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THERMODYNAMIC PROPERTIES OF LiCl IN DIMETHYL SULFOXIDE

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THERMODYNAMIC PROPERTIES OF LiCl IN DIMETHYL SULFOXIDE*

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Lawrence Radiation Laboratory, and
Department of Chemical Engineering
University of California, Berkeley

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ABSTRACT

EMF measurements were performed at 25°, 30° and 35°C on the cell:

$$Pt(s)/Li(s)/LiCl(\text{solution in DMSO})/TlCl(s)/Tl_{(Hg)}(\ell)/Pt(s).$$

For concentrations up to 0.12 molal, the activity coefficients at each temperature may be represented satisfactorily by Guggenheim's extension of the Debye-Hückel equation. The partial molal Gibbs free energy, entropy and enthalpy of transfer of LiCl from DMSO to water have been calculated to be -4.93 Kcal/mole, +25.3 cal/°K-mole and +2.61 Kcal/mole, respectively.

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Because of its high dielectric constant and stability, dimethyl sulfoxide has been of interest as an ionizing solvent for some time (Table 1). Although the chemistry of the solvent has been the subject of numerous investigations, very few thermodynamic data are available for its solutions. The only thermodynamic data which have been reported for electrolytic solutions in DMSO are some solubilities[1,2], some acid-base equilibria[3], cryoscopic data on electrolytes in the solvent[4,5,6], and the heats of solution of several iodides[7]. In addition, Cogley and Butler[8] have reported some qualitative thermodynamic results from measurements on the cell to be described below.

The present work is based on EMF measurements on the cell:

$$Pt(s)/Li(s)/LiCl(\text{solution in DMSO})/TlCl(s)/Tl_{(Hg)}(\ell)/Pt(s). \quad [1]$$

The paucity of information relevant to the behavior of inorganic salts, and of reactive metals in nonaqueous media, as well as the potential usefulness of the solvent in voltaic cells, and in electro-synthesis, justifies this choice. A halide system was chosen because of the low solubility of other salts in the solvent medium for which a reference electrode with a common anion could be found. Previous work in this laboratory established the advantages of the thallium amalgam-thallous chloride reference electrode[9]. The nature of the reference electrode restricted the choice of the anion to chlorides, and the metal cation to one of those rather high in the oxidation potential series. The lithium electrode was in part selected because of the opportunity to obtain direct thermodynamic measurements on a metal-metal ion couple which, along with the other alkali and alkaline earth metals, reacts spontaneously with most other ionizing solvent media. The potential usefulness of a lithium electrode in galvanic cells was also considered.

Table 1.

Selected Physical Properties of DMSO

		Reference
Molecular weight	78.13	
Melting point	18.58°C	*
Boiling point	189.0°C	[10]
Dielectric constant (25°C)	48.05	[10]
Density	1.0956 gm/cm^3	[11]
Entropy of vaporization (189°C)	25.8 cal/mole-°K	
Dipole moment	3.9 Debye	[12]
Debye-Hückel constant (25°C)	2.57 $(kg/mole)^{\frac{1}{2}}$	
(30°C)	2.57 $(kg/mole)^{\frac{1}{2}}$	
(35°C)	2.59 $(kg/mole)^{\frac{1}{2}}$	

* Present work.

Experimental

The vacuum tight pyrex cell constructed for this purpose (figure 1) consisted of five approximately 2 cm diameter tubes arranged in radial positions, each connected to a central tube by 6 mm glass tubing. Reference electrodes and the counter electrodes (Li) were placed in the peripheral compartments, while the central tube served to introduce the solutions.

The solution did not come in contact with stopcocks. In each experiment, two reference electrodes and three lithium electrodes were used. The solvent (Matheson, Coleman and Bell, Spectrographic grade) was purified by distillation under reduced pressure at 80°C. The product was found to contain less than 50 parts per million water by Karl Fischer titration and had a melting point of 18.58°C.

