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July 1967

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Zusammenfassung - In Konzentrationszellen ohne Ueberführung enthält eine der Elektroden gewöhnlich ein schwer lösliches Salz. Wenn die Löslichkeit dieses Salzes in der Lösung gegenüber der Konzentration des andern anwesenden Elektrolyten nicht mehr vernachlässigt werden kann, so muss der Zutritt des schwer löslichen Salzes zur andern Elektrode verhindert werden. Die in solchen Zellen existierenden Konzentrationsgradienten bewirken Abweichungen von der EMF die unter Gleichgewichtsbedingungen gemessen würde. Ein Näherungsverfahren für die Abschätzung des durch die Diffusion des schwach löslichen Salzes verursachten Fehlers wird vorgeschlagen. Die Notwendigkeit dieser Korrektur wird anhand von EMF Messungen in nichtwässrigen ionisierenden Lösungsmittlen gezeigt, in denen die Löslichkeit der Metallhalogenide i.a. grösser ist als in ihren entsprechenden wässrigen Lösungen.

Resumé - Dans les piles de concentration sans transport une des electrodes utilise généralement un sel peu soluble. Quand la solubilité de ce sel dans la solution n'est plus négligeable devant celle de l'autre electrolyte, il faut empêcher le transfert du sel peu soluble à l'autre electrode. Les gradients de concentration existant dans une telle pile entrainent des changements de F.E.M. par rapport aux mesures effectuées dans des conditions d'équilibre. Une approche est suggérée pour la determination des erreurs introduites par la diffusion du sel peu soluble. La nécessité de cette correction est prouvée dans le cas de mesures de F.E.M. de piles utilisant des solvants ioniques non-aqueux dans lesquels la solubilité des halogénures metalliques est normalement plus grande que celle de leurs equivalents aqueux.

THE EFFECT OF DIFFUSION OF A SPARINGLY SOLUBLE SALT ON THE EMF OF A CELL WITHOUT TRANSFERENCE

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Abstract

In concentration cells without transference, one of the electrodes usually involves a sparingly soluble salt. When the solubility of this salt in the solution between the electrodes is no longer negligible compared to the concentration of the other electrolyte present, access of the sparingly soluble salt to the other electrode must be prevented. The concentration gradients existing in such a cell cause deviations from the EMF measured under equilibrium conditions. An approximate treatment is suggested for the estimation of errors incurred due to diffusion of the sparingly soluble salt. The need for this correction is demonstrated for EMF measurements on cells involving nonaqueous ionizing solvents in which the solubility of metal halides is usually higher than in their aqueous analogues.

The Effect of Diffusion of a Sparingly Soluble Salt on the EMF of a Cell without Transference

For the thermodynamic treatment of cell potential, the reference state generally chosen is one in which the activity coefficient of an electrolyte approaches unity as the concentration of all solute species approaches zero. Thus the measurements in very dilute solutions and the extrapolation of cell potentials to infinite dilutions are of great importance to the determination of thermodynamic properties of solutions of all concentrations. Yet these measurements are those most subject to uncertainties arising from errors in the determination of concentration, and from the effects of spontaneous reactions and irreversible phenomena such as diffusion. It is the purpose of this discussion to outline the method of estimating the effect of diffusion on the cell potential for the special case of a cell in which there is an electrode of the second kind from which diffuses a sparingly soluble salt. It is anticipated that such an analysis will be applicable to any solvent and will be useful in providing criteria by which to select a reference electrode of the second kind for thermodynamic studies.

The discussion will be restricted to cells "without transference," which consist of:

(1) a metal electrode in contact with a solution of a salt of the metal, and;

(2) a metal electrode in contact with a sparingly soluble salt of the metal, which is in turn in contact with the solution, and;

(3) the anion of the sparingly soluble salt and the anion of the

electrolyte in solution are the same.

In concentrated solutions of the major electrolyte, one may saturate the system throughout with the low solubility salt since not only the solubility will be depressed, but also any reaction of this salt at the other electrode will cause a negligible change of solution composition. However, the nonuniform solution composition caused by diffusion must be maintained in dilute solutions. In these solutions, any reaction between the electrode of the first kind and the sparingly soluble salt may cause changes of solution composition of the same order as the bulk solution composition. Therefore, it is necessary to treat the effect of diffusion on the cell potential.

