Thermodynamics of the Association of Tri-*n*-butylammonium Cation with a Series of Lewis Bases in *o*-Dichlorobenzene and in Chlorobenzene[1]

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Abstract: The conductances of dilute solutions of tri-*n*-butylammonium picrate in *o*-dichlorobenzene solvent with added acetonitrile, acetone, pyridine, and pyridine *N*-oxide have been measured at 10, 25, 35, and 45°. Similar measurements were carried out for the same salt in chlorobenzene solvent with added acetonitrile, acetone, pyridine, pyridine *N*-oxide, tetrahydrofuran, and triphenylphosphine oxide at 10, 25, and 45°. Values of cation–ligand association constants, $K_1{}^+$, are derived from these data for each ligand at each temperature, and enthalpy and entropy changes are calculated for the association process for each ligand in the two solvents. The values of $K_1{}^+$ are almost identical for each ligand in the two solvents. The enthalpy changes in each solvent become more exothermic as ligand hydrogen-bonding basicity increases. Values of $\Delta S°$ in each solvent increase as ligand polarity (μ) increases. These results are discussed in terms of an ion dipole model for cation–ligand association.

A variety of techniques is furnishing increasing information about various aspects of specific ion–solvent interaction in solution. Ion–molecule association in the gas phase studied by mass spectroscopic techniques[2] yields thermodynamic data for the formation of the first solvation sheath about an ion in the absence of bulk solvent. Enthalpies and free energies of transfer[3,4] of salts from one polar solvent to another give information about the interactions of the ions, not only with the solvent molecules in the first solvation sphere but also with more distant solvent molecules as well. Magnetic resonance techniques have shed light on the number of solvent molecules in the first solvation sheath, the kinetics of exchange of molecules in this region with those in the bulk,[5] and the composition of the first solvation sheath as the bulk solvent composition changes in mixed solvent systems.[6]

Studies of ion–molecule association in relatively poor solvents[7-10] lead to information which bridges the gap between the areas covered by the information that may be obtained from the studies mentioned above. Studies in this laboratory have focused on the formation of 1:1 cation–molecule complexes

$$M^+ + L \rightleftharpoons ML^+ \qquad K_1{}^+ = [ML^+]/[M^+][L] \qquad (1)$$

in relatively poor solvents. Displacement of one ligand L_1 by another L_2 on the cation M^+

$$ML_1{}^+ + L_2 \rightleftharpoons ML_2{}^+ + L_1 \qquad K = K_1{}^+(2)/K_1{}^+(1) \qquad (2)$$

then is a measure of the specific solvating ability of L_2 relative to that of the first ligand under conditions where the surrounding solvent remains essentially the same and it is inferred that the disturbance of any specifically solvating solvent molecules is held to a minimum in the exchange process. The information that can be gained from these studies bears not only on the effects of variation in the structure of L (polarity and basicity)[9,11] and of M^+ (ionic radius),[7,12] but also on the effects of bulk solvent on specific ion–molecule interaction and should aid in correlating information gained from the gas phase studies of ion–molecule association with the information contained in the thermodynamic quantities related to ion transfer from one solvent to another.

A recent report from this laboratory[13] dealt with the effects of changes in temperature on the association of tri-*n*-butylammonium cation (Bu_3NH^+) with triphenylphosphine oxide (Ph_3PO) and a series of alcohols and ethers in *o*-dichlorobenzene solvent (DCB). Values of $\Delta S°$ obtained in this study gave indications of being highly dependent on the nature of the ligand for the relatively sterically unhindered ligands Ph_3PO, methanol, and tetrahydrofuran (THF). Trends in the values of $\Delta S°$ indicated that there might well be a dependence on the polarity of the ligand. Such a dependence, if established, would have strong implications concerning the nature of ion–ligand interaction in solution.

Accordingly, this is a report of a determination of the thermodynamic quantities ΔH and ΔS for reaction 1 for a series of ligands of varying polarity and basicity associating with Bu_3NH^+ in two solvents, DCB and the less polar chlorobenzene (CB). Association constants were determined at several temperatures and values of ΔH and ΔS were calculated from van't Hoff plots of log *K vs.* the reciprocal of the temperature.

Our experimental approach is based on the measurement of the increased conductivity observed when added Lewis base molecules capture cations from a salt highly associated into ion pairs. The salt tri-*n*-butylammonium picrate was selected because it is soluble in poorly solvating solvents and is only slightly dissociated into free ions in DCB ($K_{\text{diss}} = 3 \times 10^{-10}$ M^{-1} at 25°).[14] The solvents were selected on the basis of their ease of purification, limited solvating power for cations, and differing dielectric constants. The ligands examined in this study were acetone (Me_2CO), acetonitrile (MeCN), pyridine (Py), pyridine *N*-oxide (Py-O), Ph_3PO, and THF. These were selected for their range in polarity and basicity, and minimum structural steric hindrance to complex formation.

Experimental Section

o-Dichlorobenzene (Dow Chemical Co.) was filtered through a 5 × 30 cm column packed with alumina (Alcoa grade F-20) and then distilled on a 4 × 40 cm column packed with glass helices under reduced pressure (bp 43° (3 Torr)). The middle fraction was then stored in glass containers over fired alumina. Prior to use the solvent was filtered through a 2 × 30 cm column packed two-thirds with fired alumina and packed one-third with molecular sieves (Linde type 4A). The specific conductance of the solvent was 5×10^{-12} mhos cm^{-1}. Chlorobenzene (Columbia Organic Chemicals) was handled in the same manner as *o*-dichlorobenzene except that the chlorobenzene was distilled at atmospheric pressure (bp 131.5° (760 Torr)). The specific conductance of the solvent was 3×10^{-12} mhos cm^{-1}.

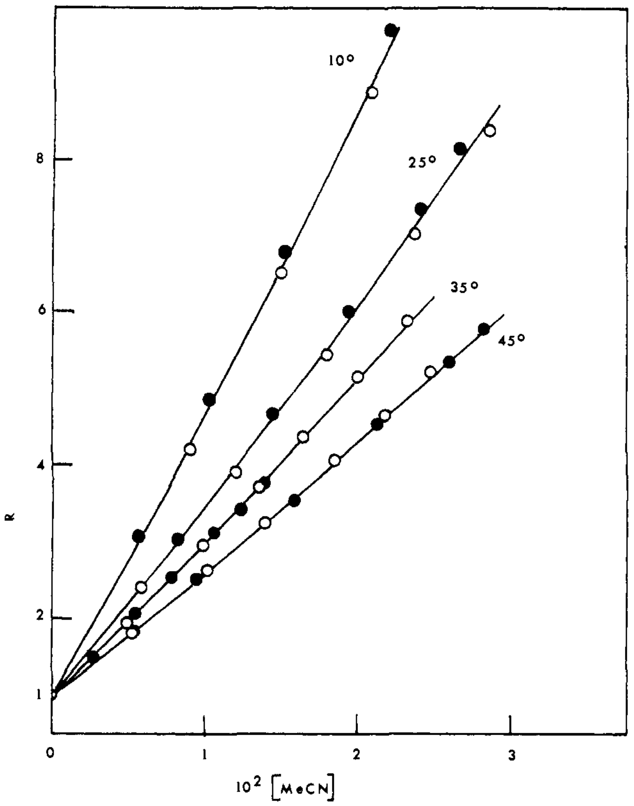

Figure 1. Ratios R for Bu_3NHPi in DCB as a function of added acetonitrile. The salt concentrations are: at 10°, (○) 0.179 mM and (●) 0.178 mM; at 25°, (○) 0.168 mM and (●) 0.174 mM; at 34.95°, (○) 0.160 mM and (●) 0.158 mM; at 45.6°, (○) 0.174 mM and (●) 0.155 mM.

