Ion–Solvent Interaction. Importance of the Dipole Moment and Basicity of the Ligand

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Abstract: Conductances of solutions of tri-*n*-butylammonium picrate in benzonitrile solvent, in *o*-dichlorobenzene with added methanol, benzonitrile, and pyridine N-oxide, and in the solvents 1,2-dichloroethane and chlorobenzene, both with added triphenylphosphine oxide and di-*n*-butylphenylphosphine oxide, have been measured at 25°. Ligand association constants for the addends with tri-*n*-butylammonium cation have been calculated. Acid–base association constants, to form the ion pair, have been determined for picric acid with pyridine, pyridine N-oxide, and triphenylphosphine oxide in *o*-dichlorobenzene at 25°. These results, in addition to those obtained previously, are discussed. The dipole moments of the ligands, in addition to their basicity, are important in determining the extent of ion–ligand association. The ligand association constants are proposed as a measure of specific ion–solvent interaction and are compared with other measures of ion–solvent interaction in the literature. The implications of the importance of the ligand dipole moment, in cation–ligand association, for ionic hydration are discussed.

Evidence has been reported[2] that the increased conductivity of solutions of tertiary ammonium salts in the presence of added amines in low dielectric solvents observed by Witschonke and Kraus[3] could be interpreted in terms of cation–ligand association

$$\mathrm{AH^+} + \mathrm{L} \rightleftarrows \mathrm{AH^+,L} \quad K_\mathrm{L} = [\mathrm{AHL^+}]/[\mathrm{AH^+}][\mathrm{L}] \tag{1}$$

and the equilibrium constants, K_L, have been determined in a number of cases. The association reaction (eq 1) is not restricted to tertiary ammonium cations. Quaternary ammonium cations have been shown[4] to associate with ligands such as triphenylphosphine oxide. Thus, the ability to form a hydrogen bond in the cation–ligand complex is not necessary for association to occur. More recently, we reported strong evidence[5] to support the hypothesis that at least one solvating solvent molecule, S, is displaced by the incoming ligand

$$\mathrm{AH^+,S} + \mathrm{L} \rightleftarrows \mathrm{AH^+,L} + \mathrm{S} \quad K_\mathrm{LS} \tag{2}$$

We have also shown[2a,4,5] for a number of ligands, and the tri-*n*-butylammonium cation, that displacement of one ligand, L, by another, L′ (eq 3) is to a good approximation independent of the solvent in which the

$$\mathrm{AH^+,L} + \mathrm{L'} \rightleftarrows \mathrm{AH^+,L'} + \mathrm{L} \tag{3}$$

displacement is carried out. All of these considerations led to our proposal[5] that the association constants, K_LS, be considered as measures of the specific cation solvating ability of solvents.

We report here additional results in a study of the effect of a wide variety of ligands on the conductance of tri-*n*-butylammonium picrate ($\mathrm{Bu_3NHPi}$) in *o*-dichlorobenzene (ODCB) and other low dielectric solvents in an effort to assess the relative importance of ligand dipole moments and ligand proton basicity in the stability of the complex formed between cation and ligand.

Experimental Results

The salt, $\mathrm{Bu_3NHPi}$, was prepared and purified as before.[2] The solvents, ODCB, 1,2-dichloroethane (EC), and chlorobenzene (PhCl), were purified as before.[2] Benzonitrile (PhCN) (Tensyn division, Velsicol Chemical Corp.) was purified according to the procedure of Coetzee and McGuire.[6] This solvent, thus prepared, has a specific conductance of 1.3×10^{-9} ohm^{-1} cm^{-1}. Methanol was purified as before.[2a] Pyridine N-oxide (PyO) (Columbia Organic Chemicals Co.) was distilled, bp 104–107° (3 torr). The resulting white solid was sublimed at 65° (1 torr), yielding white crystals. The purified PyO was stored in a desiccator and dried *in vacuo* overnight at 40° prior to each use. Triphenylphosphine oxide ($\mathrm{Ph_3PO}$) was purified as before.[4] Di-*n*-butylphenylphosphine oxide ($\mathrm{Bu_2PhPO}$) was prepared and purified as before.[5]

Conductance measurements were carried out at 25° using the cells, bridge, and thermostat previously described.[2] The physical constants of the solvents at 25° are given in the order dielectric constant, density, and viscosity: PhCN, 25.20,[7] 1.006 g/ml,[8] 1.24 cp;[9] ODCB, 10.06,[10] 1.3007 g/ml,[2] 1.272 cp;[11] PhCl, 5.621,[7] 1.1011 g/ml,[2] 0.752 cp.[12]

Visible spectrophotometric measurements were carried out using a Beckman DU spectrophotometer for the picric acid–base systems and a Cary Model 14 unit for the system vanadyl bis(acetylacetonate) ($\mathrm{VO(acac)_2}$) and PyO, using 1-cm Pyrex cells. All spectra were taken at 25 ± 2°.

$\mathrm{VO(acac)_2}$ was prepared for us by Dr. E. E. Mercer of this laboratory.

Results. The equivalent conductances, Λ, of $\mathrm{Bu_3NHPi}$ in PhCN at 25° at a number of concentrations appear in Table I. The specific conductance of the solvent was subtracted from the specific conductance of each solution to obtain that presumed due to the salt alone. The solvent conductance was no greater than 0.15% of the conductance of the most dilute solution. The resistances were determined at 1, 5, and 10 kHz. These were plotted *vs.* the inverse square root of the frequency. The intercepts at infinite frequency were taken to be the solution resistances, corrected for polarization effects. The largest correction due to polarization

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[1] Author to whom inquiries should be addressed. This work was supported in part by a grant from the Army Research Office, Durham.

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

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

[5] J. B. Ezell and W. R. Gilkerson, *ibid.*, **88**, 3486 (1966).

[6] J. F. Coetzee and D. K. McGuire, *J. Phys. Chem.*, **67**, 1810 (1963).

[7] A. A. Maryott and E. A. Smith, National Bureau of Standards Circular No. 514, U. S. Government Printing Office, Washington, D. C., Aug 10, 1951.

[8] J. Timmermans and Mme. Hennaut-Roland, *J. Chim. Phys.*, **32**, 501 (1935).

[9] A. R. Martin, *J. Chem. Soc.*, 3270 (1928).

[10] P. H. Flaherty and K. H. Stern, *J. Am. Chem. Soc.*, **80**, 1034 (1958).

[11] F. Accascina, E. L. Swarts, P. L. Mercier, and C. A. Kraus, *Proc. Natl. Acad. Sci. U. S.*, **39**, 917 (1953).

[12] R. L. McIntosh, D. J. Mead, and R. M. Fuoss, *J. Am. Chem. Soc.*, **62**, 506 (1940).