The cell

$$Pt(s),H_2(g)/HCl(\text{solution in } H_2O)/AgCl(s)/Ag(s)/Pt(s)$$

has been studied extensively in aqueous solutions[1]. Most measurements were made on solutions which had been saturated with H_2 and AgCl, which react only slowly with each other. Also, the concentration of HCl in the solution was high enough to make reaction of AgCl at the hydrogen electrode of negligible effect. The low solubility product of the AgCl necessitates that solutions of concentration of the order of 10^{-5} molal be used to detect any effect of diffusion away from the electrode of the second kind. The only measurements in this concentration range which have been reported are those of Anderson[2]. These measurements were not designed to investigate diffusion effects on the cell potential, but it was found that silver was deposited on the platinum of the hydrogen electrode in solutions of very dilute concentrations. In fact, the most dilute solution of HCl used was prepared by saturating pure water in the cell with AgCl and H_2. After a short time silver had been deposited on

the hydrogen electrode and an equivalent amount of HCl was in solution. Although this cell is illustrative of the effect of reaction of the sparingly soluble salt at the counter electrode and the consequent change of solution composition, there are no quantitative measurements of the effect of diffusion on the cell potential.

Cells utilizing the mercury-mercurous chloride electrode in water would be expected to exhibit an effect of diffusion at even lower solution concentrations than for the above cell since the solubility product of mercurous chloride is lower than that of silver chloride. No measurements have been reported on such solutions.

On the other hand, reported behavior of certain nonaqueous systems suggests that diffusion effects may have been present. In all of these systems the cell potential was lower than was expected from measurements at high concentrations. Luksha and Criss[3] used the silver-silver chloride reference electrode for measurements in N-methylformamide. Harned and Morrison[4] used the silver-silver chloride reference electrode for measurements in dioxane-water mixtures. Finally, Smyrl and Tobias[5] report the results of measurements with a thallium amalgam-thallous chloride reference electrode in dimethyl sulfoxide. This system will be the basis for the following discussion.

The EMF of the cell

$$\overset{\alpha}{Pt(s)}|\overset{\beta}{Li(s)}|\overset{\delta}{LiCl(\text{solution in DMSO})}|\overset{\epsilon}{TlCl(s)}|\overset{\phi}{Tl_{Hg}(\ell)}|\overset{\alpha'}{Pt(s)} \qquad [1]$$

has been reported as a function of LiCl concentration[5]. The reference electrode[6] employs TlCl sprinkled on the surface of the amalgam. The solubility product of TlCl in DMSO at 25°C is 5×10^{-7} as reported by Cogley and Butler[7].

Since at low bulk concentrations of LiCl the exchange reaction TlCl + Li = Tl + LiCl would significantly alter the concentration of the solution at the Li electrode surface, measurements have to be carried out before the dissolved TlCl can reach the Li surface. Thus a concentration gradient exists with respect to TlCl: the cell is saturated with respect to TlCl at the amalgam, and the TlCl concentration is, for practical purposes, zero at the LiCl electrode. As shown in figure 1, the cell potential is lower than expected from behavior at higher concentrations.

In the following, an estimate is made of the magnitude and sign of the potential deviation caused by the presence of a gradient of the sparingly soluble salt in this concentration cell "without transference."

Take two identical electrodes that are reversible to Cl^-. Insert one into the solution near the amalgam reference electrode, and the other into the solution where there is no thallous chloride and assume the concentration of TlCl varies only in one direction. These two electrodes are not to introduce any concentration gradients into the cell. One can calculate in principle the effect on the electrical potential between two identical electrodes caused by the variation in concentration between them (cf. Guggenheim[8]),

$$-F(\phi^2-\phi^1) = \int_1^2 (t^o_{Tl^+} + d\mu_{TlCl^+} + t^o_{Li} + d\mu_{LiCl}) \, . \qquad [2]$$

The integration can be made if one knows the concentration profiles, and the dependence of the transport and thermodynamic properties on the concentrations of the species throughout the region of concentration variation. Because the necessary data for such a calculation are not available even on an analogous system in aqueous solution, one must make approximations. The approximations to be made are:

(1) the solutions are dilute and the concentration of LiCl is comparable to that of TlCl;

(2) The ionic mobilities of Li^+, Cl^- and Tl^+ are equal in DMSO.

