Ion–Solvent Interaction. Displacement of Tetrahydrofuran from a Tertiary Ammonium Cation by Triphenylphosphine Oxide[1a]

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Abstract: Cation–ligand association constants, K_L, have been determined by a conductance technique for tri-*n*-butylammonium cation with triphenylphosphine oxide in *o*-dichlorobenzene (ODCB) as solvent and in tetrahydrofuran (THF); di-*n*-butylphenylphosphine oxide in both ODCB and THF; THF as ligand in ODCB solvent. All measurements were carried out at 25°. The changes in the association constants of the phosphine oxides as the solvent is changed from ODCB to THF can be accounted for (to within 5%) if a specifically solvating THF molecule in THF solvent is being displaced from the cation by the incoming phosphine oxide. The ligand association constants are interpreted as being measures of specific cation–solvent interaction and are applied to the problem of specific solvent effects on ion-pair dissociation in several solvents.

Cation–ligand association equilibria (eq 1), where A^+ is the cation, L is the ligand, and AL^+ represents

$$A^+ + L \rightleftharpoons AL^+ \qquad K_L = [AL^+]/[A^+][L] \qquad (1)$$

the cation–ligand complex, have been studied in this laboratory using a conductance method. Trialkylammonium ions have been shown[2] to form stable 1:1 complexes with ligands such as tributylamine and pyridine in *o*-dichlorobenzene (ODCB) and chlorobenzene as solvents. A tetraalkylammonium cation has been shown[3] to form a stable 1:1 complex with triphenylphosphine oxide in ODCB and ethylene chloride. The variation of the ligand association constants, K_L, with solvent led us to postulate[2] that in the case of the trialkylammonium cations, at least one specifically solvating solvent molecule, S, was being displaced from the cation by the incoming ligand (eq 2). Such a displacement had previously been proposed by D'Aprano and Fuoss[4] to explain the effects of added *p*-nitroaniline on the conductances of tetraalkylammonium salts in acetonitrile. The present work was undertaken in an effort to obtain specific evidence that, at least in one case, equilibrium 2 did occur.

$$AS^+ + L \rightleftharpoons AL^+ + S \qquad K_2 = [AL^+][S]/[AS^+][L] \qquad (2)$$

We required a solvent, S, which could act as a fairly good ligand toward tri-*n*-butylammonium (Bu_3NH^+) ion in ODCB when added in small concentrations of the order of 0.01 *M*. Tetrahydrofuran (THF) was the final choice as S. The cation was chosen on the basis of prior experience. A ligand, L, having a high affinity for Bu_3NH^+ in ODCB was desired, with the expectation that it, L, would still be able to compete for the cation when THF was used as solvent. Triphenylphosphine oxide (Ph_3PO) was selected as L. Another ligand, L′, was also needed to substantiate a previous observation[2a] that displacement of one ligand, L, by another, L′, was independent of the particular solvent used. Di-*n*-butylphenylphosphine oxide(Bu_2PhPO) was chosen as L′.

The object of the experiments was to show that the equilibrium constant for eq 2, K_2, where S is THF and L is Ph_3PO, was indeed the same in ODCB and in THF as solvent.

Experimental Section

The salt, tri-*n*-butylammonium picrate, was prepared and purified as before.[2a] ODCB and Ph_3PO were prepared as before.[3] THF (E. I. du Pont de Nemours and Co., Inc.) was passed through alumina (Alcoa grade F-20) on a 30 × 2 cm column and stored over sodium ribbon overnight. The THF was decanted from the sodium ribbon, refluxed over calcium hydride for 2 hr, and then distilled from the hydride, bp 65°. The distillate was stored over alumina which had been fired to 800° for 1 hr. Just prior to use, the THF was passed through a 30 × 2 cm column, the bottom half of which was packed with fired alumina and the top half with molecular sieve (Linde Air Products, Type 5A). The specific conductance of the solvent, 3×10^{-10} mhos/cm, was less than 0.3% of that of the most dilute salt solution used. Bu_2PhPO was prepared[5] by addition of 1 mole of dichlorophenylphosphine oxide to 3 moles of *n*-butyl bromide Grignard reagent in ether solution. The resulting solution was worked up in the usual manner. The solid Bu_2PhPO was recrystallized from ethyl acetate, and then five more times from hexane–benzene mixtures, mp 60–62°. The phosphine oxide was finally subjected to sublimation at 1 mm and 90°. Repeated purification was necessary to remove some conducting impurity. We finally were able to prepare 0.015 *M* solutions in ODCB having a specific conductance of 1.4×10^{-9} mhos/cm. The Bu_2PhPO was dried *in vacuo* at 40° overnight prior to each use.