Lithium chloride (Baker and Adamson) was dried by refluxing thionyl

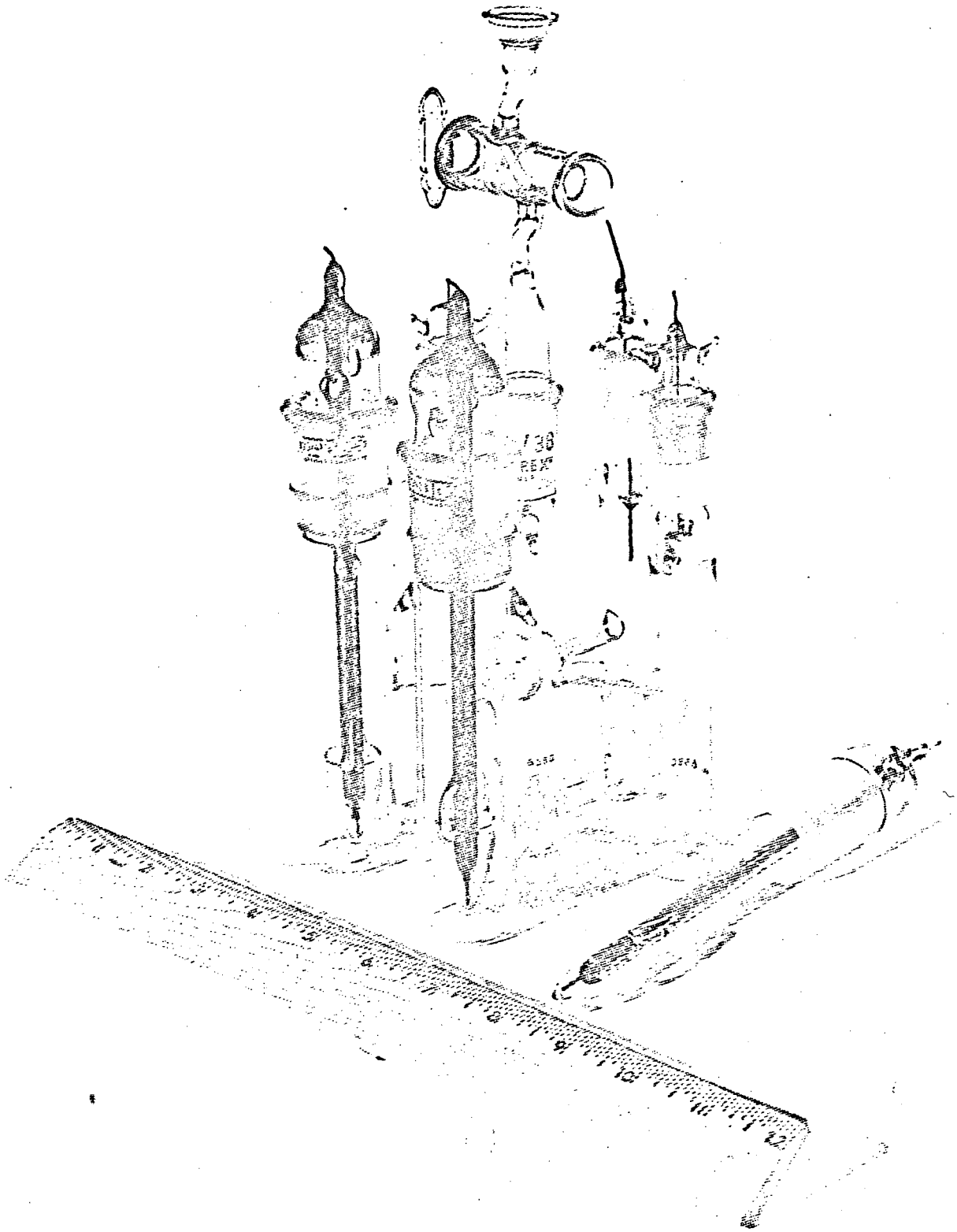

FIGURE 1. Five Compartment Cell Used For EMF Measurements.

chloride over it for two hours. The dried salt was stored in a vacuum dessicator under an atmosphere of dry argon.

The lithium metal (Lithium Corporation of America, 99.9%) was obtained commercially and stored under oil.

