

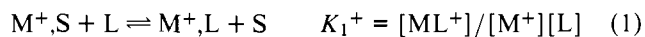
Ion-Solvent Interaction. Effects of Added Polar Compounds on the Conductances of Several Alkali Metal Salts in 2-Butanone at 25 °C

M. D. Jackson and W. R. Gilkerson*

Contribution from the Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208. Received June 26, 1978

Abstract: The conductance parameters, Λ^0 and K_A , for lithium picrate, sodium picrate, tri-*n*-butylammonium picrate, and lithium tetraphenylborate have been evaluated from the conductances measured as a function of salt concentration in solvent mixtures of 2-butanone with small amounts (up to 0.01 M) of added hexamethylphosphoric triamide (HMPA), triphenylphosphine oxide (TPPO), dimethyl sulfoxide (Me_2SO), trisethanolamine (TEA), and glyme-5. Values of cation-ligand association constants, K_1^+ , derived from the changes in limiting molar conductances, Λ^0 , are shown to be the same as those derived from changes in ion pair association constants, K_A , in the cases of lithium picrate and lithium tetraphenylborate with the ligands HMPA and TPPO. The magnitudes of K_1^+ are listed in parentheses after each ligand in the order with lithium (all ligands), with sodium (HMPA, TPPO, and TEA) and with tri-*n*-butylammonium (HMPA and TPPO only) cations for HMPA (1500, 37, 220), for TPPO (250, 18, 56), for TEA (6000, 110), for Me_2SO (12), and for glyme-5 (~ 0). It is found that, with the exception of glyme-5, there is only a small effect of changing solvent on the exchange of one ligand for another in the complex with lithium cation.

The formation of complexes of alkali metal cations with polar molecules in solution can serve as a model for one portion of the overall process: the transfer of an alkali metal cation from one polar solvent to another. The effects of changes in the cation M^+ , in the complexing polar ligand L, and in the solvent S on the equilibrium constant K_1^+ for the displacement of one specifically solvating solvent molecule by the ligand L



can give information about the factors important in specific ion-solvent interaction in the first coordination shell about the cation, and have been the subject of a number of studies recently.¹⁻⁴

We report here a study of complex formation of lithium, sodium, and tri-*n*-butylammonium cation with ligands such as hexamethylphosphoric triamide (HMPA), triphenylphosphine oxide (TPPO), trisethanolamine (TEA), dimethyl sulfoxide (Me_2SO), and glyme-5 in the relatively polar solvent 2-butanone. This is an extension of our earlier work in the less polar solvent tetrahydrofuran (THF).³ Our experimental approach is to measure the effect of added ligands on the conductance parameters, the limiting molar conductance, and ion pair association constant of salts containing the cation of interest.

Experimental Section

2-Butanone (Fisher Scientific Co.) was purified following the method of Hughes.⁵ The specific conductance of the solvent ranged from 1×10^{-8} to $1.4 \times 10^{-8} \Omega^{-1} \text{cm}^{-1}$. Hexamethylphosphoric triamide (Matheson Coleman and Bell) was stored for several days over type 4A molecular sieve (Fisher Scientific Co.) and then distilled on a $2 \times 15 \text{ cm}$ Vigreux column, a middle fraction being retained, bp 95 °C at 5 Torr. Triphenylphosphine oxide (K and K Laboratories) was recrystallized five times from ethanol and dried in vacuo before use. Trisethanolamine (Fisher) was distilled on a $2 \times 15 \text{ cm}$ Vigreux column, a middle fraction being retained, bp 182 °C at 5 Torr. Dimethyl sulfoxide (J. T. Baker Chemical Co.) was dried over type 4A molecular sieve and distilled from calcium hydride using a $2 \times 15 \text{ cm}$ Vigreux column. A middle cut was taken, bp 57 °C at 5 Torr. Bis[2-(2-methoxyethoxy)ethyl] ether (glyme-5, Eastman Kodak Co.) was distilled using a $2 \times 15 \text{ cm}$ Vigreux column, bp 122 °C at 18 Torr.

Lithium picrate was prepared from lithium carbonate (Matheson Coleman and Bell) and picric acid (Merck and Co.) by the method of Price, Crisp, and Hughes.⁶ It was recrystallized four times from an acetone-benzene mixture and dried in vacuo at the boiling point of chlorobenzene (132 °C).⁷ Lithium tetraphenylborate was prepared

in tetrahydrofuran from lithium chloride (Fisher) and sodium tetraphenylborate (Fisher) by the method of Szwarc and co-workers.⁸ It was recrystallized three times from 1,2-dichloroethane by the addition of cyclohexane and dried in vacuo at 50 °C for several days. Sodium picrate was prepared from sodium hydroxide (Fisher) and picric acid by the method of Fuoss and Coplan.⁷ It was recrystallized four times from absolute ethanol and dried in vacuo at the boiling point of chlorobenzene for several days before use. Tri-*n*-butyl picrate was prepared by the method of Kraus and Witschonke.⁹ It was recrystallized several times from absolute ethanol and dried in vacuo for several days.

The conductance cell was a Kraus-Erlenmeyer type with bright platinum electrodes. The cell constant was determined to be 0.2860 cm^{-1} by the method of Zwolenik and Fuoss.¹⁰ Conductance measurements were made using a Leeds and Northrup type 1554-A2 impedance bridge, a General Radio type 1310-B oscillator, and type 1232-A tuned amplifier and null detector. Measurements were made on the most conducting solutions at 0.5, 1.0, and 2.0 kHz and showed that the conductance varied less than 0.05% over this range. Values obtained at 1 kHz are reported here. An oil-filled thermostat, maintained at $25.00 \pm 0.005 \text{ }^\circ\text{C}$, was used.

