$CrF_6{}^{3-}$ are in qualitative agreement with those of Table IV of part I. On the other hand, the coefficients for $\psi_t{}^a$ for $CrF_6{}^{3-}$ do not agree, nor should they, due to differences in the way $\psi_t{}^a$ is defined. It would be of great interest to see a direct comparison of the present approximate average-of-configuration calculation with a more accurate open-shell average-of-configuration using Richardson's programs. Agreement would confirm that $10Dq$ can be obtained accurately as a difference in orbital energies.

It is also of interest to note in passing that the NEMO method of Newton, Boer, and Lipscomb[8] cannot be used to approximate the off-diagonal matrix elements in these calculations. Presumably their method fails because we are dealing with ions and not neutral molecules.

(8) M. D. Newton, F. P. Boer, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 88, 2353 (1966).

Conclusion

The approximations given by eq 10 are sufficiently accurate for the open-shell calculation of $10Dq$ when dealing with highly ionic systems in which $\mathfrak{F}_0{}^0$ is at least a rough approximation to $\mathfrak{F}_0$. The restriction to highly ionic systems is quite important. A recent attempt by the present author to calculate the ligand-field splitting parameters in the gaseous linear molecule NiF_2 failed owing to the very large covalency of the d orbitals. The field of two negative ions is not sufficient to raise the d-orbital diagonal elements to the point where the d orbitals are antibonding.

Thermodynamics of Lithium Chloride in Dimethylformamide

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Abstract: Potential measurements of the cell Tl(1.01 mol % in Hg)|TlCl(s)|Li$^+$,Cl$^-$,DMF|Li(1.06 mol % in Hg) have been carried out in an argon atmosphere as a function of time over a range of temperatures from 13.45 to 46.40°, and LiCl concentrations from 0.001 to 2.0 m. From these data were calculated standard potentials, free energies, enthalpies, and entropies for the reactions Li$^+$ + Cl$^-$ + Tl(s) $\rightarrow$ Li(s) + TlCl(s) and Li$^+$ + Tl(s) $\rightarrow$ Li(s) + Tl$^+$, as well as activity coefficients for LiCl in DMF. Water concentrations between 0.002 and 0.013 m have negligible effect on these measurements. Ion pairing between Li$^+$ and Cl$^-$ is found to be weak, and the Guggenheim equation gives the most accurate empirical description of the activity coefficients. Free energies, enthalpies, and entropies of transfer for LiCl from water to DMF solvents are calculated from EMF, solubility, and calorimetric measurements.

Recent interest in thermodynamics of nonaqueous electrolytes has prompted a number of potentiometric studies of activity coefficients for LiCl in dimethyl sulfoxide (DMSO)[1,2] propylene carbonate (PC),[3] and N-methylformamide (NMF).[4,5] Although enthalpy of solution data for LiCl in N,N-dimethylformamide (DMF) are available,[6,7] there is some question regarding the extent of ion pairing in this electrolyte, and neither free energy of solution nor activity coefficient data are available.

In DMSO[1,2] and propylene carbonate,[3] the cell

$$\text{Tl(Hg)}|\text{TlCl(s)}|\text{Li}^+,\text{Cl}^-,\text{solvent}|\text{Li(Hg) or Li(s)}$$
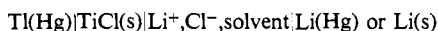
has proved to be stable and reversible, and has yielded accurate values of activity coefficients and thermodynamic potentials. Our preliminary work[8,9] showed that both the Tl(Hg) and the Li(Hg) electrodes were reversible in DMF solutions, and that the solubility of TlCl in excess chloride was small enough that liquid junction potentials could be neglected. This paper reports the results of an extensive investigation using this cell. In addition, we have critically evaluated a number of related studies in the literature, and have compared the potentiometric data with calorimetric and solubility data where these are available.

Experimental Section

Amalgams were prepared by weight from thallium rod (American Smelting and Refining Co., 99.999%), lithium rod (Foote Mineral Co., 99.97%), and mercury (Doe and Ingalls, triple-distilled). In all measurements, the thallium amalgam was 1.01 mol % (1.02 wt %) and the lithium amalgam was 1.06 mol % (0.0372 wt %). These were unsaturated and were stirred during preparation and just prior to use in the cells. Solutions of lithium chloride (Anderson Physics Laboratories, ultrapure grade) in N,N-dimethylformamide (Matheson Coleman and Bell, spectroquality) were also prepared by weight.