Table I. Conductances of Bu_3NHPi in PhCN at 25°

10^5C, M	Λ, cm^2 ohm^{-1} $equiv^{-1}$	10^5C, M	Λ, cm^2 ohm^{-1} $equiv^{-1}$
2.223	38.30	1.867	38.54
3.954	36.87	3.339	37.32
5.399	35.77	5.080	36.05
6.857	34.81	6.478	35.11
8.158	34.08	8.211	33.97
9.447	33.35	9.638	33.24
10.83	32.69	11.30	32.46

was 0.16% of the conductance. These data were treated by the method of Shedlovsky[13] (eq 4), valid when the ion-pair dissociation constant is less than 0.01. S is the Shedlovsky function[13] and $y_\pm^2$

$$1/\Lambda S = 1/\Lambda_0 + \Lambda CSy_\pm^2/K\Lambda_0^2 \quad (4)$$

is calculated from the Debye-Hückel theory. A plot of $1/\Lambda S$ *vs.* $\Lambda CSy_\pm^2$ appears in Figure 1. Λ_0 is 41.0, from the intercept, and K is 3.6×10^{-4}, from the slope. The Walden product in this solvent is $\Lambda_0\eta_0 = 0.501$ for Bu_3NHPi. This compares favorably with the value of 0.531 obtained by Witschonke and Kraus[3] in $PhNO_2$ at 25°.

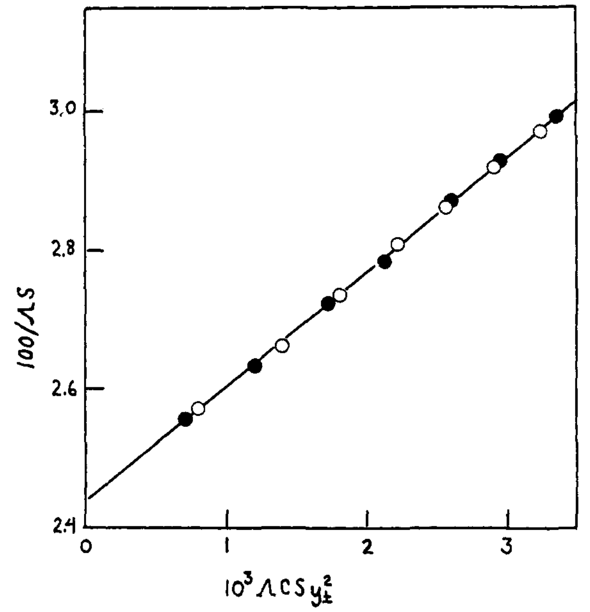

Figure 1. Shedlovsky conductance plot for tri-*n*-butylammonium picrate in benzonitrile at 25°: ○ and ● represent two separate runs.

The effects of added PyO on the conductance of Bu_3NHPi in ODCB solvent, and of Ph_3PO and Bu_2PhPO on the conductance of Bu_3NHPi in PhCl solvent, all at 25°, appear 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 salt solution at a ligand concentration [L], and g_0 is that in the absence of ligand. Figure 3 shows the effects of added Bu_2PhPO and Ph_3PO on the conductance of Bu_3NHPi in 1,2-dichloroethane (EC). Figure 4 shows the effects of added MeOH and PhCN on the conductance of Bu_3NHPi in ODCB.

The slopes of the straight-line plots in Figures 2-4, excepting MeOH, are taken[5] to be the values of the ligand association constants, K_L, eq 1. These are listed in Table II.

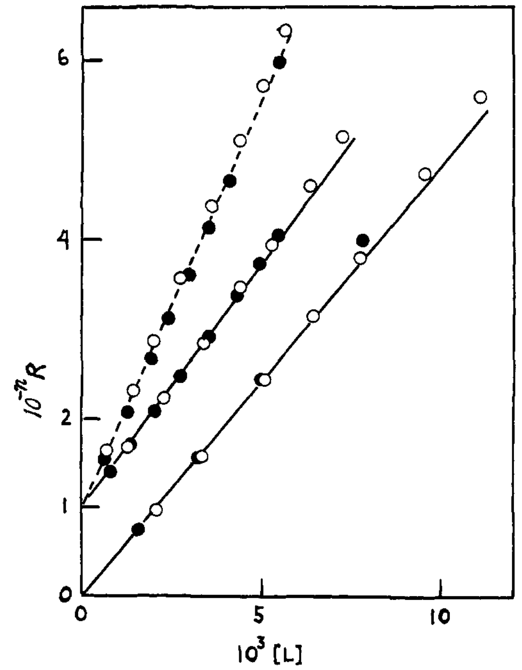

Figure 2. R for Bu_3NHPi as a function of ligand concentration at 25°. Upper dashed line, $(10^{-3}R + 1)$ for Bu_2PhPO in PhCl solvent: ○, 1.547×10^{-4} M salt; ●, 1.270×10^{-4} M salt. Middle solid line, $(10^{-3}R + 1)$ for Ph_3PO in PhCl solvent: ○, 1.353×10^{-4} M salt; ●, 2.103×10^{-4} M salt. Lower solid line, $10^{-2}R$ for PyO in ODCB solvent: ○, 1.202×10^{-4} M salt; ●, 1.302×10^{-4} M salt.

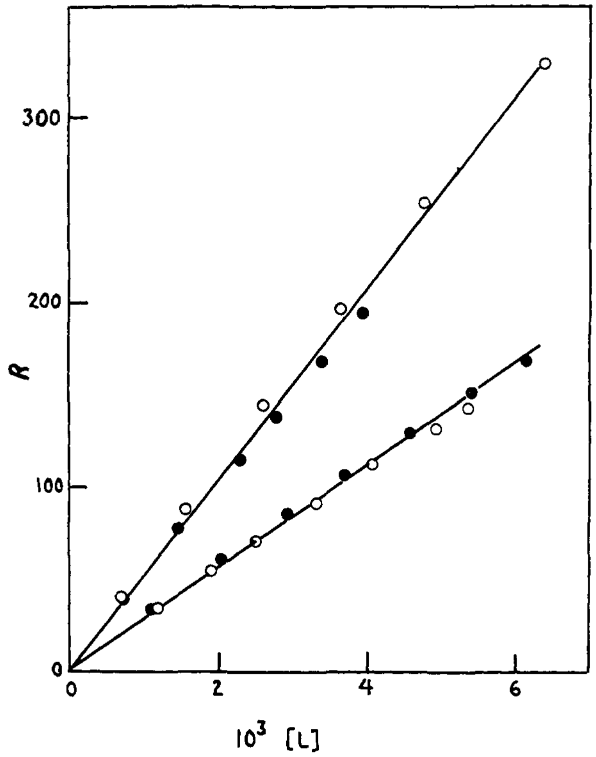

Figure 3. R for Bu_3NHPi as a function of ligand concentration in EC solvent at 25°. Upper line, Bu_2PhPO: ○, 1.897×10^{-4} M salt; ●, 1.747×10^{-4} M salt. Bottom line, Ph_3PO: ○, 0.989×10^{-4} M salt; ●, 1.064×10^{-4} M salt.