Salts were weighed in a nitrogen-filled drybox. All solutions were prepared by weight, their final concentrations being calculated taking the solution density to be that of the pure solvent. A stock solution of the ligand in the solvent was prepared and a portion placed in the conductance cell. Another portion was used to prepare a concentrated salt solution. Increments of the latter were added from a weight buret directly to the conductance cell containing the solution of ligand in solvent.

The density of 2-butanone is 0.7996 g mL^{-1} , its viscosity is 0.3774 cP , and its dielectric constant is 18.01.⁶ The densities of solutions of HMPA and of TPPO in 2-butanone were measured at 25 °C in the concentration range of 0–0.04 M using a 5-mL pycnometer having graduated side arms; the latter were calibrated with mercury. The densities increased linearly and may be represented by the equations $d = d_0 + 0.044[\text{HMPA}]$ and $d = d_0 + 0.075[\text{TPPO}]$, where the brackets represent concentrations in mol L^{-1} . Viscosities of these solutions were measured using a Cannon-Fenske viscometer; $\eta/\eta_0 = 1 + 0.80[\text{HMPA}]$ and $\eta/\eta_0 = 1 + 0.57[\text{TPPO}]$.

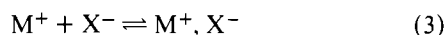
Results

The molar conductances Λ (in $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$) as a function of salt concentration C (mol L^{-1}) of lithium picrate, sodium picrate, tri-*n*-butylammonium picrate, and lithium tetraphenylborate in the pure solvent and in the various solutions of ligands in 2-butanone at 25 °C appear as supplementary material. The conductivity data have been treated using the Fuoss-Hsia 1967 conductance equation^{11a} as linearized by

Fernandez-Prini^{11b} and modified to include the Chen effect.¹² The equation governing the conductance of symmetrical electrolytes, including ion pair formation, is

$$\Lambda = \alpha[\Lambda_0 - S(C\alpha)^{1/2} + EC\alpha \log(C\alpha) + J(d)C\alpha + J_{3/2}(d)(C\alpha)^{3/2}] \quad (2)$$

The ion pair association constant for the equilibrium



is related to the fraction α of ions not associated by

$$K_A = (1 - \alpha)/C\alpha^2 y_{\pm}^2 \quad (4)$$

with the mean ionic activity coefficient y_{\pm} given by the extended Debye-Hückel equation

$$\ln y_{\pm} = -q\kappa\alpha^{1/2}/(1 + d\kappa\alpha^{1/2}) \quad (5)$$

where $q (= Z^2 e^2 / 2DkT = 15.56 \text{ \AA}^0$ in this solvent) is Bjerrum's critical distance.¹³ $\kappa\alpha^{1/2}$ is Debye's characteristic inverse distance. The parameter d that occurs in the expressions for J , $J_{3/2}$, and y_{\pm} is the distance parameter usually labeled R .

The conductance parameters Λ^0 and K_A in Table I were obtained from a least-squares treatment after setting the distance parameter $d = q$ in the expressions for J , $J_{3/2}$, and y_{\pm} .¹² For salts as associated as those we have investigated here, the values of the conductance parameters Λ^0 and K_A are not sensitive at all to the choice of distance parameter d . In a typical example, LiPi in 5.0 mM glyme-5, as d was varied (in $\sim 2\text{-\AA}$ steps) from 10 to 22 \AA , K_A increased by 1% from 6450 to 6618 M^{-1} , Λ^0 increased from 130.23 to a maximum of 130.25 (at $d = 14 \text{ \AA}$) and then decreased to 130.21 conductance units, and σ remained constant at 0.0182 until d was increased beyond 14 \AA , reaching a value of 0.0185 at $d = 22 \text{ \AA}$.

The conductance parameters for lithium and sodium picrate and for lithium tetraphenylborate may be compared with earlier values reported by Hughes and co-workers.⁶ There is satisfactory agreement in the values of K_A for lithium and sodium picrate (they report 6140 and 2190, respectively) but there are discrepancies in the values of Λ^0 which are outside experimental error, our values for these two salts being some six conductance units larger. We believe that these differences are real and due to different methods of drying these picrate salts under vacuum. We heated our salts to 132 $^{\circ}C$ while Hughes et al. apparently pumped their samples down at room temperature. Consider the following differences in Λ^0 for picrate and tetraphenylborate salts, where H designates Hughes' value and J designates that found here: one set is $\Lambda^0(KPi,H) - \Lambda^0(KBPh_4,H) = 21.12$, $\Lambda^0(LiPi,J) - \Lambda^0(LiBPh_4,J) = 22.89$, $\Lambda^0(NaPi,J) - \Lambda^0(NaBPh_4,H) = 21.58$; while another set involves Hughes' values for lithium and sodium picrates, $\Lambda^0(LiPi,H) - \Lambda^0(LiBPh_4,J) = 13.70$ and $\Lambda^0(NaPi,H) - \Lambda^0(NaBPh_4,H) = 16.08$. We believe that our results for lithium and sodium picrates are to be preferred since they are more consistent with the tetraphenylborate results and those for the potassium salts.

The molar conductances of lithium tetraphenylborate and of lithium picrate, both at a constant salt concentration of $1.0 \times 10^{-4} M$, are plotted vs. the concentration of added triphenylphosphine oxide in Figure 1 to show the very different effects the addition of a Lewis base have on an almost completely dissociated salt and one which is associated to ion pairs to a significant extent. The values of molar conductance for this graph were obtained by plotting Λ vs. C for each salt at each ligand concentration and reading off the value of Λ at $C = 1.0 \times 10^{-4} M$ for each ligand concentration.

