 2 indicates strong parallel association. If we assume a form for the potential W_0 we can deduce the temperature dependence of g from eq. (4). Thus if the potential barrier restricting rotation of neighboring pairs of dipoles in a *polar* liquid is of the form $W_0 = {}^1/_2W' (1 - \cos \gamma)$ where W' is the maximum height of the potential barrier and if z and W' are considered independent of temperature, then for high enough temperatures[11]

$$g = 1 + \frac{A}{T} \qquad (5)$$

where A is a constant depending on z, W' and the angle which the dipole moment makes with the direction of the intermolecular bond. For a few liquids (C_2H_5OH, CH_3OH, HCN) examined by the writer $g - 1$ was found roughly linear in $1/T$ in agreement with eq. (5).

In the following section the correlation parameter, g, is calculated for polar molecules in solution as a function of concentration and temperature from observed values of the dielectric constants and the densities of the solution according to eq. (2) using the indicated gaseous dipole moments to calculate the dipole moment of the molecules in solution according to eq. (3).

The Dielectric Properties of Polar Molecules in Non-polar Solvents.—In order to study association of polar molecules in non-polar solvents the correlation parameter, g, has been calculated for some typical solutions, acetone–carbon tetrachloride, nitrobenzene–hexane, n-butyl bromide–hexane, ethyl alcohol–heptane, ethyl alcohol–hexane. The results are given in Table I and II and represented in Figs. 2, 3, 4, 5 and 6. All these substances show the same general behavior of g as a function of concentration; for the pure polar liquid g is nearly equal to or greater than one, and as its concentration decreases g goes through a

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[8] G. Oster and J. G. Kirkwood, *J. Chem. Phys.*, **11**, 175 (1943).

[9] J. G. Kirkwood, Chaper 12 in E. J. Cohn and J. T. Edsall, "Proteins, Amino Acids, and Peptides," New York, 1943.

[10] G. Oster, THIS JOURNAL, **66**, 948 (1944).

[11] Compare, J. G. Kirkwood, *Ann. N. Y. Acad. Sci.*, **60**, 315 (1940).

TABLE I

CORRELATION PARAMETER AS A FUNCTION OF CONCENTRATION

Acetone–Carbon tetrachloride[a]

$P_{e_2} + P_{a_2} = 18.4$ $\mu_0 = 2.80 \times 10^{-18}$ $t = 25°$

x_2	ϵ	μ	g
0	2.230	2.88	1.00
0.10	3.28	3.22	0.89
.25	4.98	3.33	.84
.30	5.67	3.35	.85
.40	6.17	3.37	.95
1.00	21.3	3.80	1.08

Nitrobenzene–Hexane[b]

$P_{e_2} + P_{a_2} = 38.0$ $\mu_0 = 3.90 \times 10^{-18}$ $t = 25°$

x_2	ϵ	μ	g
0	1.904	4.42	1.00
0.05	2.624	4.67	0.79
.10	3.474	4.86	.76
.25	6.300	5.19	.72
.49	14.68	5.47	.91
1.00	36.10	5.60	1.18

[a] Dielectric constant and density data from I. J. Krchma and J. W. Williams, THIS JOURNAL, **49,** 2408 (1927). [b] Also from J. W. Williams and E. F. Ogg, *ibid.*, **50,** 94 (1928).

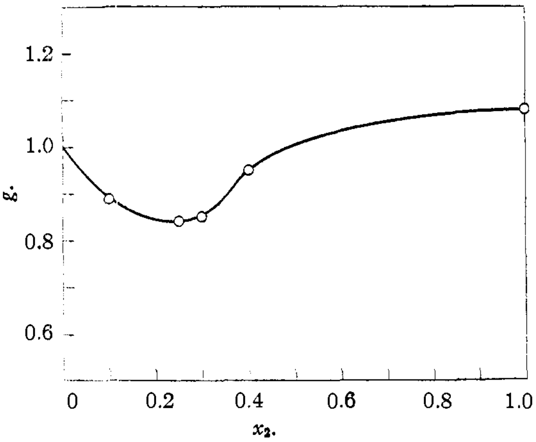

Fig. 2.—Correlation parameter of acetone–carbon tetrachloride mixtures.