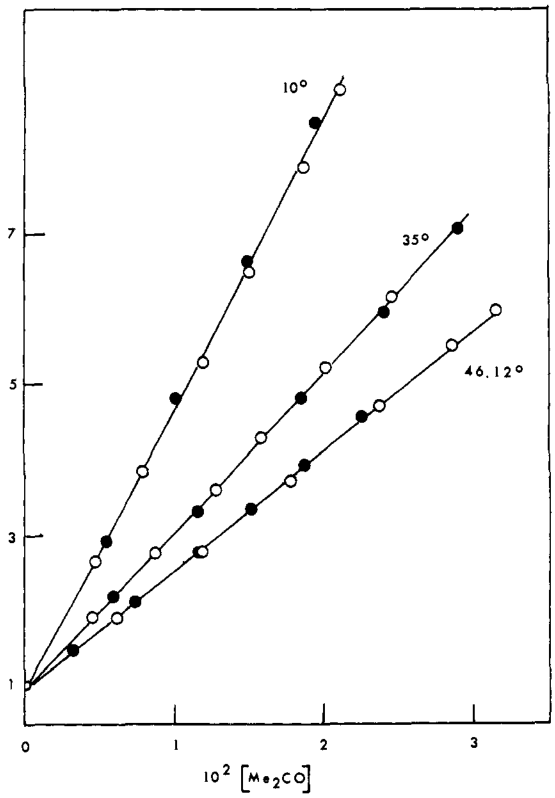

Figure 2. Ratios R for Bu_3NHPi in DCB as a function of added acetone. The salt concentrations are: at 10°, (○) 0.200 mM and (●) 0.190 mM; at 35°, (○) 0.194 mM and (●) 0.188 mM; at 46.12°, (○) 0.190 mM and (●) 0.178 mM.

Acetonitrile (B & A label Allied Chemical Co., Reagent Grade) was stored over molecular sieves (Linde type 4A) and was distilled using a 2 × 15 cm Vigreux column (bp 81° (760 Torr)). A middle fraction was then collected. Acetone (Columbia Organic Chemicals) was first distilled on a 2 × 30 cm Vigreux column; a middle fraction was then stored over molecular sieves (Linde type 4A). Prior to use this portion was distilled on a 2 × 15 cm Vigreux column (bp 57° (760 Torr)). A middle fraction was then used. Pyridine (Matheson Coleman and Bell, Reagent Grade) was refluxed for 2 hr over barium oxide and then distilled on a 2 × 15 cm Vigreux column (bp 115-116° (760 Torr)). A middle fraction was taken for use. Triphenylphosphine oxide (Columbia Organic Chemicals) was dissolved in a minimum amount of hot ethanol, filtered through a glass frit, and crystallized out of cooled ethanol solution by the addition of a minimum amount of distilled water. This procedure was repeated four times and the product was dried and stored under vacuum (mp 154-155°). Pyridine *N*-oxide (Columbia Organic Chemicals) was distilled on a 2 × 15 cm Vigreux column, under reduced pressure, and a middle fraction was obtained which was water white. Upon transferring this portion to another flask, the liquid solidified evolving a great deal of heat. This resultant solid was then sublimed (65° (1 Torr)) with steam heat onto an acetone-Dry Ice cooled cold finger, under reduced pressure. Tetrahydrofuran (B & A label Allied Chemical Co., Reagent Grade) was first treated to remove peroxides by refluxing for 0.5 hr with $Cu^{I}Cl$ and then distilling on a 2 × 15 cm Vigreux column at 760 Torr (bp 65.5°), taking a middle cut. This portion of THF was then refluxed 0.5 hr over calcium hydride followed by distillation on a 2 × 15 cm Vigreux column at atmospheric pressure.

Tri-*n*-butylammonium picrate was prepared as before.[14] The salt was then recrystallized from a minimum of hot ethanol after filtering through a glass frit. This was repeated four times. The salt (mp 106.5°) was then dried and stored under vacuum.

The salts and solid ligands were weighed in a nitrogen-filled dry box. The concentrations of the solutions were determined by weight. A dilute stock solution of electrolyte in *o*-dichlorobenzene was prepared. A portion was put in the conductance cell. Another portion was used to make up a concentrated ligand solution which is then titrated into the solution in the conductance cell. The method used in the preparation of solutions for chlorobenzene is altered from that for *o*-dichlorobenzene. A stock solution of ligand in solvent was prepared. A portion was placed in the conductance cell. Another portion was used to prepare a concentrated electrolyte titrant solution.

All measurements were carried out in oil-filled constant-temperature baths to minimize conductance leakage. The temperatures were determined using a thermometer calibrated by N.B.S. and all were maintained within ±0.01° except for the 10.0° bath which was maintained to ±0.05°.

The conductance bridge has already been described.[15] The uncertainty in the conductance measurements was about ±1% for the least conducting solutions, salt in chlorobenzene, and in other cases was about ±0.1% or less.

The cell used to determine conductance was of the Kraus-Erlenmeyer type with bright platinum electrodes. The cell constant was determined both by comparison measurements based on 0.01 Demal solutions of potassium chloride in water[16] and by a method by Fuoss[17] which is based on direct measurements of the conductance of tetrabutylammonium tetraphenylborate in *o*-dichlorobenzene solutions. The cell constant was 3.067×10^{-2} cm^{-1}.