The acid-base association constants (eq 5) for the ligands Py,

$$HPi + L \rightleftharpoons LH^+,Pi^- \quad K_a = [LH^+,Pi^-]/[HPi][L] \quad (5)$$

PyO, and Ph_3PO with picric acid, HPi, in ODCB solvent at 25° were determined spectrophotometrically. A wavelength of 400 mμ was chosen for the optical density measurements. The molar extinction coefficient of picric acid is only 130 M^{-1} cm^{-1} in ODCB at this wavelength, while that of the picrate anion in the pyridinium picrate ion pair is 8000 M^{-1} cm^{-1}. Typically, the optical density of a solution of picric acid (10^{-4} M) in ODCB was determined as

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(13) T. Shedlovsky, *J. Franklin Inst.*, **225**, 739 (1938).

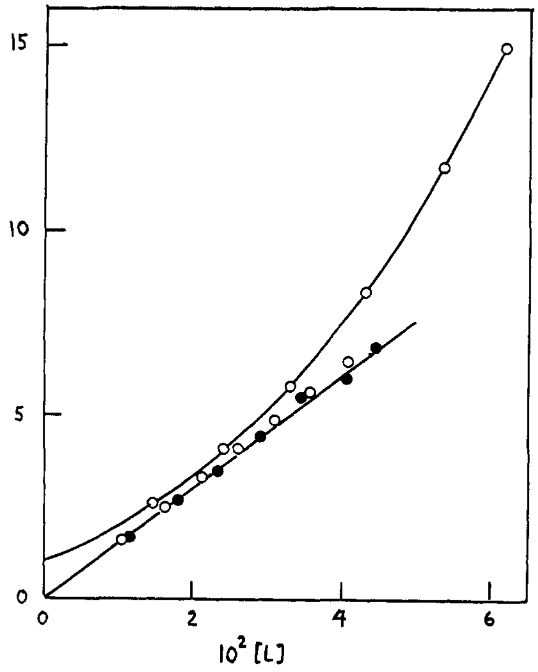

Figure 4. R for Bu_3NHPi as a function of ligand concentration in ODCB solvent at 25°. Upper curve, MeOH in 1.157×10^{-4} M salt. Lower line, (R − 1) for PhCN: ○, 1.353×10^{-4} M salt; ●, 1.169×10^{-4} M salt.

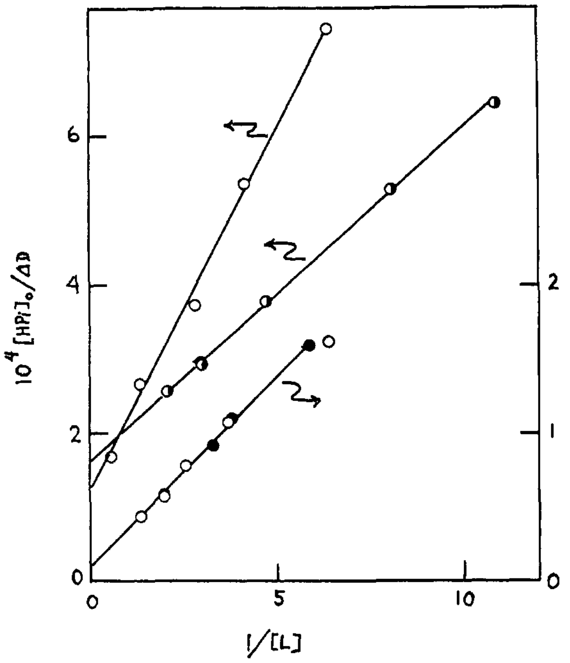

Figure 5. Plots of eq 6 for HPi in ODCB solvent at 25° with: ○, Py ($10^{-4}/[L]_c$); ◑, PyO ($10^{-2}/[L]_c$); and lower line, ○ and ●, two separate runs with Ph_3PO ($10^{-2}/[L]_c$), right-hand ordinate.

successive additions of ligand were made to the solution. The data were treated in a manner similar to that of Pearson and Vogelsong[14]

$$l[HPi]_0/\Delta D = 1/\Delta\epsilon + 1/\Delta\epsilon K_a[L]_c \qquad (6)$$

(eq 6), where l is the cell path length, $[HPi]_0$ is the initial concentration of picric acid, ΔD is the optical density of solution of ligand concentration [L] less that with no added ligand, $\Delta\epsilon$ is the molar extinction coefficient of the ion pair minus that of the picric acid, and $[L]_c$ is the total concentration of ligand minus that in the form of the ion pair. Plots of $l[HPi]_0/\Delta D$ *vs.* 1/[L] gave a first approximation to $\Delta\epsilon$. The latter was then used to calculate $[L]_c$ and another plot was made. The final plots appear in Figure 5. Values of K_a and $\Delta\epsilon$, in that order, for the several ligands are: pyridine, 9600 M^{-1} and 8000 M^{-1} cm^{-1}; PyO, 300 M^{-1} and 6700 M^{-1} cm^{-1}; Ph_3PO, 35 M^{-1} and 1100 M^{-1} cm^{-1}.

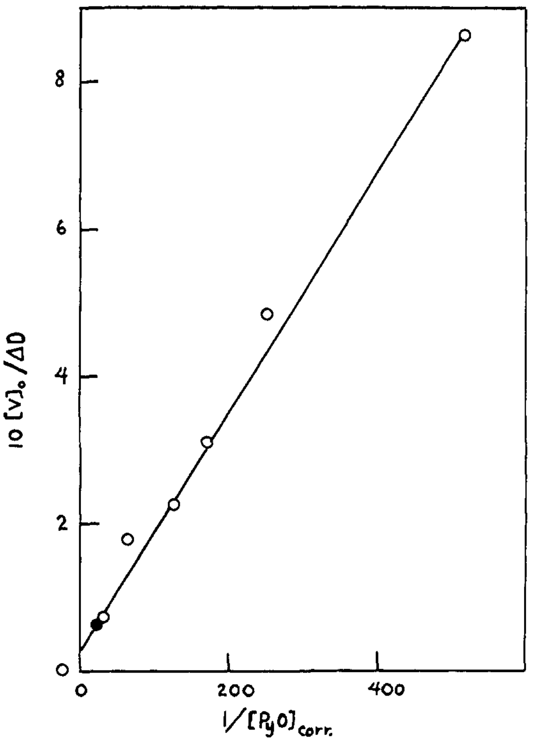

Figure 6. Plot of eq 6 for $VO(acac)_2$ in $PhNO_2$ at 25°: ○, 7.77×10^{-3} M $VO(acac)_2$; ●, 3.89×10^{-3} M $VO(acac)_2$.

