[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ARKANSAS]

Electrolyte-Solvent Interactions. Polar Properties of Electrolytes in Low Dielectric Solvents[1]

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The contact distances of the tetrabutylammonium picrate and tetrabutylammonium bromide ion pairs are determined from dielectric measurements. Different methods of calculation are critically compared. The effect of different solvents on the distance is examined. It is shown that the extent of the formation of ionic aggregates in a mixed polar-nonpolar solvent depends on the concentration of polar solvent and not on the dielectric constant of the mixture.

Introduction

It has been shown recently[3,4] that the equations which are used to calculate ion pair contact distances (a) from conductance data[5-7] yield considerably different a values from the same experimental dissociation constants. Also, a values for a given electrolyte in different solvents differ when the same equation is used. The latter variation may be explained qualitatively in terms of differences in polarization of the electrolyte by different solvents—although differences of more than 1 Å. seem rather large. The former variation probably reflects differences in the assumptions made in the various theories. It should be recognized that the chain of reasoning which leads from an "experimental" K (K itself results from a rather elaborate theory) to a "contact distance" is long. Any theory of solutions which may be developed from molecular considerations will require accurate distance parameters. From this viewpoint the present situation is rather unsatisfactory. That all theories yield "reasonable" a values, *i.e.*, of molecular dimensions, is no great consolation. A simple method for determining a values consists of measuring the dipole moment of ion pairs. Formally the charge–charge distance of an ion-pair may be treated just like the corresponding distance within a polar molecule, *i.e.*, $\mu = ae$. Surprisingly, the only study of this kind was carried out by Kraus and co-workers[8,9] about twenty-five years ago, when many of the theoretical tools now available for analysis (*e.g.*, the Onsager and Kirkwood theories) did not exist. Using the Debye equation and a simple extrapolation of solute polarization to infinite dilution, they found that the a values thus obtained for a large number of electrolytes in benzene were less than the corresponding a's calculated from the Bjerrum theory.

It is the purpose of this paper to re-examine the problem of determining a values of ion-pairs from dielectric measurements in the light of recent theories, using measurements of tetrabutylammonium picrate in benzene, to extend the work to other solvents and finally to present some results of the application of dielectric measurements to a study of ion association in mixed solvents.

Experimental

Apparatus.—Dielectric measurements were carried out at 100 kc. using an apparatus designed by Testerman and Scherer[10] which employs the resonance method. The total capacitance of a General Radio precision condenser (722-N) and the measuring cell is kept constant in this method. The cell, of about 170 $\mu\mu$f capacitance, follows a design of Smyth[11] but uses three concentric nickel cylinders as electrodes. It was calibrated using benzene (purified as described below) to which was assigned at 25° a dielectric constant of 2.2730.[12] All measurements reported here are referred to this value. Measurements were carried out at 25, 35 and 45° by moving the cell from one oil-filled bath to another. The geometry of the system at each temperature was held constant by mounting all lead wires rigidly and keeping the cell position in each bath fixed with a weighted, wooden cell holder set in it. The temperature in each bath was constant to ± 0.002°.

Materials.—**Tetrabutylammonium bromide** was prepared from the corresponding iodide (Eastman Kodak) in this way. The iodide, after being recrystallized three times from benzene–petroleum ether mixtures, was dissolved in an ethanol-water solution and treated with a silver oxide slurry. After filtration, the resulting solution was titrated to pH 7 with dilute HBr solution and evaporated, first on a steam-bath, then under vacuum. The dried salt was recrystallized three times from benzene–petroleum ether mixtures or ethyl acetate and dried three weeks over anhydrous $Mg(ClO_4)_2$ before use. Its melting point (for various batches) ranged from 119.4 to 116.0°, compared with a literature value[13] of 119.5.

Tetrabutylammonium picrate was prepared similarly but employing the reaction of the iodide with silver picrate. Its melting point was 89.5°, in agreement with previous work.[3,8]

Benzene,[14] **dioxane**,[15] **toluene**,[16] **methanol**,[17] and **nitrobenzene**[18] were purified by the methods described in the respective references.

Preparation of Solutions.—All solutions were prepared by weight, using dilution techniques. Sufficient material was used to yield five significant figures in the concentration. In the case of the mixed solvent systems it was found that a stock solution stored in a mixing flask changes its composition slightly on standing since the more volatile component vaporizes preferentially. This is indicated by a fourth place change in the dielectric constant of the mixture over a 24 hr. period. This change in dielectric constant was therefore determined in a separate run and an appropriate correction applied to all subsequent solution measurements in this solvent.

Density Measurements.—The density of the one or two most concentrated solutions was determined in a Lipkin

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(2) From the M.S. Thesis of E. A. Richardson.

(3) P. H. Flaherty and K. H. Stern, THIS JOURNAL, **80**, 1034 (1958).

(4) K. H. Stern and E. S. Amis, *Chem. Revs.*, **59**, 1 (1959).

(5) N. Bjerrum, *Kgl. Danske Videnskab. Selskab.*, **7**, No. 9 (1926).

(6) J. T. Denison and J. B. Ramsey, THIS JOURNAL, **77**, 2615 (1955).

(7) W. R. Gilkerson, *J. Chem. Phys.*, **25**, 119 (1956).

(8) J. A. Geddes and C. A. Kraus, *Trans. Faraday Soc.*, **32**, 585 (1936).

(9) G. S. Hooper and C. A. Kraus, THIS JOURNAL, **56**, 2265 (1934).

(10) P. C. Scherer and M. K. Testerman, *J. Polymer Sci.*, **7**, 549 (1951).

(11) C. P. Smyth and S. O. Morgan, THIS JOURNAL, **50**, 1547 (1928).

(12) R. M. Davies, *Phil. Mag.*, **VII**, 211, 1008 (1936).

(13) H. Sadek and R. M. Fuoss, THIS JOURNAL, **72**, 301 (1950).

(14) N. J. Leonard and L. E. Sutton, *ibid.*, **70**, 1564 (1948).