The DMF used in one set of measurements was dried using Linde 4A molecular sieves, which were dried before use by heating in a quartz tube under a stream of argon at 375° for 24 hr. They were

(1) D. R. Cogley and J. N. Butler, *J. Electrochem. Soc.*, 113, 1074 (1966); G. Holleck, D. R. Cogley, and J. N. Butler, *ibid.*, 116, 952 (1969).
(2) W. H. Smyrl and C. W. Tobias, *ibid.*, 115, 33 (1968).
(3) M. Salomon, *J. Phys. Chem.*, 73, 3299 (1969); *J. Electrochem. Soc.*, 116, 1392 (1969).
(4) R. P. Held and C. M. Criss, *J. Phys. Chem.*, 69, 2611 (1965).
(5) E. Luksha and C. M. Criss, *ibid.*, 70, 1496 (1966).
(6) R. P. Held and C. M. Criss, *ibid.*, 71, 2487 (1967).
(7) L. Weeda and G. Somsen, *Rec. Trav. Chim. Pays-Bas.*, 86, 893 (1967).

(8) J. C. Synnott and J. N. Butler, *Anal. Chem.*, 41, 1890 (1969).
(9) J. N. Butler, *Advan. Electrochem. Electrochem. Eng.*, 7, 77 (1970).

then transferred to a Pyrex flask and cooled under vacuum in the antechamber of the drybox and flushed with argon, to minimize absorption of water from air. They were used in drying solvent as soon as they were cooled.

The solvents, and the solutions prepared using them, were analyzed by gas chromatography (Barber-Coleman, Model 5340, Poropak Q column, helium carrier gas, thermal conductivity detection) for water. DMF as received contained approximately 240 ppm $(1.3 \times 10^{-2} M)$ water, and the sieve-dried DMF contained less than 40 ppm $(2 \times 10^{-3} M)$ water. Since DMF can be hydrolyzed at higher temperatures (e.g., in the injector port of a chromatograph), chromatography was found not to be a reliable means of establishing the organic impurity content in the solvent. The manufacturer's specifications for the solvent indicate a uv cutoff at 270 mμ with absorbance of 1.0, which we have verified, and a maximum evaporation residue of 5 ppm. Fluorescence, as quinine base, is given as 0.5 ppb.

In a typical run, cells of two compartments in an H configuration, separated by a frit and equipped with platinum leads, were placed in an aluminum block whose temperature was maintained within $\pm 0.1°$ by use of a Haake circulator. In one compartment, the lithium amalgam was placed, while, in the other, thallium amalgam was placed with thallous chloride (Fisher Scientific Co., purified) sprinkled over it. The lithium chloride solutions were introduced from the lithium amalgam side of the cell to minimize transfer of thallium ion to the lithium amalgam electrode. Measurements of potential were made using a Fluke high-impedance (Model 821A) voltmeter. Potentials were measured to 0.1 mV in all cases, and to greater precision where stability permitted.

Preparation of solutions and all measurements were carried out in a dry argon atmosphere, using a Vacuum Atmospheres Corp. drybox. The argon used contained <1 ppm O_2, <1 ppm N_2, and the gas was continuously circulated through a purification train to remove O_2, N_3, H_2O, and organic vapors.

Results

Approximately 400 measurements of the potential of the cell

$$Tl(Hg)_iTlCl(s)_iLi^+,Cl^-,DMF_iLi(Hg)$$
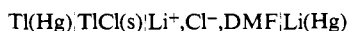
were made as a function of time, temperature, and concentration.[10] If the electrodes are perfectly reversible and LiCl is a completely dissociated electrolyte, the potential E should be given by the Nernst equation

$$E = E_1° + \frac{2RT}{F} \ln (m\gamma_\pm) \tag{1}$$

where $E_1°$ is the standard potential of the above cell, R is the gas constant, T is the absolute temperature, F is the Faraday constant, m is the concentration (mol/kg of solvent) of LiCl in DMF, and $\gamma_\pm$ is the mean molal activity coefficient. The potential of the cell as written is negative in accordance with the IUPAC convention. The activity coefficient is expected to be given approximately by the Debye-Hückel theory

$$\ln \gamma_\pm = \frac{-A\sqrt{m}}{1 + Ba\sqrt{m}} \tag{2}$$

where $A = (4.203 \times 10^6)(\epsilon T)^{-1/2}$, $B = 50.3(\epsilon T)^{-1/2}$, and a is an adjustable parameter which corresponds roughly to the average size of a solvated ion. Using $\epsilon = 37.4$ for the dielectric constant of DMF,[11] one calculates at 25°, $A = 3.572$, $B = 0.476$. For our pre-

(10) Tables of original data, and some details of the calculations, including computer programs, have been deposited as Document No. NAPS-00888 with the ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 3rd Ave., New York, N. Y. 10022. See also J. N. Butler, et al., Final Report on Contract No. AF 19(628)-6131 (Sept 1969). Report No. AFCRL-69-0470.

