Chloride Reversible Electrodes for Use in Aprotic Organic Solvents

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ALTHOUGH A LARGE number of electrochemical studies have been made using aprotic solvents, little systematic work has been done on reference electrodes, particularly of the second kind, for these solvents. Interest in such electrodes is not confined to their usefulness in potential measurements, since most battery cathode systems are of this type.

Investigations of the thallous chloride/thallium amalgam electrode in dimethyl sulfoxide (DMSO) have established its reversibility and provided data on the solubility and complex formation constants of thallous chloride in DMSO. Other studies have established the reversibility of the cadmium chloride/cadmium amalgam electrode in N,N-dimethyl formamide (DMF) and of the silver ion/silver couple in many solvents (1).

This paper presents the results of some preliminary studies of chloride reversible reference electrodes for use in the solvents DMSO, DMF, and propylene carbonate (PC), as well as solubility data relevant to these studies.

EXPERIMENTAL

Solubility Studies. DMSO and DMF (Matheson, Coleman and Bell, "Spectroquality") were used as received in the preparation of solutions, while PC (Jefferson Chemical Co.) was purified by distillation (2). Supporting electrolytes were tetraethylammonium chloride and tetraethylammonium perchlorate (Eastman Organic Chemicals). Standard solutions were prepared by dissolution of known weights of

(1) J. N. Butler, *Advan. Electrochem. Electrochem. Eng.*, **7**, 77 (1969).

(2) R. Jasinski and S. Kirkland, ANAL. CHEM., **39**, 1663 (1967).

thallous perchlorate (K&K Laboratories, "Highest Purity"), lead chloride (Fisher Scientific Co. Reagent), or cadmium chloride (Fisher Scientific Co. Reagent) in each of the solvents, all of which were $0.1M$ in either Et_4NCl or Et_4NClO_4. Saturated solutions of thallous chloride (Fisher Scientific Co., "Purified"), lead chloride, and cadmium chloride were prepared in solvents of various chloride concentrations (Table I) and allowed to equilibrate, with occasional stirring, for 24 hr. Samples of the solutions were analyzed after the experiments by gas chromatography (Barber-Colman, model 5340, Poropak Q column, thermal conductivity detection) for water content and were found to contain less than 0.04% water in all cases. Earlier work (3) suggested that such amounts of water probably have little effect on the solubility data sought.

Polarographic analysis was carried out using a Sargent model XV polarograph with a dropping mercury (Doe and Ingalls, triply distilled) electrode and an aqueous saturated calomel electrode (Fisher Scientific Co.). Sample size was 25 ml, and correction for background current was made using measurements in the supporting electrolyte above. Concentrations of Tl, Cd, or Pb in unknown solutions were obtained using calibration solutions matched as closely as possible to the unknowns.

The solubility of LiCl in PC was measured by saturating the solvent with anhydrous LiCl (Anderson Physics Laboratories) and allowing the saturated solution to stand, with occasional stirring, for several days at room temperature. The supernatant liquid was analyzed by potentiometric titration with standard aqueous silver nitrate, and was found to be $4.0 \times 10^{-2}M$ in LiCl.

Potential and Polarization Resistance Measurements. DMSO and DMF (Fisher, Certified) were dried with Linde 4A Molecular Sieves and analyzed by gas chromatography. Less than 50 ppm of volatile impurities, including water, were present. PC was purified by distillation (2) and contained less than 10 ppm of volatile impurities. Salts were reagent grade, anhydrous, and were dried for at least 7 days over anhydrous $CaSO_4$ before solutions were prepared. Experiments were carried out in a dry nitrogen atmosphere at 25 ± 2 °C.

Potential measurements were made with a Fluke high impedance differential voltmeter and were accurate within 0.1 mV. Polarization measurements were made using a 135-V battery and a bank of resistors as a constant current source. In the first set of experiments, cells consisting of two identical amalgam electrodes (approximately 1 cm^2 in surface area) separated by a glass frit were covered with the finely powdered chloride of the metal dissolved in the amalgam. The electrolyte in each case was $1M$ Et_4NCl in the solvent of interest. The bias potential was measured as a function of time and, at times, polarization curves were obtained.