(15) C. A. Kraus and R. A. Vingee, *ibid.*, **56**, 511 (1934).

(16) A. I. Vogel, *J. Chem. Soc.*, 607 (1948).

(17) N. G. Foster and E. S. Amis, *Z. physik Chem. (Frankfurt)*, 3, 365 (1955).

(18) J. Meisenheimer and O. Dorner, *Ann. Chem.*, **482**, 130 (1930).

pycnometer at 25, 35 and 45°. It was assumed that the density varied linearly with concentration in these dilute solutions. The pycnometer was calibrated with conductivity water.

Refractive Index.—All pure solvents and the most concentrated solutions were measured with a Bausch and Lomb Dipping Refractometer at 25, 35 and 45°. More dilute solutions were measured until their refractive index was indistinguishable from that of the pure solvents. All measurements are standardized to $n_D = 1.49797$ for benzene at 25°.

Experimental Results

Table I lists the dielectric constants, refractive indexes and densities of the pure solvents and of solutions of Bu_4NPi in benzene, dioxane and toluene in two benzene–methanol mixtures. Mole fraction units have been used throughout. The densities are expressed as linear equations in X_2(BuNPi) to save space, and the refractive indices of the solutions are the same as those of the pure solvents, except where indicated. Table II contains similar data for Bu_4NBr solutions.

TABLE I

Bu_4NPi IN VARIOUS SOLVENTS

$X_2 \times 10^4$	$\epsilon_{12}(25°)$	$\epsilon_{12}(35°)$	$\epsilon_{12}(45°)$	d_{12} and $[n]_D^t$
(1) Benzene				
0.0	2.2693	2.2520	2.2344	25° $d_{12} = 0.87368 + 2.04X_2$
.083924	2.2720	2.2547	2.2355	$n_{12} = 1.49799$
.16694	2.2755	2.2581	2.2389	35° $d_{12} = 0.86316 + 1.58X_2$
.43505	2.2864	2.2672	2.2480	$n_{12} = 1.49347$
.88890	2.3052	2.2872	2.2662	45° $d_{12} = 0.85233 + 1.31X_2$
1.6942	2.3274	2.3077	2.2867	$n_{12} = 1.48721$
2.2190[a]	2.3474	2.3254	2.3043	
3.7160[b]	2.3818	2.3671	2.3443	
(2) Dioxane				
0.0	2.2219	2.2046	2.1894	25° $d_{12} = 1.02673 + 0.63X_2$
.092330	2.2259	2.2108	2.1937	$n_{12} = 1.42335$
.16644	2.2299	2.2131	2.1962	35° $d_{12} = 1.01558 + 0.46X_2$
.31058	2.2333	2.2194	2.2008	$n_{12} = 1.41941$
.53572	2.2447	2.2268	2.2093	45° $d_{12} = 1.00430 + 0.38X_2$
1.3286	2.2738	2.2575	2.2395	$n_{12} = 1.41470$
2.4260	2.3132	2.2940	2.2759	
3.8410	2.3611	2.3436	2.3214	
4.7460	2.3902	2.3703	2.3504	
7.9150	2.4723	2.4496	2.4317	
(3) Toluene				
0.0	2.3691	2.3480	2.3251	25° $d_{12} = 0.86160 + 1.06X_2$
.12132	2.3737	2.3535	2.3293	$n_{12} = 1.49310$
.36460	2.3799	2.3605	2.3353	35° $d_{12} = 0.85219 + 1.41X_2$
.75490	2.3907	2.3700	2.3456	$n_{12} = 1.48869$
1.4917	2.4091	2.3892	2.3616	35° $d_{12} = 0.84263 + 1.70X_2$
2.1526	2.4286	2.4071	2.3809	$n_{12} = 1.48349$
3.8793	2.4683	2.4457	2.4216	
Bu_4NPi IN BENZENE–METHANOL MIXTURES				
(4) Mole fraction MeOH = 0.00046552 in benzene				
0.0	2.2708	2.2578	2.2361	Values same as for pure benzene solutions (see 1)
.036380	2.2725	2.2573	2.2371	
.066219	2.2753	2.2582	2.2397	
.15081	2.2785	2.2625	2.2427	
.39805	2.2864	2.2695	2.2498	
1.0902	2.3110	2.2938	2.2724	
(5) Mole fraction MeOH = 0.047565 in benzene				
0.0	2.4828	2.4538	2.4191	25° $d_{12} = 0.87198 + 3.00X_2$
0.76695	2.5150	2.4854	2.4403	35° $d_{12} = .86141 + 3.15X_2$
1.3981	2.5374	2.5078	2.4724	45° $d_{12} = .85060 + 2.14X_2$
1.9820	2.5594	2.5296	2.4930	
3.5067	2.6098	2.5786	2.5417	

[a] $[n_{12}]^{25}D = 1.49793$, $[n_{12}]^{35}D = 1.49325$, $[n_{12}]^{45}D = 1.48688$. [b] $[n_{12}]^{25}D = 1.49745$, $[n_{12}]^{35}D = 1.49277$, $[n_{12}]^{45}D = 1.48647$.

In all cases agreement with literature values is satisfactory. Because of slight variations of the constants for the same material prepared at different times, the measured value for the actual solvent material used in a given run is listed with that run. For example, although the cell was calibrated with benzene to which a dielectric constant of 2.2730 had been assigned, the benzene used for the first run in Table I measured 2.2693 with the calibrated cell.

Results and Discussion

In order to assess the effect of different methods of calculation on the dipole moment of ion pairs we employ our data on Bu_4NPi in benzene.

Geddes and Kraus[8] calculated the dipole moment using the simple Debye equation and assumed that the solution polarization is a weighted average of the mole fractions of the components, *i.e.*, $P_{12} = P_1X_1 + P_2X_2$. The dipole moment then was obtained by direct extrapolation of P_2 to infinite dilution. This method is strictly applicable only to gases and yields quasi-vapor values when applied to solutions. The molar refraction is approximated sufficiently well for these large ions by adding up bond refractions.