Conductance measurements were carried out using bridge, bath, and cells previously described.[2a] Solutions were prepared as previously described.[2a] All measurements were carried out at 25.00 ± 0.005°. Physical constants for THF have been taken[6] to be: dielectric constant, 7.39; coefficient of viscosity, 4.60 mpoise; density, 0.880 g/ml.

Results

Values of Λ for solutions of Bu_3NHPi in THF without any addends are listed in Table I. In each case, the specific conductance of the solvent was subtracted from that of the solution to obtain the specific conductance presumed due to salt. In no case did this correction exceed 0.3%. The equivalent conductances in Table I are an order of magnitude smaller at comparable con-

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(1) (a) This research was supported in part by a grant from the U. S. Army Research Office, Durham, N. C.; (b) author to whom inquiries should be addressed.

(2) (a) E. R. Ralph, III, and W. R. Gilkerson, *J. Am. Chem. Soc.*, **86**, 4783 (1964); (b) W. R. Gilkerson and E. R. Ralph, III, *ibid.*, **87**, 175 (1965).

(3) W. R. Gilkerson and J. B. Ezell, *ibid.*, 87, 3812 (1965).

(4) A. D'Aprano and R. M. Fuoss, *J. Phys. Chem.*, **67**, 1722 (1963).

(5) See Acknowledgment.

(6) D. N. Battacharyya, C. L. Lee, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **69**, 608 (1965).

Table I. Tributylammonium Picrate in THF at 25°

10^4C	Λ	10^4C	Λ
0.2682	3.989	1.948	1.546
0.5073	2.941	0.3303	3.636
0.7009	2.520	0.5778	2.781
0.9420	2.190	0.8255	2.344
1.099	2.033	1.028	2.113
1.285	1.886	1.308	1.883
1.677	1.661	1.894	1.578

centrations than those for the alkali metal tetraphenylborates reported by Szwarc, *et al.*[6] We have already found[2a] that tributylammonium picrate undergoes acid–base dissociation (eq 3) in ODCB (D = 10.06)

$$\mathrm{Bu_3NH^+,Pi^-} \rightleftharpoons \mathrm{Bu_3N + HPi} \qquad K_d = [\mathrm{Bu_3N}][\mathrm{HPi}]/[\mathrm{Bu_3NH^+,Pi^-}] \quad (3)$$

and ethylene chloride (D = 10.23) to such an extent as to affect the magnitudes of the conductances. If K_d is of the same order of magnitude as the ion-pair dissociation constant, K_0 (eq 4), then the Fuoss conductance function, applicable in solvents of dielectric constant 10 or less, becomes[7] eq 5, where F is a factor given

$$\mathrm{Bu_3NH^+,Pi^-} \rightleftharpoons \mathrm{Bu_3NH^+ + Pi^-} \qquad K_0 = [\mathrm{Bu_3NH^+}][\mathrm{Pi^-}]/[\mathrm{Bu_3NH^+,Pi^-}] \quad (4)$$

$$F/\Lambda = [1 + y_\pm(K_d/K_0)^{1/2}]/\Lambda_0 + \Lambda C y_\pm^{2}/F\Lambda_0^{2}K_0 \quad (5)$$