(11) R. Payne, private communication (data at 25°, 1 MHz). Compare with G. R. Leader and J. F. Gormley, J. Amer. Chem. Soc., 73, 5731 (1951), who give $\epsilon = 36.71$, at 25° and 10 MHz.
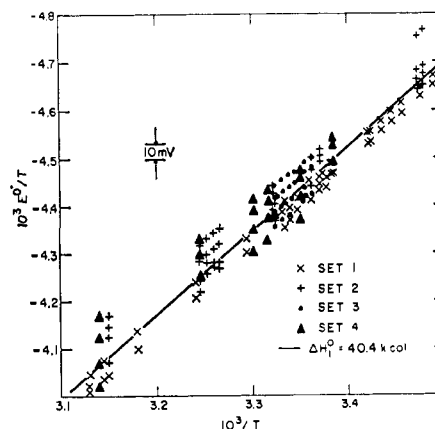

Figure 1. Temperature dependence of cell potential. The raw data have been approximately corrected for the concentration dependence using the Debye-Hückel equation (2) with $a = 3$, but no extrapolations to zero concentration or zero time have been made.

liminary calculations we chose a to be 3 Å, by analogy with water and DMSO.

As a first approximation to $E_1°$, we calculated

$$E°' = E - \frac{2RT}{F} \ln (m\gamma_\pm) \tag{3}$$

(where $\gamma_\pm$ is given by eq 2) and examined its dependence on temperature. Figure 1 shows a representative display of data obtained in the four series of experiments. Sets 1-3 were obtained using DMF containing approximately 0.013 m water, and set 4 was obtained using dried solvent containing <0.002 m water. Although there is considerable spread in the data because of the dependence of $E°'$ on time and concentration, there is no significant difference between the results obtained in the two different samples of solvent. This lack of dependence on water concentration will be shown more accurately later. The thermodynamic functions of the cell reaction

$$Li^+ + Cl^- + Tl(Hg) \longrightarrow Li(Hg) + TlCl(s)$$
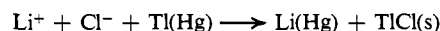
were calculated from the values of $E_1°$ by the usual relations.

The line drawn in Figure 1 was fitted by the method of least squares and corresponds to $\Delta H_1° = 40.4$ kcal/mol. Values of $\Delta G_1°$ and $\Delta S_1°$ were also calculated from these same data, and the results are listed in Table I. Separate statistical treatments were given to set 4 (dry) and the combination of sets 1, 2, and 3 (wet). Note that these agree well within the confidence limits. Treatment of all data together gave the same results as the combination of sets 1, 2, and 3.

The bulk of the data was obtained in a region close to 25°, and those values from experiments at 25 $\pm$ 3° were corrected to 25.00° using the experimentally determined temperature coefficient corresponding to the line in Figure 1. For these data the time and concentration dependence was examined more closely. Figure 2 shows typical curves of the time dependence (on a logarithmic scale) from 1 to 400 hr. Within the first hour, as equilibrium was approached, erratic changes in potential were often observed. From 1 to 20 hr, the potential was steady within 1 mV, but in every case drifted toward more positive values (discharge of cell). Observations at much longer times

Table I. Thermodynamic Parameters for the Cell Reaction[a] $Li^+ + Cl^- + Tl(Hg) \rightarrow Li(Hg) + TlCl(s)$

Method	Set[b]	$E_1°$, V	$\Delta G_1°$, kcal/mol	$\Delta H_1°$, kcal/mol	$\Delta S_1°$, cal/(deg mol)
Least squares[c]	1,2,3	-1.324 ± 0.005	30.53 ± 0.12	40.4 ± 1.1	33 ± 4
	4	-1.325 ± 0.014	30.56 ± 0.32	37 ± 4	22 ± 12
Extrapolation[d]	1,2,3	-1.326 ± 0.002	30.58 ± 0.05		
	4	-1.330 ± 0.005	30.67 ± 0.12		
Guggenheim[e]	1,2,3,4	-1.331 ± 0.0005	30.69 ± 0.01		33 ± 4[f]

[a] Li(Hg) concentration 1.06 mol %, Tl(Hg) concentration 1.01 mol %, Li^+ and Cl^- at unit activity in DMF.   [b] For sets 1, 2, and 3 the solvent contained 0.013 m H_2O. For set 4 the solvent contained <0.002 m H_2O.   [c] Treatment of $E°'$ values as an approximation to $E_1°$. Errors are statistical 95% confidence limits.   [d] $E°'$ values obtained in the range $25 \pm 2°$ corrected to $25.00°$ and extrapolated to zero concentration and zero time. Errors are estimated 95% confidence limits based both on linear and curvilinear extrapolations.   [e] The 25° data for $m > 0.1$ were extrapolated using the Guggenheim equation with $\beta = +0.07$ (see Table II) and the errors are statistical 95% confidence limits.   [f] Calculated using $\Delta S° = (\Delta H° - \Delta G°)/T$ with $\Delta H° = 40.4 \pm 1.1$.

showed a continuous drift in the same direction. If this drift were the result of a slow establishment of solubility equilibrium, it would be expected that the plot of E vs. log t would approach an asymptotic constant value at long times; but this is clearly not the case in Figure 2.
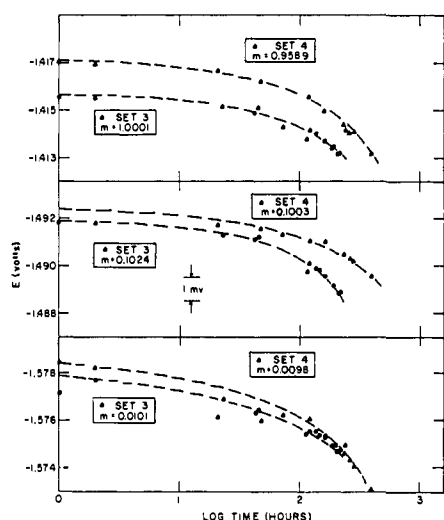

Figure 2. Time dependence of cell potential. Data obtained near 25° have been corrected to 25.00° using the temperature coefficient indicated by the line on Figure 1.