Discussion

Figure 1 shows clearly at least two of the effects that may occur upon the addition of Lewis bases (or acids for that

Table I. Conductance Parameters for Salts in 2-Butanone at 25 $^{\circ}C$

ligand concn, mM	Λ^0	σ_0^a	K_A	σ_K^b	σ^c
Lithium Picrate					
none	130.45	0.18	6609	29	0.028
HMPA					
1.10	125.51	0.10	3022	35	0.085
2.50	123.39	0.18	2111	34	0.130
5.16	122.61	0.08	1585	9	0.055
10.10	122.07	0.12	1173	8	0.064
TEA					
1.00	124.97	0.11	1366	19	0.091
3.31	123.58	0.07	799	6	0.051
6.18	123.25	0.04	671	4	0.031
8.45	122.84	0.05	616	5	0.042
TPPO					
1.00	126.56	0.12	5316	49	0.090
2.30	121.63	0.11	4214	28	0.069
5.17	117.38	0.13	2903	20	0.071
10.08	114.05	0.20	1899	18	0.095
Me ₂ SO					
2.81	130.20	0.02	6326	4	0.007
4.56	130.02	0.13	6104	27	0.049
9.86	130.53	0.07	5295	12	0.025
glyme-5 no change in Λ^0 or K_A within experimental error up to 9.9 mM ligand					
Sodium Picrate					
none	131.06	0.05	2374	5	0.024
HMPA					
2.44	130.36	0.10	2160	18	0.072
4.95	129.45	0.02	2003	3	0.014
7.47	128.09	0.04	1824	4	0.024
10.11	127.46	0.11	1684	10	0.063
TPPO					
2.41	129.93	0.06	2269	12	0.044
4.99	128.07	0.07	2176	8	0.041
7.45	127.60	0.05	2118	6	0.033
10.08	126.12	0.08	2018	8	0.044
TEA					
0.99	130.03	0.13	2122	23	0.092
2.86	129.21	0.04	1876	5	0.028
5.44	127.56	0.05	1592	5	0.032
7.80	126.59	0.09	1422	9	0.058
Tri- <i>n</i> -butylammonium Picrate					
none	128.60	0.15	4494	20	0.044
HMPA					
1.05	127.64	0.05	3665	8	0.027
3.47	125.96	0.04	2521	5	0.020
6.88	125.06	0.04	1789	5	0.029
TPPO					
0.98	126.64	0.05	4026	21	0.041
4.97	125.01	0.02	3494	4	0.012
9.96	123.34	0.04	2905	5	0.018
Lithium Tetraphenylborate					
none	107.32	0.02	101	1	0.014
HMPA					
0.96	101.46	0.05	66	12	0.051
5.18	98.90	0.03	89	3	0.026
10.18	98.24	0.07	110	6	0.064
TPPO					
0.92	102.97	0.05	83	11	0.047
5.10	94.61	0.04	77	3	0.031
9.84	90.06	0.05	69	4	0.044

^a Calculated values of the standard deviation in Λ^0 . At least six data pairs were measured and used for each solvent-ligand mixture.

^b Calculated values of the standard deviation in K_A . ^c Calculated values of the standard deviation of the fit of $\Lambda(\text{calcd})$ to $\Lambda(\text{obsd})$.

matter) to appropriate salt solutions. The decrease in the molar conductance of the slightly associated ($\sim 1\%$) lithium tetraphenylborate as triphenylphosphine oxide is added can be at-

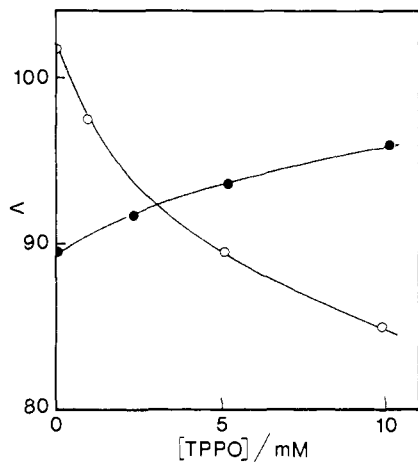
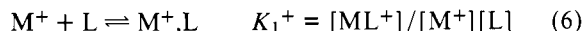


Figure 1. Molar conductances of lithium tetraphenylborate (open circles) and lithium picrate (closed circles) in 2-butanone at 25 °C as a function of the concentration of added triphenylphosphine oxide. The salt concentration is 0.1 mM in each case.

tributed to a decrease in ion mobility upon formation of the cation ligand complex.



Here $[M^+]$ represents the molar concentration of M^+ . The activity coefficients of the two cations in the dilute solutions encountered here are taken to be identical while the activities of uncharged species are taken to be equal to their molar concentrations. If no ions are associated to form nonconducting ion pairs (or at infinite dilution) the molar conductance represented by Λ^0 here becomes

$$\Lambda^0 = \alpha_{M^+} \Lambda_0^0 + \alpha_{ML^+} \Lambda_1^0 \quad (7)$$

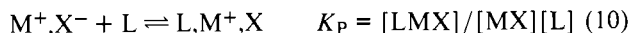
where α_{M^+} is the fraction of uncomplexed salt having a limiting molar conductance Λ_0^0 , and α_{ML^+} is the fraction of salt in the form of the cation-ligand complex with limiting molar conductance Λ_1^0 . Introducing eq 6 into eq 7 we have

$$\Lambda^0 = (\Lambda_0^0 + \Lambda_1^0 K_1^+ [L]) / (1 + K_1^+ [L]) \quad (8)$$