Allen[19] recently has developed an extrapolation method which yields P_2^0, the molar polarization at infinite dilution, when the polarization and density are linear functions of the composition. We have used only that portion of our data where this is the case.

It has been pointed out by Onsager[20] that in solution the polarization of the solvent is affected by the solute so as to give rise to a reaction field at the dipole. There results for the polarization per unit volume the term $(\epsilon - 1)(2\epsilon + 2)/9\epsilon$ instead of $(\epsilon - 1)/(\epsilon + 2)$. Kirkwood[21] has modified this theory to take hindered rotation into account. Oster[22] has applied the Kirkwood theory to dilute solutions of polar solutes in non-polar solvents. He obtains for the solution polarization

$$P_{12} = X_1P_1 + X_2P_2 = \frac{(\epsilon_{12} - 1)(2\epsilon_{12} + 1)}{9\epsilon_{12}} \frac{M_{12}}{d_{12}} \quad (1)$$

and

$$P_2^0 = R_2^0 + \frac{4\pi N}{3} \frac{\mu^2{}_0 g}{3kT} \quad (2)$$

where g is a factor accounting for hindered rotation which is nearly unity in these systems.

Oster obtains P_2^0 by direct extrapolation of P_2 to $X_2 = 0$. The difficulties inherent in such extrapolations have been discussed extensively by Smith.[23] Allen[19] developed his extrapolation method to overcome these difficulties but with respect to the Debye equation. Applying his method to equations 1 and 2 we obtain

$$\frac{(\epsilon_{12} - 1)(2\epsilon_{12} + 1)}{9\epsilon_{12}} = \frac{(\epsilon_1 - 1)(2\epsilon_1 + 1)}{9\epsilon_1} + cX_2 \quad (3)$$

$$d_{12} = d_1 + bX_2 \quad (4)$$

from which[19]

$$P_2^0 = \frac{P_1M_2}{M_1} + \frac{cM_1 - bP_1}{d_1} \quad (5)$$

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(19) K. A. Allen, *J. Phys. Chem.*, **62**, 363 (1958).

(20) L. Onsager, THIS JOURNAL, **58**, 1486 (1936).

(21) J. G. Kirkwood, *J. Chem. Phys.*, **7**, 911 (1939).

(22) G. Oster, THIS JOURNAL, **68**, 2036 (1946).

(23) J. V. Smith, "Electric Dipole Moments," Butterworth, London, 1955.

TABLE II

Bu_4NBr IN VARIOUS SOLVENTS

$X_2 \times 10^4$	$\epsilon_{12}(25°)$	$\epsilon_{12}(35°)$	$\epsilon_{12}(45°)$	d_{12} and $[n_{12}]_{\mathrm{D}}^{t}$
(1) Benzene				
0.0	2.2698	2.2524	2.2327	25° $d_{12} = 0.87368 + 0.907X_2$
0.57026	2.2727	2.2564	2.2378	$n_{12} = 1.49799$
1.1291	2.2761	2.2593	2.2406	35° $d_{12} = 0.86311 + 0.845X_2$
2.5506	2.2824	2.2650	2.2457	$n_{12} = 1.49347$
3.6692	2.2864	2.2695	2.2531	45° $d_{12} = 0.85230 + 0.790X_2$
5.5377	2.2921	2.2758	2.2594	$n_{12} = 1.48721$
8.1764	2.3023	2.2860	2.2697	
12.667	2.3195	2.3059	2.2895	
(2) Toluene				
0.0	2.3691	2.3480	2.3251	25° $d_{12} = 0.86160 + 0.907X_2$
1.5612	2.3730	2.3524	2.3323	$n_{12} = 1.49310$
3.0366	2.3758	2.3568	2.3362	35° $d_{12} = 0.85219 + 0.845X_2$
4.9761	2.3798	2.3605	2.3388	$n_{12} = 1.48869$
				45° $d_{12} = 0.84263 + 0.790X_2$
				$n_{12} = 1.48349$

Bu_4NBr IN MIXED SOLVENTS[a]