Solutions were made either by direct weighing of solute and solvent, or by dilution of more concentrated solutions. The solutions were prepared and stored in a glove box under an atmosphere of dry argon. The lithium electrodes were prepared by etching the surface in an HCl solution in DMSO, carefully rinsing with solvent and then rinsing with a portion of the solution to be used in the cell. The cell was assembled, the solution introduced and the cell was removed from the glove box and suspended in a grounded water bath. Temperature was controlled within ±0.01°C.

On each cell the measuring procedure began fifteen minutes after thermal equilibrium at 25°C had been attained. The measurements were made with a Leeds and Northrup K-3 potentiometer, using carefully calibrated standard cells. The second set of measurements at 25°C was made one hour later and if there was less than 0.1 millivolt difference between the readings, the temperature was raised to 30°C, and 35°C, respectively, where the measurements were repeated. The temperature was then reduced to 25°C and another set of measurements were made. The last measurement at 25°C always agreed within less than 0.1 millivolt with the earlier measurements at 25° if the temperature cycle was shorter than twelve hours. The bias potential between the reference electrodes was always less than 0.05 millivolt, and for the lithium electrodes was less than 0.1 millivolt.

The thallium amalgams used in the present studies were all in the concentration order of 10^{-2} mole fraction thallium. The voltage of the cell [1], was "corrected" to solid thallium metal by using the EMF data on thallium amalgam concentration cells of Richards and Daniels[14]. The relative potentials of the amalgams employed are given in Tables 2, 3, and 4.

In Tables 5, 6, and 7 are given the results of the cell measurements at 25°, 30°, and 35°C, respectively. In the first column is given the molality of LiCl in solution. The measured cell voltage, E, and the amalgam are listed in the second and third columns, respectively. The cell voltage "corrected" to solid thallium, E', is given in the fourth column. E' is related to the standard cell potential and the solution concentration by

$$E' = E^{o} - \frac{2RT}{F} \ln m_{LiCl}\gamma_{LiCl} \qquad [2]$$

where both E^{o} and γ_{LiCl} are unknowns. The usual arbitrary definition is adopted: the activity coefficient of lithium chloride approaches unity as the concentration of lithium chloride approaches zero. The limiting equation proposed by Guggenheim[13] is employed to facilitate extrapolation to infinite dilution, i.e.,

$$\ln \gamma_{LiCl} = - \frac{\alpha z_{+}|z_{-}|I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} + 2\beta_{LiCl}\, m_{LiCl} \,. \qquad [3]$$

Here, α = Debye-Hückel constant,

$$I = \text{ionic strength} = \tfrac{1}{2} \sum_{i} z_i^2 m_i \,,$$

β_{LiCl} = constant, independent of molality.

From [2],

$$E' - \frac{\alpha z_+ |z_-| I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} \left(\frac{2RT}{F}\right) + \frac{2RT}{F} \ln m = E^{o\prime} = E^{o} - \frac{4RT}{F} \beta_{LiCl} m \ , \quad [4]$$

where equation [4] defines $E^{o\prime}$. The function $E^{o\prime}$ is listed in the fifth column of Tables 5, 6, and 7.

By constructing a plot of $E^{o\prime}$ vs m, according to equation [4], one should obtain a straight line. Extrapolating to $m \rightarrow 0$, one can obtain E^{o} and then γ_{LiCl}, for other concentrations at which the cell EMF is measured.

Table 2.

Relative Potentials of Thallium Amalgams at 20°C.

mole fraction Tl[a]	Amalgam	ε[b]
9.67×10^{-3}	1	0
9.32×10^{-3}	3	-0.00107
1.035×10^{-2}	2	+0.00193
9.71×10^{-3}	4	+0.00012
1		+0.14690

Table 3.

Relative Potentials of Thallium Amalgams at 30°C.

mole fraction Tl[a]	Amalgam	ε[b]
9.67×10^{-3}	1	0
9.32×10^{-3}	3	-0.00107
1.035×10^{-2}	2	+0.00199
9.71×10^{-3}	4	+0.00012
1		+0.15091

Table 4.

Relative Potentials of Thallium Amalgams at 40°C.

mole fraction Tl[a]	Amalgam	ε[b]
9.67×10^{-3}	1	0
9.32×10^{-3}	3	-0.00111
1.035×10^{-2}	2	+0.00203
9.71×10^{-3}	4	+0.00012
1		+0.15483

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[a] Calculated using molecular weights based on $C^{12} = 12.000$.