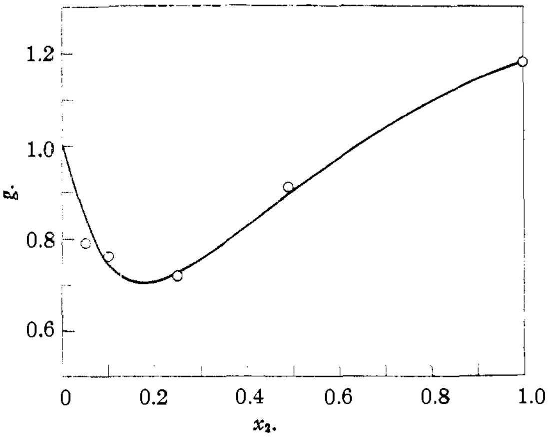

Fig. 3.—Correlation parameter of nitrobenzene–hexane mixtures.

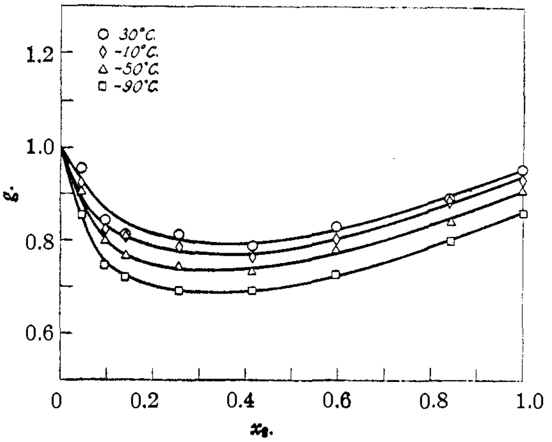

Fig. 4.—Correlation parameter of *n*-butyl bromide–heptane mixtures.

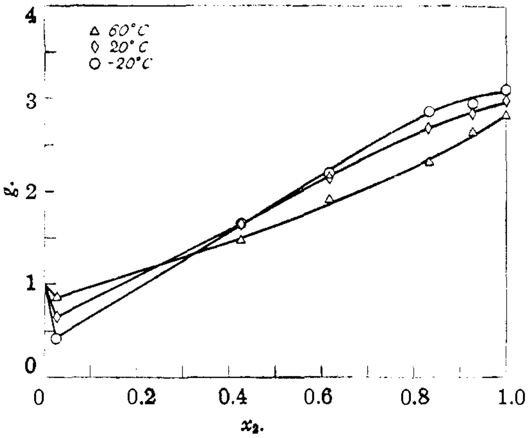

Fig. 5.—Correlation parameter of ethyl alcohol–heptane mixtures.

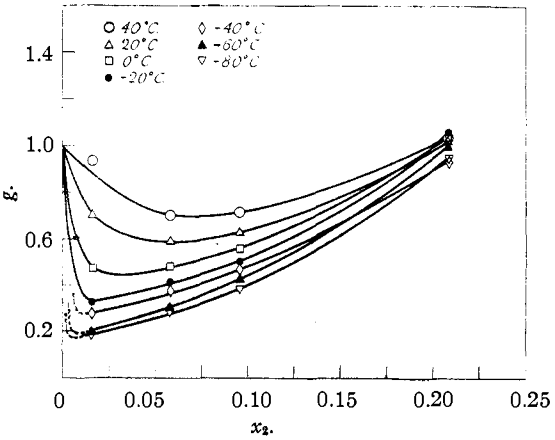

Fig. 6.—Correlation parameter of ethyl alcohol–hexane mixtures.

minimum and increases again at still further dilution becoming, by definition, unity at infinite dilution. The minimum in the g curve corresponds to a concentration where the polar molecules are associated in a configuration resulting,

TABLE II

CORRELATION PARAMETER AS A FUNCTION OF CONCENTRATION AND TEMPERATURE

n-BUTYL BROMIDE–HEPTANE[a]

$P_{e2} + P_{a2} = 46.1 \quad \mu_0 = 1.85 \times 10^{-18}$

	x_2	0.0456	0.0930	0.1409	0.2579	0.4154	0.5959	0.8413	1.000
	ϵ	2.349	2.588	2.854	3.548	4.687	6.280	8.970	11.08
−90°	μ	2.15	2.18	2.20	2.26	2.33	2.40	2.45	2.48
	g	0.856	0.748	0.722	0.692	0.694	0.729	0.800	0.860
	ϵ	2.239	2.441	2.653	3.226	4.119	5.405	7.565	9.258
−50	μ	2.11	2.14	2.17	2.22	2.28	2.33	2.40	2.42
	g	0.904	0.800	0.768	0.745	0.736	0.782	0.841	0.908
	ϵ	2.149	2.310	2.491	2.957	3.679	4.732	6.474	7.880
−10	μ	2.09	2.11	2.13	2.18	2.23	2.28	2.32	2.37
	g	0.925	0.822	0.809	0.789	0.763	0.802	0.886	0.933
	ϵ	2.064	2.197	2.346	2.737	3.336	4.203	5.640	6.799
30	μ	2.07	2.09	2.11	2.14	2.19	2.24	2.29	2.32
	g	0.955	0.842	0.810	0.813	0.789	0.830	0.891	0.955