$X_2 \times 10^4$	$\epsilon_{123}(25°)$	$\epsilon_{123}(35°)$	$\epsilon_{123}(45°)$	d_{123} and $[n_{123}]_{\mathrm{D}}^{t}$
(3) Mole fraction MeOH = 0.0003998 in benzene				
0.0	2.2718	2.2542	2.2337	25° $d_{123} = 0.87368 + 0.907X_3$
.078020	2.2731	2.2570	2.2353	$n_{123} = 1.49799$
.35175	2.2770	2.2605	2.2395	35° $d_{123} = 0.86311 + 0.841X_3$
.97032	2.2792	2.2634	2.2408	$n_{123} = 1.49347$
2.0712	2.2835	2.2671	2.2468	45° $d_{123} = 0.85230 + 0.782X_3$
7.0472	2.3019	2.2848	2.2647	$n_{123} = 1.48721$
12.055	2.3193	2.3051	2.2860	
(4) Mole fraction MeOH = 0.005134 in benzene				
0.0	2.2873	2.2700	2.2491	25° $d_{123} = 0.87350 + 0.823X_3$
0.38273	2.2932	2.2765	2.2557	$n_{123} = 1.49759$
1.0396	2.2983	2.2843	2.2613	35° $d_{123} = 0.86293 + 0.841X_3$
2.2849	2.3078	2.2907	2.2702	$n_{123} = 1.49301$
5.5859	2.3271	2.3104	2.2883	45° $d_{123} = 0.85212 + 0.841X_3$
				$n_{123} = 1.48676$
(5) Mole fraction MeOH = 0.01073 in benzene				
0.0	2.3083	2.2879	2.2650	25° $d_{123} = 0.87330 + 0.907X_3$
0.56191	2.3193	2.3015	2.2747	35° $d_{123} = .86278 + .845X_3$
1.2980	2.3299	2.3083	2.2839	45° $d_{123} = .85195 + .790X_3$
3.1551	2.3481	2.3235	2.3011	
4.9885	2.3703	2.3497	2.3251	
(6) Mole fraction MeOH = 0.02090 in benzene				
0.0	2.3525	2.3303	2.3048	25° $d_{123} = 0.87293 + 0.907X_3$
0.25135	2.3583	2.3327	2.3080	35° $d_{123} = .86341 + .845X_3$
0.60999	2.3659	2.3422	2.3161	45° $d_{123} = .85158 + .790X_3$
1.0179	2.3745	2.3516	2.3268	
1.6428	2.3880	2.3630	2.3380	
2.2485	2.3960	2.3730	2.3460	
3.0968	2.4120	2.3890	2.3590	
(7) Mole fraction MeOH = 0.02814 in benzene				
0.0	2.3894	2.3630	2.3334	25° $d_{123} = 0.87268 + 0.907X_3$
1.6526	2.4191	2.4020	2.3727	35° $d_{123} = .86216 + .845X_3$
2.9851	2.4503	2.4227	2.3929	45° $d_{123} = .85133 + .790X_3$
(8) Mole fraction MeOH = 0.07290 in benzene				
0.0	2.6299	2.5915	2.5492	25° $d_{123} = 0.87108 + 0.907X_3$
0.50954	2.6415	2.6044	2.5609	$n_{123} = 1.49237$
1.5379	2.6641	2.6289	2.5844	35° $d_{123} = 0.86051 + 0.845X_3$
2.4491	2.6804	2.6455	2.6012	$n_{123} = 1.48647$
2.9469	2.6939	2.6586	2.6143	45° $d_{123} = 0.84970 + 0.790X_3$
5.4137	2.7521	2.7225	2.6685	$n_{123} = 1.48048$
(9) Mole fraction MeOH = 0.13784 in benzene				
0.0	3.1166	3.0474	2.9699	25° $d_{123} = 0.86814 + 2.27X_3$
0.63245	3.1258	3.0570	2.9835	$n_{123} = 1.48610$
1.0481	3.1410	3.0761	2.9988	35° $d_{123} = 0.85750 + 1.20X_3$
2.1648	3.1722	3.1111	3.0337	$n_{123} = 1.48123$
				45° $d_{123} = 0.84651 + 1.24X_3$
				$n_{123} = 1.47517$

$X_3 \times 10^4$	$\epsilon_{123}(25°)$	$d_{123}(25°)$
(10) Mole fraction nitrobenzene = 0.005418 in benzene		
0.0	2.3891	$d_{123} = 0.87571 + 0.907X_3$
0.73177	2.3955	
1.5069	2.3988	
2.4702	2.4047	
(11) Mole fraction nitrobenzene = 0.02069 in benzene		
0.0	2.7356	$d_{123} = 0.88143 + 0.907X_3$
0.58184	2.7453	
1.8590	2.7565	
3.0769	2.7658	
(12) Mole fraction nitrobenzene = 0.04854 in benzene		
0.0	3.6245	$d_{123} = 0.89186 + 0.907X_3$
.40825	3.6308	
.64513	3.6398	
1.1660	3.6486	
(13) Mole fraction nitrobenzene = 0.08009 in benzene		
0.0	4.1014	$d_{123} = 0.90368 + 0.907X_3$
.14554	4.1072	
.30224	4.1121	
.62436	4.1211	

[a] For meaning of subscripts see Discussion.

μ_0 then is calculated from equation 2. An examination of our data shows that (3) is linear over a somewhat wider range of concentration than the Debye equation.

In Table III are listed values of P_2^0 and μ_0 obtained by the various methods of calculation.

TABLE III

COMPARISON OF METHODS OF CALCULATION: Bu_4NPi IN BENZENE (25°)

Method	P_o(ml.)[b]	μ_0(D)	a(Å.)
Debye[a]	6740	17.8	3.71
Allen[19]	5886	16.8	3.50
Oster (Eq. 1,2)	8597	20.6	4.28
Oster–Allen (Eq. 5)	8860	20.8	4.34

[a] Ref. 8. [b] R_2 = 127 ml.

The first two μ_0 values are for a quasi-vapor, the last two are solution moments. It is possible, however, to convert solution to vapor values using Onsager's equation

$$\mu_{\text{sol}} = \left(\frac{2\epsilon_{12} + 1}{2\epsilon_{12} + n_2^2} \cdot \frac{n_2^2 + 2}{3}\right) \mu_{\text{gas}} = A \cdot \mu_{\text{gas}} \qquad (6)$$

which is strictly valid only for spherical molecules but nearly correct for elliptical ones also. With solid solutes n_2 cannot be obtained directly but can be calculated from the molar refraction, *i.e.*

$$R_2 = \frac{n_2^2 - 1}{n_2^2 \times 2} \cdot \frac{M_2}{d_2} \qquad (7)$$

where R_2 is obtained by adding bond refractions and d_2 is calculated from solution measurements assuming additivity. Using data for $X_2 = 3.716 \times 10^{-4}$ we obtain d_2 = 1.5 g./ml., n_2 = 1.75 and A = 1.25. Calculations for other X_2 values yield the same result. Using this value of A to convert the solution contact distances to (hypothetical) vapor values, we obtain 3.42 and 3.47 Å. by the Oster and Oster–Allen methods, in excellent agreement with the Allen method using the Lorentz field. Since the Onsager field is clearly more appropriate for solutions all our subsequent discussion will employ equation 5.

To study the effect of solvent on the dipole moment of ion pairs we compare Bu_4NPi in benzene, dioxane, toluene and in a benzene–methanol mixture. For molecular solutes many studies of this kind, primarily in non-polar solvents, have been reported,[24] but there seems to be no previous work of this kind for electrolytes. Particularly

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(24) For an extensive discussion in terms of molecular interactions *cf.* ref. 23, chapter 6.

for the large and highly polarizable ions of Bu_4NPi considerable variations in dipole moment might be expected.