The second set of experiments was made using cells of the following type:
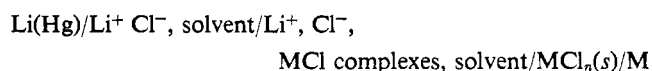
$$Li(Hg)/Li^+\ Cl^-, \text{solvent}/Li^+, Cl^-,$$
$$MCl\ \text{complexes, solvent}/MCl_n(s)/M$$

Table I. Solubility Data

Solvent	Salt	C_{Cl}	Ionic strength[a]	Solubility
DMF	TlCl	0	0.1001	5.48×10^{-5}
		0.0098	0.1000	1.04×10^{-4}
		0.0996	0.0996	8.40×10^{-4}
	CdCl$_2$	0	0.1001	6.09×10^{-2}
		0.0100	0.1000	6.70×10^{-2}
		0.1001	0.1001	1.47×10^{-1}
	PbCl$_2$	0	0.1001	9.97×10^{-2}
		0.0100	0.1000	1.09×10^{-1}
		0.1001	0.1001	2.61×10^{-2}
PC	TlCl	0	0.1003	6.07×10^{-7}
		0.0109	0.1119	4.86×10^{-7}
		0.1004	0.1004	7.90×10^{-6}
	CdCl$_2$	0	0.1001	2.35×10^{-3}
		0.0101	0.1000	9.23×10^{-3}
		0.1001	0.1001	1.61×10^{-1}
	PbCl$_2$	0	0.1001	7.30×10^{-5}
		0.0101	0.1000	8.38×10^{-4}
		0.1001	0.1001	9.57×10^{-3}
DMSO	TlCl	0	0.1004	1.76×10^{-3}
		0.0103	0.1003	1.30×10^{-3}
		0.0995	0.0995	2.54×10^{-3}

[a] Ionic strength = $[Et_4NCl] + [Et_4NClO_4]$; all concentrations in mol/l.

(3) J. C. Synnott and J. N. Butler, *J. Phys. Chem.*, **73**, 1470 (1969).

Table II. Polarization Characteristics of $MCl_n/M(Hg)$ Electrodes

Solvent	MCl_n	Solubility MCl_n[a]	Amalgam composition, %	ΔE, mV	dE/di, Kohm
DMF	TlCl	8.40×10^{-4}	12.9	0.2	3.4
	$CdCl_2$	0.147	Sat'd ($\sim 5\%$)	0.1 (4)	Ohmic
	$PbCl_2$	2.61×10^{-2}	1	0.5	5.4
PC	TlCl	7.90×10^{-6}	2, 20	0.3	5.2
	$CdCl_2$	0.161	4	5–8	68–72
	$PbCl_2$	9.57×10^{-3}	1	1–2	10–12
DMSO	TlCl	2.54×10^{-3}	1, 40	0.01 (5, 6)	Ohmic
	$CdCl_2$	2.81 (7)	4	0.1	7.2
	$PbCl_2$	0.547 (7)	1	1–2	13.5

[a] Molal solubility in $0.1M$ Et_4NCl electrolyte from Table I, except for $CdCl_2$ and $PbCl_2$ in DMSO for which the solubility in the pure solvent is given.

Table III. Potential and Polarization Resistance of Cells
$Li(Hg)/LiCl$ (0.1m), Solvent/$MCl_n(s)$/M

Solvent	M	Amalgam composition, %	MCl_n	E, V	dE/di, Kohm	Solubility MCl_n, M
DMF	Ag	...	AgCl	1.982 ± 0.005	5.6	0.1
	Tl(Hg)	12.9	TlCl	1.377 ± 0.001	12	0.0008
	Pb(Hg)	1	$PbCl_2$	1.845 ?	14	0.2
	Cd(Hg)	4	$CdCl_2$	1.652 ± 0.001	15	0.15
DMSO	Ag	...	AgCl	2.265 ± 0.005	34	0.1
	Tl(Hg)	6.5	TlCl	1.543 ± 0.001[a]	Ohmic	0.003
	Pb(Hg)	1	$PbCl_2$	1.777 ± 0.001	28	0.5 (7)
	Cd(Hg)	4	$CdCl_2$	1.550 ± 0.005	18	2.8 (7)

[a] Li(Hg) was 0.818 mol % (see reference 9). For all other entries, Li(Hg) was 1.22 mol %.

where M was silver, thallium amalgam, lead amalgam, or cadmium amalgam, and the solvent was DMSO or DMF. In each case, the concentration of LiCl was $0.1M$ and the Li amalgam contained 0.043 wt % (1.22 mol %) Li. The potential of the cell was measured as a function of time and polarization curves were obtained.