There are two simple explanations for the continuous discharge of the cell. The first is that the lithium amalgam is reacting with the solvent, water in the solvent, or an organic impurity in the solvent. This is refuted by the data displayed in Figure 2, for the following reasons. (1) If the lithium amalgam were reacting with water in the solvent, one would expect a substantially slower drift of potential for the data of set 4 (<0.002 m H_2O) than for those of set 3 (0.013 m H_2O). The shape of the curves for these two sets is approximately the same over a 100-fold range of concentration. (2) If the lithium amalgam were reacting with the solvent, or an organic impurity in the solvent, this reaction would proceed at the same rate (or perhaps even faster, because of the more negative potential) in dilute LiCl solutions as in concentrated LiCl solutions. The percentage change in Li^+ concentration near the electrode surface could thus be as much as 100 times greater in the 0.01 m solution as in the 1 m solution, and one would expect to see considerably larger changes in potential with time in the dilute solution. Figure 2

shows clearly that the time dependence of potential is essentially independent of concentration.

The second explanation, that thallium-containing species are diffusing from the Tl(Hg)|TlCl electrode to the Li(Hg) electrode, is supported by the data in Figure 2 in several respects. (1) The time scale for appreciable diffusion over distances of the order of 1 cm is approximately 10^5 sec or 30 hr, approximately the time required for appreciable deviations in potential to become apparent. This implies that diffusion is occurring over the entire length of the cell, not merely over a short distance near the electrode. (2) The shape of the curves in Figure 2 is virtually independent of the LiCl concentration and water content. This observation implies that the diffusing species is $TlCl_2^-$, rather than Tl^+ or $TlCl$. The equilibrium concentration of $TlCl_2^-$ in saturated $TlCl$ solutions is directly proportional to the chloride concentration, whereas $[TlCl]$ is independent of chloride concentration and $[Tl^+]$ is inversely proportional to chloride concentration. Furthermore, in the concentration range from 0.01 to 1.0 m, $TlCl_2^-$ is the predominant species in solution.[8,9] The relatively small effect of water content indicates that K_{s2} is little affected by this parameter.

At each concentration for which sufficient time dependence data existed, we extrapolated to zero time using a curve of roughly the shape shown for the four data sets in Figure 2. Extrapolated values of potential at 25° and zero time are given in Table II. However, there were systematic deviations from eq 1 and 2 which were outside the estimated errors of interpolation and extrapolation. For example, $E°'$ was not independent of concentration, as might be expected, and extrapolation to zero concentration was unsatisfactory because of the systematic curvature of the plot (Figure 3). Depending on the concentration range considered to be most reliable, values anywhere from -1.32 to -1.34 could be obtained. (These may be compared with the average $E°'$ of 1.326 ± 0.0020.)

An alternative method of extrapolation is to use the Guggenheim form

$$\ln \gamma_\pm = \frac{-A\sqrt{m}}{1 + \sqrt{m}} + 2\beta m \tag{4}$$

which has been used successfully to describe the activity coefficients of LiCl and LiBr in dimethyl sulfoxide[2,3] and in propylene carbonate.[3] In the fourth column of Table II are listed the values of

$$E°'' = E - \frac{2RT}{F}\left(\ln m - \frac{A\sqrt{m}}{1 + \sqrt{m}}\right) \tag{5}$$