[b] Absolute volts.

Table 5.

Results of Cell Potential Measurements at 25°C.

m(moles/kg)	E(volts)	Amalgam	E'(volts)	$E^{o\prime}$(volts)
0.87877	2.47341	1	2.32451	2.25398
0.30177	2.52252	3	2.37255	2.26417
0.16389	2.54697	4	2.39819	2.26722
0.12450	2.55971	3	2.40974	2.26825*
0.12213	2.56064	3	2.41067	2.26843*
0.08803	2.57327	1	2.42437	2.26930*
0.08775	2.57324	1	2.42434	2.26915*
0.07592	2.57932	4	2.43054	2.26956*
0.05821	2.59230	3	2.44233	2.27055*
0.05821	2.59110	4	2.44232	2.27054*
0.02821	2.62266	4	2.47388	2.27156*
0.01775	2.64319	1	2.49429	2.27164*
0.00988	2.66970	1	2.52080	2.27163
0.00891	2.67465	1	2.52575	2.27182
0.00884	2.67500	1	2.52610	2.27180
0.00768	2.67933	2	2.53236	2.27157
0.00677	2.68436	2	2.53739	2.27072
0.00456	2.70491	1	2.55601	2.27115
0.00383	2.71131	2	2.56434	2.27075
0.00356	2.71687	1	2.56797	2.27099
0.00332	2.71830	2	2.57133	2.27060
0.00275	2.72604	2	2.57907	2.26958
0.00190	2.74340	2	2.59643	2.26900
0.00178	2.74803	1	2.59913	2.26849
0.00089	2.77455	2	2.62758	2.26288
0.00084	2.77662	2	2.62965	2.26208
0.00045	2.79921	2	2.65224	2.25358

* Data used in least squares analysis.

Table 6.

Results of Cell Potential Measurements at 30°C.

m(moles/kg)	E(volts)	Amalgam	E'(volts)	$E^{o'}$(volts)
0.30177	2.52102	3	2.36904	2.25885
0.16389	2.54550	4	2.39471	2.26154*
0.12450	2.55880	3	2.40682	2.26296*
0.12213	2.55951	3	2.40753	2.26291*
0.07592	2.57825	4	2.42746	2.26378*
0.05821	2.59156	3	2.43958	2.26492*
0.05821	2.59039	4	2.43960	2.26494*
0.02821	2.62241	4	2.47162	2.26591*
0.00988	2.67002	2	2.52110	2.26576
0.00768	2.67988	2	2.53096	2.26575
0.00677	2.68496	2	2.53604	2.26488
0.00456	2.70393	2	2.55501	2.26489
0.00383	2.71222	2	2.56330	2.26474
0.00357	2.71765	1	2.56674	2.26478
0.00275	2.72716	2	2.57824	2.26352
0.00190	2.74477	2	2.59585	2.26315
0.00178	2.74936	1	2.59845	2.26226
0.00089	2.77639	2	2.62747	2.25661
0.00084	2.77798	2	2.62906	2.25529
0.00045	2.80111	2	2.65219	2.24679

* Data used in least squares analysis.

Table 7.

Results of Cell Potential Measurements at 35°C.

m(moles/kg)	E(volts)	Amalgam	E'(volts)	E^{o}'(volts)
0.30177	2.51946	3	2.36550	2.25310
0.16389	2.54423	4	2.39148	2.25581*
0.12450	2.55773	3	2.40377	2.25726*
0.12213	2.55842	3	2.40446	2.25717*
0.07592	2.57747	4	2.42472	2.25810*
0.05821	2.59072	3	2.43676	2.25902*
0.05821	2.58964	4	2.43689	2.25915*
0.02821	2.62214	4	2.46939	2.26013*
0.00988	2.67039	1	2.51752	2.25989
0.00768	2.68038	2	2.53032	2.23987
0.00677	2.68587	2	2.53581	2.25950
0.00383	2.71319	2	2.56313	2.25879
0.00357	2.71865	1	2.56578	2.25878
0.00275	2.72829	2	2.57823	2.25747
0.00190	2.74617	2	2.59611	2.25683
0.00178	2.75068	1	2.59781	2.25603
0.00089	2.77775	2	2.62769	2.24637
0.00084	2.77939	2	2.62933	2.24515
0.00045	2.80276	2	2.65270	2.23982

* Data used in least squares analysis.