The density of *o*-dichlorobenzene was measured at 10.0° with a 25-ml volumetric flask. Water was used as a calibrating liquid. The uncertainty in the density is ±0.05%. The densities of *o*-dichlorobenzene and chlorobenzene at other temperatures were taken from Timmermans' compilation.[18]

Results

***o*-Dichlorobenzene Solvent.** Values of the molar conductance, Λ, at various molar concentrations, c, of the salt Bu_3NHPi at 10, 25, 35, and 45° in the presence of added acetone, acetonitrile, pyridine, and pyridine *N*-oxide are listed in Table V of the microfilm edition of this journal.[19]

The ratio R is defined as $(\Lambda_L/\Lambda)^2$, where Λ is the molar conductance of the salt in the absence of ligand, and Λ_L is

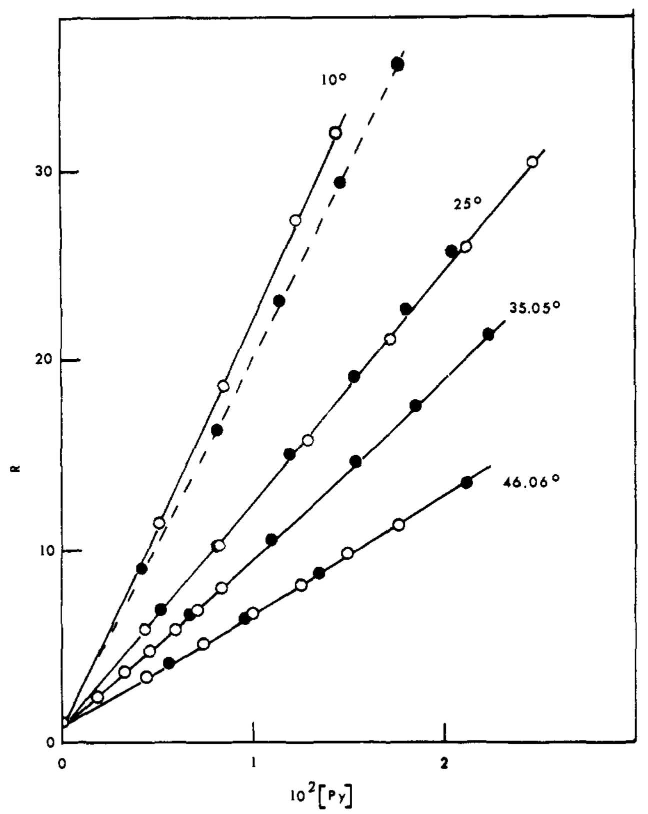

Figure 3. Ratios R for Bu_3NHPi in DCB as a function of added pyridine. The salt concentrations are: at 10°, (○) 0.200 mM and (●) 0.211 mM; at 25°, (○) 0.181 mM and (●) 0.180 mM; at 35.05°, (○) 0.186 mM and (●) 0.188 mM; at 46.06°, (○) 0.181 mM and (●) 0.183 mM.

the molar conductance of the salt solution with a ligand concentration [L]. Figures 1 through 4 show the ratio R as a function of ligand concentration for the ligands acetonitrile (MeCN), acetone (Me_2CO), pyridine (Py), and pyridine N-oxide (PyO) at 10, 25, 35, and 45°. The increases are large; for a 0.01 M ligand solution, the increases in conductance range from 63% for acetonitrile at 45° to 3000% for pyridine N-oxide at 10°. It has been previously shown[9,12,14,20] that conductance increases occurring upon the addition of Lewis bases such as those used here to solutions of Bu_3NHPi in DCB are due to the association of the cation with a molecule of Lewis base to form a 1:1 cation-ligand complex, eq 1.

A 10^{-4} M solution of Bu_3NHPi in DCB is only slightly dissociated into free ions

$$Bu_3NH^+, Pi^- \rightleftharpoons Bu_3NH^+ + Pi^- \qquad (3)$$

$$K_0 = [Bu_3NH^+][Pi^-]y_\pm^2/[Bu_3NHPi]$$

Here $[Bu_3NHPi]$ is the molar concentration of ion pairs whose activity coefficient is taken to be unity, and $y_\pm$ is the mean ionic activity coefficient, taken to be given by a form of the Debye-Hückel limiting law.[21] The Shedlovsky conductance equation,[22] which may be used to represent the conductance when ion pair association is large,[21] may be put into the form

$$K = (\Lambda S/\Lambda_0)^2 c y_\pm^2/(1 - \Lambda S/\Lambda_0) \qquad (4)$$

The factor $\Lambda S/\Lambda_0$ is γ, the fraction of free ions, and S is the Shedlovsky function,[22] correcting Λ for ion atmosphere effects. S and $y_\pm^2$ are both very close to unity at the ion concentrations we deal with here. Formation of ion triples and higher aggregates than ion pairs is known to be unimportant in DCB for the salt concentrations used here. Making the assumption that the limiting molar conductance of the tertiary ammonium salt in which the cation is complexed with ligand is the same as that of the uncomplexed salt, it has been shown[9,23,24] that for the kind of salt-ligand systems we deal with here, the conductance ratio $R = (\Lambda_L/\Lambda)^2$ is to a good approximation equal to the apparent ion pair dissociation constant K of the salt in the presence of ligand divided by that, K_0, in the absence of ligand.

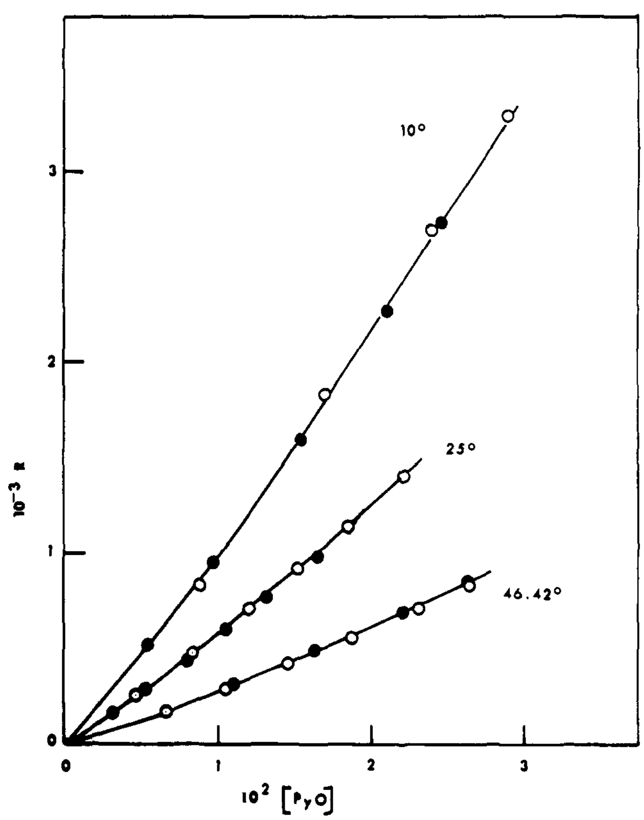

Figure 4. Ratios R for Bu_3NHPi in DCB as a function of added pyridine N-oxide. The salt concentrations are: at 10°, (○) 0.199 mM and (●) 0.208 mM; at 25°, (○) 0.199 mM and (●) 0.196 mM; at 46.42°, (○) 0.190 mM and (●) 0.192 mM.

$$R = (\Lambda_L/\Lambda)^2 = K/K_0 \qquad (5)$$

When ligand is added to the salt solution, one or more complexes may form between ligand and the salt species present, eq 6.