Table II. Condensed Experimental Data and Activity Coefficients at 25°

Set[a]	m	E[b]	E°'[c]	E°''[d]	Log γ±[e]	Log γ±[f]	β[f]	a[f]	Log γ±[g]
4	0.00100	−1.6703	−1.3098	−1.3097	0.090	0.132			−0.047
1	0.00102	−1.6790	−1.3195	−1.3194	0.007	0.050			−0.047
3	0.00102	−1.6832	−1.3237	−1.3236	−0.027	0.014			−0.047
1	0.00203	−1.6462	−1.3199	−1.3197	−0.013	0.028			−0.066
2	0.00203	−1.6535	−1.3272	−1.3270	−0.075	−0.033			−0.066
1	0.00502	−1.6048	−1.3210	−1.3206	−0.057	−0.014			−0.102
4	0.00980	−1.5784	−1.3248	−1.3242	−0.124	−0.082			−0.139
3	0.01005	−1.5779	−1.3254	−1.3248	−0.131	−0.089			−0.140
1	0.01005	−1.5775	−1.3250	−1.3244	−0.127	−0.085			−0.140
2	0.0512	−1.5161	−1.3320	−1.3295	−0.316	−0.273	0.281?	2.62?	−0.283
4	0.1003	−1.4924	−1.3342	−1.3301	−0.407	−0.365	0.088	2.28	−0.367
3	0.1024	−1.4920	−1.3346	−1.3304	−0.413	−0.371	0.056	2.22	−0.369
2	0.5047	−1.4392	−1.3393	−1.3278	−0.659	−0.617	0.061	2.32	−0.614
4	0.9589	−1.4171	−1.3400	−1.3241	−0.751	−0.709	0.070	2.45	−0.710
3	1.0001	−1.4156	−1.3400	−1.3238	−0.757	−0.715	0.070	2.46	−0.716
2	1.9997	−1.3890	−1.3386	−1.3171	−0.833	−0.791	0.068	2.63	−0.790
							Av 0.069	Av 2.39	

[a] Solvent as received (0.013 m H_2O) for sets 1, 2, 3; dried (< 0.002 m H_2O) for series 4. [b] Data obtained in range 25 ± 3° corrected to 25.00° and extrapolated to zero time (Figure 2). [c] Based on Debye–Hückel equation with $a = 3$. [d] Based on Guggenheim equation. [e] Calculated directly from E and m assuming $E_1° = -1.326$. [f] Calculated directly from E and m assuming $E_1° = -1.331$. [g] "Best values." Calculated from the Guggenheim equation with $\beta = +0.068$.

which should be a linear function of m with slope $4RT\beta/F$ if the Guggenheim equation is obeyed precisely. These values are plotted in Figure 3. Note that for $m > 0.1$, the plot is almost perfectly linear, and can easily be extrapolated to $m = 0$.

The steep systematic deviations to less negative potentials at low concentrations are consistent with the establishment of a diffusion potential between the compartments of the cell because of the presence of dissolved thallium species.[12] Quantitative correction for these deviations cannot be made without knowledge of transport numbers for the various species involved, but qualitatively, we expect this effect to be least at relatively high concentrations because the dissolved thallium species $TlCl_2^-$ is of the same charge type as the chloride ions it replaces. Thus an extrapolation of the data for $m > 0.1$ to $m = 0$ may be justifiable under the circumstances. A least-squares straight line fit to these values of $E°''$ gives an intercept $E° = -1.3310 \pm 0.0005$ V (errors are 95% confidence limits), and a slope corresponding to $\beta = +0.068 \pm 0.004$.

Values of activity coefficient for LiCl in DMF can be calculated directly from each experimental point once a value of $E°$ is known

$$\ln \gamma_\pm = (E - E°)\left(\frac{F}{2RT}\right) - \ln m \qquad (6)$$

and two columns of Table II give alternative sets of $\gamma_\pm$ values, the first obtained using $E_1° = -1.326$, and the second obtained using $E_1° = -1.3310$. From each experimental point, one can also calculate a value of a from the Debye–Hückel equation (2) or a value of β from the Guggenheim equation (9). These are large and positive at low concentrations, because of the systematic deviations noted in Figure 3, but at high concentrations yield relatively consistent values. As expected, β obtained by this method agrees with that obtained above from the plot of Figure 3. The average value of the Debye–Hückel ion-size parameter a is approximately 2.4 Å, which is considerably smaller than the values giving the best fit in aqueous solutions

(12) W. H. Smyrl and C. W. Tobias, *Electrochim. Acta*, **13**, 1581 (1968).

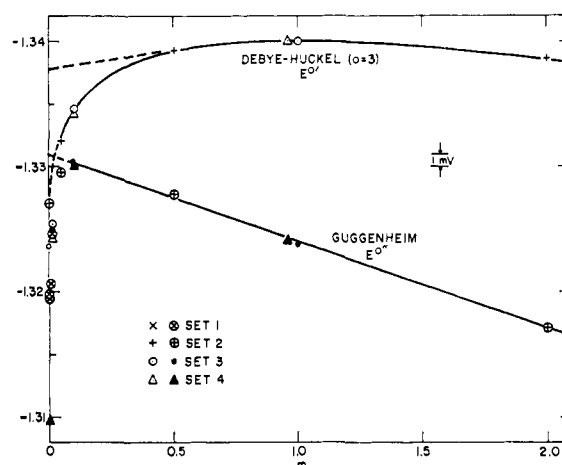(4–5 Å).[13] The significance of these values will be discussed in the next section.

Figure 3. Alternative extrapolations to zero concentration using the Debye–Hückel (eq 2) and Guggenheim (eq 4) forms.

The last column of Table II lists our "best values" of activity coefficients, which are calculated from the Guggenheim equation with $\beta = +0.068$. These are in agreement with the experimental data for $m > 0.1$ and are probably a better estimate of the true activity coefficients for $m < 0.1$ than are the experimental values.