by Fuoss[8] correcting Λ for ion atmosphere effects, being dependent upon Λ_0, the solvent dielectric constant D, and viscosity. The mean ionic activity coefficient, $y_\pm$, is calculated using the Debye–Hückel equation. Inspection of eq 5 shows that a value of Λ_0 cannot be obtained directly from the intercept of a plot of F/Λ *vs.* $\Lambda C y_\pm^2/F$. We must employ an estimate of Λ_0 obtained by some other means. The Walden product, $\Lambda_0\eta_0$, for tetrabutylammonium tetraphenylborate has been found[6] to be almost the same in THF ($\Lambda_0\eta_0$ = 0.388) as in nitrobenzene[9] ($\Lambda_0\eta_0$ = 0.411) at 25°. The Walden product for $\mathrm{Bu_3NHPi}$ is[10] 0.531 in nitrobenzene at 25°. If we assume the Walden product for this latter salt is the same in THF as in nitrobenzene, we estimate a Λ_0 value of 115 in THF. We do not believe that this estimate of Λ_0 is in error by more than 15%. A plot of values of F/Λ *vs.* $\Lambda C y_\pm^2/F$, calculated using Λ_0 = 115, appears in Figure 1. A least-squares treatment of these data yields an apparent Λ_0' of 50 with a probable error of ±6. This uncertainty is principally due to the necessarily long extrapolation to the intercept, since the probable error in the lowest calculated value of F/Λ, when compared to the observed value, is only 1%. The slope of the plot (with a probable error of 0.5%) and the assumed value of Λ_0 yield a value of $K_0 = (3.3 \pm 1.0) \times 10^{-8}$. The uncertainty in K_0 was taken to be due primarily to the estimated uncertainty in the assumed value of Λ_0. Equation 6 may be obtained from

$$\Lambda_0' = \Lambda_0/[1 + (K_d/K_0)^{1/2}] \quad (6)$$

eq 5, since the factor $y_\pm$ becomes unity at infinite dilution. We calculate a value of $K_d = (1.2 \pm 0.4) \times 10^{-8}$ from eq 6 and the values of Λ_0', Λ_0, and K_0 mentioned above. It is difficult to assess the reliability of the foregoing values of K_0 and K_d, since there is no independent method whereby we could obtain a value of Λ_0. Addition of picric acid to solutions of $\mathrm{Bu_3NHPi}$ would have repressed the acid–base dissociation,[7] but the conductances of solutions of picric acid itself in as basic a solvent as THF[11] would be expected to contribute enough to the total conductance to make such measurements difficult to interpret.

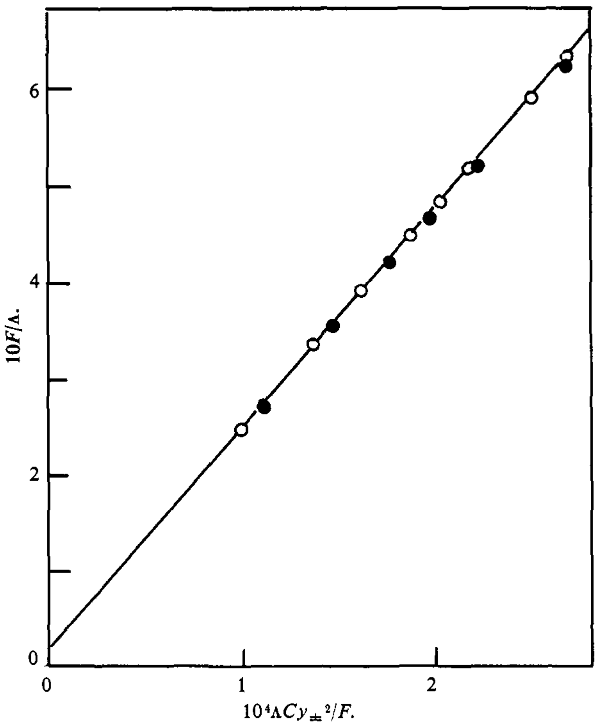

Figure 1. Fuoss conductance plot for tri-*n*-butylammonium picrate in THF at 25°: ○ and ● represent two separate runs.