Table II. Ligand Association Constants with Bu_3NH^+ at 25°

Ligand	Solvent	K_L
PyO	ODCB	49,000 ± 1000
PhCN	ODCB	150 ± 10
MeOH[a]	ODCB	85 ± 20
Ph_3PO	PhCl	560,000 ± 20,000
	EC	27,400 ± 600
Bu_2PhPO	PhCl	930,000 ± 30,000
	EC	51,000 ± 1600

[a] Calculated as described in the Discussion.

The association equilibrium constant of PyO with $VO(acac)_2$ in nitrobenzene at 25° was determined spectrophotometrically at 600 mμ, following Carlin and Walker.[15] A plot of eq 6, $l[VO(acac)_2]/\Delta D$ *vs.* $1/[PyO]_c$, appears in Figure 6. The association constant is found to be 20 M^{-1} and $\Delta\epsilon$ is 33 M^{-1} cm^{-1}.

Discussion

The ion-pair dissociation constant for Bu_3NHPi in PhCN at 25° ($K = 3.6 \times 10^{-4}$) is almost twice the value (1.9×10^{-4}) reported by Kraus[3] in $PhNO_2$ at 25°. This is surprising when one recalls that the dielectric constant of PhCN, D = 25.20, is almost 10 units less than that of $PhNO_2$, D = 34.7. We presume that the explanation of this apparent anomaly is that the specific solvent interaction of PhCN with Bu_3NH^+ is much greater than that of $PhNO_2$ and Bu_3NH^+. We have not determined K_L for Ph_3PO with Bu_3NH^+

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(14) R. G. Pearson and D. C. Vogelsong, *J. Am. Chem. Soc.*, **80**, 1038 (1958).

(15) R. L. Carlin and F. A. Walker, *ibid.*, **87**, 2128 (1965).

in PhCN solvent but estimate a value for it as follows: the equilibrium constant for the displacement of PhCN by Ph_3PO from Bu_3NH^+ in ODCB solvent is given by $K_D = K_L(Ph_3PO)/K_L(PhCN)$ and has a numerical value of 2440, where $K_L(Ph_3PO)$ has been reported elsewhere,[5] and $K_L(PhCN)$ is listed in Table II. If we assume that K_D is the same in PhCN as it is in ODCB solvent (see introductory section), then $K_D = K_L[PhCN]$, where K_L is the desired value of the ligand association constant in PhCN solvent, and [PhCN] (=9.75 *M*) is the molar concentration of PhCN in itself as solvent. We then obtain the estimate that $K_L \sim 250$ for Ph_3PO with Bu_3NH^+ in PhCN. This is to be compared with a previous estimate[5] of $K_L \sim 1800$ for the same cation–ligand system in $PhNO_2$ solvent. The larger the value of K_L, the less effective is the solvent in specifically solvating the cation.

In the previous paper in this series[5] we had applied the ligand association constants for Bu_3NH^+ with Ph_3PO and other ligands to the problem of the specific effects on the ion-pair dissociation equilibrium of Bu_3NHPi of the solvents $PhNO_2$, ODCB, THF, and PhCl. We are now in a position to add PhCN and ethylene chloride (EC) to the list of solvents. A plot of $-\log K$ *vs.* $1/D$, where K_0 is the ion-pair dissociation constant (eq 7) of Bu_3NHPi in the solvent S, of dielectric constant *D*, appears in Figure 7.

$$Bu_3NH^+,Pi^- + S \rightleftarrows Bu_3NH^+S + Pi^- \quad K_0 = \frac{[Bu_3NH^+S][Pi^-]}{[Bu_3NH^+,Pi^-]} \tag{7}$$

If eq 2, with L = Ph_3PO, is added to eq 7, we obtain eq 8. A plot of $-\log K_{OL}$ *vs.* $1/D$ appears in Figure 7, including the new data for PhCN and EC solvents. The scatter in the log K_0 plot is much reduced in the log K_{OL} plot, indicating[5] that most of the effects due to specific ion–solvent interaction have been eliminated.

$$Bu_3NH^+,Pi^- + Ph_3PO \rightleftarrows Bu_3NH^+,OPPh_3 + Pi^-$$
$$K_{OL} = [Bu_3NH^+,OPPh_3][Pi^-]/[Bu_3NH^+,Pi^-]/[Ph_3PO] \tag{8}$$

Methanol as a ligand (Figure 4) presents special features which should be examined before proceeding to consideration of the general nature of the interaction of Bu_3NH^+ with the ligands studied to date. The upward curvature of *R* (Figure 4) as the MeOH concentration increases indicates participation of more than one methanol molecule in complex formation with the Bu_3NH^+ cation. If a series of equilibria is postulated, representing successive additions of methanol molecules to the cation (eq 9), then the ratio, *R*, becomes

$$Bu_3NH^+,L + L \rightleftarrows Bu_3NH^+,L_2 \quad K_2$$
$$Bu_3NH^+,L_2 + L \rightleftarrows Bu_3NH^+,L_3 \quad K_3 \tag{9}$$

$$R = 1 + K_L[L] + K_LK_2[L]^2 + K_LK_2K_3[L]^3 \tag{10}$$

A trial plot of $(R - 1)/[L]$ *vs.* [L] showed decided curvature up at higher methanol concentrations. It was clear that using the scheme (eq 9) at least a cubic term in [MeOH] would have to be included. The intercept, 85 M^{-1}, of the trial plot, as [MeOH] → 0, was taken as a first approximation to K_L. The quantity $(R - 1 - 85[L])/[L]^2$ was then plotted *vs.* [L]. The slope of the resulting line at high [L] values was taken to be the value of $K_LK_2K_3 = 15{,}300\ M^{-3}$. Then a plot of $(R - 1 - 15{,}300[L]^3)/[L]$ *vs.* [L] was made. The intercept, at [L] → 0, of this plot yielded $K_L = 85\ M^{-1}$ and the slope gave $K_LK_2 = 1340\ M^{-2}$. The smooth curve drawn through the points in Figure 4 was calculated using