Discussion

Ion Pairing. Studies by Prue and Sherrington[14] of the conductance in LiCl in DMF have shown deviations from the Fuoss–Onsager equation which were consistent with incomplete dissociation of the salt. The association constant K_1 is defined by

$$[LiCl] = K_1[Li^+][Cl^-](\gamma')^2 \qquad (7)$$

(13) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworth and Co., London, 1959, p 246.
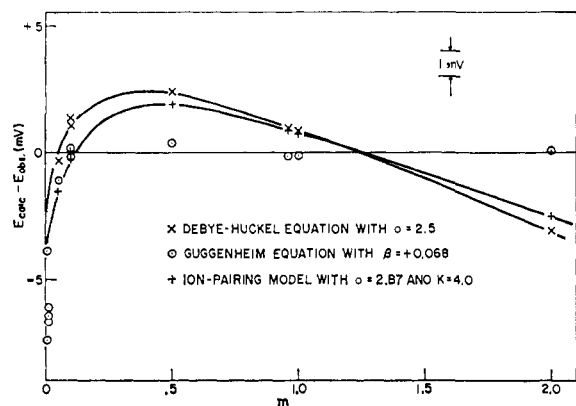(14) J. E. Prue and P. J. Sherrington, *Trans. Faraday Soc.*, **57**, 1795 (1961).

Figure 4. Deviation of calculated from observed potential values corresponding to three mathematical models: Debye–Hückel (eq 2), Guggenheim (eq 4), and ion pairing (eq 8). In each case the parameters were adjusted to give the best fit (minimum U in eq 9) to the data for $m > 0.1$. Only the Guggenheim equation fits within experimental error.

where brackets represent molal concentrations, γ' is the mean activity coefficient of the free Li^+ and Cl^- ions, and the activity coefficient of the neutral species is assumed to be unity. Prue and Sherrington[14] found that K_1 was approximately 35, and was relatively independent of the ion size parameter used to calculate the activity coefficient of the free ions. Held and Criss,[6] on the basis of a strong concentration dependence at low concentrations of the enthalpy of solution of LiCl in DMF, suggested that ion pairing was even stronger, and calculated $K_1 = 2 \times 10^3$, with a heat of dissociation of 6 kcal/mol. However, the enthalpy of solution was approximately constant for concentrations greater than 10^{-3} m, and this has been independently verified.[7] Thus there is some inconsistency in these data, and it is of interest to inquire whether our activity coefficient data can give some independent information regarding the extent of ion pairing.

The relatively small value of a (2.4 Å, Table II) which we obtained from the Debye–Hückel equation might be construed as an indication of moderate ion pairing in LiCl–DMF solutions. The value of β obtained from the Guggenheim equation points in this direction also. Our value of $+0.068$ is less positive than for aprotic solvent systems where there is known to be little association between ions ($\beta = +0.325 \pm 0.040$ for LiCl–DMSO[2] and $+0.485$ for LiBr–DMSO[3]), but is more positive than in systems where there is some ion association ($\beta = -0.28$ for LiBr–PC[3] and -8.89 for LiCl–PC[3]).

For our ion-pairing calculations, the potential of the cell was assumed to be controlled only by the activities of the free ions (not the ion pair) and thus

$$E = E_1° + \frac{RT}{F} \ln([Li^+][Cl^-]) + \frac{2RT}{F} \ln \gamma' \quad (8)$$

The activity coefficient γ' was calculated from an equation similar to eq 2, with m replaced by $[Li^+]$, which is equal to the ionic strength if there is ion pairing.

Both the ion-size parameter a in eq 2 and the equilibrium constant K_1 in eq 7 were adjusted to give the best fit using a nonlinear least-squares method.[15] The function

(15) N. Ingri and L. G. Sillén, Acta Chem. Scand., 16, 159 (1962).

$$U = \sum(E_{calcd} - E_{obsd})^2 \quad (9)$$

was adjusted to be a minimum, and the confidence limits of the parameters a and K_1 were calculated from the shape of the pit. Details are given elsewhere.[10] The data set on which these calculations were performed was the six experimental points in Table II for $m > 0.1$, with $E°$ taken to be -1.331 V. There was a definite minimum to the valley at $K_1 = 4.0 \pm 0.4$ and $a = 2.88 \pm 0.05$.

Note that although the "best" equilibrium constant is much smaller than the K_1 values obtained from conductance[14] or from enthalpy of solution,[6] the ion-size parameter for the free ions is also smaller than expected and tends to compensate for the low K_1. From the conductance data,[14] one would predict a between 3 and 5 Å. From transference numbers,[16] the size of a solvated Li^+ ion is found to be 4.66 Å, and the Cl^- ion is found to be 1.95 Å, implying $a = 3.3$.