The effects of added $\mathrm{Ph_3PO}$ and $\mathrm{Bu_2PHPO}$ on the conductances of solutions of $\mathrm{Bu_3NHPi}$ in ODCB at 25° are shown in Figure 2. We have plotted the ratio R *vs.* [L], where R is $(g/g_0)^2$. g is the specific conductance of the solution at a ligand concentration [L], and g_0 is that in the absence of ligand. Figure 3 shows the effect of added THF as ligand on the conductance of $\mathrm{Bu_3NHPi}$ in ODCB at 25°. Figure 4 shows the effects of added $\mathrm{Ph_3PO}$ and $\mathrm{Bu_2PhPO}$ on the conductances of solutions of $\mathrm{Bu_3NHPi}$ in THF as solvent at 25°. The slopes (the average of two runs in each case) of these plots, designated K_L, are listed in Table II.

Table II. Ligand Association with $\mathrm{Bu_3NH^+}$ at 25°

Ligand	Solvent	K_L
$\mathrm{Ph_3PO}$	ODCB	366,000 ± 4000
	THF	229 ± 3
$\mathrm{Bu_2PhPO}$	ODCB	630,000 ± 40,000
	THF	416 ± 16
THF	ODCB	124 ± 6

Discussion

The extent of ion-pair dissociation of $\mathrm{Bu_3NHPi}$ is small in the 10^{-4} M concentration range in both ODCB

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(7) (a) M. A. Elliott and R. M. Fuoss, *J. Am. Chem. Soc.*, **61**, 294 (1939); (b) E. G. Taylor and C. A. Kraus, *ibid.*, **69**, 1731 (1947).

(8) R. M. Fuoss and C. A. Kraus, *ibid.*, **55**, 476 (1933).

(9) R. M. Fuoss and E. Hirsch, *ibid.*, **82**, 1013 (1960).

(10) C. R. Witschonke and C. A. Kraus, *ibid.*, **69**, 2472 (1947).

(11) E. M. Arnett, *Progr. Phys. Org. Chem.*, **1**, 360 (1963).

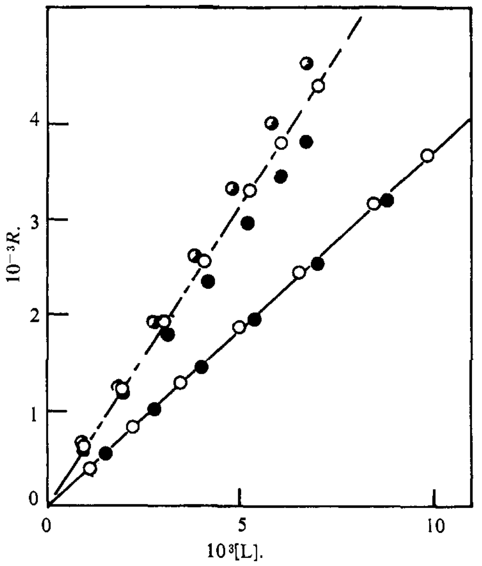

Figure 2. R (defined in text) for Bu_3NHPi as a function of ligand concentration in ODCB at 25°. Lower solid line (L = triphenylphosphine oxide): ○ and ● represent two separate series of runs at the same initial salt concentration, 1.518×10^{-4} M salt. Upper dashed line (L = dibutylphenylphosphine oxide): ○, 1.684×10^{-4} M salt; ◑, 1.744×10^{-4} M salt; ●, 1.840×10^{-4} M salt.

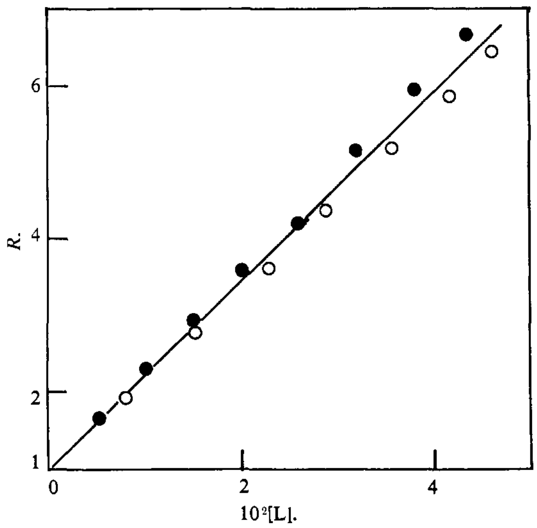

Figure 3. R for Bu_3NHPi as a function of THF (the ligand) concentration in ODCB at 25°: ○, 1.346×10^{-4} M salt; ●, 0.827×10^{-4} M salt.