It has been shown[3] already that a values of Bu_4NPi as determined from conductance measurements in *polar* solvents differ considerably. Unfortunately corresponding dielectric measurements are of little value because the theoretical treatment for such systems is as yet not sufficiently advanced. We therefore have restricted ourselves to studying this problem in some typical non-polar and very slightly polar (toluene $\mu = 0.4 \times 10^{-18}$ e.s.u., benzene–methanol), ($X \simeq 0.05$) solvents. The original data are given in Table I, and a plot of $\epsilon_{12} - \epsilon_1 = \Delta\epsilon$ *vs.* X_2 for these systems is shown in Fig. 1. The slope of these plots is very roughly proportional to the solute polarization and hence increases with increasing solute dipole moment. The curve for toluene is somewhat lower than for the others. The slight curvature in benzene can be attributed to quadrupole association at higher concentrations. This is known to occur from molecular weight determinations.[25] The addition of MeOH seems to decrease this association. This will be discussed in the next section. $P_2{}^0$ and μ_0 calculated from equations 3–5 are given in Table IV. There is a distinct change in a with solvent which is well outside experimental error but there is no obvious correlation with the dielectric constant of the solvent.

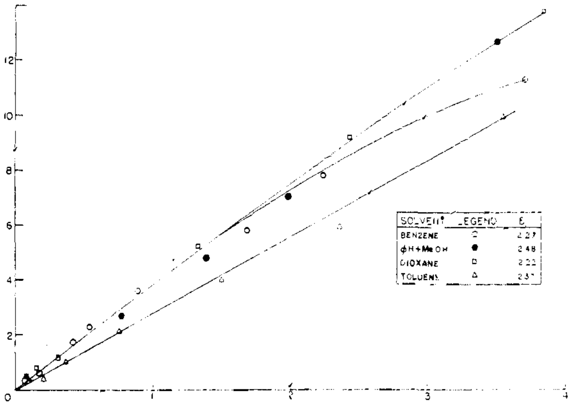

Fig. 1.—The change in dielectric constant on the addition of Bu_4NPi to various solvents.

TABLE IV

POLARIZATION AND DIPOLE MOMENT OF Bu_4NPi IN BENZENE, DIOXANE AND TOLUENE AT 25°

Solvent	$P_2{}^0$ (ml.)	$P\mu$(ml.)	μ_0 sol(D.)	a (Å.)
Benzene	8860	8733	20.8	4.34
Dioxane	8292	8165	19.9	4.15
Toluene	6591	6464	17.8	3.71
Benzene–Methanol ($X_{MeOH} = 0.0476$)	8272	8145	20.0	4.17

Over the range of temperature studied a is independent of temperature. No direct comparison with conductance a values is possible, but in general the values are considerably closer to those obtained in seven slightly polar solvents[3] using the Bjerrum equation[5] ($a_B = 4.67$Å., $\sigma = 0.18$) than with the Denison–Ramsey[6] equation ($a_{DR} = 5.83$Å., $\sigma = 0.38$). The use of the Onsager field does, however, bring dielectric constant and conductance values into closer agreement.

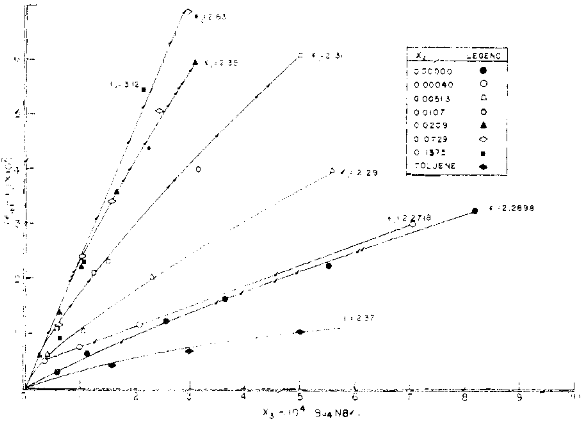

Fig. 2.—The change in dielectric constant on the addition of Bu_4NBr to benzene–methanol mixtures and to toluene.

The Effect of Solvent Composition on the Degree of Association of Electrolytes.—As shown in Fig. 1 and Table IV the addition of MeOH to benzene produces little change in the polarization of Bu_4NPi. What change does occur is consistent with a decreased association of ion pairs to quadrupoles at higher concentrations.

It seemed to be of interest therefore to study an electrolyte whose association to quadrupoles and higher aggregates is very pronounced. Freezing point determinations on similar salts[25] indicate that Bu_4NBr should have a molecular weight of several times the formula weight in even very dilute solutions in benzene. We have now investigated the effect of adding a small amount of a polar molecular solvent to such a solution. The systems studied are (a) benzene–methanol–Bu_4NBr and (b) benzene–nitrobenzene–Bu_4NBr, with the majority of data having been obtained for the first of these systems. For what follows the subscripts 1, 2, 3 refer, respectively, to the non-polar solvent, the polar solvent and the electrolyte. Since the two systems differ in some respects they will be discussed separately. We first take up (a).

(a) **The Benzene–Methanol–Tetrabutylammonium Bromide System.**—Figure 2 exhibits plots of $(\epsilon_{123} - \epsilon_{12}) = \Delta\epsilon$ as a function of X_3 for a series of solutions of different X_2. It can be seen that a very small amount of MeOH noticeably increases $\Delta\epsilon$. Each new addition of MeOH further increases $\Delta\epsilon$, but there is a limiting concentration of MeOH ($X_2 = 0.0729$, $\epsilon_{12} = 2.63$) beyond which the further addition of MeOH does not increase $\Delta\epsilon$ significantly. At somewhat lower values of X_3 the limiting value of X_2 is 0.0209, $\epsilon_{12} = 2.35$. At or above this limit $\Delta\epsilon$ is essentially a linear function of salt concentration instead of curving convexly as it does for $X_2 < 0.0729$. Thus the major change occurs as the dielectric constant of the solvent mixture (ϵ_{12}) increases from 2.27 ($X_2 = 0$) to 2.35 ($X_2 = 0.0209$). It is not difficult to show that this change in dielectric constant is not responsible for the observed effect since a

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[25] F. M. Batson and C. A. Kraus, THIS JOURNAL, **56**, 2017 (1934).