ETHYL ALCOHOL–HEPTANE[b]

$P_{e2} + P_{a2} = 13.6 \quad \mu_0 = 1.70 \times 10^{-18}$

	x_2	0.0256	0.4252	0.6142	0.8300	0.9260	1.000
	ϵ	2.015	5.55	10.49	20.3	25.5	30.7
−20°	μ	1.87	2.06	2.12	2.16	2.17	2.18
	g	0.43	1.65	2.20	2.83	2.95	3.10
	ϵ	1.968	4.59	8.40	15.5	19.8	23.8
20	μ	1.86	2.00	2.08	2.12	2.14	2.14
	g	0.66	1.63	2.16	2.68	2.84	2.98
	ϵ	1.915	3.76	6.48	11.8	15.2	18.7
60	μ	1.85	1.97	2.04	2.08	2.10	2.11
	g	0.88	1.49	1.92	2.31	2.64	2.82

ETHYL ALCOHOL–HEXANE[b]

$P_{e2} + P_{a2} = 13.6 \quad \mu_0 = 1.70 \times 10^{-18}$

	x_2	0.0153	0.0578	0.0962	0.2076
	ϵ	2.077	2.144	2.248	3.360
−80°	μ	1.88	1.89	1.90	2.00
	g	0.188	0.286	0.381	0.950
	ϵ	2.045	2.114	2.214	3.225
−60	μ	1.88	1.89	1.90	1.98
	g	0.198	0.305	0.421	1.000
	ϵ	2.016	2.083	2.179	3.075
−40	μ	1.87	1.88	1.89	1.97
	g	0.280	0.379	0.472	0.940
	ϵ	1.989	2.054	2.145	2.913
−20	μ	1.87	1.88	1.89	1.95
	g	0.332	0.416	0.508	1.065
	ϵ	1.964	2.026	2.111	2.755
0	μ	1.86	1.87	1.88	1.94
	g	0.478	0.484	0.562	1.045
	ϵ	1.940	2.002	2.082	2.622
20	μ	1.85	1.86	1.88	1.92
	g	0.707	0.592	0.633	1.035
	ϵ	1.914	1.978	2.054	2.507
40	μ	1.85	1.86	1.88	1.91
	g	0.942	0.704	0.718	1.040

[a] Dielectric constant and density data from C. P. Smyth and H. E. Rogers, THIS JOURNAL, **52,** 2227 (1930). [b] Also from C. P. Smyth and W. N. Stoops, *ibid.*, **51,** 3312 (1929).

on an average, in the smallest effective dipole moment per molecule over the entire concentration range. It is interesting to compare the curves for acetone (Fig. 2) and nitrobenzene (Fig. 3). Nitrobenzene has a larger dipole moment than has acetone. Furthermore, because of the flat benzene ring attached to the nitro group there may be a tendency for the dipoles in pure nitrobenzene to become slightly aligned. Thus pure nitrobenzene exhibits a greater value of g than does acetone. At a mole fraction of 0.17 in the polar component g for nitrobenzene decreases to 0.7 suggesting a tendency toward antiparallel arrangement of pairs of dipoles. The value of g increases for greater dilutions where the dipoles become free from each other and they are completely unhindered in their rotations at infinite dilution. The minimum occurs at low concentrations of the polar component since it is necessary to dilute the nitrobenzene liquid structure in order to allow the dipoles to orient into their antiparallel positions. At further dilutions the tendency for this arrangement is decreased. Acetone however not having such a large dipole moment nor such packing possibilities as nitrobenzene has a lower g in the pure liquid state and has a minimum in g at a higher concentration and the minimum is less pronounced than that for nitrobenzene.