$E^{o'}$ is plotted versus molality in figures 2, 3 and 4. The EMF-s of the cells were found to be well behaved for concentrated solutions of lithium chloride. As the concentration is decreased, the function $E^{o'}$ becomes a linear function of molality. The sharp decrease of $E^{o'}$ at concentrations below 2×10^{-2} molal was quite unexpected. This behavior could not be explained by random scatter of data; the decrease persisted at all three temperatures. Several independent sets of solutions, made by both methods, were used and the data was found to be reproducible and not due to errors in solutions concentration. A reaction in the cell could not have caused this behavior because the cell voltage was constant over the period of the temperature cycle. After twelve hours the lithium electrodes became discolored, and the cell potential began to decrease steadily due to the reaction

$$Li(s) + TlCl(soln) \rightarrow Tl(s) + LiCl(soln) \ . \qquad [5]$$

The unexpected decrease of $E^{o'}$ occurred in solutions where the concentration of LiCl was approaching that of TlCl. The solubility product of TlCl in dimethyl sulfoxide is 5×10^{-7}.[8] Since TlCl must be kept away from the lithium electrode, where it will react, a concentration gradient of TlCl exists in the cell. The cell potential will be lower than expected when there is diffusion of the sparingly soluble salt from the reference electrode. At higher concentrations of LiCl, it would be expected that the nonuniform concentration distribution would be of no effect, and the effect should become greater as the solution concentration of LiCl decreases. The departure of the potential from the linear extension of the line obtained by least squares fit of the data at higher concentrations can be, to a good approximation, explained by quantitative consideration of the effect of diffusion of TlCl[15].