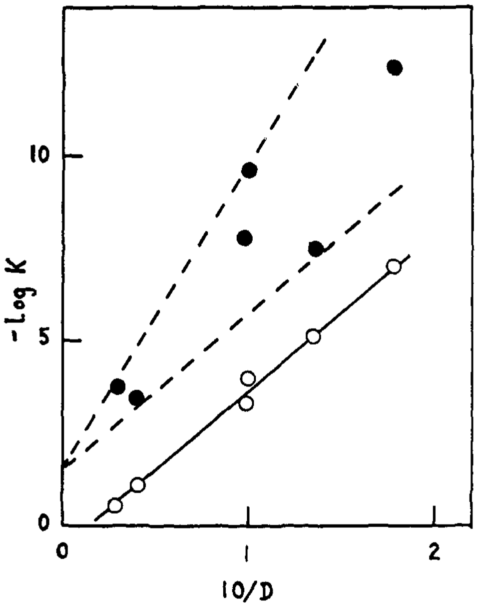

Figure 7. Filled circles represent log K_0 for Bu_3NHPi at 25° in (from left to right in the figure) $PhNO_2$, PhCN, EC, ODCB, THF, and PhCl. Open circles represent log K_{OL}, calculated as described in the text.

$$R = 1 + 85[\text{MeOH}] + 1340[\text{MeOH}]^2 + 15{,}300[\text{MeOH}]^3 \tag{11}$$

We do not believe the nonlinear terms in eq 11 are due to activity effects. Methanol tends to behave as if it forms dimers and higher *n*-mers at higher concentration in low dielectric solvents. Thompson and Kraus[16] examined the effects of added methanol and triphenylcarbinol (in the 0.05 to 0.8 *M* concentration range) on solutions of tetramethylammonium and tetrabutylammonium picrates in ethylene chloride. Added methanol resulted in increased conductances while the tertiary alcohol decreased the conductances of both salts. Kraus and Thompson observed *linear* increases in conductance with added methanol, in contrast to our results with Bu_3NHPi here, and in EC solvent.[2a] It seems reasonable that the relatively open region around the N–H bond in Bu_3NH^+ allows space for more than one small MeOH molecule to approach the center of positive charge. Further speculation concerning the nonlinear terms in eq 11, while interesting, will be postponed until further studies of alcohol–salt systems can be carried out. We do believe that K_L, for the first-order term, does correspond to eq 1, complex formation involving the cation with one methanol molecule.

A relative scale of ion–solvent (ligand) interaction can be set up using equilibrium constants, K_S, at 25° for the reaction

$$Bu_3NH^+,OPPh_3 + S \rightleftarrows Bu_3NH^+,S + Ph_3PO$$
$$K_S = [Bu_3NH^+,S][Ph_3PO]/[Bu_3NH^+,OPPh_3][S] \tag{12}$$

where S may represent a solvent or ligand molecule in the sense that we have used these terms in this paper. We have chosen Ph_3PO as the reference ligand. We have accumulated more data using Ph_3PO than any

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[16] W. E. Thompson and C. A. Kraus, *J. Am. Chem. Soc.*, **69**, 1016 (1947).

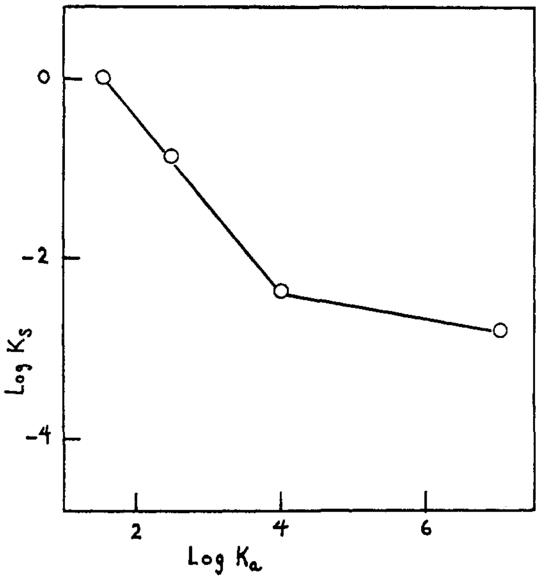

Figure 8. Solvating power *vs.* basicity for the ligands (from left to right in the figure) Ph_3PO, PyO, Py, and Bu_3N.

other. The values of log K_S which we have accumulated to date appear in Table III. We have calculated K_S for the solvents ODCB, PhCl, and EC using the relation $K_S = 1/K_L(Ph_3PO)[S]$, where $K_L(Ph_3PO)$ is the ligand association constant of Ph_3PO with Bu_3NH^+ in the particular solvent of molarity [S]. K_S for $PhNO_2$ was calculated using our previous estimate[5] of K_L (Ph_3PO) in that solvent. K_S for PhCN was calculated using the estimate of $K_L(Ph_3PO)$ in PhCN obtained as described at the beginning of this discussion. We have also included in Table III the equilibrium constant for reaction 12 with S = Bu_3NH^+,Br^- in ODCB. The triplet ion association constant for this system has been reported elsewhere.[2a]

Table III. Solvating Power Values[a] at 25°

No.	S (or L)	$-$Log K_S	μ_S, D.
1	PhCl	6.74	1.75
2	ODCB[b]	6.50	2.51
3	EC	5.54	1.2 (2.54)
4	$PhNO_2$[b]	4.20	4.28
5	PhCN	3.32	4.14
6	MeCN[c]	3.18	3.97
7	Bu_3NHBr[c]	0.20	7.66
8	4-CNPy[c]	3.97	-1.63
9	MeOH	3.80	1.69
10	Bu_3N[c]	2.81	0.78
11	THF[b]	3.43	1.63
12	Py[c]	2.37	2.15
13	4-MePy[c]	2.06	2.57
14	PyO	0.88	4.24
15	Ph_3PO[b]	0	4.31
16	Bu_2PhPO[b]	-0.23	3.98

[a] This work unless otherwise noted. [b] Reference 5. [c] Reference 2a.

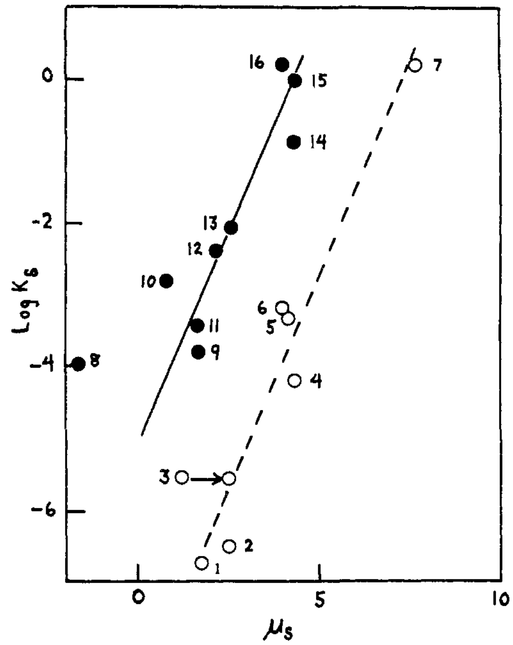

Figure 9. Solvating power, log K_S, *vs.* dipole moment, μ_S. The numbers by the data points correspond to those in Table III.