RESULTS AND DISCUSSION

Solubility. The values listed in Table I for C_{Cl} are the concentrations of Et_4NCl in each electrolyte. The values for "ionic strength" are the sum of Et_4NCl and Et_4NClO_4 concentrations, but do not include any possible contribution from the dissolved TlCl, $CdCl_2$, or $PbCl_2$, since the nature of the ionic species resulting from these materials is obtainable only by a considerably more detailed investigation than we have carried out. Thus, the true ionic strength of the saturated solution is somewhat greater than the nominal $0.1M$ value for some of the $CdCl_2$ and $PbCl_2$ solutions.

The solubility of the salts was obtained from the polarographic diffusion current in the saturated solution. Concentration was assumed to be proportional to diffusion current after correction for background current, and calibration solutions were matched as closely as possible to the concentration of the unknown solution.

Polarization Characteristics. The results of the first set of experiments are summarized in Table II for the cell

$$M(Hg)/MCl_n(s)/1M Et_4NCl/MCl_n(s)/M(Hg)$$

The area of the identical electrodes was approximately 1 cm^2.

In DMF, the thallium, lead, and cadmium chloride electrodes were all stable, but the $CdCl_2$ was apparently the most stable. Although the data in Table I show an increase in solubility of $CdCl_2$ when excess chloride is added, this increase is not large, which implies that complexes such as $ClCl_3^-$ are relatively weak. This conclusion was reached earlier from similar measurements (8). Thus, the predominant soluble species is probably $CdCl_2$, the neutral complex, and although cadmium chloride is moderately soluble in DMF, the liquid junction between a solution of (for example) LiCl and a similar solution saturated with cadmium chloride may not contribute an appreciable potential to the cell, if the concentration of lithium and chloride ions is large compared to the concentrations of the cationic (e.g., $CdCl^+$) or anionic (e.g., $CdCl_3^-$) complexes. The $PbCl_2$ electrode was initially unstable, but became reversible after standing for $1^1/_2$ hr, and deteriorated over a period of 2 days. The solubility of $PbCl_2$ in DMF apparently decreases as excess chloride is added, which implies the predominance of cationic species (Pb^{2+} or $PbCl^+$, for example) in the solution. The data of Table I show a slight maximum in solubility which is not consistent with any simple equilibrium scheme and may reflect the changes in ionic strength of the equilibrium solution resulting from the additional lead-containing and chloride ions added by the dissolving salt.

(4) L. W. Marple, ANAL. CHEM., **39**, 844 (1967).
(5) D. R. Cogley and J. N. Butler, J. Electrochem. Soc., **113**, 1074 (1966).
(6) W. H. Smyrl and C. W. Tobias, ibid., p 754.
(7) C. A. Melendres, Thesis, University of California, Berkeley, 1965, UCRL 16330.
(8) P. A. Malachesky, Tyco Laboratories, Waltham, Mass., 1968, private communication.
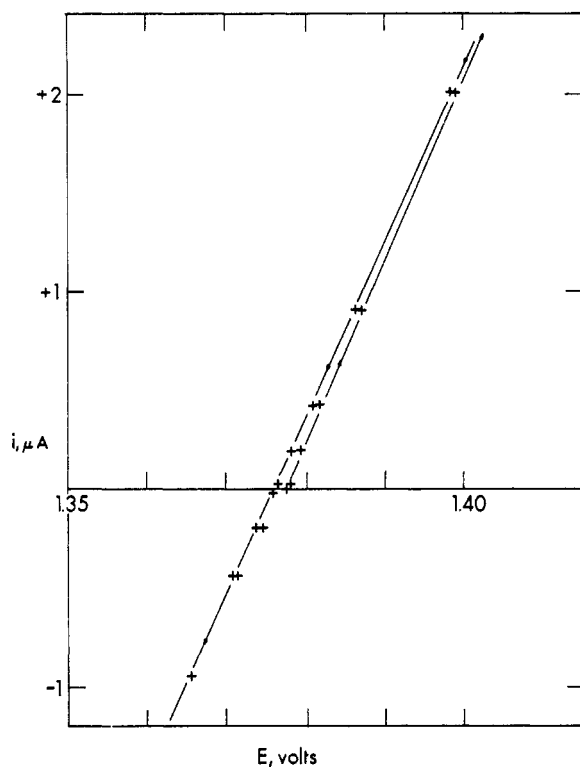(9) G. Holleck, D. R. Cogley, and J. N. Butler, J. Electrochem. Soc., **116**, 952 (1969).