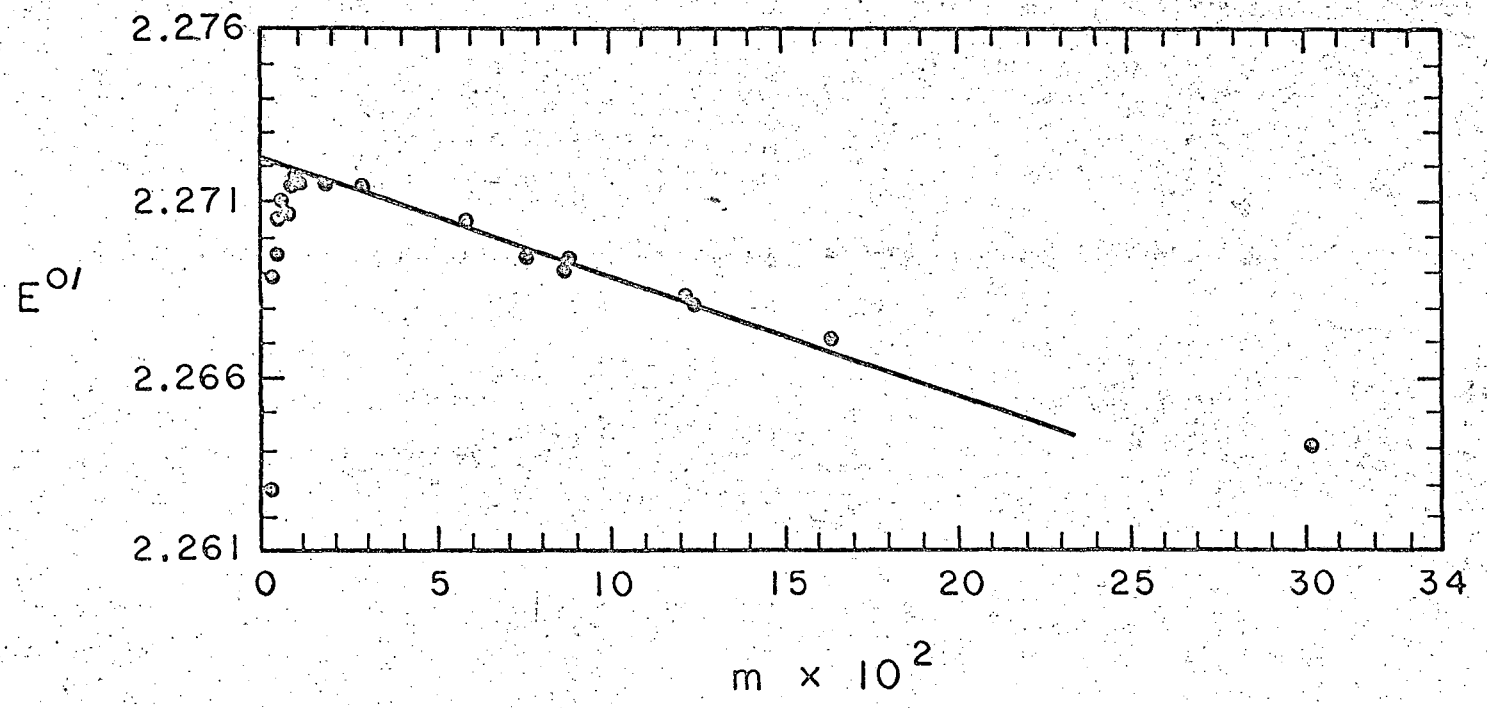

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FIGURE 2. Extrapolation of EMF Data to Infinite Dilution at 25°C.

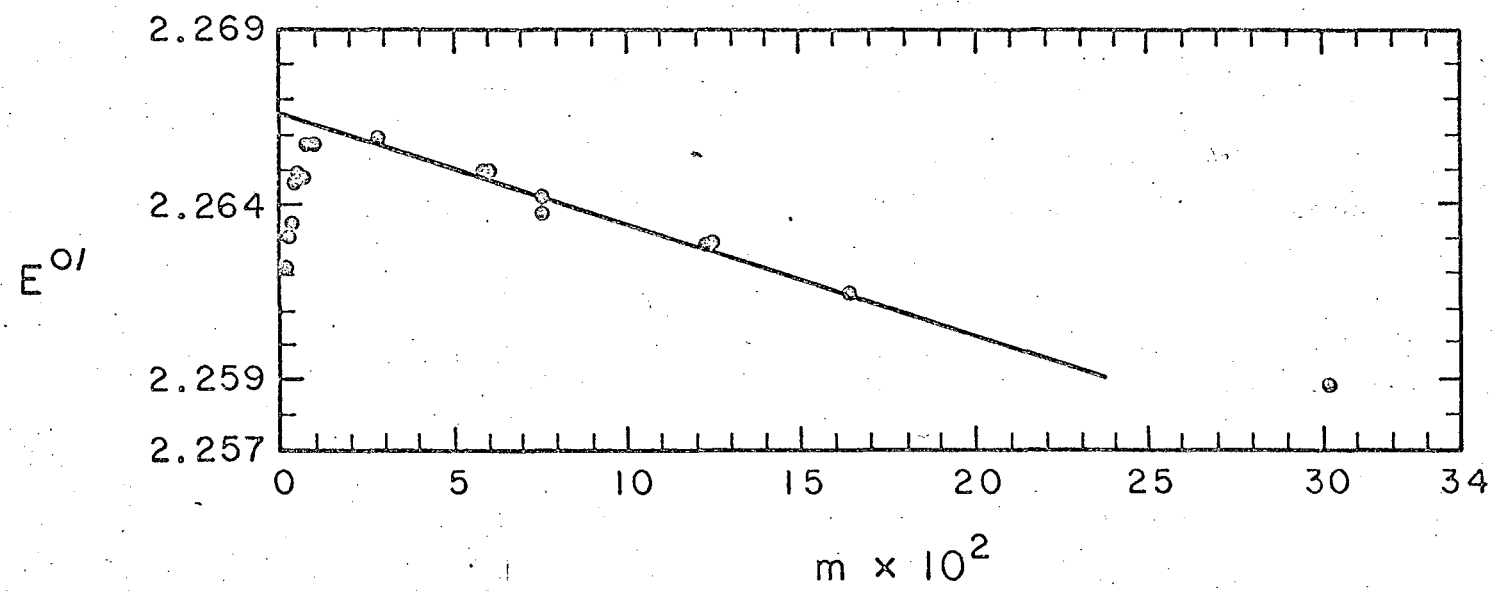

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FIGURE 3. Extrapolation of EMF Data to Infinite Dilution at 30°C.