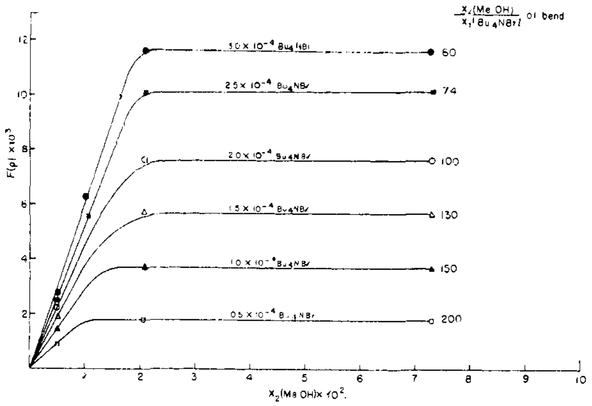

Fig. 3.—$F(p)$ plot for Bu_4NBr in the benzene–methanol system. For definition of $F(p)$ see equation 22.

similar curve for toluene ($\epsilon_1 = 2.37$) lies below that for pure benzene. To analyze the data further we first define

$$p_{123} = \frac{(\epsilon_{123} - 1)(2\epsilon_{123} + 1)}{9\epsilon_{123}} \tag{8}$$

$$p_{13} = \frac{(\epsilon_{13} - 1)(2\epsilon_{13} + 1)}{9\epsilon_{13}} \tag{9}$$

$$p_{12} = \frac{(\epsilon_{12} - 1)(2\epsilon_{12} + 1)}{9\epsilon_{12}} \tag{10}$$

$$p_1 = \frac{(\epsilon_1 - 1)(2\epsilon_1 + 1)}{9\epsilon_1} \tag{11}$$

where the p's are the volume polarizations of the respective solutions given by the Onsager equation.

Using the measured dielectric constants one may plot $(p_{123} - p_{12})$ *vs.* X_3. This plot looks qualitatively just like Fig. 2 and hence is not reproduced. We now define "normal" behavior by the equations

$$p_{12} = p_1 + cX_2 \tag{12}$$

$$p_{13} = p_1 + bX_3 \tag{13}$$

$$p_{123} = p_{12} + bX_3 \tag{14}$$

$$p_{123} = p_{13} + cX_2 \tag{15}$$

This is the behavior to be expected in dilute solution if no great changes in the state of aggregation of dipole moments of the components occur with changes in concentration. Thus equation 12 holds, for example, for dilute solutions of MeOH in benzene and equation 14 holds for Bu_4NPi in benzene–MeOH mixtures. The obvious failure of equation 14 to apply to Bu_4NBr argues that its behavior is not "normal." It might be reasonable to suppose that with increasing X_2 larger aggregates (which have a lower molar polarization) are breaking down to ion pairs. When this breakdown is complete any further addition of polar component has only minor effects.

To analyze this situation more quantitatively we proceed by defining a function

$$F(p) = (p_{123} - p_{12}) - (p_{13} - p_1) \tag{16}$$

Using the intercepts on the family of curves $(p_{123} - p_{12})$ *vs.* X_3 for various constant values of X_2, we now construct a plot of $F(p)$ *vs.* X_2 at various constant X_3. Such a plot again produces a family of curves (one for each value of X_3). This is shown in Fig. 3. Each curve consists of a rising and a flat portion with a fairly definite break in between. Qualitatively $F(p)$ may be described as a kind of polarization which is a function of X_2 up to some critical value and is nearly constant thereafter. From the definition of $F(p)$ it evidently arises from the electrolyte since the actual contribution of the polar molecules has been subtracted, yet it depends on X_2. This is again consistent with the breakdown of higher aggregates to ion pairs up to a critical value of X_2. Figure 3 allows us to compute the critical molar ratio X_2^c/X_3, *i.e.*, the number of moles of polar component necessary for the complete breakdown. These numbers have been placed to the right of the curves in Fig. 3. The inverse relation between the ratio and X_3 may be rationalized as follows: for low values of X_3 the size of the aggregates probably is small: thus if a sufficiently large region of polar molecules is required to produce dissociation to ion pairs, the number of moles of polar molecules per mole of electrolyte is fairly large, because the number of electrolyte clusters per mole is large. Conversely, when X_3 is large the electrolyte clusters are larger, but there are fewer of them per mole of material. Consequently fewer polar molecules will be needed per mole of electrolyte to produce dissociation.

We now proceed to a more detailed consideration of the situation just described. For any particular value of X_3 there exists a critical value of $X_2 = X_2^c$ necessary to complete the breakdown of aggregates. One may then ask whether (1) for $X_2 > X_2^c$ there is some regular relation between $F(p)$ and X_3—in this region $F(p)$ is independent of X_2—and (2) whether the solutions behave "normally" as defined by equations 14 and 15. The answer to the first question[2] is that $F(p)$ is a linear function of X_3, *i.e.*

$$F(p) = 38.7X_3 \simeq bX_3 \tag{17}$$

To investigate normal behavior we substitute equation 12 in 14 to obtain

$$p_{123} = p_1 + cX_2 + bX_3 \tag{18}$$

Normal behavior then implies that c is independent of X_3 and b is independent of X_2. An analysis of our data[2] for $X_2 > X_2^c$ shows that b is somewhat dependent on X_2 and that

$$p_{123} = p_1 + 1.28X_2 + 43.6X_3 + 136X_2X_3 \tag{19}$$

The last term thus measures the interaction between methanol and Bu_4NBr, if one assumes the benzene to be unchanged. Since presumably no changes in the degree of aggregation are occurring in this region, equation (19) can be interpreted as a change in the dipole moment of either component produced by the other. The results of such a calculation are shown in Table V.