We found, as expected, that a and K_1 were closely interdependent, and a map of U showed a long diagonal valley where, for example, $K_1 = 10$ and $a = 3.95$ gave almost as good a fit as did $K_1 = 3$ and $a = 2.76$. We also compared our best fit to the ion-pairing model with the mathematically much simpler expressions of eq 2 and 4. It is clear from Figure 4 that the Guggenheim equation gives by far the best fit to our data. In quantitative terms, the minimum value of the deviation function (for $E° = 1.331$, using the six points with $m > 0.1$) was found to be $U_{min} = 2.5 \times 10^{-7}$ for the Guggenheim equation ($\beta = 0.068$); this is 100 times smaller than U_{min} (2.0×10^{-5}) for the Debye–Hückel equation ($a = 2.50$) and $U_{min} = 1.15 \times 10^{-5}$ for the ion-pairing model ($K_1 = 4.0$, $a = 2.88$). Note particularly that the two-parameter ion-pairing model gives a fit not much better than the one-parameter Debye–Hückel equation.[17]

Standard Potentials and Thermodynamic Functions. Because the standard potentials given in Table I are for particular concentrations of lithium and thallium amalgams, they cannot be easily compared with data obtained by other methods or in other solvents. For this purpose, it is necessary to correct for the free energies of amalgamation. The standard potential $E_2°$ of the cell

$$Tl(s)|TlCl(s)|Li^+,Cl^-,DMF|Li(s)$$
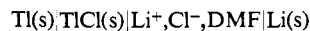
is obtained from Table I by means of the relation

$$E_2° = E_1° + E_{Tl} + E_{Li} \quad (10)$$

where the last two terms are the potentials of the cells

$$Tl(s)|Tl^+|Tl(Hg)$$

$$Li(Hg)|Li^+|Li(s)$$
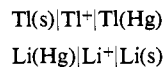
For the concentrations of amalgams used in our experiments, E_{Tl} is -0.1477 V[2,18] and E_{Li} is -0.9515 V[19]

(16) R. C. Paul, J. P. Singla, and S. P. Narula, J. Phys. Chem., 73, 741 (1969).

(17) Note that for the ion-pairing model the values of K_1 and a also depend on the standard potential $E_1°$. The best fit with $E_1° = -1.326$, using a larger set of data points with $m > 0.01$, gave $K_1 = 12.5$ and $a = 3.5$, which are in better agreement with the conductance data.[14] The value of U_{min}, calculated using these parameters with the same data set as used in all our other calculations, was 2.77×10^{-5}. Thus, the fit was not nearly as good as the one obtained above.

(18) T. W. Richards and F. Daniels, J. Amer. Chem. Soc., 41, 1732 (1919); G. N. Lewis and M. Randall, ibid., 43, 233 (1921).

(19) D. R. Cogley and J. N. Butler, J. Phys. Chem., 72, 1017 (1968).

at 25°. The values of $E_2°$ corresponding to two estimates of the standard potential of our experimental cell are given in Table III. The difference in standard potentials $E_3°$ between the lithium and thallium electrodes is also listed in Table III. This is given in terms

Table III. Standard Potentials and Thermodynamic Parameters at 298 °K[a]

$E_1°$ = -1.3310 ± 0.0005 V[b]	$\Delta G_t°$ = $+1.23 \pm 0.01$ kcal/mol
$E_2°$ = -2.4302 ± 0.0006 V	$\Delta H_t°$ = -1.8 ± 1.1 kcal/mol
$\Delta G_2°$ = $+56.04 \pm 0.01$ kcal/mol	$\Delta H_t°$ = -2.97 ± 0.08 kcal/mol[e]
$\Delta H_2°$ = $+59.5 \pm 1.1$ kcal/mol[c]	$\Delta S_t°$ = -11 ± 4 cal/(mol deg)[f]
$\Delta S_2°$ = 12 ± 4 cal/(mol deg)	$\Delta S_t°$ = -14.1 ± 0.3 cal/(mol deg)[g]
$-\text{Log } K_{so}$ = 9.0 ± 0.2[d]	$\Delta G_t°(Cl^-)$ = $+12.3$ kcal/mol[h]
$E_3°$ = -2.96 ± 0.01 V	$\Delta G_t°(Li^+)$ = -11.0 kcal/mol

[a] Standard potentials defined as follows: $E_1°$, Tl(Hg)|TlCl(s) Li$^+$Cl$^-$ (solvent)|Li(Hg); $E_2°$, Tl(s)|TlCl(s)|Li$^+$Cl$^-$ (solvent)|Li(s); $E_3°$, Tl(s)|Tl$^+$ (solvent)||Li$^+$ (solvent)|Li(s); cell reaction 2, Li$^+$ + Cl$^-$ + Tl(s) → Li(s) + TlCl(s). Subscript t refers to transfer of LiCl from H$_2$O to DMF. [b] Best estimate of $E°$, using Guggenheim eq 4 with data for $m > 0.1$. [c] Calculated from data in Table I using $+0.7$ kcal[18] for the heat of amalgamation of Tl and -19.81 ± 0.04 for the heat of amalgamation of Li.[19] [d] Reference 8. [e] Enthalpy of solution, -11.82 ± 0.06 (ref 7). [f] Corresponding to $\Delta H_t°$ = -1.8. [g] Corresponding to $\Delta H_t°$ = -2.97. [h] A. J. Parker, *Chem. Rev.*, **69**, 1 (1969).

of measurable quantities by

$$E_3° = E_2° + \frac{RT}{F} \ln K_{so} \qquad (11)$$

where K_{so} is the solubility product of TlCl.