If Λ_1^0 is less than Λ_0^0 then Λ^0 will decrease as the concentration of ligand decreases, as is observed with lithium tetraphenylborate. The increase in the conductance of 1×10^{-4} M lithium picrate as triphenylphosphine oxide is added (Figure 1) is indicative that in addition to a decrease in ion mobility, the extent of ion pair association must decrease as well. Consider the following equilibria in addition to cation-ligand complex formation: dissociation of ion pairs



ion pair-ligand complex formation



Taking $C\alpha$ as the total free ion concentration

$$C\alpha = [M^+] + [ML^+] = [X^-]$$

while

$$C(1 - \alpha) = [MX] + [LMX]$$

The experimental ion pair association constant in the presence of ligand, eq 4, becomes, upon introduction of eq 6 and 10

$$K_A = ([MX]/[M^+][X^-])_{\gamma_{\pm}^2} (1 + K_P [L]) / (1 + K_1^+ [L]) \quad (11)$$

Recalling that the first factor in parentheses on the right-hand side of eq 11 is K_A^0 , the ion pair association constant in the

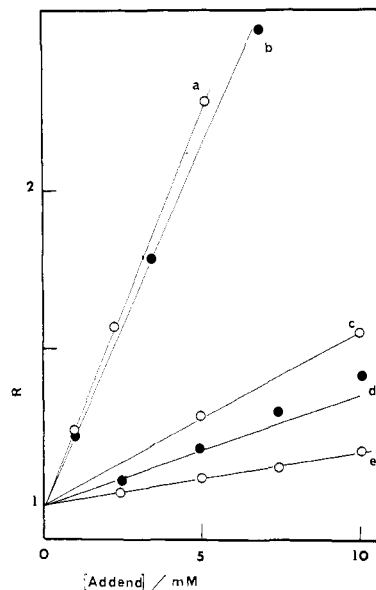


Figure 2. The ratio R of ion pair association constants in 2-butanone as a function of the concentration of ligands (addends): (a) lithium picrate plus TPPO, (b) tri-*n*-butylammonium picrate plus HMPA, (c) tri-*n*-butylammonium picrate plus TPPO, (d) sodium picrate plus HMPA, and (e) sodium picrate plus TPPO.

absence of ligand, eq 9, then eq 11 can be rearranged to yield the ratio

$$(K_A^0/K_A) = (1 + K_1^+ [L]) / (1 + K_P [L]) \quad (12)$$

One can expect that in general the affinity of a Lewis base for an unassociated cation will be greater than its affinity for an ion pair so that $K_1^+ > K_P$. Thus the extent of ion pair association should decrease as ligand concentration increases. It is clear from Figure 1 that for lithium picrate this latter effect occurs to a large enough extent to overshadow the effect due to ion mobility.

There are other factors that might influence the changes in Λ^0 and K_A given in Table I. Changes in the solvent viscosity affect the ion mobility. Assuming that the limiting molar conductances in these systems obey Walden's rule, $\Lambda^0 \eta = \text{constant}$, then the values of Λ^0 can be corrected for changes in solvent viscosity when these are known. These effects are small here, amounting to no more than a 0.7% decrease in Λ^0 for lithium tetraphenylborate at the highest concentration of added HMPA. The total observed decrease of Λ^0 is 9% for this system.

Changes in solvent dielectric constant will, of course, influence the extent of ion pair association and thus K_A . Huyskens and co-workers¹⁴ have made a determined effort to account for this factor in their approach to these kinds of effects by measuring the value of K_A as a function of dielectric constant when a nonpolar, noninteracting solute is added to the solvent. The problem this approach introduces is that specific interaction of the polar solvent itself with the ions might be affected by addition of the nonpolar solute. It is our opinion that the changes in dielectric constant of the Lewis base-2-butanone solvent mixtures are small enough at the concentrations utilized here to not be a significant factor in the changes we observe in K_A .

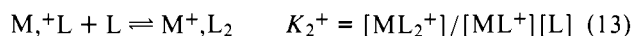
The plots of K_A^0/K_A (Figure 2) for lithium picrate with added TPPO, and for both sodium picrate and tri-*n*-butylammonium picrate with added HMPA and TPPO, are all sufficiently linear to indicate that cation-ligand complex formation is the principal source of the changes in K_A in these systems and no other complexes need be considered. Accordingly the slopes of these graphs are taken to be values of K_1^+ and are listed in Table II.

Table II. Cation-Ligand Association Constants in 2-Butanone at 25 °C

salt	ligand	K_1^+	Δ_1^0	$\Delta\Delta^{0b}$
LiPi	HMPA	1500		
	HMPA	1100 ^a	121.9	8.5
LiBPh ₄	HMPA	2000 ^a	98.6	8.7
	TPPO	250		
LiPi	TPPO	200 ^a	105.4	25.0
	TPPO	240 ^a	84.1	23.2
LiPi	TEA	6000		
	Me ₂ SO	12		
	glyme-5	~0		
NaPi	HMPA	37		
	TPPO	18		
	TEA	110		
Bu ₃ NHPi	HMPA	220		
	TPPO	56		

^a From values of limiting equivalent conductances. ^b $\Delta_0^0 - \Delta_1^0$.