The transference numbers which appear in equation [2] are rather complicated functions of the concentrations and transport properties of all the species present. However, one may introduce a considerable simplification in the case of dilute solutions. The transference numbers appropriate for dilute solutions (cf. MacInnes[9]) are defined by

$$t_i = \frac{z_i^2 U_i c_i}{\sum_j z_j^2 U_j c_j} \qquad [3]$$

in which U_i = mobility of ionic species, $\frac{cm^2\text{-mole}}{sec\text{-joule}}$,

c_i = concentration (mole/cm^3) for ionic species,

z_i = charge number.

From the assumption of equal ionic mobilities, the transference number is found to be

$$t_i = \frac{z_i^2 c_i}{\sum_i z_i^2 c_i} \quad . \qquad [4]$$

For the case at hand,

$$t_i = \frac{c_i}{2(c_{TlCl}+c_{LiCl})} = \frac{c_i}{2c_{Cl^-}} \quad . \qquad [5]$$

This relationship between the transference number and concentration allows one to write

$$-F(\phi^2-\phi^1) = \frac{1}{2}\int_1^2 \left[\frac{c_{Tl^+}}{c_{Cl^-}}\, d\mu_{TlCl} + \frac{c_{Li^+}}{c_{Cl^-}}\, d\mu_{LiCl}\right] . \qquad [6]$$

The thermodynamic relations

$$\mu_{TlCl} = \mu^{\theta}_{TlCl} + 2RT\, ln\, (m\gamma_{\pm})_{TlCl}$$

$$\mu_{LiCl} = \mu^{\theta}_{LiCl} + 2RT\, ln\, (m\gamma_{\pm})_{LiCl}$$

may be differentiated to yield

$$-F(\phi^2-\phi^1) = \frac{1}{2}\,(2RT)\left\{\int_1^2 \frac{d(m_{TlCl} + m_{LiCl})}{(m_{TlCl} + m_{LiCl})}\right.$$

$$\left. + \int_1^2 \left[\frac{m_{Tl^+}}{m_{Cl^-}}\, d(ln\, \gamma_{\pm TlCl}) + \frac{m_{Li^+}}{m_{Cl^-}}\, d(ln\, \gamma_{\pm LiCl})\right]\right\} \qquad [7]$$

in which it has been assumed

$$\frac{m_{Tl^+}}{m_{Cl^-}} = \frac{c_{Tl^+}}{c_{Cl^-}} \quad \text{and} \quad \frac{m_{Li^+}}{m_{Cl^-}} = \frac{c_{Li^+}}{c_{Cl^-}} .$$

The molalities have been introduced strictly for convenience.

The first term of equation [7] involving only the concentrations may be integrated immediately. The much smaller term may be reasonably well approximated by

$$d(ln\, \gamma_{\pm TlCl}) = d(ln\, \gamma_{\pm LiCl}) = -d(\alpha z_+ |z_-| I^{\frac{1}{2}})$$

since the activity coefficient of all electrolytes of the same charge type should have equal activity coefficients in solutions of equal ionic strength, for solutions of low ionic strength. The integration then yields

$$-F(\phi_2-\phi_1) = RT\ ln \frac{(m_{TlCl} + m_{LiCl})_2}{(m_{TlCl} + m_{LiCl})_1} - RT\ \alpha[I_2^{\frac{1}{2}} - I_1^{\frac{1}{2}}] \ . \qquad [8]$$

The upper limit denotes the region adjacent to the reference electrode which is saturated with TlCl, and the lower limit may denote any other region of the electrolytic solution.

The result is not restricted to the solvent dimethyl sulfoxide and the electrolytes TlCl and LiCl; i.e., one could apply it to other systems which satisfy the assumptions listed above. For systems in which the concentration of the sparingly soluble salt is much lower than that of the other electrolyte, the potential calculated from equation [8] is zero as one would expect. Also, when the concentration of the slightly soluble salt is uniform throughout the cell, the potential calculated from equation [8] is again zero. Diffusion of the slightly soluble salt away from the reference electrode causes the reference electrode in the region of high ionic strength to be of a negative potential with respect to an identical reference electrode in the region of lower ionic strength.

In the development above, a "continuous mixture" junction has been assumed. The same results are obtained for "free diffusion" of TlCl from a reference electrode freshly introduced into a cell of uniform concentration of LiCl but free of TlCl. The cell potential will be constant, after the first few minutes, until the diffusing salt reaches the lithium electrode. The "continuous mixture" junction and the "free diffusion" junction should give the same results since it has been assumed that the mobilities of all the ions are equal.