Figure 1. Polarization of cell

Li(Hg)/LiCl, DMF/TlCl(s)/Tl(Hg)

Figure 2. Polarization of cell

Li(Hg)/LiCl, DMF/PbCl₂(s)/Pb(Hg)

Although the $CdCl_2$ and $PbCl_2$ electrodes are reversible in DMSO, the solubility of the salts is so large that a substantial liquid junction potential seems inevitable, even if the charged complexes are of low concentration compared to the uncharged complexes, since both cadmium and lead form complexes with chloride in this solvent. The reversibility and stability of the thallium amalgam–thallous chloride electrode in DMSO is well documented, and this electrode has been used successfully in cells without liquid junction (*1*). The effect of the small amount of thallium which dissolves in dilute chloride solutions has been quantitatively treated elsewhere (*10*).

In PC, the $PbCl_2$ and $CdCl_2$ electrodes were relatively irreversible. They gave polarization resistances (Table II) which were appreciably higher than the estimated ohmic resistance of the cell (3 to 7 Kohm), a result which is consistent with the relatively unstable bias potentials of these electrodes. The solubilities of $PbCl_2$ and $CdCl_2$ are relatively large in PC, and both increase with increasing chloride concentration. The Tl(Hg)/TlCl electrode was initially unstable in PC, but became stable to within ±0.3 mV after several polarizations. This process may involve the formation of an adsorbed chloride layer on the amalgam by a mechanism similar to that by which an aqueous calomel electrode is made reversible.

A second set of experiments measured potentials and polarization resistances of cells of the type

Li(Hg)/Li⁺, Cl⁻, solvent/Li⁺, Cl⁻, MCL complexes,

solvent/MCL_n(s)/M
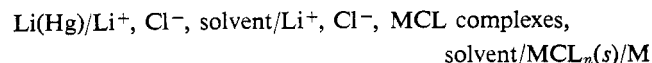
where M was Ag, Tl(Hg), Pb(Hg), or Cd(Hg), and the solvent was DMF or DMSO. The results are summarized in Table III. Specific comments follow.

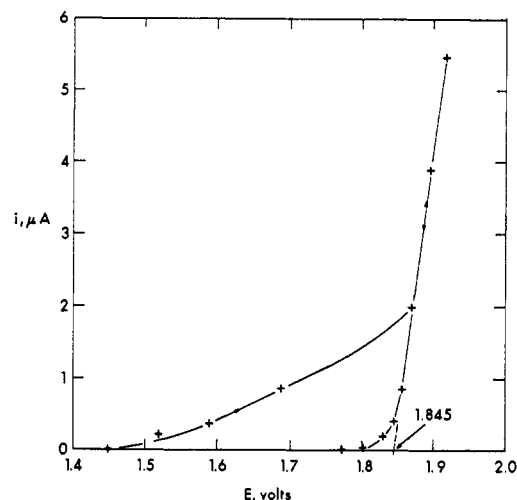(10) W. H. Smyrl and C. W. Tobias, *Electrochim. Acta*, 13, 1581 (1968).

DMF–Ag/AgCl. The initial potential of 1.954 V had increased to 1.969 V after 3 hr, and the value (1.982 V) given in Table III was obtained after 9 hr. Within 30 min after cell preparation, a black precipitate formed on the lithium amalgam electrode.

DMF–Tl(Hg)/TlCl. The initial potential value of 1.382 V decreased to 1.370 V in less than 1 hr and remained constant over the next 4 hr. The value of 1.377 V in Table III was obtained after 19 hr. This change may have resulted from a temperature decrease of 5 °C. The corresponding DMSO cell shows a potential increase of 0.2 mV/deg with decreasing temperature which tends to confirm this hypothesis. Figure 1 shows the extremely good reversibility of the electrode.

DMF–Pb(Hg)/PbCl₂. Initially, the potential of this cell was unstable (approximately 1.48 ± 0.02 V) and decreased over a 9-hr period to an apparently steady value of 1.375 V. The polarization resistance measured 2 hr after preparation was approximately 200 Kohm. Figure 2 shows the polarization curve after 12 hr. On application of a small charging current, the potential shifted from approximately 1.4 to 1.85 V, where an apparently reversible ohmic resistance was observed. With decreases in current, the potential drifted to lower values again. The extrapolated intercept of the reversible portion of the curve was 1.845 V, as given in Table III. The formation of a black precipitate on the lithium amalgam electrode and the large shift in potential for small applied current (Figure 2) probably reflect the consumption of soluble lead complexes which had diffused into the lithium amalgam compartment.