The values of the ratio $R = K_A^0/K_A$ for the systems lithium picrate plus HMPA and TEA and for sodium picrate plus TEA show curvature down when plotted vs. ligand concentration. The ratio R shows curvature up in a similar plot for lithium picrate plus Me₂SO. The latter results indicate that we should consider the addition of a second ligand to the ion-ligand complex



The ratio R becomes

$$R = (1 + K_1^+[L] + K_1^+K_2^+[L]^2)/(1 + K_p[L])$$

and rearrangement leads to

$$(R - 1)/[L] = K_1^+ + K_1^+K_2^+[L] - K_pR \quad (14)$$

A decrease in $(R - 1)/[L]$ as the ligand concentration (or R) increases indicates that addition of a ligand molecule to the ion pair is important. In either of these two complicating cases, extrapolation of $(R - 1)/[L]$ to zero ligand concentration, or to $R = 0$, gives the intercept as K_1^+ . The plots of $(R - 1)/[L]$ vs. R for lithium picrate with HMPA and with TEA and for sodium picrate with TEA appear in Figure 3; the values of K_1^+ from these graphs are listed in Table II. The values of $(R - 1)/[L]$ for lithium picrate with added Me₂SO are plotted vs. ligand concentration in Figure 3 and the value of K_1^+ obtained from this is listed in Table II.

The changes in K_A for lithium tetraphenylborate in the presence of added ligand are much greater than the standard deviations in K_A listed in Table I but it must be remembered that these are the results for systems where the fraction of salt associated to ion pairs is only 1–2%. Values of K_A obtained for such systems should be regarded as curve-fitting parameters. We should have to extend our measurements to much higher salt concentrations in order to obtain reliable values of K_A . Larger salt concentrations would require higher ligand concentrations, thus compounding errors due to changes in viscosity and dielectric constant. We can obtain the information of interest from the variations in the values of the limiting molar conductances. Rearrangement of eq 8 yields

$$(\Delta_0^0 - \Delta^0)/[L] = K_1^+ \Delta^0 - K_1^+ \Delta_1^0 \quad (15)$$

The left-hand side of eq 15 is plotted vs. Δ^0 for lithium tetraphenylborate with added HMPA and TPPO in Figure 4. Also included are similar plots for lithium picrate with these two ligands. The lines through the data points were fitted using a least-squares procedure. Values of K_1^+ and Δ_1^0 calculated from these are listed in Table II.

The uncertainties in the values of K_1^+ listed are estimated

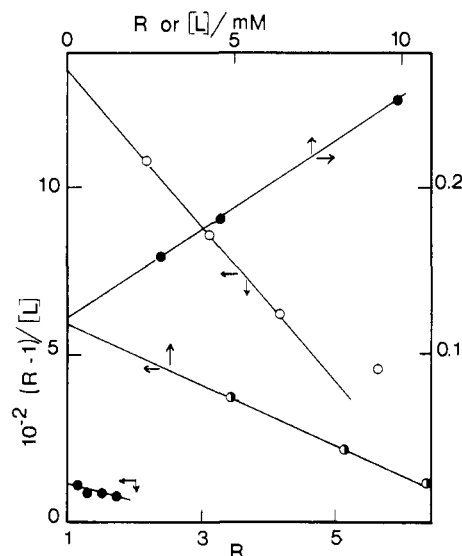


Figure 3. The function $(R - 1)/[L]$ plotted vs. R for lithium picrate with added HMPA (open circles, left-hand ordinate, lower abscissa), vs. R for sodium picrate with added TEA (lower set of filled circles, left-hand ordinate, lower abscissa), vs. R for lithium picrate with added TEA (half-filled circles, left-hand ordinate $\times 0.1$, upper abscissa), and vs. ligand concentration for lithium picrate with added Me₂SO (upper set of filled circles, right-hand ordinate, upper abscissa), all in 2-butanone solvent.

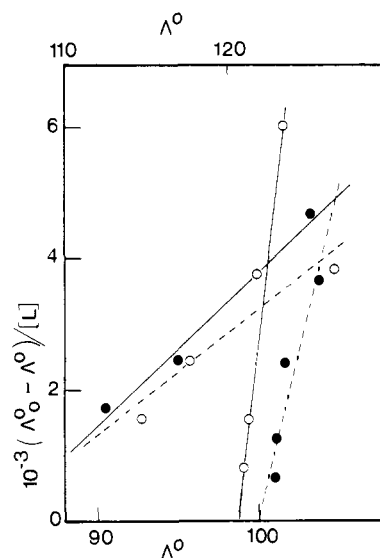


Figure 4. The conductance function $(\Delta_0^0 - \Delta^0)/[L]$ plotted vs. Δ^0 (corrected for viscosity changes) for lithium tetraphenylborate (solid lines, lower abscissa) and for lithium picrate (dashed lines, upper abscissa) in the presence of added HMPA (pair of data sets with the largest slopes) and in the presence of added TPPO (pair of data sets with the smaller slopes).

to be $\pm 10\%$ for the values obtained from K_A for the picrate salts and so are listed to only two significant figures. The 33% discrepancy between the value of K_1^+ for lithium ion with HMPA calculated using the limiting molar conductances and that from K_A is taken to be due to the relatively small change in Δ^0 upon complexation with HMPA. The agreement between the value of K_1^+ calculated from ion mobility and that from ion association constants is better for TPPO as ligand with lithium ion; the bulk of this ligand results in a relatively greater change in Δ^0 on complexation with both the picrate and the tetraphenylborate salts. The decrease in Δ^0 upon complexation, $\Delta\Delta^0 = \Delta_0^0 - \Delta_1^0$, is seen to be essentially the same for both salts with HMPA as a ligand and with TPPO as a ligand.