TABLE V

THE EFFECT OF METHANOL ON THE POLAR PROPERTIES OF Bu_4NBr IN BENZENE SOLUTIONS

X_2	ϵ_{12}	P(ml.)	$\mu \times 10^{18}$ (e.s.u.)	a(Å.)
0.000	2.268		13.9	2.90
.0209	2.353	4090	14.0	2.92
.0281	2.389	4360	14.4	3.00
.0729	2.630	4360	14.4	3.00
.138	3.117	5200	15.8	3.29

Conversely, it can be shown that the dipole moment of methanol increases from 1.42 D. in pure benzene to 1.73 D. in a solvent in which $X_3 = 3 \times 10^{-4}$. Mechanistically both effects can be interpreted as a mutual polarization of the molecules and ion pairs which tends to increase the charge separation in both.

When $X_2 < X_2^c$ $F(p)$ depends on X_2 as well as on X_3. An examination of the data[2] shows that the dependence is represented quite well by

$$F(p) = (S\sqrt{X_3} + \theta)X_2 \qquad (20)$$

where $S = 41.2$ and $\theta = -0.11$, *i.e.*, the slopes in Fig. 3 are proportional to $\sqrt{X_3}$, in contrast to equation 19, which expresses p_{123} as a simple additive function in the first power of mole fractions and is close to normal behavior (the term in X_2X_3 is small) for $X_2 > X_2^c$. Below X_2^c

$$p_{123} = p_{13} + (S\sqrt{X_3} + \theta + c)X_2 \qquad (21)$$

Thus in these solutions p_{123} can no longer be expressed as a simple linear equation in X_2 and X_3. The increase in solution polarization of a benzene–Bu_4NBr solution as MeOH is added to it now depends not only on the concentration of MeOH but on the square-root of the salt concentration already present.

We now propose a simple model consistent with equation 21. Suppose that the only electrolyte species present are ion pairs (I) and aggregates which do not contribute appreciably to the polarization. These may be formally designated as quadrupoles ($Q = \pm \mp$). In that case we can express p_{13} as

$$p_{13} = p_1 + bI \qquad (22)$$

where b is obtained from equation 14 ($X_2 > X_2^c$) and I represents the mole fraction of ion pairs. It then follows that

$$p_{123} = p_1 + bI + cX_2 \qquad (23)$$

But, experimentally (*cf.* eq. 21)

$$p_{123} = p_{13} + cX_2 + bX_2\sqrt{X_3} \qquad (24)$$

where the small constant θ has been neglected and we have used the approximate numerical equality of b and S.

Now consider two solutions with the same formal salt concentration (X_3), but different X_2. In each of the solutions we assume an equilibrium of the type $Q \rightleftharpoons 2\ I$, where $Q = X_3 - I$. A formal equilibrium constant for this reaction is $K = I^2/(X_3 - I)$ and hence

$$I = \frac{-K \pm (K^2 + 4KX_3)^{1/2}}{2} \simeq -K/2 + \sqrt{KX_3} \qquad (25)$$

The two solutions above will then have different values of I, K increasing with increasing X_2. From (24)

$$p_{123}'' - p_{123}' = c(X_2'' - X_2') + b\sqrt{X_3}\,(X_2'' - X_2')$$

But from (23)

$$p_{123}'' - p_{123}' = b(I'' - I') + c(X_2'' - X_2')$$

and therefore

$$I'' - I' = (X_2'' - X_2')\sqrt{X_3} \qquad (26)$$

i.e., the change in ion pair concentration is proportional to the change in X_2. If equation 23 is valid $F(p)$ then becomes (at constant X_3)

$$F(p) = b(I - I^0)$$

where I^0 represents the concentration of ion pairs when $X_2 = 0$ and I for any values of $X_2 < X_2^c$. I^0 can be calculated since $F(p)$ is nearly constant above X_2^c, *i.e.* $F^c(p) = d(X_3 - I^0)$ from which the equilibrium constant $K^0 = (I^0)^2/(X_3 - I^0)$ can be calculated. Moreover, if I^0 is known, I and the corresponding K then can be calculated for any $X_2 < X_2^c$. The constancy of K with change of X_3 can be taken as an argument for the validity of the calculation.

The results of such a calculation are shown in Table VI for $X_2 = 0$ and $X_2 = 0.5 \times 10^{-2}$. For the former K is constant within a factor of two over a six-fold change in X_3 which is all that can be expected from such a crude calculation. The addition of methanol clearly causes an increase in K, but this increase is abnormally large for the highest two values of X_3, *i.e.*, whereas for $0.5 \times 10^{-4} \leq X_2 \leq 2.0 \times 10^{-4}$ K increases by about 50% or less, for $X_3 \geq 2.5 \times 10^{-4}$ K increases by a factor of five. This may be related to the observation made earlier that at high salt concentrations a given concentration of methanol is more effective in breaking up ionic aggregates than at low salt concentrations.

TABLE VI

DISSOCIATION CONSTANT FOR THE FORMAL REACTION $Q \rightleftharpoons 2\ I$

$X_3 \times 10^4$	$I^0 \times 10^5$	$K(X_2 = 0) \times 10^6$	$K(X_2 = 0.5 \times 10^{-2}) \times 10^6$
0.5	0.9	2.0	3.1
1.0	1.5	2.7	3.5
1.5	1.9	2.8	3.8
2.0	2.4	3.3	3.9
2.5	1.8	1.4	8.9
3.0	2.1	1.6	8.7

(b) **The Benzene–Nitrobenzene–Tetrabutylammonium System.**—A plot of $(\epsilon_{123} - \epsilon_{12}) = \Delta\epsilon$ *vs.* X_3 for several constant values of X_2 is shown in Fig. 4. Salt concentrations (X_3) used are lower than in system (a) because the addition of a given quantity of nitrobenzene to benzene increases the dielectric constant of the mixture (and consequently the conductivity of the solution when salt is added) far more than the same amount of methanol does. This has prevented us from obtaining data for $X_2 > 0.08$ in this system.