and THF. The first term on the right-hand side of eq 5 then is small compared to either of the remaining terms in the equation. Equation 5 then reduces to the relation, $\Lambda_0^2K_0 = \Lambda^2Cy_\pm^2/F^2$. Let K be the ion-pair dissociation constant for salt at ligand concentration [L], and K_0 be that in the absence of added ligand. Further assume that the value of Λ_0 for the hypothetical ligand-complexed salt is almost the same as that for the uncomplexed salt.[12] The ratio R becomes

$$R = (g/g_0)^2 = (K/K_0)(I/I_0)^2C/C_0$$

where I is $F/y_\pm$ at [L], I_0 is the same ion atmosphere correction factor in the absence of ligand, C is the salt concentration at [L], and C_0 is that at [L] = 0. In a typical titration of salt solution, Figure 4, adding small increments of Ph_3PO dissolved in THF from a weight buret, the total decrease in salt concentration at the maximum concentration of L was only 5%. The increasing free ion concentration results in an increase in the ratio $(I/I_0)^2$ of 4.4% over the same interval. The changes in these two factors essentially cancel one another during the course of a titration so that the ratio R is approximately equal to K/K_0 at a particular [L]. It has been shown[2a] that

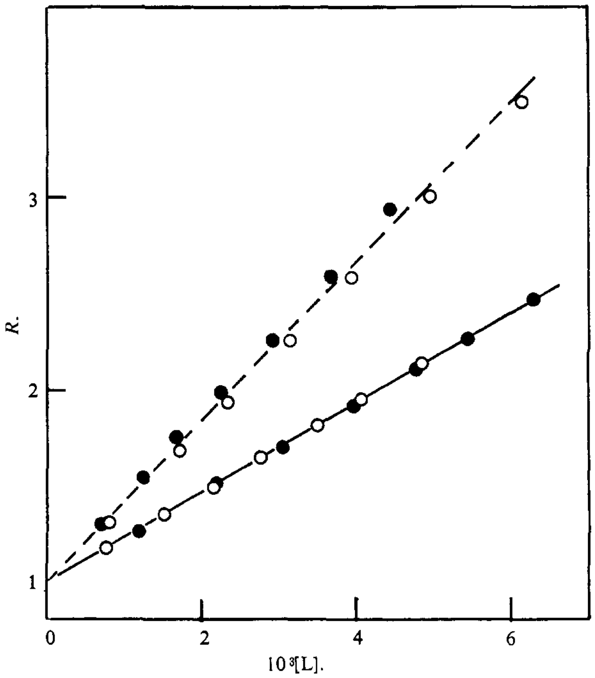

Figure 4. R for Bu_3NHPi as a function of ligand concentration in THF solvent at 25°. Lower solid line (L = triphenylphosphine oxide): ○, 0.878×10^{-4} M salt; ●, 1.620×10^{-4} M salt. Upper dashed line (L = dibutylphenylphosphine oxide): ○, 1.894×10^{-4} M salt; ●, 1.147×10^{-4} M salt.

$$K/K_0 = 1 + K_L[L] \qquad (7)$$

if the Λ_0's for complexed and uncomplexed salts are about the same. The slopes of the plots of R vs. [L] then give the values of the ligand association constants, K_L, as they were designated in Table II.