The effects on cation-ligand complex formation of changing

Table III. Effect of Solvent on Cation-Ligand Association at 25 °C

solvent	K_1^+ / M^{-1} with			
	HMPA	TPPO	Me ₂ SO	TEA
	Bu ₃ NH ⁺			
nitrobenzene	1750 ^a	363 ^b	100 ^a	
2-butanone	220	56		
<i>o</i> -dichlorobenzene ^{c,d}	2.25×10^6	0.37×10^6	37×10^3	
tetrahydrofuran	880 ^a	230 ^e		
	Li ⁺			
2-butanone	1500	250	12	6000
acetonitrile ^f	2100		49	
tetrahydrofuran		3500 ^e		50 000 ^g
	Na ⁺			
2-butanone	37	18		110
acetonitrile	29			
tetrahydrofuran		250 ^e		4800 ^g

^a M. D. Jackson, Ph.D. Dissertation, University of South Carolina, 1977. ^b J. B. Ezell and W. R. Gilkerson, *J. Phys. Chem.*, **72**, 144 (1968). ^c HMPA and Me₂SO: H. W. Aitken and W. R. Gilkerson, *J. Am. Chem. Soc.*, **95**, 8551 (1973). ^d TPPO: H. B. Flora and W. R. Gilkerson, *ibid.*, **92**, 3273 (1970). ^e Reference 3a. ^f Reference 15. ^g Reference 3b.

the cation from lithium to sodium can be seen using the values of the ratio K_1^+ (for Li⁺)/ K_1^+ (for Na⁺); this ratio is 41 for HMPA, 54 for TEA, and 14 for TPPO as ligand in 2-butanone. In THF,³ this ratio is 10 for TEA and 14 for TPPO. Nakamura finds this ratio to be 72 for HMPA in acetonitrile solvent.¹⁹

We had found^{3b} that for glyme-5 with lithium cation in THF solvent K_1^+ was 1900, slightly more than one-half that with TPPO as ligand. Early in the present work K_1^+ was found to be 250 for lithium cation with TPPO in 2-butanone. Accordingly, we expected K_1^+ for glyme-5 to be around 100, easily measurable under the conditions of our experiments. We have no explanation to offer for the result that added glyme-5 has no detectable effect on either Δ^0 or K_A for lithium picrate in 2-butanone. Clearly, more information is needed before we can understand this result.

The effects of changing the solvent on cation-ligand complex formation with a number of ligands can be seen in Table III, where values of K_1^+ are listed for Bu₃NH⁺ with HMPA, TPPO, and Me₂SO in nitrobenzene, 2-butanone, *o*-dichlorobenzene, and tetrahydrofuran, for lithium and sodium cation with HMPA, TPPO, Me₂SO, and TEA in 2-butanone and tetrahydrofuran, and with several of these ligands in acetonitrile solvent.¹⁵ The values of K_1^+ for Bu₃NH⁺ with both HMPA and TPPO are seen to decrease by a factor of less than 2 when the solvent is changed from the polar (dielectric constant $D = 34.7$) but poorly solvating (qualitative, based on salt solubility) nitrobenzene to the relatively low dielectric ($D = 7.4$) but highly solvating tetrahydrofuran. In contrast, the values of K_1^+ for these two ligands and for Me₂SO increase by factors of 1300, 1000, and 370, respectively, when the solvent is changed from nitrobenzene to the lower dielectric ($D = 10.0$) and poorly solvating solvent *o*-dichlorobenzene.

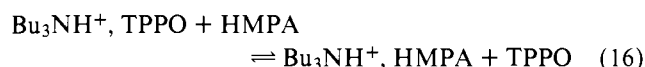
We have already presented evidence that cation-ligand association in solvating solvents involves the displacement of at least one solvent molecule from the primary solvation sheath of the cation by the incoming ligand as depicted in eq 1.¹⁶ If specific solvation of the cation is the principal cause of the variations in values of K_1^+ for a particular cation-ligand pair shown in Table III, then the exchange equilibrium constants for displacement of one ligand by another ligand should exhibit a smaller variation than does K_1^+ as the bulk solvent is changed. The values of K_{ex} for the displacement of TPPO by HMPA on Bu₃NH⁺ (calculated as the ratio K_1^+ (for

Table IV. Ligand Displacement of THF from Lithium Cation at 25 °C

ligand	$-\Delta G_{ex}^0$ ^a	$-\delta\Delta G_{HB}^0$ ^b	μ ^c
HMPA	7.38	3.15	5.38 ^d
TPPO	6.32	2.62	4.30
Me ₂ SO	4.52	1.76	3.90
AN	1.10	-0.27	3.96
Q	2.42	1.88	1.2 ^e
MEK	1.65	-0.07	2.78
THF	0	0	1.65

^a In kcal mol⁻¹. Values calculated as described in text. ^b $\delta\Delta G_{HB}^0 = \Delta G_{f(L)}^0 - \Delta G_{f(THF)}^0$, where $\Delta G_{f(L)}^0$ is for the formation of a hydrogen-bonded complex with *p*-fluorophenol, ref 25. ^c These values of dipole moment, in debyes, are all taken, unless otherwise noted, from A. L. McClellan, "Tables of Experimental Dipole Moments", W. H. Freeman, San Francisco, Calif., 1963. ^d J.-E. Dubois and H. Viellard, *J. Chim. Phys. Phys.-Chim. Biol.*, **62**, 699 (1965). ^e B. Lassier, C. Brot, and N. Dat-Xuong, *Mol. Phys.*, **27**, 1697 (1974).

HMPA)/ K_1^+ (for TPPO)), the reaction given by



are found to be 4.8, 3.9, 6.1, and 3.8, respectively, in the solvents nitrobenzene, 2-butanone, *o*-dichlorobenzene, and tetrahydrofuran. Similarly, the values of K_{ex} for the displacement of Me₂SO by TPPO on Bu₃NH⁺ are found to be 3.6 in nitrobenzene and 10 in *o*-dichlorobenzene. The much smaller variations in the displacement equilibrium constants when compared with the variations in the values of K_1^+ as the solvent is changed are indicative to us that our hypothesis is correct; the incoming ligand apparently displaces a specifically solvating solvent molecule to form the cation-ligand complex.