Several similarities and differences between systems (a) and (b) may be noted. For low values of X_2 the plots in Fig. 4 are similar to those in Fig. 2, indicating decreased aggregate formation with increasing nitrobenzene concentration. However, it takes about twice as much nitrobenzene as methanol to reach the same value of $\Delta\epsilon$, *i.e.*, nitrobenzene is less effective in producing the breakdown of aggregates to ion pairs. At $X_2 = 0.04854$ $\Delta\epsilon$ is a linear function of X_3. The dipole moment of Bu_4NBr calculated at this concentration is 14.8 D., in good agreement with the values in Table V. However, the behavior of the electrolyte upon further addition of nitrobenzene is strikingly different from system (a). There, when sufficient methanol has been added to cause breakdown of aggregates to ion pairs, the further addi-

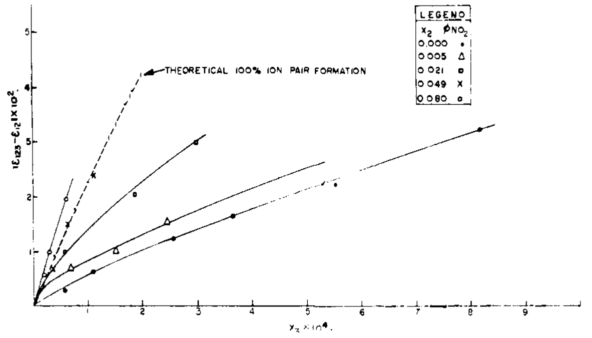

Fig. 4.—The change in dielectric constant on the addition of Bu_4NBr to benzene–nitrobenzene mixtures.

tion of methanol has no more effect. On the other hand, the further addition of nitrobenzene further increases the slope in Fig. 4. This would indicate a further increase in polarization of the solute, *i.e.*, an increase in the dipole moment. Thus at $X_2 = 0.080$ the ion pair dipole moment is 17.3 D., a rather large increase.[26] This is reflected also in a $F(p)$ *vs.* X_2 plot (Fig. 5) which is linear and shows no plateau. This implies that the rate of increase in electrolyte polarization above the "critical" concentration of nitrobenzene required to just break up aggregates to ion pairs is the same as below it. Evidently the high charge density and dipole moment of nitrobenzene increase the bromide–N^+ distance considerably (from 3.08 to 3.60Å.) whereas methanol does not do so as much (*cf.* Table V). This increase need not imply an actual movement of electrons within the ions but may result only from a rearrangement of the butyl chains.

By comparison Fuoss and Kraus[27] report a = 4.21 Å. from conductance for ion pairs in actual contact in dioxane–water mixtures. This parallels the situation described for Bu_4NPi that conductance a's are greater than dipole a's. Sadek and Fuoss[28] have suggested that the conductance of Bu_4NBr in nitrobenzene–CCl_4 mixture can be accounted for by assuming that one distance of a = 4.25 Å. describes an ion pair with a molecule of nitrobenzene squeezed in between the ions over nearly the entire range of solvent composition, whereas a's calculated from a continuum model for the solvent decrease systematically with increasing nitrobenzene concentration. In contrast to the solvent composition range studied by Sadek and Fuoss, our solutions are on the non-polar solvent rich side. The model suggested by these authors would then imply that as the nitrobenzene concentration is increased beyond the critical value, nitrobenzene molecules begin to squeeze in between the ions in the ion pairs. However, methanol molecules do not do this—or, alternatively, nitrobenzene molecules are trapped between ions forming an ion pair, but methanol molecules are not. This is difficult to accept. An examination of some reasonable models[2] of ion pairs solvated with nitrobenzene molecules (*e.g.*, with the nitrobenzenes oriented at zero and small angles with the ion pair dipole axis but not between the ions) shows that the high charge density around the nitro group considerably decreases anion–cation attraction by introducing repulsive forces between the molecules solvating one ion and the other ion. This factor is much less important when the solvating molecules are methanol.

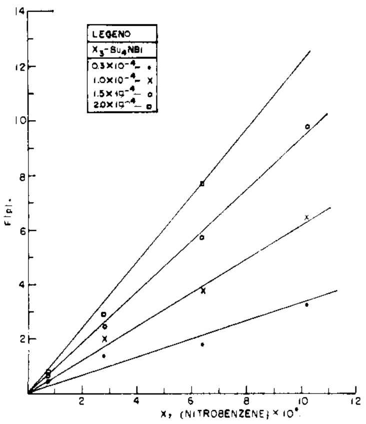

Fig. 5.—$F(p)$ plot for Bu_4NBr in the benzene–nitrobenzene system.

The results presented here suggest that interactions between electrolytes and polar molecules can be studied by dielectric measurements. These should be useful in complementing conductance studies since they focus on the non-conducting part of the solution which can only be inferred by the latter.

Conclusions

1. Values of the dipole moment of Bu_4NPi in benzene as calculated by different equations are in very good agreement, far better than the corresponding contact distances calculated from conductance.

2. The use of the Onsager field which yields dipole moments in solution improves the agreement between ion pair contact distances obtained from dielectric and conductance measurements, but in all cases reported here values from the former are several tenths of an ångström less.

3. The addition of small amounts of polar solvent to a non-polar one markedly reduces the formation of higher ionic aggregates and favors the formation of ion pairs. The effect depends on the concentration of the polar solvent and not on the dielectric constant of the mixture. A method for calculating an equilibrium constant between (postulated) non-polar quadrupoles and ion pairs is presented.

4. It is suggested that dielectric studies of dilute solutions of polar molecules and electrolytes in a non-polar solvent may be useful in elucidating ion-dipole interactions and structure in these solutions.

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[26] We have assumed that a linear plot is evidence for a single dipolar electrolyte species in solution, *i.e.*, ion pairs only.

[27] R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **79**, 3304 (1957).

[28] H. Sadek and R. M. Fuoss, *ibid.*, **76**, 5905 (1954).