To determine the behavior of the cell potential as a function of LiCl concentration, calculations have been made using equation [8]. Examples are given below:

Case I.

Let $(m_{LiCl})_2 = (m_{LiCl})_1 = 10^{-3}$ molal. From the solubility product of TlCl, i.e., $K_{sp} = 5 \times 10^{-7}$, one finds

$$(m_{TlCl})_2 \cong 3.6 \times 10^{-4}$$

$$(m_{TlCl})_1 = 0 ,$$

one calculates

$$(I)_2 = 1.4 \times 10^{-3}, \quad (I)_2^{\frac{1}{2}} = 3.70 \times 10^{-2}$$

$$(I)_1 = 10^{-3} \quad , \quad (I)_1^{\frac{1}{2}} = 3.16 \times 10^{-2}$$

and

$$-F(\phi^2-\phi^1) = RT \ln (1.4) - RT\, \alpha(0.7 \times 10^{-2}) .$$

At 25°C in dimethyl sulfoxide,

$$\frac{RT}{F} = 25.69 \times 10^{-3}, \quad \alpha = 2.57$$

from which one calculates

$$-(\phi^2-\phi^1) = 7.7 \times 10^{-3} \text{ volts.}$$

Therefore, the cell potential will be smaller by 7.7 millivolts than it would be for the same cell if diffusion were negligible.

Case II.

Let $(m_{LiCl})_2 = (m_{LiCl})_1 = 10^{-4}$

and $(m_{TlCl})_2 = 6.6 \times 10^{-4}$

$(m_{TlCl})_1 = 0$

$$I_2 = 7.6 \times 10^{-4} \quad I_2^{\frac{1}{2}} = 2.8 \times 10^{-2}$$

$$I_1 = 10^{-4} \quad I_1^{\frac{1}{2}} = 10^{-2}.$$

This yields

$$-(\phi^2-\phi^1) = 51 \times 10^{-3} \text{ volts.}$$

The cell potential will be smaller by 51 millivolts than for the same cell if diffusion were negligible.

Case III.

For the cell

$Pt(s),H_2(g)/HCl$ solution in $H_2O/AgCl(s)/Ag(s)/Pt(s)$ [9]

let

$$(m_{HCl})_2 = (m_{HCl})_1 = 10^{-4}$$

$$(m_{AgCl})_2 \cong 10^{-6}$$

from which one calculates

$$I_2 = 1.01 \times 10^{-4} \qquad (I_2)^{\frac{1}{2}} = 1.005 \times 10^{-2}$$

$$I_1 = 10^{-4} \qquad (I_1)^{\frac{1}{2}} = 10^{-2}$$

$$(\phi^2 - \phi^1) = 2.6 \times 10^{-4} \text{ volts} .$$

The cell potential will be smaller by 0.3 millivolts than for the corresponding cell if the concentration gradients were negligible.

Summarized below are the results of calculations for DMSO with the concentration of LiCl listed in the first column. It may be seen that the effect of the nonuniform distribution of TlCl becomes larger as the concentration of LiCl decreases. That this is the observed experimental behavior is seen in figure 4. There the function $E^{o'}$ is plotted versus m_{LiCl}. The function $E^{o'}$ is related to the measured cell potential difference, E, by

$$E + \frac{2RT}{F}\left[\ln m - \frac{\alpha\, m_{LiCl}^{\frac{1}{2}}}{1+m_{LiCl}^{\frac{1}{2}}}\right] = E^{o'} . \qquad [10]$$

This is in turn related to the standard cell potential E^o and the molality by

$$E^{o'} = E^o - \frac{4RT}{F}\,\beta_{LiCl}\, m_{LiCl} . \qquad [11]$$

The experimental data are represented by open circles. The solid

straight line is an extension of the least squares fit of the data in the linear region. The dotted line represents the expected cell behavior including the effect of diffusion of the thallous chloride from the reference electrode. According to Cogley and Butler[7], the fraction of TlCl present in a complex form in the presence of excess chloride ion should be negligible at the chloride ion concentrations used in these measurements.