The minimum for *n*-butyl bromide (Fig. 4) occurs at even greater concentrations of the polar constituent. *n*-Butyl bromide has a relatively small dipole moment which is deeply imbedded in the molecules. The values of g at the minima decrease with decreasing temperature.

The effects discussed above are much more pronounced in the case of ethyl alcohol. X-Ray diffraction studies of ethyl alcohol[12] show that pure alcohol has a highly coördinated structure with tendencies for the alcohol molecules to align end to end because of hydrogen bonding. This results in abnormal thermodynamic behavior of the liquid and in a high dielectric constant although the individual alcohol molecules do not have large dipole moments.[8] Thus g is quite large for pure alcohol but, as shown by the curves in Fig. 5, it is necessary to go to very low concentrations (less than mole fraction 0.10) in order to loosen up the coördinated structure of the pure liquid in order to form complexes having low dipole moments. The effect of lowering the temperature is to enhance the coördination of the molecules in the pure liquid with a consequent increase in g. However, lowering the temperature increases the stability of the complex of associated molecules in the low concentration region, thus g is lowered there. Lowering the temperature increases the stability of any associated structure, therefore the curves for g *versus* concentration at different temperatures cross in a region where the coördinated structure is reverting to the other association of molecules which gives a lower dipole moment per molecule. The effect of increasing the temperature is to flatten the curves and in the case of infinitely high temperature g is equal to unity at all concentrations, *i.e.*, completely independent dipoles. The influence of temperature on the minimum of g is better illustrated in Fig. 6, the correlation parameter as a function of temperature at small concentrations. The minimum of g is decreased with decreasing temperature, furthermore as the temperature is lowered the minimum appears at lower concentrations. Apparently the lower the temperature the more dilute the polar liquid must be in order to loosen up its increasingly more stable coördinated structure.

The slopes of the g *versus* mole fraction curves on the very dilute concentration side of the minima can be approximately accounted for by a dipole–dipole interaction theory due to Fuoss.[13] However the experimental measurements do not extend to sufficiently dilute concentrations at various temperatures to warrant a quantitative comparison with that theory.

The systems discussed above are fairly typical of many other systems of dipole molecules in non-polar solvents examined by the writer. A more quantitative analysis of the nature and extent of association in these systems as has been done for water and alcohol requires further information concerning the structure of these solutions especially that which can be obtained from data on X-ray scattering as a function of concentration and temperature.

Dielectric Properties of Polar Molecules in Polar Solvents

Relatively little experimental work has been done on the measurement of the dielectric constants of mixtures of polar substances with the exception of dilute aqueous solutions of polar molecules. In the general case interpretation of the data would be expected to be difficult since one must not only consider the interactions of each molecule with one similar to it (g_1 and g_2) but also the interaction of polar molecules of different type (g_{12}). However in the case of dilute aqueous solutions of polar molecules the situation turns out to be rather simple.

We shall assume, as a crude approximation, that the addition of small amounts of a polar substance to water contributes a mere additive effect to water, *i.e.*, assume $P = x_1P_1 + x_2P_2$ or

$$\frac{(\epsilon - 1)(2\epsilon + 1)}{9\epsilon}\, v = \frac{(\epsilon_1 - 1)(2\epsilon_1 + 1)}{9\epsilon_1}\, x_1v_1 + \frac{(\epsilon_2 - 1)(2\epsilon_2 + 1)}{9\epsilon_2}\, x_2v_2 \quad (6)$$

where v is the mean molar volume. If subscript 1 represents water and since we are dealing with dilute aqueous solutions, at room temperature, both ϵ and ϵ_1 are much greater than one. Also if we assume an additivity of volumes, *i.e.*, $v = x_1v_1 + x_2v_2$ then eq. (6) becomes to a good approximation after rearranging

$$\epsilon = \epsilon_1 + \left[\frac{(\epsilon_2 - 1)(2\epsilon_2 + 1)}{2\epsilon_2} - (\epsilon_1 - 1)\right] \frac{x_2v_2}{v} \quad (7)$$

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(12) W. H. Zachariasen, *J. Chem. Phys.*, **3**, 158 (1935); W. C. Pierce and D. P. MacMillan, THIS JOURNAL, **60**, 779 (1938); G. C. Harvey, *J. Chem. Phys.*, **7**, 878 (1939).