Values of K_1^+ for lithium and sodium cations with TPPO and TEA as ligands increase by factors of 8.3 or greater as the solvent is changed from 2-butanone to tetrahydrofuran. The value of K_{ex} for the displacement of TPPO by TEA on lithium cation is 24 in 2-butanone and decreases by a factor of 1.7 to 14 in tetrahydrofuran. The value of K_{ex} for the displacement of TPPO by TEA on sodium is 6.1 in 2-butanone and increases by a factor of 3.1 to 19.2 in tetrahydrofuran.

These changes in K_{ex} may be due to changes in ligand-solvent interaction, or to changes in cation-ligand interaction as a result of changes in the rest of the primary solvation sheath around the cation and in the next nearest layer of solvent molecules. Changes in bulk dielectric constant may play some part but there is no trend in values of K_{ex} to indicate that this factor is a major contributor. The changes in K_{ex} as solvent is changed, in those cases we have investigated, are larger in the cases of the alkali metal cations Li⁺ and Na⁺ than for Bu₃NH⁺ but we believe that they are significantly less than the changes observed in values of K_1^+ as solvent is changed.

The value of K_{ex} for displacement of the solvent molecule S by a given ligand L from a cation M⁺ is related to K_1^+ by the expression $K_{LS} = K_1^+[S]$, where the activity of solvent has been taken to be equal to its molar concentration, [S].¹⁶ Using this expression, we can include the solvents tetrahydrofuran (THF), 2-butanone (MEK), and acetonitrile (AN) in a list of ligand exchange equilibrium constants (or free energies) if it is assumed that the values of K_{ex} are (almost) independent of solvent. We will compare values of ΔG_{ex}^0 , so that an uncertainty of a factor of 3 in K_{ex} introduces an uncertainty of 0.65 kcal mol⁻¹ in ΔG_{ex}^0 at 25 °C. Values of ΔG_{ex}^0 so calculated appear in Table IV. THF is chosen as the reference substance since it has the smallest affinity for lithium of the substances included in Table III. The equilibrium constant K_{ex} for the displacement of THF by TPPO was calculated using earlier results.³ The value of K_{ex} for displacement of THF by HMPA

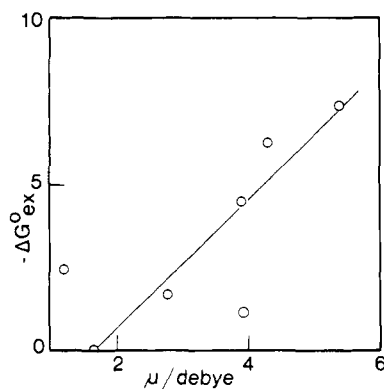


Figure 5. The free energy of exchange, ΔG°_{ex} , in kcal mol⁻¹, for displacement of THF by ligand on lithium cation as a function of the ligand dipole moment in debyes.

was obtained by combining that for TPPO with the value of K_{ex} for the displacement of TPPO by HMPA in 2-butanone (this work). The value of K_{ex} for displacement of THF by Me₂SO was calculated by combining that for TPPO in THF with the value of K_{ex} for displacement of TPPO by Me₂SO in 2-butanone (this work). The value of K_{ex} for displacement of THF by acetonitrile (AN) was obtained by combining the K_{ex} for displacement of AN by HMPA (Nakamura¹⁵) with the value of K_{ex} already calculated for displacement of THF by HMPA. K_{ex} for the displacement of THF by quinuclidine (Q) was calculated from earlier results.^{3b} The value of K_{ex} for the displacement of THF by MEK was calculated by combining K_{ex} for the displacement of MEK by TPPO (this work) with the value of K_{ex} for the displacement of THF by TPPO.³ Values of $\Delta G^{\circ}_{ex} (= -RT \ln K_{ex})$ were calculated and appear in Table IV. Figure 5 shows a plot of ΔG°_{ex} vs. the dipole moment of displacing ligand. The affinity of these ligands for lithium ion does increase roughly as the ligand dipole moment increases. Indeed, the correlation between ΔG°_{ex} and μ_L appears to be much better¹⁷ than was obtained in an earlier comparison of values of K_1^+ for a series of ligands with tri-*n*-butylammonium cation.^{18,19} We do not maintain that a simple electrostatic ion-dipole relationship governs these short-range interactions in solution (note the departure of the points for quinuclidine and acetonitrile from the line drawn through the points in Figure 5), but the magnitude of the moment does seem to be a fair measure of the factors that control ion-polar molecule interaction in solution.

It had been pointed out earlier¹⁹ that there is a good correlation between values of K_1^+ for tri-*n*-butylammonium cation with a large number of Lewis bases in *o*-dichlorobenzene solvent and the hydrogen bond formation constants measured by Taft et al.²⁰ for the same bases with *p*-fluorophenol in carbon tetrachloride. We find a similar correlation between binding to lithium cation as measured by ΔG°_{ex} and hydrogen bond complex formation with *p*-fluorophenol as measured by ΔG°_{HB} ;²¹ see Figure 6.

A comparison of our results for lithium cation-ligand complex exchange with other measures of solvent affinity for Lewis acids such as Gutmann's donor numbers²² and Popov's ²³Na NMR chemical shifts²³ must await our accumulation of more data; we do not at present have data on enough ligands in common with these other measures to say more than that there does *seem* to be a correlation with these other measures, as one would expect.