Effect of Diffusion on Cell Potential

LiCl conc. molality	$-(\phi^2-\phi^1)$ mv
1×10^{-2}	0.056
5×10^{-3}	0.45
1×10^{-3}	7.67
7×10^{-4}	12.03
5×10^{-4}	17.20
3×10^{-4}	26.63
1×10^{-4}	50.84

Similar behavior of the cell EMF in dilute solutions in the presence of an electrode of the second kind (Ag, AgCl, Cl^-) was observed among others by Luksha and Criss[3(Fig.1,2)], and by Harned and Morrison[4(Fig.3)]. Unfortunately, the correction procedure presented above requires the knowledge of the solubility product of AgCl in the respective solvents. In the case of N-methylformamide[3], Povarov et al[10] found that the solubility of AgCl is 6×10^{-6} molal at 18°C, increasing to 4×10^{-2} in a 0.5 molal solution of NaCl. Luksha and Criss do not propose an explanation for the phenomena. It seems likely that the diffusion of AgCl from the reference electrode has caused the "humped" curve. Thus their extrapolations, represented by the dashed lines, may be several tens of millivolts too low. It is not possible to treat these systems quantitatively without taking complex formation into account. For the

dioxane-water system investigated by Harned and Morrison, according to the qualitative statement by Krahtovil and Tezak[11], AgCl is more soluble than in water. Harned and Owen[12] propose that the "humped" curve which appears in dioxane-rich mixtures, can be accounted for by the Gronwall extension to the Debye-Hückel equation. Guggenheim[13] has discussed the failure of the Gronwall extension to account for effects neglected in the Debye-Hückel theory. Further, such an explanation would hardly seem appropriate for the N-methylformamide systems where the behavior is similar, since the solvent has a large dielectric constant (171)[14]. Therefore, we propose that the dotted line, which represents their extrapolation to infinite dilution, is several millivolts too low, and we prefer the extrapolation represented by the solid line. It is not possible to confirm that diffusion of AgCl has caused the behavior, since the solubility of AgCl in the system is not known.

The behavior of these systems reveals the importance of the choice of the reference electrode for thermodynamic measurements. If the reference electrode is an electrode of the second kind, the solid salt should be of low solubility both in the pure solvent and in the solutions employed in the concentration cells. From the knowledge of the solubility, it is possible to estimate the concentration at which the effect of diffusion of the sparingly soluble salt will be appreciable by applying the correction procedure discussed above. A more accurate calculation would necessitate a knowledge of the mobilities of all the ions in the diffusion region, the activity coefficients of the two electrolytes in this region, and any complexation constants.

Conclusion

In measurements of EMF-s involving electrodes of the second kind, a concentration gradient of the sparingly soluble salt in the electrolyte has been shown to be responsible for anomalous behavior at high dilutions of the other solute electrolyte. Consideration of this effect may be particularly important in work with nonaqueous ionizing solvents, in which the solubility of the metal halides usually employed in aqueous work is often significantly higher than in water. Knowledge of the solubility of the sparingly soluble salt allows a reasonable estimation of the deviation of the EMF from the case when there are no concentration gradients in the system.