Comparison of the values of K_L for the two phosphine oxides in the two solvents shows that displacement of one ligand by another (eq 8) is not affected by changing

$$Bu_3NH^+,OPPh_3 + OPPhBu_2 \rightleftharpoons Bu_3NH^+,OPPhBu_2 + OPPh_3 \qquad (8)$$

the solvent from ODCB to THF. The equilibrium constant, K_8, for the displacement is equal to the ratio $K_L(OPPhBu_2)/K_L(OPPh_3)$. In ODCB this ratio is 1.72 ± 0.13; in THF the ratio is 1.82 ± 0.09. These two values are equal within experimental error even though the individual K_L's change by a factor of 1000 in going from ODCB solvent to THF. The constancy of K_8 upon changing solvents is similar to the behavior[2a] of the complexes of 4-methylpyridine and pyridine with Bu_3NH^+ in ODCB and chlorobenzene.

The decrease in K_L for both phosphine oxides in THF compared with ODCB is due to the greater specific cation–solvent interaction in THF. The equilibrium

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(12) The addition of 1 mole of Ph_3PO to tributylmethylammonium perchlorate in ODCB resulted in only a 15% increase in the limiting equivalent conductance.[3]

constant, K_2, for the displacement of THF from Bu_3NH^+ by Ph_3PO (eq 9) is given by the relation $K_2 = K_L(Ph_3PO)/K_L(THF) = 2950$ in ODCB as solvent. If a molecule of THF is being displaced from Bu_3NH^+ by the incoming phosphine oxide in THF solvent, then the value of the equilibrium constant corresponding to eq 9 in THF is $K_2 = K_L(Ph_3PO)[THF]$, where $K_L(Ph_3PO)$ is the observed ligand association constant for Ph_3PO and Bu_3NH^+ in THF, and [THF] is the molar concentration of THF in THF solvent. $K_2 = 229 \times 12.2 = 2800$ in THF, the same within experimental error as that obtained in ODCB solvent. We regard the constancy of K_2 in these two solvents as convincing evidence that at least one solvent molecule is displaced from Bu_3NH^+ by the incoming ligand. We shall extend this to such poorly solvating solvents as chlorobenzene in order to explain the variations observed in K_L as one changes solvents. The free energy of such solvation should only depend on the nature of the cation (charge, steric requirements, and presence of polarizable groups), the nature of the solvent molecule, and the molar concentration of the latter in the bulk solvent.

$$Bu_3NH^+,THF + Ph_3PO \rightleftharpoons Bu_3NH^+,OPPh_3 + THF \quad (9)$$

Determinations of K_L for a cation and ligand in a number of solvents should yield the relative free energies of solvation of the cation (by one solvent molecule) in the various solvents. There is at least one drawback to this procedure; we have neglected activity coefficients completely in evaluating the constants, K_L. Consider the thermodynamic equilibrium constant ($K_{L,S}$) for eq 2

$$K_{L,S} = [Bu_3NH^+,L]y_+'[S]y_S/[Bu_3NH^+,S]y_+[L]y_L \quad (10)$$

y_+ and y_+' are the activity coefficients for solvated cation and cation–ligand complex, respectively, while y_S and y_L are the activity coefficients for solvent and ligand, dissolved in solvent. y_+ is not the usual Debye–Hückel mean ionic activity coefficient. The latter accounts for departures from ideality due to ion–ion interaction only. That source is small here owing to the small ion concentrations usually employed. The y_+'s here include interaction with surrounding solvent as well as ion–ion interaction. The relative steric requirements of S and of L and the relative interactions with surrounding solvent of those portions of the molecules L and S which project into the surrounding solvent determine the ratio y_+'/y_+. We have, hopefully, set this latter ratio equal to unity, since the major portion of the interaction between cation, solvated or complexed, and surrounding solvent will be determined by the Born charging process,[13] which should result in roughly the same free-energy change for either type cation in a given solvent. y_S is set equal to unity in accordance with the usual choice of standard state for solvent. A convenient standard state for ligand would be pure ligand (solid or liquid) at the temperature of interest. It is known[14] that Henry's law constants for benzoyl chloride vary by a factor of 4.6 in transferring from dioxane solvent to ethanol solvent. The value of y_L may exhibit similar variations. Specific information on this point is laboriously obtained. We will set y_L equal to unity until such information becomes available. A convenient, but necessarily approximate, check on this latter assumption would be the variation in the ligand displacement equilibrium constant, K_{L_1}/K_{L_2} in several solvents using two or more ligands of significantly different structure. A report on such experiments will be published in the near future.