We have shown here that one can obtain the same values (within experimental error) for ion-molecule complex formation constants from the variation with concentration of

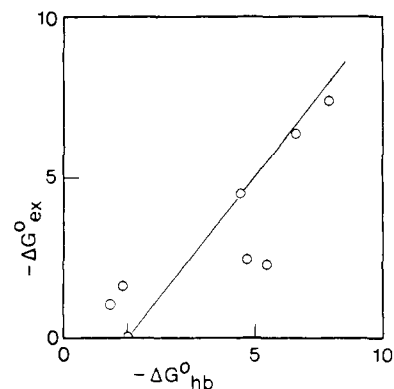


Figure 6. The free energy of exchange, ΔG°_{ex} , for the displacement of THF by ligand on lithium cation as a function of ΔG°_{HB} , the free energy of hydrogen-bond formation of the ligand with *p*-fluorophenol, both in kcal mol⁻¹.

added ligand of ion pair association constants and of limiting equivalent conductances of certain alkali metal salts in 2-butanone. Our results for the cation-ligand complex formation constants are indicative that in ion-polar solvent interaction, a major portion of the interaction is specific and short range, involving principally those solvent molecules in the first coordination shell around the ions. This is not a novel conclusion²⁴ but our results certainly reinforce this view.

Supplementary Material Available: Table V, molar conductances of lithium picrate in 2-butanone-ligand mixtures at 25 °C; Table VI, molar conductances of lithium tetraphenylborate in 2-butanone-ligand mixtures at 25 °C; Table VII, molar conductances of sodium picrate in 2-butanone-ligand mixtures at 25 °C; Table VIII, molar conductances of tri-*n*-butylammonium picrate in 2-butanone-ligand mixtures at 25 °C (6 pages). Ordering information is given on any current masthead page.

References and Notes

- (1) D. R. Cogley, J. N. Butler, and E. Grunwald, *J. Phys. Chem.*, **75**, 1477 (1971).
- (2) (a) B. G. Cox, A. J. Parker, and W. E. Waghorne, *J. Phys. Chem.*, **78**, 1731 (1974); (b) G. Clune, W. E. Waghorne, and B. G. Cox, *J. Chem. Soc., Faraday Trans. 1*, **72**, 1294 (1976).
- (3) (a) H. B. Flora and W. R. Gilkerson, *J. Phys. Chem.*, **77**, 1421 (1973); (b) *ibid.*, **80**, 679 (1976).
- (4) A. Hourdakakis and A. I. Popov, *J. Solution Chem.*, **6**, 299 (1977).
- (5) S. R. C. Hughes and S. H. White, *J. Chem. Soc. A*, 1216 (1966).
- (6) S. Crisp, S. R. C. Hughes, and D. H. Price, *J. Chem. Soc. A*, 603 (1968).
- (7) M. A. Coplan and R. M. Fuoss, *J. Phys. Chem.*, **68**, 1177 (1964).
- (8) D. N. Battacharyya, C. L. Lee, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **69**, 608 (1965).
- (9) C. R. Witschonke and C. A. Kraus, *J. Am. Chem. Soc.*, **69**, 2472 (1947).
- (10) J. J. Zwolenik and R. M. Fuoss, *J. Phys. Chem.*, **68**, 903 (1964).
- (11) (a) R. M. Fuoss and K. L. Hsia, *Proc. Natl. Acad. Sci. U.S.A.*, **57**, 1550 (1967); (b) R. Fernandez-Prini, *Trans. Faraday Soc.*, **65**, 3311 (1969).
- (12) (a) C. Treiner and J.-C. Justice, *J. Chim. Phys. Phys.-Chim. Biol.*, **68**, 56 (1971); (b) M. S. Chen, Ph.D. Dissertation, Yale University, 1969; (c) A. D. Pethybridge and D. J. Spiers, *J. Chem. Soc., Faraday Trans. 1*, **72**, 64, 73 (1976).
- (13) N. Bjerrum, *K. Dan. Vidensk. Selsk.*, **7**, No. 9 (1926).
- (14) M. C. Haulait and P. L. Huyskens, *J. Solution Chem.*, **4**, 853 (1975).
- (15) T. Nakamura, *Bull. Chem. Soc. Jpn.*, **48**, 1447 (1975).
- (16) J. B. Ezell and W. R. Gilkerson, *J. Am. Chem. Soc.*, **88**, 3486 (1966).
- (17) Eyeball estimate only. The assumptions used to arrive at values of ΔG°_{ex} make a more sophisticated treatment of the goodness of fit of doubtful worth.
- (18) M. L. Junker and W. R. Gilkerson, *J. Am. Chem. Soc.*, **97**, 493 (1975).
- (19) H. W. Aitken and W. R. Gilkerson, *J. Am. Chem. Soc.*, **95**, 855 (1973).
- (20) (a) D. Gurka and R. W. Taft, *J. Am. Chem. Soc.*, **91**, 4794 (1969); (b) L. Joris, J. Mitsky, and R. W. Taft, *ibid.*, **94**, 3438 (1972).
- (21) See E. M. Arnett, E. J. Mitchell, and T. S. S. Murty, *J. Am. Chem. Soc.*, **96**, 3875 (1974), for a recent comprehensive compilation of the thermodynamic parameters for both hydrogen bond formation and proton transfer.
- (22) V. Gutmann, *Electrochim. Acta*, **21**, 661 (1976).
- (23) R. H. Erlich, R. Roach, and A. J. Popov, *J. Am. Chem. Soc.*, **92**, 4989 (1970).
- (24) See, for instance, ref 1 and 2a.