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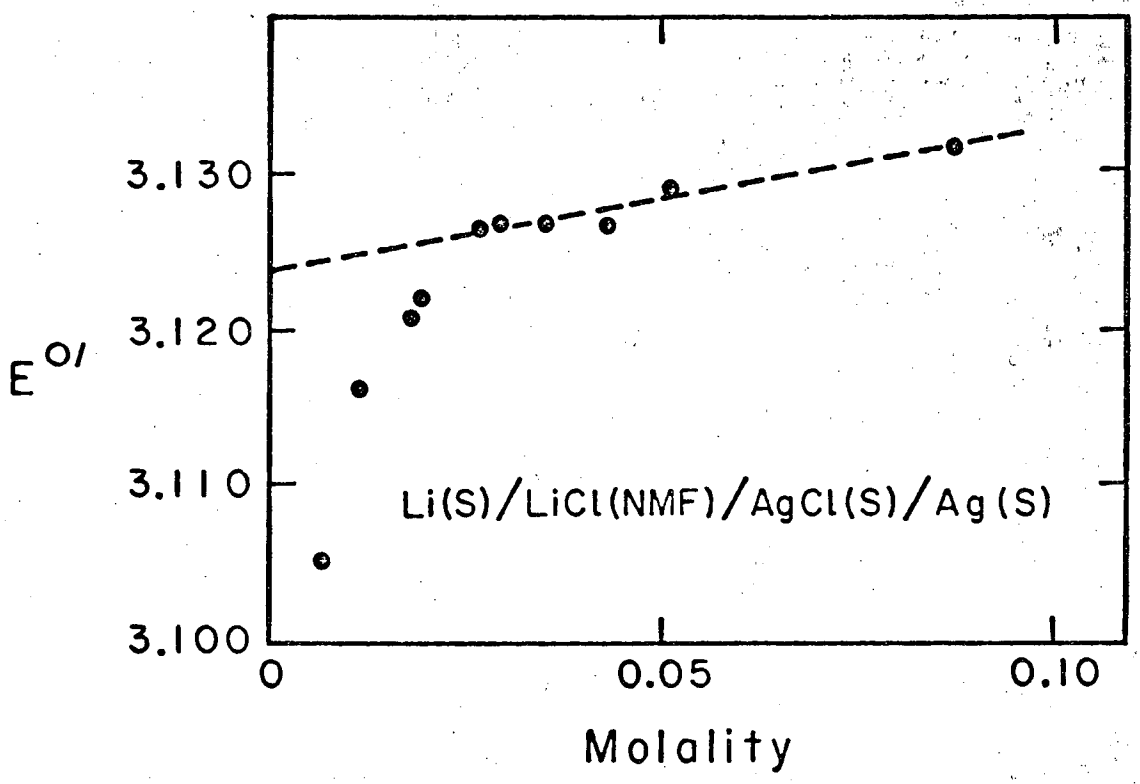
Figure 1. Cell EMF data in N-methylformamide. The experimental data of Luksha and Criss[3] was treated according to equations [9] and [10] and is plotted as open circles. The dashed line represents Luksha and Criss' extrapolation.

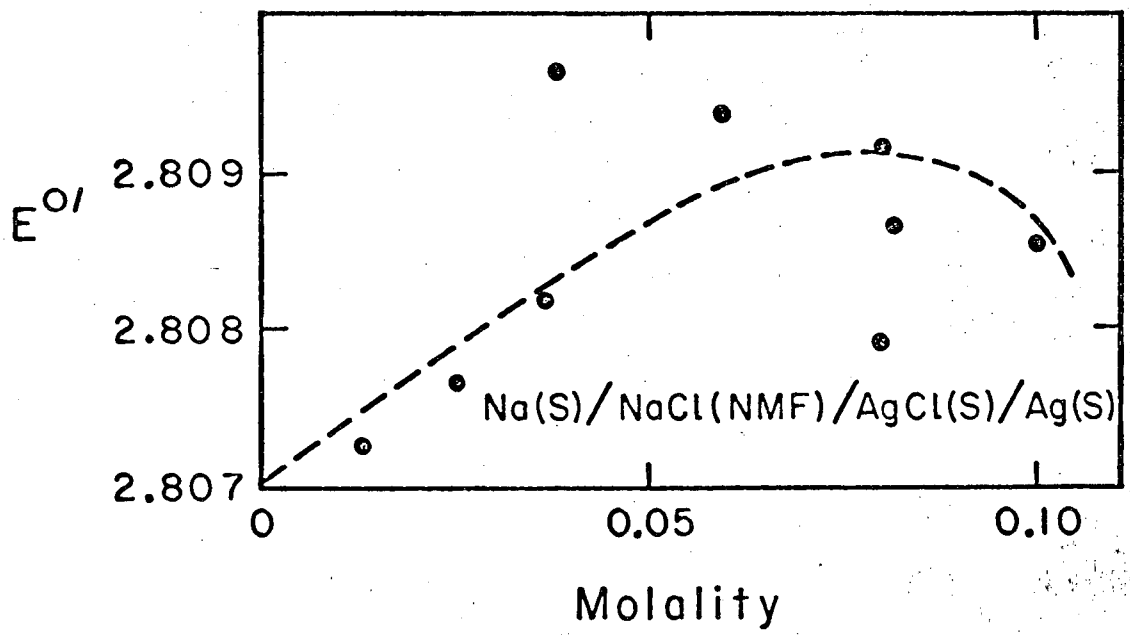
Figure 2. Cell EMF data in N-methylformamide. The experimental data of Luksha anc Criss[3] was treated according to equations [9] and [10] and is plotted as open circles. The dashed line represents Luksha and Criss' extrapolation.

Figure 3. Cell EMF data in 70% Dioxane-30% Water. The experimental data reported by Harned and Morrison[4] was treated by equations [9] and [10] based on Guggenheim's extension to the Debye-Hückel equation, and is represented by the open circles. The dashed line corresponds to the extrapolation proposed by Harned and Morrison. The solid line is our proposed extrapolation, neglecting the three points in the most dilute solutions.