DMF–Cd(Hg)/CdCl₂. In contrast to the $PbCl_2$ cell, the $CdCl_2$ cell was extremely stable in potential, as shown in Figure 3. The initial potential, 1.653 V, varied by less than 1 mV over the next 12 hr. A polarization curve was made after 12 hr, and the zero current potential shifted by less than 1 mV after polarization at up to 5 μA over a period of an hour. This amount can be accounted for by concentration changes at the electrodes. The considerable solubility of $CdCl_2$ [black precipitate at Li(Hg) electrode] did not appear to affect the stability or reversibility of the cell.

DMSO–Ag/AgCl. The initial potential of the cell was 2.427 V, and decreased by only 3 mV during the first hour. A rapid decrease in potential to approximately 2.3 V was observed. After 18 hr, the potential was 2.282 V and was still decreasing. A steady decrease could result from self-

discharge of the cell because of silver complexes diffusing to the lithium amalgam electrode, since the estimated solubility of AgCl is at least $0.1M$ in this electrolyte. Previous work (3, 11) has given $K_{s2} = 10^{+1.5}$ for AgCl in DMSO, implying that essentially all the chloride is tied up as $AgCl_2^-$ complexes.

DMSO–Tl(Hg)/TlCl. This cell was extremely stable and reversible and has been discussed in other papers (1, 9).

DMSO–Pb(Hg)/PbCl$_2$. The initial potential of this cell was 1.752 V, increasing to 1.769 V after 8 hr and to 1.777 V after 26 hr. Reversibility was good, and the potential returned to within 1 mV of the same zero current value after polarization to ± 5 μA. A black precipitate formed on the Li(Hg) electrode almost immediately, which is consistent with the high solubility (7) of PbCl$_2$ in DMSO.

DMSO–Cd(Hg)/CdCl$_2$. The initial potential was extremely unsteady (0.8 to 1.5 V), and a black precipitate formed on the Li(Hg) electrode as expected because of the high solubility of CdCl$_2$ in DMSO (7). The polarization resistance after 3 hr was very large (300 Kohm), but after this polarization the potential reached a steady value of 1.519 V. After 24 hr, the potential was 1.550 V (Table III) and the polarization resistance had dropped to 18 Kohm, which is only slightly higher than the expected ohmic resistance of the cell.

PC–Tl(Hg)/TlCl. After this work was completed, we became aware of a study in another laboratory (12) of the cell

$$\text{Li}(s)/\text{LiCl in PC}/\text{TlCl}(s)/\text{Tl(Hg)}$$

at a number of temperatures. More than a day was required to establish reversibility of the thallous chloride electrode, a result which is consistent with our observation that the thallous chloride electrode in PC must be aged or polarized before reversibility is attained. A further observation was made that lithium amalgam in contact with PC solutions apparently reacted with the solvent, producing a clear waxy substance of unidentified composition. This was confirmed by observations in our own laboratory. Such a reaction is much slower with lithium metal [although its potential is 1V more negative than the amalgam (13)], but the stability and reversibility of lithium metal in PC solutions has been verified on many occasions (1). Further investigations of this phenomenon are clearly required.

The stability and reversibility of the silver/silver chloride electrode has been established previously (1, 3), but the high solubility of AgCl in solutions containing excess chloride means that liquid junction potentials can be minimized only by using a relatively high concentration of an inert ionic medium (such as Et$_4$NClO$_4$) compared to the total concentrations of silver and chloride. For cells with liquid junctions, the silver/silver chloride electrode is quite satisfactory. Similar considerations can be made in the cases of the PbCl$_2$ and CdCl$_2$ electrodes. The thallium amalgam/thallous chloride electrode has been found to be stable and reversible in all three solvents, and the solubility of thallous chloride in solutions containing excess chloride is low enough that cells without appreciable liquid junction potential can be constructed using this electrode.