We are now in a position to ask: what factor or factors in the ligand (solvent) structure determine the solvation power of solvent molecules as measured by K_S? It is natural to expect the proton basicity of the ligands, as measured by the acid–base association constant, K_a, with picric acid (eq 5) to be related to the ligand strength, relative to Ph_3PO, as measured by K_S. A plot of log K_S *vs.* log K_a appears in Figure 8 for Bu_3N, Py, PyO, and Ph_3PO. The value of $K_a = 1.1 \times 10^7$ for Bu_3N in ODCB has been reported previously.[2] The ligand strength *increases* as the proton basicity decreases! This does not mean of course that proton basicity may not be of some importance. The bases used here are each of quite different structure. A clearer picture begins to emerge if one plots log K_S *vs.* μ_S, the dipole moment of the solvating molecule (Figure 9). The moments used in this plot are listed in Table III and with one exception[17] were taken from the compilation of McClellan.[18] Gas-phase values were chosen where available. The value of μ_S for EC in parentheses is that calculated[19] for the *gauche* form of the molecule. This latter value of μ_S is indicated in Figure 9. The net observed moment of 4-cyanopyridine (4CNPy), 1.63 D., is taken to have the negative end of the dipole vector pointing toward the nitrile group and away from the ring nitrogen. The solid and dashed lines in Figure 9 were drawn in to show that the ligands fall naturally into two groups: group a, along the dashed line in Figure 9, consists of substituted benzene compounds, ethylene chloride, acetonitrile, and the ion pair, $Bu_3NH^+Br^-$, each of these being polar but not having any basicity in the usual sense; group b, along the solid line in Figure 9, consists of compounds definitely basic in character. The separation between the two groups is marked, members of group b in general being stronger in solvating power (by three orders of magnitude as measured by K_S) than members of group a having similar dipole moments.

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(17) The value for Bu_2PhPO is an unpublished result from J. B. Ezell, Ph.D. Dissertation, University of South Carolina, 1965. The moment was determined from dielectric measurements of benzene solutions at 25°. No correction for atom polarization was made.

(18) A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman and Co., San Francisco, Calif., 1963.

(19) I. Watanabe, S. Mizushima, and Y. Morino, *Sci. Papers Inst. Phys. Chem. Res.* (Tokyo), **39**, 401 (1942).

We feel that the behavior of the members of group a, their points lying as close along a straight line (Figure 9) as they do in a plot of log K_S *vs.* μ_S, furnish strong justification for our prior treatment[2,5,20] of specific ion–solvent interaction in terms of short-range ion–dipole interaction. The behavior of members of group b, each having one or more lone pairs of electrons on the nucleophilic atom in the molecule, illustrates that, in addition to ion–dipole interaction, short-range ion–lone pair interaction is of great importance, as one would expect. This latter interaction could be variously described as due to H bonding or proton basicity of the solvating molecules. Note that, despite the variety of basic groups bearing lone pairs involved, $\geqslant$N, >O, $\geqslant$P–O, $\geqslant$N–O, they are all behaving as if the lone pair(s) is contributing a dipole moment of about 3 D. to the effective dipole operative in the ion–dipole interaction. It is well known that the idealized dipole description of molecules must break down at the intermolecular distances involved in the ion–ligand complex. With this realization in mind, we still prefer to discuss specific ion–solvent interaction within the framework of the ion–dipole approximation as long as this approach remains fruitful.

Log K_S for Bu_3N is almost 2 log units above the solid line through the points for the base group (b). We believe that this is a reflection of the high basicity of Bu_3N, compared to the other members of the group (Figure 8). The point representing log K_S for 4-cyanopyridine is far to the left of (or above) the solid line in Figure 9; this ligand interacts with Bu_3NH^+ more strongly than its net dipole moment would indicate. Acetonitrile is a much weaker ligand than is pyridine (Table III; see also ref 2) so we do not expect that it is the nitrile end of the 4-cyanopyridine which is forming the complex with the cation. The ring nitrogen is assumed to be the site of interaction with the cation. Polar groups in the 4 position on the pyridine ring are much farther removed from the cation charge than is the ring nitrogen lone pair. The energy of interaction between an ion and a dipole decreases as the square of the distance between them. If the net dipole moment of the 4-substituted pyridines is divided into the effective moment of the ring nitrogen and its lone pair, and the group moment of the group substituted in the 4-position, then it is easily seen that one might expect the solvating power of the 4-substituted pyridines to be less than their net dipole moments would indicate. A line, designated as line c, roughly connecting the data points for 4-cyanopyridine, pyridine, and 4-methylpyridine, has a slope less than that for the solid line in Figure 9, by the factor $^1/_{2.7}$. It would be of interest to study this effect more thoroughly with a greater number of substituted ligands.

Log K_S for 1,2-dichloroethane falls closer to the dashed line in Figure 9, for the polar ligands, if the moment of the *gauche* form for the molecule is used rather than the net observed dipole moment. The latter value is a weighted mean for the equilibrium mixture of rotational isomers.[19] Following the arguments of Ramsey[21] and co-workers, it appears that the enhanced ion-solvating power of EC over that which one would expect from its observed dipole moment is due to at least one EC molecule assuming the *gauche* form in specifically solvating the Bu_3NH^+ cation. Ramsey[21] prefers to view this effect with other cations in terms of an increase in the local dielectric constant around the ions.

A number of other measures of ion-solvating power have been proposed. One having some solvents (ligands) in common with the present study is Kosower's[22] *Z*-value series. The *Z* values for three solvents are in the order MeOH > MeCN > Py, while the order of log K_S values is just the reverse. It might be noted that the magnitudes of the apparent molar extinction coefficients for the iodide salt used by Kosower are in the same order as log K_S for these three solvents. Garst's E_T values[23] for three solvents are in the order Et_3N > THF > Py, while for log K_S, the order is Py > THF > Bu_3N. It is interesting to note that Dimroth's[24] E_T values using certain betaines increase linearly as Garst's values decrease in a variety of solvents. Thus, our log K_S values would parallel Dimroth's E_T values. Pincock[25] has suggested that the rates of pyridine-catalyzed decomposition of *t*-butylperoxy formate serve as a measure of ion-solvating power for a series of solvents. Our values of log K_S do parallel his values of log k_2 (k_2 is the rate constant for the decomposition); for log k_2, $PhNO_2 > CH_2Cl_2 >$ PhCl, while for log K_S, $PhNO_2 > CH_2ClCH_2Cl >$ PhCl. Each of the various measures of ion-solvating power cited above, *Z*, E_T, and log k_2, deals with the effect of solvent acting as a bulk dielectric fluid in addition to any specific interaction between solvent and solute. On the other hand, log K_S should serve as a measure of specific solvent effects, such as those causing deviations from what one would expect if the solvent were acting merely as a structureless dielectric fluid.