Figure 4. Cell EMF data in Dimethyl Sulfoxide. The open circles represent experimental data treated according to equations [9] and [10]. The solid line is the extrapolation to infinite dilution based on Guggenheim's extension of the Debye-Hückel equation, neglecting the data below 0.01 molal. The dashed line represents the expected cell behavior, taking into account diffusion of the sparingly soluble salt, based on equation [8].


3.130
3.120
3.110
3.100
E°'
Li(S)/LiCl(NMF)/AgCl(S)/Ag(S)
0
0.05
0.10
Molality

XBL 678-3736



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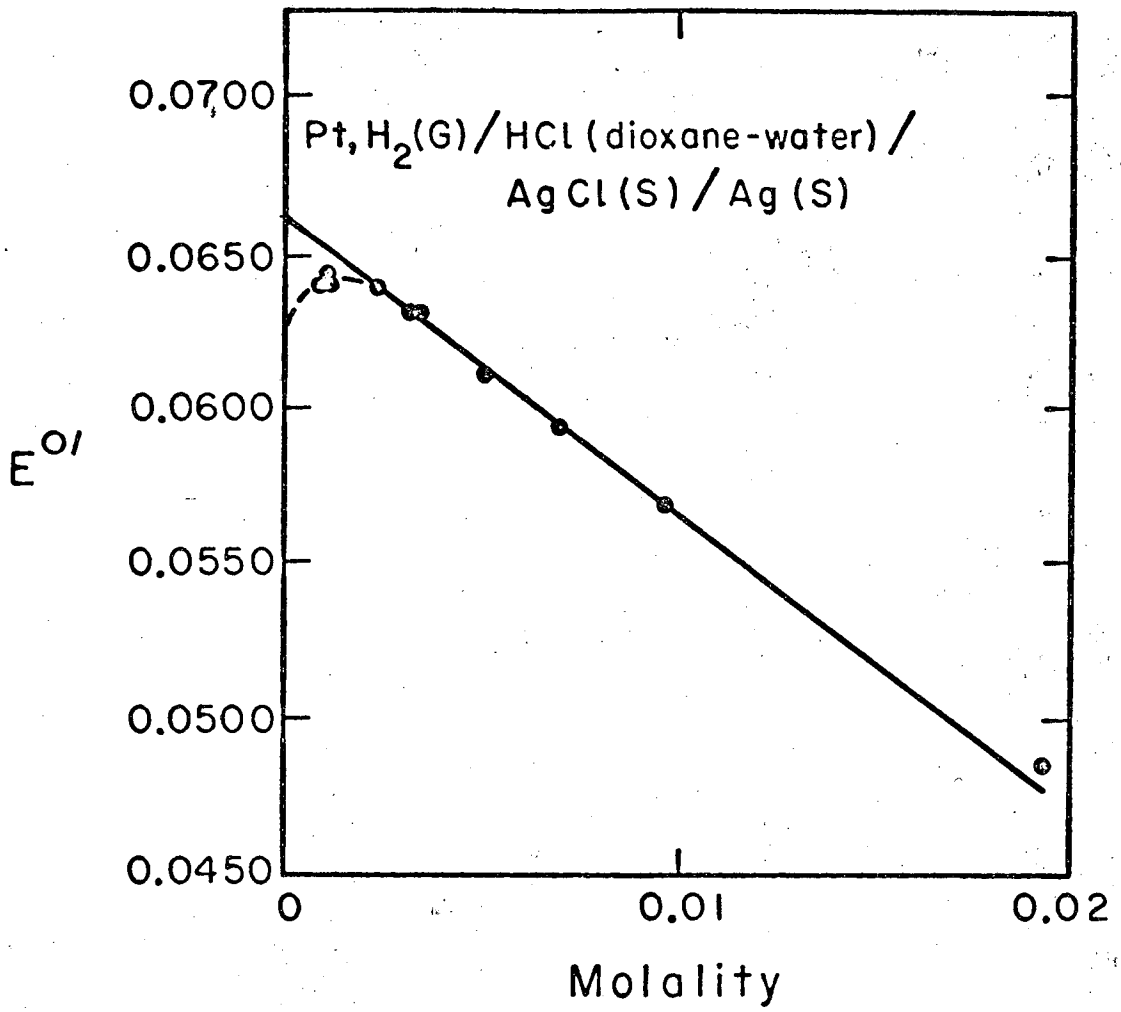
Pt, H_2(G) / HCl (dioxane-water) /
AgCl (S) / Ag (S)
0.0700
0.0650
0.0600
0.0550
0.0500
0.0450
$E^{o\prime}$
0
0.01
0.02
Molality