$$BH^+ + L \rightleftharpoons BH^+, L \quad K_1^+ = [BHL^+]/[BH^+][L] \qquad (6a)$$

$$BH^+, L + L \rightleftharpoons BH^+, L_2 \qquad (6b)$$

$$K_2^+ = [BH^+L_2]/[BHL^+][L]$$

$$Pi^- + L \rightleftharpoons Pi^-, L \quad K_1^- = [PiL^-]/[Pi^-][L] \qquad (6c)$$

$$BH^+, Pi^- + L \rightleftharpoons BH^+, L, Pi^- \qquad (6d)$$

$$K_p = [BHLPi]/[BHPi][L]$$

An expression has been derived[8,25] for the ratio K/K_0 in terms of the equilibrium constants in eq 6.

$$K/K_0 = (1 + K_1^+[L] + K_1^+K_2^+[L]^2)(1 + K_1^-[L])/(1 + K_p[L]) \qquad (7)$$

Slight upward curvature can be noted in the case of each ligand, Figures 1 through 4, indicative[9] that more than one ligand is reacting with the cation, eq 6b, or another is interacting with the anion, eq 6c. For the Lewis bases used as ligands here the latter alternative has been shown to be un-

Table I. Ligand Association Constant with Bu_3NH^+ in DCB

Ligand	10°	25°	35°	55°
		K_1^+, M^{-1}		
MeCN	347	236	196[a]	155[b]
	350	242	193[a]	159[b]
Me_2CO	353	248	197	150[c]
	363	250	200	149[c]
Py	2040	1120	800[d]	540[e]
	1870	1130	830[d]	550[e]
PyO	91,000	52,000		25,300[f]
	94,000	53,000		25,100[f]

[a] Actual temperature 34.95°. [b] Actual temperature 45.65°. [c] Actual temperature 46.12°. [d] Actual temperature 35.05°. [e] Actual temperature 46.06°. [f] Actual temperature 46.41°.

Table II. Thermodynamics of Association with Bu_3NH^+ in DCB

Ligand	$\Delta H_1°$, kcal mol^{-1}	$\Delta S°_1$, cal deg^{-1} mol^{-1}	μ_L[b]
MeCN	-4.01 ± 0.04	-2.54 ± 0.14	3.97
Me_2CO	-4.32 ± 0.06	-3.56 ± 0.21	2.85
Py	-6.30 ± 0.12	-7.17 ± 0.39	2.15
PyO	-6.43 ± 0.08	0.04 ± 0.26	4.24
THF[a]	-4.82 ± 0.26	-6.38 ± 0.86	1.65
Ph_3PO[a]	-6.58 ± 0.17	3.30 ± 0.58	4.30

[a] Reference 13. In the interest of internal self-consistency, values of K_1^+ for these ligands were recalculated from Flora's conductance data using the same procedure as in this work. This resulted in values of K_1^+ slightly different from those reported in ref 13, and thus small differences in the values of $\Delta H°$ reported in ref 13 (-4.84 ± 0.24 for THF and -6.56 ± 0.20 for Ph_3PO) and here. Similar differences may be noted in the values of $\Delta S°$ reported there (-6.40 ± 0.8 for THF and $+3.37 \pm 0.6$ for Ph_3PO) and here. [b] Reference 26.

important.[9] If the types of reactions represented by eq 6c and 6d are unimportant, then eq 7 reduces to

$$K/K_0 = 1 + K_1^+[L] + K_1^+K_2^+[L]^2 \tag{8}$$

Since $K/K_0 = R$, then eq 8 can be rearranged to

$$(R - 1)/[L] = K_1^+ + K_1^+K_2^+[L] \tag{9}$$

Plots of $(R - 1)/[L]$ *vs.* [L] were made for each of the ligands at each temperature. The intercepts as $[L] \rightarrow 0$ were taken to be values of K_1^+. The slopes of these plots are not listed because approximations made in the derivation of eq 9 and the experimental uncertainty make interpretation of these values in terms of K_2^+ of doubtful validity.

Two titration experiments were carried out in each case, and the two values of K_1^+ determined as outlined above at each temperature are listed in Table I. It can be seen that the reproducibility of the values of K_1^+ determined here is better than ±5%. Several of the values of K_1^+, Table I, at 25°, may be compared with values previously reported for this solvent. Ralph[14] found $K_1^+ = 1370$ M^{-1} for pyridine compared with the value 1120 M^{-1} found here, and Ralph found, for MeCN, $K_1^+ = 212$ M^{-1} while a mean value of 239 M^{-1} is found here. Ralph used a slightly different method to determine the values of K_1^+ in DCB than that used here in DCB; apparent values of ion pair dissociation constants for the salt were determined by measuring the conductivity at various salt concentrations in each of several solvent mixtures of DCB and ligand. This method is used here to determine values of K_1^+ in CB (see below). Ezell reported[11] a value of $K_1^+ = 49{,}000$ M^{-1} for PyO while that found here is 52,000 M^{-1}. In view of the reproducibility of the values of K_1^+ by different investigators using somewhat different methods of determination, it is believed that the absolute values of K_1^+ reported in Table I are uncertain by ±10%.

The thermodynamic quantities $\Delta H°_1$ and $\Delta S°_1$ for the formation of the 1:1 cation-ligand complex, eq 6a, were evaluated by a least-squares fit of the equation

$$\log K_1^+ = (\Delta S°_1/2.303R) - (\Delta H°_1/2.303R)(1/T) \tag{10}$$

assuming both $\Delta H°_1$ and $\Delta S°_1$ are constant over the range of temperature studied here. These results along with their probable errors are listed in Table II.

Chlorobenzene Solvent. Values of Λ at various concentrations C of Bu_3NHPi in pure CB, and in solutions of CB and the ligands acetonitrile, acetone, pyridine, pyridine *N*-oxide, tetrahydrofuran, and triphenylphosphine oxide at 10, 25, and 45° are listed in Table VI of the microfilm edition of this journal.[19]

Chlorobenzene has a dielectric constant of 5.62[27] at 25° while that of *o*-dichlorobenzene is 10.06[28] at this temperature. At a given salt concentration in the range of 10^{-4} M formation of ion triples can compete with ligand-cation complexation in CB

$$BHPi + BH^+ \rightleftharpoons (BH)_2Pi^+ \tag{11a}$$

$$BHPi + Pi^- \rightleftharpoons BH(Pi)_2^- \tag{11b}$$

in the formation of new conducting species.[14,29] Earlier it was believed that the effects of triple ions in the determination of K_1^+ values were not serious in the case of tertiary ammonium salts such as Bu_3NHPi.[24] A series of experiments using PyO as the ligand titrating solutions of Bu_3NHPi in CB at 10° show that as the salt concentration is increased the slopes of R *vs.* [L] become smaller.[30] Accordingly the titration method used to determine the ratio K/K_0 is inappropriate for CB. The method developed by Ralph,[14] alluded to above, was adopted for these experiments. Here the product $\Lambda_0K^{1/2}$ is determined at a number of concentrations of ligand in CB by the method of Fuoss and Kraus.[29] The conductance of salt in each ligand-CB solvent mixture is measured as a function of salt concentration. At concentrations of Bu_3NPHi in CB of the order of 2×10^{-4} M, the free ion concentration is so small ($\Lambda \leq 0.1$ in the solutions here) that ion atmosphere effects are negligible. Fuoss' equation for the conductance in such a system[30] reduces to eq 12

$$\Lambda C^{1/2} = \Lambda_0K^{1/2} + AC \tag{12}$$

where A is a constant characteristic of salt and solvent. The intercept as $C \rightarrow 0$ of a plot of $\Lambda C^{1/2}$ *vs.* C then yields values of $\Lambda_0K^{1/2}$ corrected for effects due to ion triples.