Equilibrium constants for complex formation involving vanadyl bis(acetylacetonate), $VO(acac)_2$, and a series of ligands have been determined by Carlin and Walker[15] in $PhNO_2$ and benzene solvent using a spectrophotometric method. The reaction is

$$V + L \rightleftarrows V,L \quad K_V = [V,L]/[V][L] \qquad (13)$$

where V represents $VO(acac)_2$ and V,L the complex. A plot for log K_S *vs.* log K_V appears in Figure 10, including the value of K_V for L = PyO, determined in the present work. In this comparison, we have paired our K_S for Bu_3N with K_V for Bu_2NH. The solid line through the amines appears to include MeOH as well. The correspondence between these two measures is extremely close, except for PyO and Ph_3PO. Centering our attention on the amines and methanol, the close correspondence between these two measures of cation–ligand interaction would appear to rule out H bonding as making any significant contribution to the stability of the Bu_3NH^+,L complexes, beyond that ascribable to interaction of an electrostatic nature. While the complex $VO(acac)_2$ is neutral, residual positive charge remains on the central V atom. If the ion–dipole model[2,5] can be applied to each of the these equilibria,

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[21] H. Y. Inami, H. K. Bodenseh, and J. B. Ramsey, *J. Am. Chem. Soc.*, **83**, 4745 (1961), and other references cited therein.

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[23] (a) J. F. Garst, D. Walmsley, C. Hewitt, W. R. Richards, and E. R. Zabolotny, *ibid.*, **86**, 412 (1964); (b) J. F. Garst, R. A. Klein, D. Walmsley, and E. R. Zabolotny, *ibid.*, **87**, 4080 (1965).

[24] K. Dimroth, private communication to J. F. Garst; see ref. 23b.

[25] R. E. Pincock, *J. Am. Chem. Soc.*, **86**, 1820 (1964).

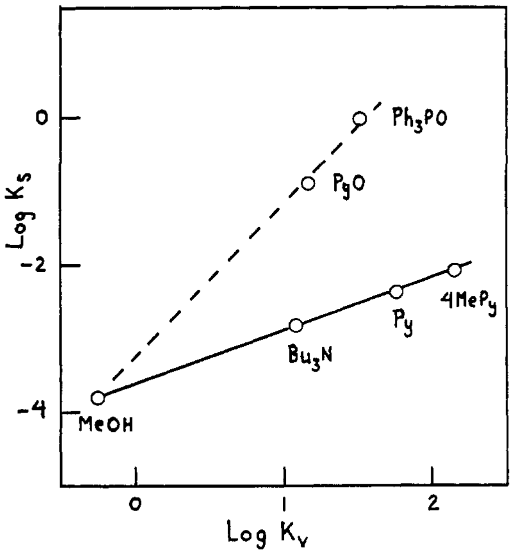

Figure 10. Comparison of association of ligands with Bu_3NH^+, log K_S, to association with $VO(acac)_2$, log K_V.

then log K_S should be given by

$$\log K_S = A + Z_S e\mu_S/2.30kTr_S^2 \qquad (14)$$

where A is a constant, Z_S is the charge on Bu_3NH^+ (= 1), and log K_V should be given by

$$\log K_V = A' + Z_V e\mu_S/2.30kTr_S^2 \qquad (15)$$

where A' is another constant, Z_V is the effective charge on vanadium in $VO(acac)_2$, and it is assumed that the distance, r_S, between charge and dipole is the same for the two systems. Combination of eq 14 and 15 and slight rearrangement yields

$$\log K_S = \frac{1}{Z_V}\log K_V + A''' \qquad (16)$$

where we have eliminated the (approximately) constant factor, $e\mu_S/2.30kTr_S^2$, from eq 14 and 15. The slope of the solid line in Figure 10 then should be equal to $1/Z_V$, the ratio of the charge on Bu_3NH^+ to that on V in $VO(acac)_2$. The slope is 0.78, so that $Z_V = +1.3$. The slope of the dashed line through the oxides yields a charge on vanadium of +0.42. These two values of Z_V bracket calculated values of the formal charge on vanadium(IV) in several complexes. A MO treatment by Ballhausen and Gray[26] of the $VO \cdot 5H_2O^{2+}$ ion yielded a formal charge on V of +0.97. A recent similar treatment of VF_6^{3-} by Tyree[27] placed a formal charge of +0.51 on V(III) in this complex. A refinement of the calculation on VF_6^{3-} by Fenske[28] gave the formal charge on V(III) as 1.94. If a calculation of the Fenske type were carried out on $VO(acac)_2$, it might well be that the formal charge would be increased from +0.97 to the neighborhood of +1.5. Such a comparison as we have made here is straining credibility, however, since it is quite likely that the coordination of the amine ligands, and possibly even the oxides, with vanadium in $VO(acac)_2$ involves forces other than pure ion–dipole forces.

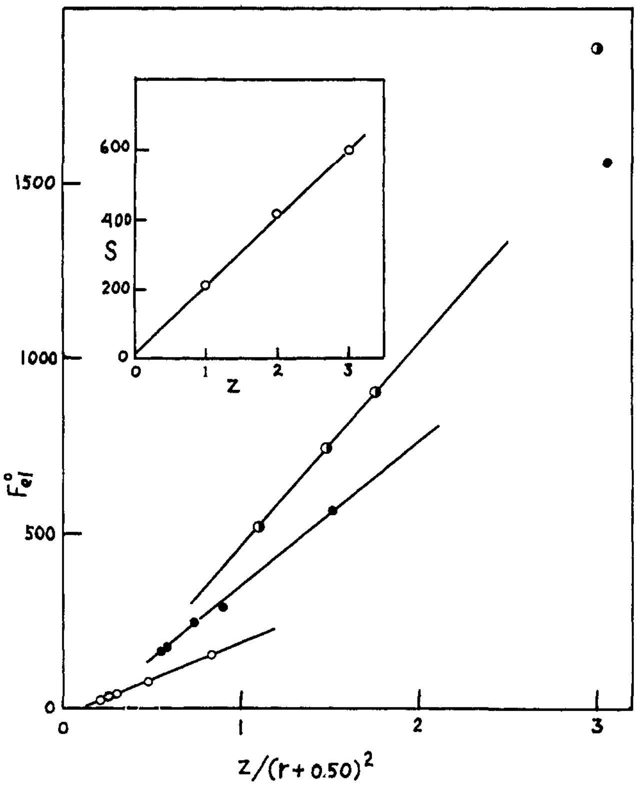

Figure 11. Electrical contribution to the free energy of hydration of cations in water, F°_{el}, in kcal/mole, *vs.* $Z/(r + 0.50)^2$, in A^{-2}: ○, $Z = +1$; ●, $Z = +2$; ◐, $Z = +3$. In the insert, S, the slopes of the straight lines in the main figure, are plotted *vs.* the cation charge type, Z.