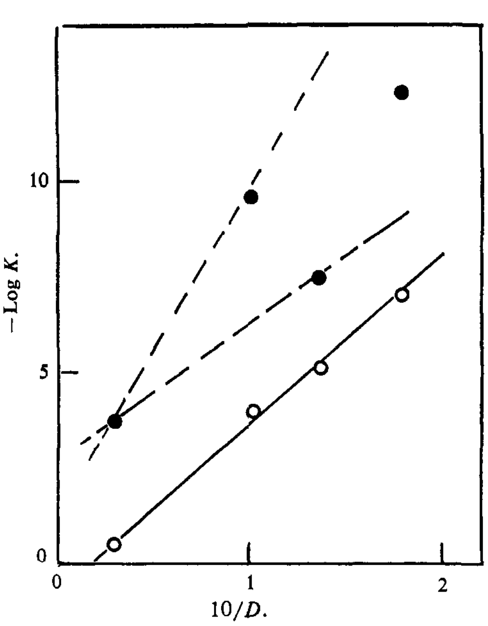

Figure 5. Filled circles represent the ion-pair dissociation constants for Bu_3NHPi in (left to right) nitrobenzene, ODCB, THF, and chlorobenzene, all at 25°, as a function of the dielectric constant, D. Open circles represent the ion-pair dissociation constants, corrected as described in the text, to eliminate specific solvent effects.

If a specifically solvating solvent molecule is displaced from Bu_3NH^+ by an incoming ligand, then in ion-pair formation we expect S to be displaced by picrate anion in forming the contact ion pair, eq 11 (in reverse). If

$$Bu_3NH^+,Pi^- + S \rightleftharpoons Bu_3NH^+S + Pi^- \qquad K_S = K_0/[S] \quad (11)$$

specific solvation occurs during the pair dissociation process, then it has been shown[15] that the contact ion-pair[15b] dissociation constant should obey the relation

$$\ln K_0 = \ln (3000/4\pi Na^3) - E_S/RT - e^2/akTD \quad (12)$$

where a is the distance of closest approach of the solvated ions, E_S is the free energy of specific solvation of the ions (pair → dissociated ions), and the remaining symbols have their usual significance. If E_S were to show large enough variation from solvent to solvent, then the usual[16] plot of log K *vs.* $1/D$ for a salt in a number of solvents at constant temperature may not be linear. Such a plot for Bu_3NHPi in nitrobenzene,[10] ODCB,[2] THF (this work), and chlorobenzene[2] appears in Figure 5 (closed circles). Note the scatter of points. The dashed lines have no significance other than to enclose the observed points. Large specific solvent

$$Bu_3NH^+,Pi^- + L \longrightarrow Bu_3NH^+,L + Pi^- \qquad K_{0L} = K_0K_L \quad (13)$$

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[14] W. J. Miller and E. Grunwald, *J. Phys. Chem.*, **68**, 1285 (1964).

[15] (a) W. R. Gilkerson, *J. Chem. Phys.*, **25**, 1199 (1956); (b) R. M. Fuoss, *J. Am. Chem. Soc.*, **80**, 5059 (1958); H. Sadek and R. M. Fuoss, *ibid.*, **81**, 4511 (1959).

[16] H. Y. Inami, H. K. Bodenseh, and J. B. Ramsey, *ibid.*, **83**, 4745 (1961).

effects are apparent. If we add eq 2 to eq 11, we obtain eq 13. A plot of log (K_{0L}) *vs.* $1/D$ also appears in Figure 5 (open circles) for Ph_3PO as ligand. The data used in this plot are listed in Table III. Log K_{0L} is remarkably linear in $1/D$; specific solvent effects have disappeared. We regard this latter result as strong supporting evidence that even such weakly solvating solvents as ODCB do solvate the tributylammonium ion in a specific manner.