Figure 5 shows such a plot for Bu_3NHPi in pure CB at 10, 25, and 46.4°. The average values of $\Lambda_0K_1^{1/2}$ at each temperature are $(1.27 \pm 0.05) \times 10^{-5}$ at 10°, $(2.26 \pm 0.04) \times 10^{-5}$ at 25°, and $(4.84 \pm 0.02) \times 10^{-5}$ at 46.4°. These values were used to calculate the ratios $R = K/K_0$ for the ligands in CB. The present data at 25° are not in agreement with those reported by Ralph.[14] Ralph found $\Lambda_0K_0^{1/2} = 3.0 \times 10^{-5}$ at 25°, compared with the value 2.26×10^{-5} found in this study. The latest data, the results from three runs at 25° and two runs each at 10 and 46.4°, are self consistent in that the average values at the three temperatures fall on the same straight line in a plot of $\log \Lambda_0K_0^{1/2}$ *vs.* $1/T$. The value of $\Lambda_0K_0^{1/2}$ at 45° was obtained from this graph by interpolation.

Figure 6 shows plots of $\Lambda C^{1/2}$ *vs.* C for Bu_3NHPi in CB at 10, 25, and 45° in the presence of added acetonitrile. The intercepts as $C \rightarrow 0$ are taken to be values of $\Lambda_0K^{1/2}$ for the salt at various ligand concentrations. The values of R at each ligand concentration were then calculated by dividing the square of the intercept in the presence of ligand by the square of the intercept in the absence of ligand. These

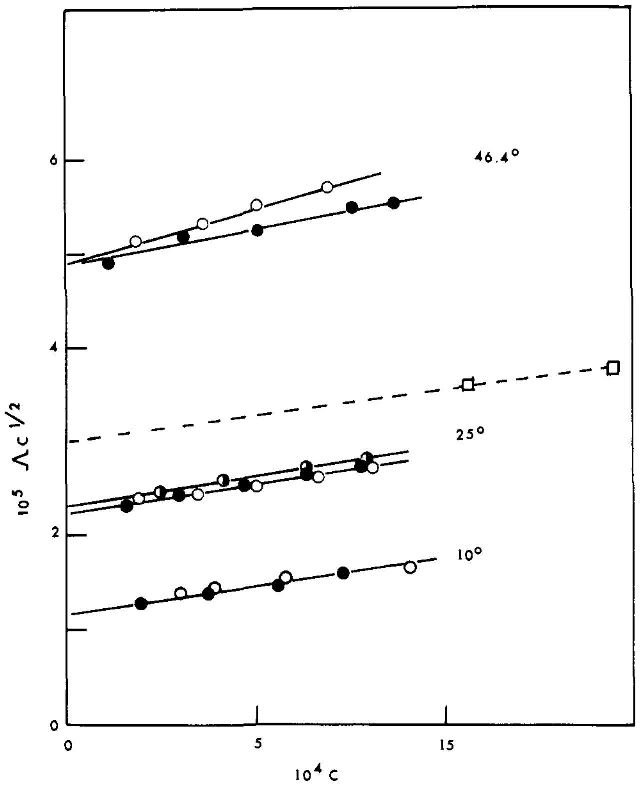

Figure 5. Fuoss-Kraus triple-ion plots for Bu_3NHPi in CB. Open, filled, and half-filled circles represent repeated runs. The squares represent data at the two lowest concentrations reported by Ralph (ref 14). The dashed line passes through Ralph's data points at the higher salt concentrations.

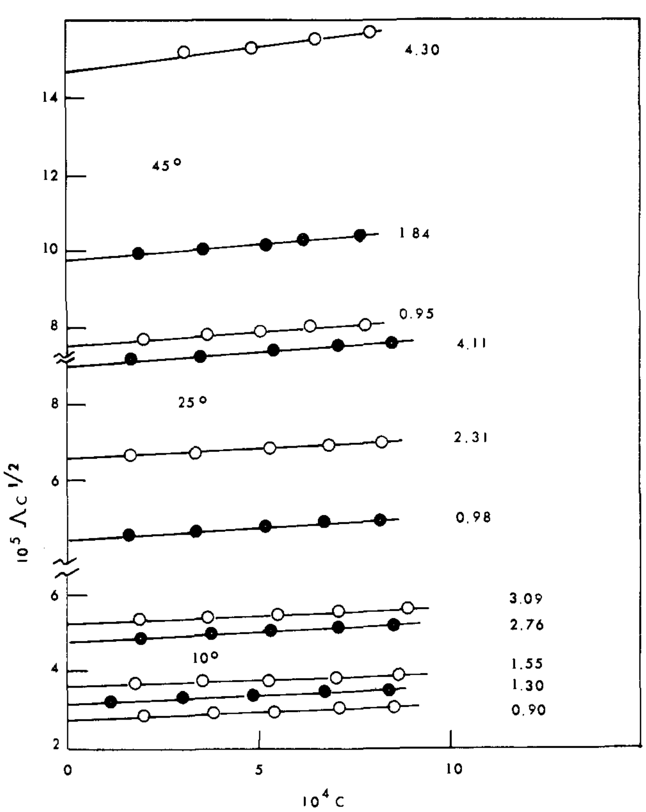

Figure 6. Fuoss-Kraus triple-ion plots for Bu_3NHPi in CB in the presence of added acetonitrile. The numbers on the right-hand side in the figure are concentrations of acetonitrile in units of centimolarity (10^{-2} M).