Atkinson's recent report[29] that MeOH, but not $PhNO_2$, appears to specifically solvate Bu_4N^+ and perhaps Br^- is a reasonable one in the light of our results and those of Kraus.[16] MeOH is only six times better than $PhNO_2$ in forming a complex with Bu_3NH^+, but its smaller size might facilitate attachment of one or more of these molecules to the Bu_4N^+ cation and possibly to the anion.

We conclude from the studies reported here that cation–solvent (ligand) interaction in low dielectric solvents depends upon the dipole moment as well as the basic character of the ligand, and not on the dielectric constant of the bulk solvent. Our results successfully account for specific solvent effects on the ion pairing of Bu_3NHPi in a number of solvents.

The free energies of hydration of a number of cations and anions have been treated in several reports[30] using variations of the Born equation (eq 17) for a charge,

$$\Delta F_{el} = -\frac{Z^2e^2}{2r}\left(1 - \frac{1}{\epsilon}\right) \qquad (17)$$

Ze, of radius r, transferred from gas to a medium of dielectric constant ϵ. These treatments have required replacing ϵ by some ϵ_{eff}[30b–d] and/or replacing r by some value other than the crystal radius[30a,d] in order to fit the experimental data. Our results (Figure 9) indicate that specific ion–solvent interaction depends upon μ_S, the dipole moment of the solvent molecule.

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[30] (a) W. M. Latimer, K. S. Pitzer, and C. M. Slansky, *J. Chem. Phys.*, **7**, 108 (1939); (b) R. M. Noyes, *J. Am. Chem. Soc.*, **84**, 513 (1962); (c) *ibid.*, **86**, 971 (1964); (d) R. H. Stokes, *ibid.*, **86**, 979 (1964).

This observation leads[31] to the proposal that the principal term in the free energy of hydration of ions should be an ion–dipole term

$$F^\circ_{\mathrm{el}} = Zen_{\mathrm{S}}\mu_{\mathrm{S}}/(r + r_{\mathrm{S}})^2 \qquad (18)$$

where n_{S} is the number of solvent molecules of radius r_{S} in the hydration sphere. Intimations that this equation might apply were put forward by Blandemer and Symons.[32] We have plotted Noyes' revised values[30c] of $\bar{F}^\circ_{\mathrm{el}}$, the electrical contribution to the partial molar free energies of the ions in water at 25°, *vs.* $Z/(r + 0.50)^2$ in Figure 11. We found that setting the distance between charge and solvating dipole to be $r + 0.50$ A gave separate straight lines for mono-, di- and trivalent cations. We used Pauling's crystal radii as listed by Noyes[30c] for the ionic radii, *r*. The smaller high-charge cations, Be^{2+} and Al^{3+}, lie above the di- and trivalent lines. This could either be real, owing to some degree of covalent bonding between solvent and ion, or an artifact, owing to use of incorrect values for the ionic radii. The slopes, *S*, of the three lines increase linearly with charge type (insert, Figure 11). This might be expected if polarization of the solvent dipoles by the ions is important; it should be important at the small distances involved. We do not wish to carry out an extensive investigation along the lines mentioned above. Our principal purpose is to point out to those investigators who are interested that a more fruitful point of departure in considering hydration of ions in water might be the ion–dipole relation (eq 18) rather than the Born equation.

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Octahedral Cobalt(III) Complexes in Dipolar Aprotic Solvents. IX.[1] Solvent Exchange of Some Dimethyl Sulfoxide Containing Bis(ethylenediamine)cobalt(III) Complexes and Solvent-Interchange Reactions of Some *cis*-Chloro(solvent)bis(ethylenediamine)cobalt(III) Ions and the *trans*-Chloroaquobis(ethylenediamine)cobalt(III) Ion in Dimethyl Sulfoxide, N,N-Dimethylformamide, and N,N-Dimethylacetamide

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Abstract: Rate constants for replacement by the solvent of coordinated molecules have been determined for the following systems at a number of temperatures: *cis*-chloro(dimethylacetamide)bis(ethylenediamine)cobalt(III) ion (*cis*-$[CoCl(DMA)(en)_2]^{2+}$) in anhydrous N,N-dimethylformamide (DMF) and *trans*-chloroaquobis(ethylenediamine)cobalt(III) ion (*trans*-$[CoCl(H_2O)(en)_2]^{2+}$) in acidified DMF; *cis*-$[CoCl(DMA)(en)_2]^{2+}$ and *cis*-chloro(dimethylformamide)bis(ethylenediamine)cobalt(III) ion (*cis*-$[CoCl(DMF)(en)_2]^{2+}$) in anhydrous dimethyl sulfoxide (DMSO) and *trans*-$[CoCl(H_2O)(en)_2]^{2+}$ in acidified DMSO; *cis*-$[CoCl(DMF)(en)_2]^{2+}$ and *cis*-$[CoCl(DMSO)(en)_2]^{2+}$ in anhydrous N,N-dimethylacetamide (DMA). Activation parameters have been obtained for most reactions. The steric course of these reactions is interpreted as proceeding by an SN1 mechanism, involving trigonal bipyramidal transition states, to yield *cis*- and *trans*-chloro(solvent)bis(ethylenediamine)cobalt(III) ions. The *trans*-chloro(solvent)bis(ethylenediamine)cobalt(III) isomers formed have not yet been isolated as they are unstable and isomerize to give the *cis* isomer, but the rate of isomerization and the spectra of the two isomers have been obtained. Rate constants for the exchange of DMSO in the following complexes have been determined at 35°: *cis*-chloro(dimethyl sulfoxide)bis(ethylenediamine)cobalt(III) ion and *cis*-$[CoCl(DMSO)(en)_2]^{2+}$ in the presence of bromide ion, *cis*-bromo(dimethyl sulfoxide)bis(ethylenediamine)cobalt(III) ion, *cis*-nitro(dimethyl sulfoxide)bis(ethylenediamine)cobalt(III) ion, and *cis*-bis(dimethyl sulfoxide)bis(ethylenediamine)cobalt(III) ion. The strength of the solvents as ligands is shown to be $H_2O \simeq DMA \ll DMF < DMSO$.

Some recently investigated anation reactions in dipolar aprotic solvents[2–4] have been interpreted as having an SN1 mechanism, and others as having an SN2 mechanism. While data on the rate of solvent exchange in each of these systems would conclusively show the correctness of these assignments, we have only recently developed a method for determining

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