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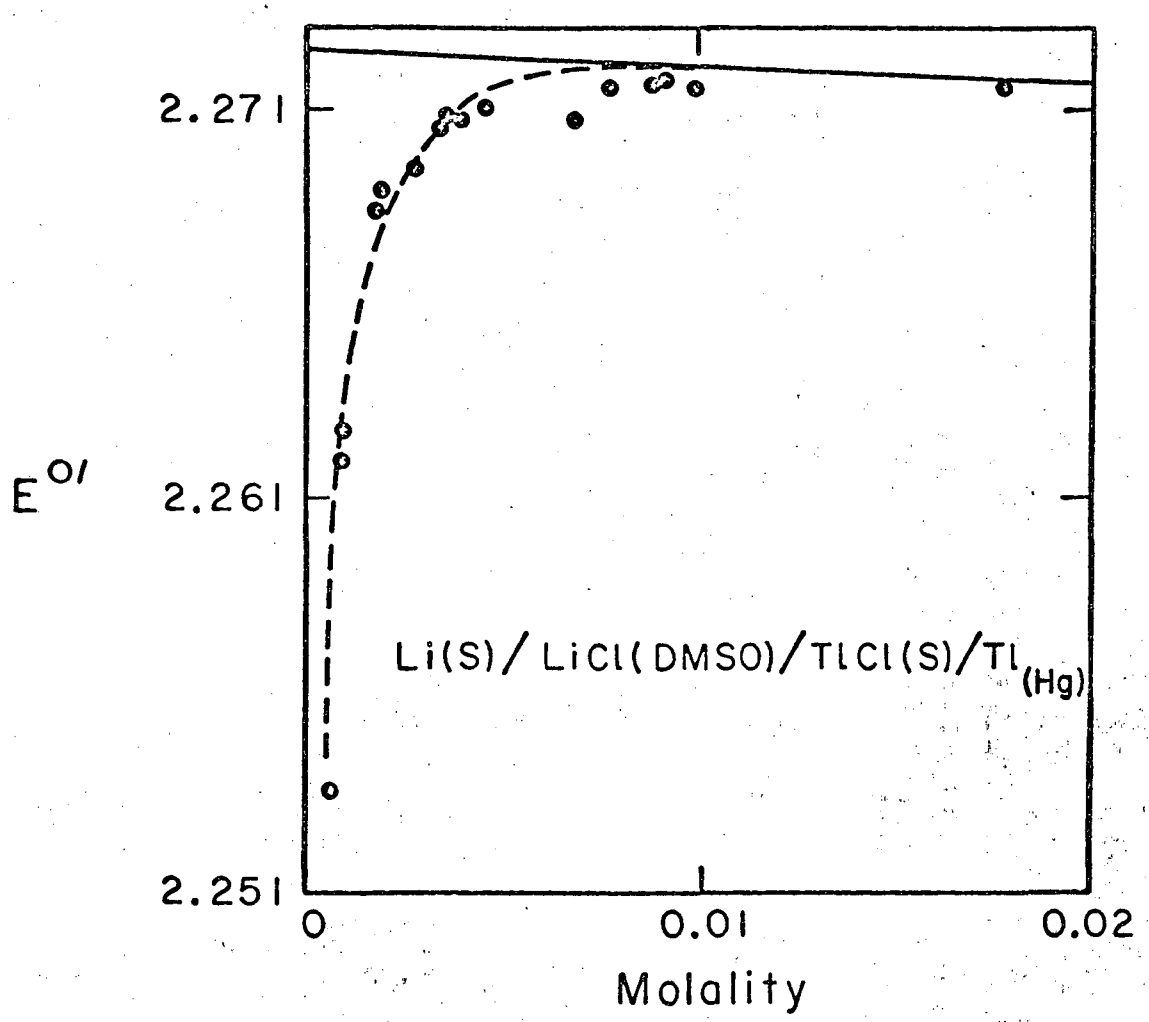

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