Table III. Bu_3NHPi in Several Solvents at 25°

Solvent	−Log K_0	L	Log K_L	D
$PhNO_2$[a]	3.72	Pyridine	0.79	34.7
		Ph_3PO[b]	3.21	
ODCB	9.54	Pyridine[c]	3.14	10.06
		Ph_3PO[d]	5.56	
THF	7.48	Ph_3PO[d]	2.36	7.39
PhCl	12.32	Pyridine[c]	2.91	5.62
		Ph_3PO[b]	5.32	

[a] Reference 10; K_L calculated (ref 2a) from data obtained by Witschonke and Kraus. [b] Calculated assuming $K_L(Ph_3PO)/K_L(py)$, obtained in ODCB, does not vary from solvent to solvent. [c] Reference 2a. [d] This work.

The reaction between ligand and ion pair to form the cation–ligand complex and the free anion may be described[17] as a two-step process: (i) insertion of ligand between cation and anion to form a "ligand-separated" ion pair analogous to the "solvent-separated" ion pairs introduced by Winstein, *et al.*;[18] (ii) subsequent dissociation of the ligand-separated ion pair to produce free cation–ligand complex and the free anion. Following Fuoss,[17a] we assume process i depends only on the nature of the ion pair and the cation affinity of the ligand and is independent of the macroscopic dielectric constant of the solvent. Process ii is dielectric dependent, the distance of closest approach being that for the ligand-separated ion pair. This distance of closest approach, a, calculated from the slope of the log K_{0L} *vs.* $1/D$ line in Figure 5, is 5.53 A. Ramsey and co-workers[16] report the slope of a plot of log K_0 *vs.* $1/D$ for Bu_4NPi in a similar series of solvents, from which a value of $a = 5.30$ A may be calculated for this latter salt. Thus, we find that the replacement of the triphenylphosphine oxide by a butyl group results in only a 0.2-A reduction in the a value. Separating log K_{0L} into its two components, we have

$$Bu_3NH^+,Pi^- + L \rightleftharpoons Bu_3NH^+,L,Pi^- \qquad K_i$$

$$Bu_3NH^+,L,Pi^- \rightleftharpoons Bu_3NH^+,L + Pi^- \qquad K_{ii}$$

Taking $\log K_{ii} = \log (3000/4\pi N a^3) - e^2/2.303akTD$, then the intercept of the log K_{0L} *vs.* $1/D$ plot as $1/D \rightarrow 0$ is $I = \log (3000/4\pi N a^3) + \log K_i$. Knowing a from the slope, we calculate from the intercept that $K_i = 0.09$. At this stage, we cannot attach a great deal of physical significance to values of K_i calculated in the foregoing manner. It remains to be seen whether equilibria of the type corresponding to K_i do, or do not, depend on solvent when L is not a solvent molecule. We have already reported[2a] that there is good evidence from conductance measurements that a molecule of Bu_3N does form some complex with the ion pair Bu_3NH^+,Pi^- in ODCB at 25°, with an association constant of 25 M^{-1}. Whether formation of this complex results in increased charge separation (a reasonable criterion for identifying ligand-separated ion pairs) or not is not known at present. Hogen-Esch and Smid[19] have recently presented evidence based on both spectroscopic and conductance measurements that alkali metal fluorenyl salts form both contact and solvent-separated ion pairs in THF solvent, the relative amounts of each depending on the cation and temperature. Atkinson and Kor,[20] using sound absorption techniques, have presented further confirmation of Eigen and Tamm's[21] three-step mechanism for pair formation of Mn^{2+} and SO_4^{2-} ions in water and water–organic solvent mixtures. Apparently, successive waters of solvation are removed in discrete steps as the ions form the contact ion pair. The use of ion–ligand equilibrium constants as a tool for studying ion–solvent interaction is, we believe, placed on rather secure foundations by the experimental results in this report. Such studies, in addition to those involving the techniques cited above,[19,20] are expected to add greatly to our knowledge of the physical chemistry of electrolyte solutions in the near future. Further reports on work already completed in this laboratory will be forthcoming.

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