(13) R. M. Fuoss, THIS JOURNAL, **56**, 1031 (1934). See also J. N. Wilson, *loc. cit.*

For dilute solutions we can replace x_2/v by $c_2/1000$ where c_2 is the concentration of the solute in moles per liter. Then eq. (7) becomes

$$\epsilon = \epsilon_1 + \delta c_2$$
$$\delta = \left[\frac{(\epsilon_2 - 1)(2\epsilon_2 + 1)}{2\epsilon_2} - (\epsilon_1 - 1)\right]\frac{v_2}{1000} \quad (8)$$

Eq. (8) has the form of a well-known experimental result which states that for dilute aqueous solutions the dielectric constant is a linear function of the concentration, the slope, δ, being characteristic of the solute and is independent of the concentration for low concentrations.[14] In Table III are given the values of the dielectric increment, δ, for various aqueous solutions as calculated from eq. (8). All the values are for 25° (ϵ_1 = 78.5) and are compared with the observed values compiled by Edsall.[14] The agreement with observed values is fairly good considering the crudeness of the assumptions. Better agreement is achieved by replacing the molal volume of the solute in eq. (8) by the apparent molal volume; however, the apparent molal volumes in water for many of these substances have not been reported in the literature. Good agreement with experiment would be expected for those substances which have correlation parameters, g, equal to unity in the pure liquid state and do not form complex associations with water. An interesting example of probable complex association with water is the case of 1,4-dioxane (ϵ_2 = 2.1, v_2 = 85.0). The dielectric increment calculated for aqueous solutions of this substance is −6.45 compared with the observed value of −8.3. Whereas for the substances in Table III the calculated dielectric increment is generally less negative than the observed values, dioxane shows a very much *larger* negative value. This suggests that dioxane forms a complex association, probably between the protons of the water molecules and the oxygen atoms of the dioxane heterocyclic ring, which partially destroy the highly coördinated structure of water with a consequent decrease in the effective dipole moment of the water molecules. There is evidence from viscosity studies of dioxane–water mixtures that a hydrate of dioxane with four or five water molecules is formed.[15] The fact that dioxane is one of the few zero dipole moment substances which are completely miscible in water indicates that some such association does take place.

TABLE III

CALCULATED AND OBSERVED VALUES OF THE DIELECTRIC INCREMENT FOR AQUEOUS SOLUTIONS AT 25°

	ϵ_2	v_2	$-\delta$ (calcd.)	$-\delta$ (obs.)
Methyl alcohol	33.7	40.5	1.79	1.4
Ethyl alcohol	25.1	58.7	3.11	2.6
n-Propyl alcohol	21.8	75.1	4.22	4.0
t-Butyl alcohol	11.4	94.2	6.26	6.3
Acetone	21.5	73.4	4.13	3.2
Ether	4.5	103.0	7.57	7.1
Glycol	41.2	55.0	2.04	1.8
Aniline	7.2	90.1	6.40	7.6
Methyl acetate	7.3	80.0	5.65	5
Pyridine	12.5	80.6	5.27	4.2
Acetonitrile	38.8	52.5	2.08	1.7
Nitromethane	39.4	54.2	2.11	2.0

Summary

The Onsager–Kirkwood theory of dielectric polarization of polar liquids is applied to solutions of polar molecules. A correlation parameter, whose value differing from unity is a measure of the hindering effect of a molecule on its neighbors, is calculated for solutions of polar molecules in non-polar solvents. This parameter is a direct measure of the extent and nature of molecular association. All of the systems examined show the same general behavior: parallel association of dipoles in solutions of large concentrations of the polar components and antiparallel association at some lower concentrations. At extremely dilute solutions the dipoles become free of each other. Lowering the temperature enhances both parallel and antiparallel associations, the latter arrangement becomes more pronounced at lower concentrations.

Low concentrations of various polar molecules in water generally alter the dielectric constant of the water in a predictable manner. However, dioxane lowers the dielectric constant of water much more than predicted by theory, indicating strong interaction with water.

PRINCETON, N. J.
RECEIVED MAY 28, 1946

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(14) J. T. Edsall, in C. L. A. Schmidt, "The Chemistry of Amino Acids and Proteins," C. V. Mosby Co., Springfield, Ill., 1938, p. 882; J. Wyman, *Chem. Rev.*, **19**, 213 (1936); W. P. Conner, R. P. Clarke and C. P. Smyth, THIS JOURNAL, **64**, 1379 (1942).

(15) J. A. Geddes, *ibid.*, **55**, 4832 (1933); E. Mariani, *Chem. Zentr.*, **113**, I, 1737 (1942).