values of R at the three temperatures are plotted *vs.* ligand concentration, Figure 7. There is an increase of the slopes of these plots at higher ligand concentrations. A plot of the function $(R - 1)/[L]$ *vs.* [L] was made, Figure 8, and the intercepts, taken to be values of $K_1{}^+$ for acetonitrile, are listed in Table III. Conductance data for each of the other ligands were treated in the same manner. Plots of $(R - 1)/[L]$ *vs.* [L] for each of these ligands were prepared. The values of $K_1{}^+$ obtained from these graphs are listed in Table III. It is believed that the uncertainty in these values of $K_1{}^+$ is of the order of ±10%. There are large discrepancies between the values of $K_1{}^+$ reported here and those reported earlier from this laboratory for the ligands Py[14] and Ph_3PO.[11] These discrepancies are not due to differences in the conductances of the salt solutions in the presence of ligand; these are the same within experimental error. The differences are in the conductancies of the salt in pure solvent in the absence of ligand. Values of $\Lambda C^{1/2}$ ($\sim\Lambda_0 K^{1/2}$) plotted *vs.* [L] for the present work are shown in Figure 9, compared with past results for Py[14] and Ph_3PO.[11] In the case of Py as ligand Ralph used the same method as that used here to obtain values of $\Lambda_0 K^{1/2}$ at different pyridine concentrations. Ezell used the method of adding Ph_3PO to salt solution (that used here in DCB solvent) to determine the values of $\Lambda C^{1/2}$ plotted in Figure 9. The differences observed in conductances of the salt in solvent alone then will be ascribed as due either to trace impurities in the solvent or to impurities in the salt in the earlier experiments.

The thermodynamic quantities $\Delta H°$ and $\Delta S°$ for cation-ligand complex formation were calculated just as they were in DCB solvent (above) and appear tabulated in Table IV.

Table III. Ligand Association Constants with Bu_3NH^+ in CB

Ligand	10°	25°	45°
	$K_1{}^+$, M^{-1}		
MeCN	404	290	168
Me_2CO	402	270	166
Py	2560	1380	600
PyO	136,000	76,000	32,400
THF	234	149	80
Ph_3PO	1,830,000	920,000	368,000

Discussion

Few thermodynamic studies of ion-molecule association in solution have been reported. Arnett[31] has employed titrimetric calorimetry to determine the enthalpy of reaction of various ligands with Na^+ in acetone at 25°. While the heats observed by Arnett, *et al.*, are small, they fall in the same sequence as those reported here for the ligands common to the two studies; Arnett found the enthalpies to decrease in the order MeCN > Me_2CO > THF > Py. Izatt, Christensen, and coworkers[32] have carried out a calorimetric study of the interactions of a series of uni- and bivalent metal cations with a polycyclic ether in aqueous solutions. The authors remarked that the magnitudes of the thermodynamic quantities are strongly dependent on the solvent. The thermodynamic quantities for the reactions studied here show relatively small changes upon changing the solvent from *o*-dichlorobenzene to chlorobenzene. Specific effects due to hydrogen bonding were certainly present in the systems considered by Izatt and coworkers and are absent in the systems considered in this study.

Table IV. Thermodynamics of Association with Bu_3NH^+ in CB

Ligand	$\Delta H°_1$, kcal^{-1} mol^{-1}	$\Delta S°_1$, cal deg^{-1} mol^{-1}
MeCN	−4.51 ± 0.28	−3.95 ± 0.95
Me_2CO	−4.52 ± 0.07	−4.03 ± 0.24
Py	−7.43 ± 0.19	−10.62 ± 0.62
PyO	−7.10 ± 0.18	−1.55 ± 0.59
THF	−5.50 ± 0.17	−8.56 ± 0.57
Ph_3PO	−8.22 ± 0.18	−0.33 ± 0.59

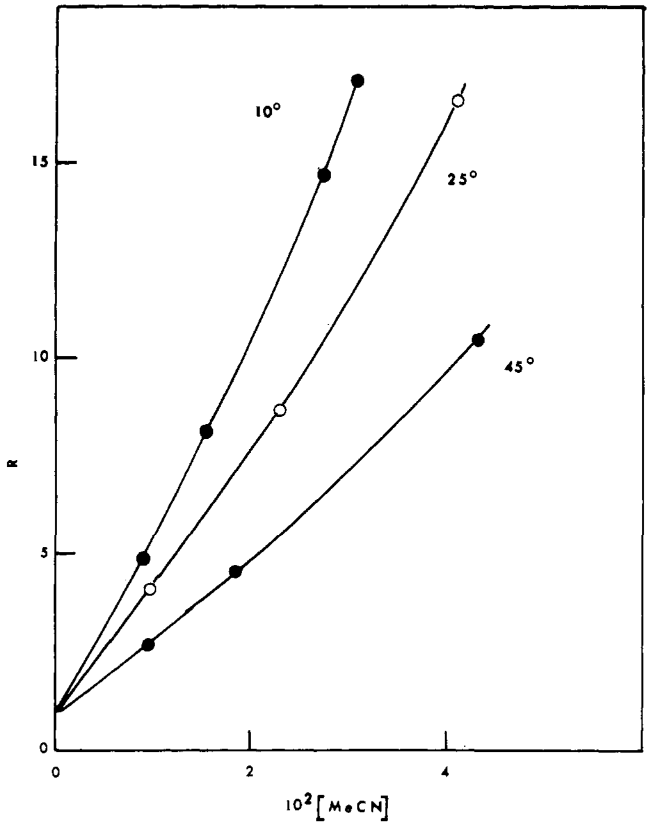

Figure 7. Ratios R for Bu_3NHPi in CB as a function of added acetonitrile. The ratios were calculated from the intercepts on the ordinate axis of the graphs in Figures 5 and 6 as described in the text.

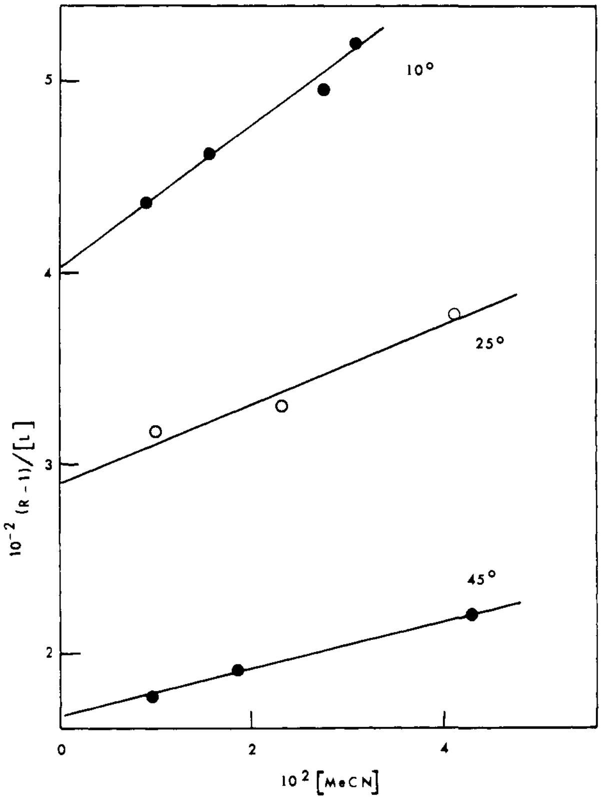

Figure 8. The function $(R - 1)/[L]$ plotted *vs.* acetonitrile concentration for Bu_3NHPi in CB.