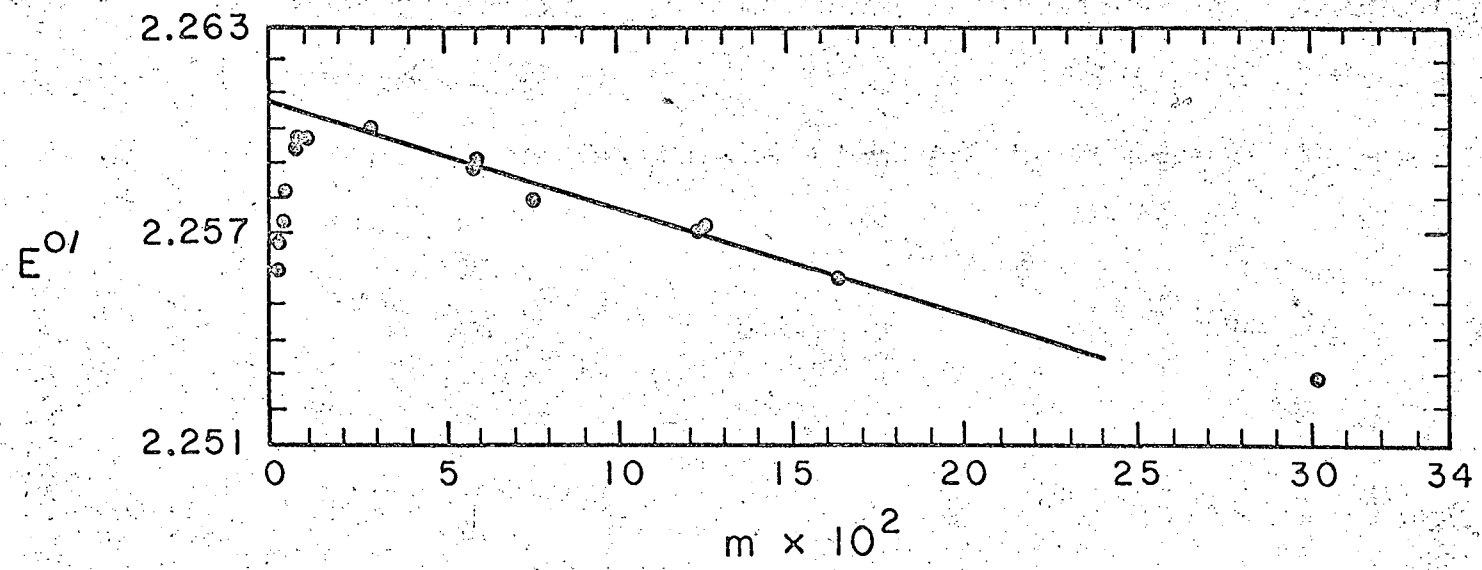

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FIGURE 4. Extrapolation of EMF Data to Infinite Dilution at 35°C.

With the foregoing consideration in mind, the extrapolation to infinite dilution was made by fitting a least squares line to the data in the linear region. The results of the data analysis is summarized in Table 8. From these results were calculated ΔG^o, ΔH^o and ΔS^o for the cell reaction. These thermodynamic functions are given in Table 9.

The same calculations may be carried out for aqueous solutions. The quantity $\Delta\bar{G}^o$ for the transfer at 25°C,

$$\text{LiCl(soln in DMSO},\gamma_\pm=1) + 55.55 \text{ moles } H_2O \rightarrow \text{LiCl(soln in } H_2O,\gamma_\pm=1) + 12.799 \text{ moles DMSO} \qquad [6]$$

is found to be

$$\Delta\bar{G}^o = -4.93 \text{ kcal/mole} .$$

The entropy of transfer at this temperature is calculated to be +25.3 cal/°K-mole, after correcting for the difference in partial molal volume of the two solvents.