The thermodynamic functions of the cell reaction

$$Li^+ + Cl^- + Tl(s) \longrightarrow Li(s) + TlCl(s)$$
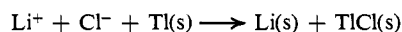
are also given in Table III. $\Delta G_2°$ corresponds to $E_2°$ which we calculated from $E_1°$ obtained using the Guggenheim equation. The enthalpy $\Delta H_1°$ listed in Table I was corrected for the heat of amalgamation of Tl[18] and the heat of amalgamation of Li.[19]

Free energies, enthalpies, and entropies of the process

$$LiCl(H_2O) \longrightarrow LiCl(DMF)$$
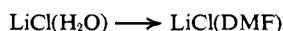
are given in Table III. These quantities can also be obtained from differences in free energies and enthalpies of solution and solvation as well as from the standard potentials of other nonaqueous cells.

The enthalpy of transfer for LiCl from water to DMF obtained from Weeda and Somsen's calorimetric data[7] is in good agreement with the value obtained from the temperature coefficient of our cell. There is substantial disagreement with Held and Criss's extrapolation[6] of their heats of solution at low concentration (which give $\Delta H_t°$ = -5.6 kcal/mol) but good agreement with their high-concentration values, which are the same as those of Weeda and Somsen.[7]

Criss and Luksha[20] measured the solubilities of a number of alkali halides (but not LiCl) and calculated free energies of solution, which were then used to eval-

uate individual ionic free energies. The combination of their values for Li$^+$ and Cl$^-$ in DMF gives a total free energy of solvation for LiCl of -193.5 kcal/mol. Combining this with Izmailov's[21] free energy of solvation (-191.5 kcal/mol) for LiCl in H$_2$O, one obtains $\Delta G_t°$ = 2.0, which is in amazingly good agreement with our direct measurement. (Other calculations of the free energy of solvation for Li$^+$ and Cl$^-$ lead to free energies of transfer varying from $+1.5$ to $+4.5$ kcal/mol, which gives a more realistic estimate of the error in this calculation.)

Since the solubility of LiCl in DMF is known[22] to be 2.60 mol/kg solvent, it should be possible to obtain a value for the free energy of solution of LiCl in DMF by extrapolating our activity coefficient data to 2.60 m. Using the Guggenheim equation with β = 0.068, we obtain $\gamma_{\pm}$ = 0.157 at saturation. The standard free energy of solution is then

$$\Delta G_{soln}° = -2RT \ln (m \gamma)_{sat} = +1.06 \pm 0.02 \text{ kcal/mol}$$

which leads to a free energy of transfer of $+10.82 \pm 0.07$ kcal/mol, completely outside the limits of error of our estimate from $E_2°$ ($+1.23 \pm 0.01$). This discrepancy can probably be attributed to solvate formation: the solid phase in equilibrium with the saturation solution is not LiCl but a solvate of LiCl with DMF. The difference (-9.6 kcal/mol) represents the free energy of formation of the (stable) solvate. To agree with our free energy of transfer value, the free energy of solution would have to be approximately -8.6 kcal/mol, which corresponds to a saturation limit of 48 m.

Our measured free energy of transfer for LiCl from water to DMF can be combined with quasi-thermodynamic data to obtain free energies of transfer for single ions ("solvent activity coefficients"). The value for $G_t°$ of Cl$^-$ listed in Table III was estimated by Parker,[23] and the corresponding value for Li$^+$ obtained by difference from the value for LiCl, assuming complete dissociation. The free energy of transfer (-11.0 kcal/mol) for Li$^+$ thus obtained is much more negative than for DMSO (-6.0) or PC ($+0.9$), much more negative than for other cations (Ag$^+$, -5.8; K$^+$, -3.0) in DMF, and indicates bonding which may make Li$^+$ in DMF one of the most strongly solvated cations known.

(21) N. A. Izmailov, *Dokl. Akad. Nauk SSSR*, **149**, 884 (1963); *Zh. Fiz. Khim.*, **34**, 2414 (1960); *Russ. J. Phys. Chem.*, **34**, 1142 (1960).
(22) R. S. Kittila, "DMF–Chemical Uses," E. I. du Pont de Nemours and Co., Wilmington, Del., 1967, p 226.
(23) See Table III, footnote h.

(20) C. M. Criss and E. Luksha, *J. Phys. Chem.*, **72**, 2966 (1968).