A strong correlation had been noted recently[9] of values of K_l^+ with values of K_f, the equilibrium constant for formation of hydrogen-bonded complexes between p-fluorophenol

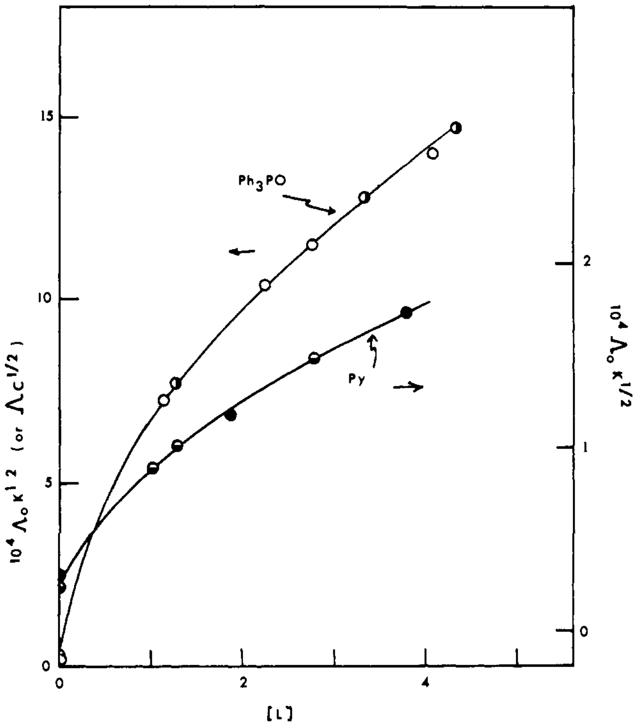

Figure 9. The conductance function $\Lambda_0 K^{1/2}$ (or $\Lambda c^{1/2}$) for Bu_3NHPi in CB as a function of added Ph_3PO or Py; a comparison of present results with earlier results. For Ph_3PO the open circles represent values of $\Lambda_0 K^{1/2}$ (this work), left-hand ordinate, *vs.* $[L] = 1000 \times [Ph_3PO]$; right half-filled circles are values of $\Lambda c^{1/2}$ in 0.135 mM salt solutions reported by Gilkerson and Ezell (ref 11). The right half-filled circles represent values of $\Lambda_0 K^{1/2}$ with pyridine as ligand (this work), right-hand ordinate, *vs.* $[L] = 100 \times [Py]$ while filled circles represent results reported by Ralph and Gilkerson (ref 14).

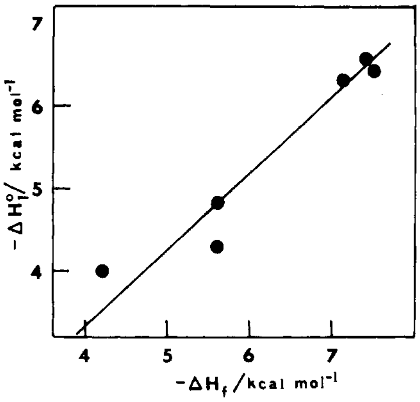

Figure 10. Enthalpies of association of Bu_3NH^+ with Lewis bases in DCB, $\Delta H^\circ{}_l$ *vs.* hydrogen bonding enthalpies, $\Delta H^\circ{}_f$.

and Lewis bases in CCl_4 reported by Taft and coworkers,[33] eq 13. Arnett and Schleyer have carried out extensive stud-

$$p\text{-}FC_6H_4OH + L \rightleftharpoons p\text{-}FC_6H_4OH\ldots L \qquad (13)$$

ies of the thermodynamics of this reaction.[34] A comparison of values of $\Delta H^\circ{}_l$ for association of Bu_3NH^+ with the Lewis bases used in this study in DCB solvent with the values of $\Delta H^\circ{}_f$, the enthalpy changes for the same ligands forming hydrogen-bonded complexes with p-fluorophenol, is shown in Figure 10. Values of $\Delta H^\circ{}_l$ in CB solvent yield a similar diagram. The correlation of enthalpy changes for the two different processes is good. The absolute magnitudes of the enthalpy changes for the two different processes are very similar, but this is thought to be fortuitous. Evidence has been presented[23] that association of Bu_3NH^+

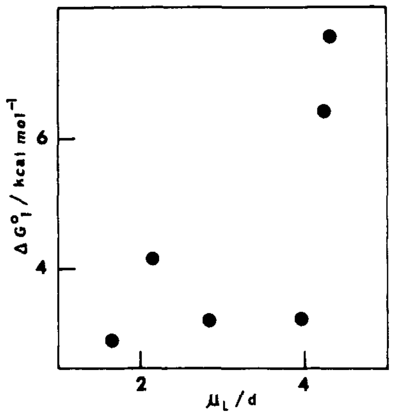

Figure 11. Free energies of association of Bu_3NH^+ with Lewis bases in DCB at 25°, $\Delta G^\circ{}_{l}$ *vs.* ligand dipole moment.

with ligands of the type considered here involved displacement of at least one solvating solvent molecule S from the cation by the ligand, eq 14. The equilibrium constant for

$$BH^+, S + L \rightleftharpoons BH^+, L + S \qquad (14)$$

this reaction is given by $K_{LS} = K_l{}^+[S]$, where [S] is the molar concentration of solvent. The entropy change for this reaction might be expected to be approximately zero; no changes in charge type occur, no changes in the number of kinetic species occur and the ligands are relatively sterically unhindered. If this were the case then for the reaction corresponding to eq 1, $\Delta S^\circ{}_l = -(R \ln [S])(1 + T\,\partial \ln \rho_0/\partial T)$ where ρ_0 is the solvent density. This expression yields a value of $\Delta S^\circ{}_l = -3.11$ for DCB at 25° and would change slightly with a change in solvent. The entropy changes observed here in cation-ligand complex formation, within ±5 eu of −2 eu in DCB and within ±5 eu of −5 eu in CB solvent, are consistent with the view given above that the incoming ligand is displacing a relatively tightly bound solvent molecule. Values of $\Delta H^\circ{}_l$ then would represent the differences between two larger energies of interaction, with the implication that the enthalpy of interaction of Bu_3NH^+ with either DCB or CB is significantly larger than is the enthalpy of interaction of *p*-fluorophenol with carbon tetrachloride.

The lack of correlation of log $K_l{}^+$ with aqueous pK_a values of the ligands has already been noted,[11] and is consistent with the observations of Taft and Schleyer[35] and of Arnett[36] concerning the lack of correlation of the energetics of hydrogen bond formation with those of proton transfer.