Activity coefficients were determined as a function of concentration at the measured temperatures. Activity coefficients obtained from the smoothed data are given in Table 10 at rounded concentrations.

Table 8.

Standard Cell Potentials at 25°, 30° and 35°C.

T(°K)	E^o(volts)	β_{LiCl}(kg/mole)
298.15	2.27234 ± 0.00045	0.325 ± 0.040
303.15	2.26665 ± 0.00072	0.298 ± 0.052
308.15	2.26083 ± 0.00064	0.286 ± 0.045

Table 9.

ΔG^o, ΔS^o and ΔH^o for the Reaction:

$$\text{Li(s)} + \text{TlCl(s)} + 12.799 \text{ moles DMSO} \rightleftarrows \text{LiCl(soln in DMSO}, \gamma_\pm=1) + \text{Tl(s)}$$

T(°K)	ΔG^o(kcal/mole)	ΔS^o(cal/°K-mole)	ΔH^o(kcal/mole)
298.15	-52.402	-26.5	-60.31
303.15	-52.271	-26.5	-60.31
308.15	-52.136	-26.5	-60.31

Table 10.

Activity Coefficients of Lithium Chloride at 25°, 30° and 35°C.

m moles/kg	$-\ln \gamma_{LiCl}$		
	25°	30°	35°
0.005	0.152	0.160	0.165
0.010	0.220	0.230	0.230
0.015	0.270	0.275	0.275
0.020	0.306	0.310	0.310
0.025	0.335	0.339	0.340
0.030	0.360	0.364	0.365
0.035	0.383	0.385	0.392
0.040	0.404	0.405	0.414
0.045	0.422	0.423	0.430
0.050	0.440	0.440	0.447
0.060	0.470	0.470	0.475
0.080	0.511	0.520	0.525
0.100	0.548	0.560	0.565
0.120	0.582	0.592	0.600

The behavior of the activity coefficient of LiCl indicates that it is a completely dissociated salt in very dilute solutions. We arrive at this interpretation from the value of β_{LiCl} which is positive, as in aqueous solutions. In aqueous solutions, a negative value of β is interpreted as an indication of ion-pairing[18]. Although the magnitude of β_{LiCl} in dimethyl sulfoxide is larger than in water, we attach less significance to the magnitude than to the sign. Further interpretation must await further data on other electrolytes in dimethyl sulfoxide.

The activity coefficients from the present study (25°) are consistently higher than those reported by Dunnett and Gasser (18.5°) obtained

from freezing point depression studies[4]. According to our measurements, correction for temperature would increase the discrepancy. Analysis of the results of Dunnett and Gasser according to the method suggested by Brown and Prue[*16], yields a value of $\beta_{LiCl} = -2.11$. The reasons for the disagreement with the present study are not understood. It seems possible that traces of water may have caused anomalous freezing point readings in the dilute solutions, those most important for the determination of β_{LiCl}. Also the value of the cryoscopic constant (4.36) used by Dunnett and Gasser is subject to question. This value reported by Lindberg, Kenttämaa and Nissema[17] is based on cryoscopic measurements on solutions of benzene in dimethyl sulfoxide, but the most dilute solution used was 0.88 molal. If one used the cryoscopic constant of Skerlak, et al[5], i.e., 3.97, for the above analysis, the value of β_{LiCl} becomes positive. The value of 3.97 is also consistent with the data of Lindberg, et al.

According to the present results the free energy and entropy of transfer of LiCl from dimethyl sulfoxide to water are in the direction one would predict from the relative dielectric constant of the two solvents. Calculations of the dielectric constant effect according to the Born equation do not account quantitatively for the free energy and entropy of transfer. Similar conclusions were reached for several other solvents by Strehlow[19]. The heat of transfer of LiCl from DMSO to H_2O is calculated to be +2.61 kcal. This may be compared to the recent measurements of the heats of transfer of several iodides from DMSO to H_2O[7], for which the heats of transfer, as expected, are larger - in the order of +10 kcal.

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* In these calculations we used for the dielectric constant 49.15[10], 18.55°C as the melting point of the solvent[4], 1.1000 g/cm^3 for the density[11], and 4.36[17] for the molal cryoscopic constant.

Acknowledgement

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