At one time there appeared to be a correlation of the values of the free energy of cation-ligand complex formation with ligand dipole moments.[11] The free energy changes obtained in this study in either DCB solvent or CB solvent, when plotted *vs.* ligand dipole moment indicate a trend to more negative values as ligand moment increases but the data points are badly scattered; such a plot is shown in Figure 11 for DCB solvent. Values of $\Delta H^\circ{}_l$ for either solvent show more scatter and no trend whatsoever when plotted *vs.* ligand dipole moment. In contrast, the entropy changes, $\Delta S^\circ{}_l$, for cation-ligand complex formation show a clear trend to increase as the ligand moment increases; plots of $\Delta S^\circ{}_l$ *vs.* μ_L for both DCB and CB solvent appear in Figure 12. It appears that changes in the free energies of cation-ligand complex formation are dominated by changes in the enthalpies of complex formation, and that these latter quantities are determined by structural factors which are not reflected in molecular dipole moments. A better understanding of the role that molecular structural changes play in the strengths of intermolecular interactions of the kind discussed here must await development of approaches to theoretical calculations of the energies as a function of distance and orientation for the relatively large polyatomic molecules and ions such as those we consider here.

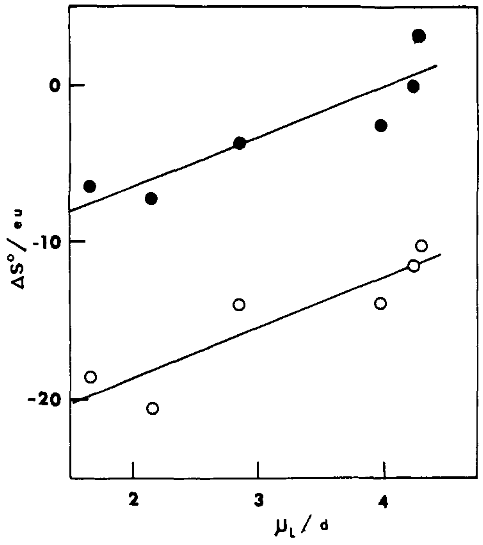

Figure 12. Entropies of cation-ligand complex formation, $\Delta S^\circ{}_l$ *vs.* ligand dipole moments. Filled circles, DCB solvent. Open circles, $\Delta S^\circ{}_l - 10$ eu for CB solvent.

The correlation, such as it is, between changes in entropy, $\Delta S^\circ{}_l$, and dipole moment, Figure 12, can be interpreted in terms of the crude electrostatic model of cation-dipole interaction proposed earlier,[11,12,14,37] eq 15, where $\Delta G^\circ{}_{el}$ is

$$\Delta G^\circ = \Delta G^\circ{}_{ch} + \Delta G^\circ{}_{el} \qquad (15)$$

the electrostatic portion of the free energy change corresponding to eq 14 and $\Delta G^\circ{}_{ch}$ is that portion of the free energy change due to short-range forces not represented by the ion-dipole model. $\Delta G^\circ{}_{el}$ is taken[38,39,12] to be given by eq 16, where r_L is the distance separating the charge on the

$$\Delta G^\circ{}_{el} = -(Nze/\epsilon_e)(\mu_L/r_L{}^2 - \mu_S/r_S{}^2) \qquad (16)$$

cation from the center of the ligand dipole in the complex, r_S is the corresponding distance for the solvent molecule, and ϵ_e is the effective dielectric constant modifying the ion-dipole potential energy of interaction. The thermodynamic quantities become[40] $\Delta S^\circ{}_{el} = \Delta G^\circ{}_{el}(\partial \ln \epsilon_e/\partial T)$ and $\Delta H^\circ{}_{el} = \Delta G^\circ{}_{el}(1 + T\partial \ln \epsilon_e/\partial T)$. It is not known *a priori* whether to take ϵ_e to be small (~1.0 as *in vacuo*) or to be equal to ϵ, the bulk dielectric constant of the solvent. The factor $\partial \ln \epsilon_e/\partial T$ is zero for $\epsilon_e = 1$ and is -0.0037 deg^{-1} for DCB at 25°. The contribution of $\Delta H^\circ{}_{el}$ to the overall enthalpy changes for the reactions considered here may be seen to be small if ϵ_e is equal to the bulk dielectric constant; however, $\Delta S^\circ{}_{el}$ does make a sizable contribution to the overall entropy change if this is the case. On the other hand, if ϵ_e is more nearly that *in vacuo* ($\epsilon_0 = 1$) then $\partial \ln \epsilon_e/\partial T = 0$ so that $\Delta S^\circ{}_{el} = 0$ and $\Delta H^\circ{}_{el} = \Delta G^\circ{}_{el}$. The facts that ΔG° does not change much as solvent dielectric constant changes, and that the values of $\Delta S^\circ{}_l$ in DCB and in CB are not constant and are roughly proportional to the ligand dipole moments, are taken to indicate that ϵ_e lies somewhere between the vacuum value and the bulk dielectric constant of the solvent, and that ϵ_e is some function of the bulk value of ϵ so that $(\partial \ln \epsilon_e/\partial T)$ is nonzero. Then

$$\Delta S^\circ{}_{el} = -(Nze/\epsilon_e)(\mu_L/r_L{}^2 - \mu_S/r_S{}^2)(\partial \ln \epsilon_e/\partial T) \qquad (17)$$

and if r_L does not change much for the series of ligands considered here, then $\Delta S^\circ{}_{el}$ will be approximately linear in μ_L, with a positive slope. The number of disposable parameters in the equation corresponding to the model, eq 17, are too great to make further quantitative comparison of model and experiment profitable.

When studies of the thermodynamics of ion-molecule association reactions in low-dielectric solvents were first undertaken in this laboratory,[13] it was expected that values of $\Delta S°$ for unhindered ligands would be constant for eq 1 and zero for eq 13, so that values of $\Delta G°$ would be almost equal to $\Delta H°$. It is found here that values of $\Delta H°_1$ are related most closely to short-range effects of the same nature as those operating in the formation of hydrogen bonds. The small changes in $\Delta S°_1$ that do occur with ligand appear to give some information on the nature of the electrostatic portion of the ion-ligand interaction as modified by surrounding solvent. The variations of $\Delta S°_1$ with ligand dipole moment are in accord with the model of cation-ligand interaction proposed earlier[12] to account for the changes in $\Delta G°$ with cation radius for a series of alkali metal cations associating with Ph_3PO in THF solvent.

The strengths of the interactions of Bu_3NH^+ (or *p*-fluorophenol) with the variety of Lewis bases examined here are not simply related to observables such as ligand dipole moment, but are more complex in nature and will require a more detailed understanding of the electron distributions in base and in cation (or acid) in order to appreciate the effects structural changes have on these binding energies.

Acknowledgment. We wish to thank the referees for their helpful comments and in particular for pointing out that a possible correlation existed between enthalpies of cation-ligand complex formation and enthalpies of hydrogen bond formation as determined by Arnett and coworkers.

Supplementary Material Available. Conductance data will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number JACS-75-493.

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