From our solubility data for TlCl in these three solvents, we have estimated the equilibrium constants for complex

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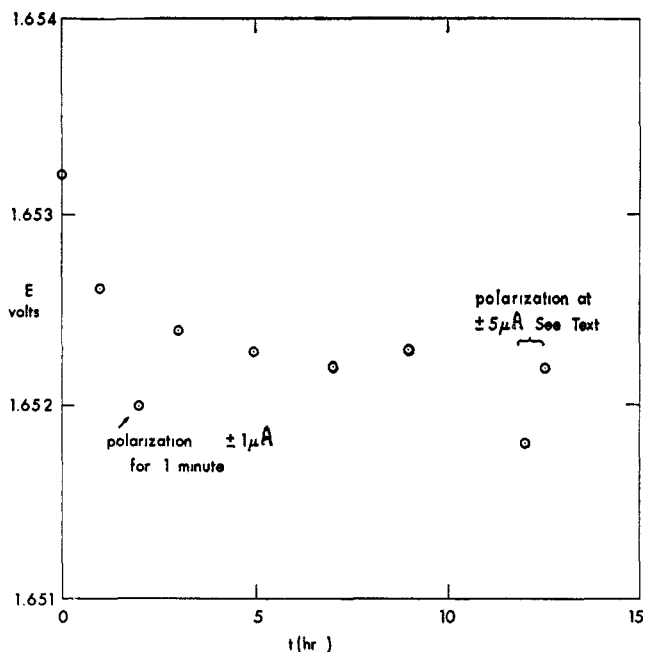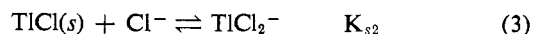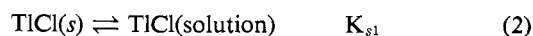(13) D. R. Cogley and J. N. Butler, *J. Phys. Chem.*, **72**, 1017 (1968).

Figure 3. Time dependence of potential of cell

Li(Hg)/LiCl, DMF/CdCl$_2$(s)/Cd(Hg)

formation. To calculate these constants, we assumed that the equilibria were the same as in water, (14):

$$\text{TlCl}(s) \rightleftharpoons \text{Tl}^+ + \text{Cl}^- \qquad K_{s0} \qquad (1)$$

$$\text{TlCl}(s) \rightleftharpoons \text{TlCl(solution)} \qquad K_{s1} \qquad (2)$$

$$\text{TlCl}(s) + \text{Cl}^- \rightleftharpoons \text{TlCl}_2^- \qquad K_{s2} \qquad (3)$$

Since we have measured the solubility (S) at three concentrations of added chloride (C), the three equilibrium constants can be determined through the mass balance equations:

$$S = K_{s2}[\text{Cl}^-] + K_{s1} + K_{s0}/[\text{Cl}^-] \qquad (4)$$

$$C = (1 + K_{s2})[\text{Cl}^-] - K_{s0}/[\text{Cl}^-] \qquad (5)$$

provided that the activity coefficients are assumed to be independent of the composition of the ionic medium. The variation is probably not more than 10% in the various solutions used in our studies. Since the principal change is the substitution of chloride for perchlorate, the total concentration of thallium-containing species is small in all solutions, and any specific effects (15) of the Et$_4$N$^+$ ion are constant. Using the above equations, values (Table IV) were obtained for the equilibrium constants K_{s0}, K_{s1}, and K_{s2}. Not enough

(14) L. G. Sillen and A. E. Martell, "Stability Constants," The Chemical Society, London, 1964, pp 294–6.
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Table IV. Approximate Equilibrium Constants for Thallous Chloride Complexes in Aprotic Solvents

Solvent	Logarithm of Equilibrium Constant		
	K_{s0}	K_{s1}	K_{s2}
DMF	−9.0	−4.6	−2.1
PC	−12.4	<−6.4	−4.1
DMSO	−6.4	−2.95	−1.8
DMSO (5)	−6.26 ± 0.04	−3.5± 0.1	−2.3 ± 0.1

data were available to set limits of error on the constants, but a reasonable estimate is less than ± 0.5 logarithmic unit.

In Table IV we have also given the values for these constants obtained previously (5) in $0.5M$ LiClO$_4$–DMSO supporting electrolyte by potentiometric measurements with a thallium amalgam electrode. The agreement is good, considering the approximations inherent in our calculations from such sparse data and the different ionic media employed. Ion pairing of Li$^+$ with Cl$^-$ would be expected to be stronger than with TlCl$_2^-$, and this difference would be reduced or effectively eliminated (i.e., Et$_4$N$^+$ medium). Thus, K_{s2} is expected to be larger (log K_{s2} more positive) in the Et$_4$N$^+$ medium than in the Li$^+$ medium, and this is observed. A similar argument implies that K_{s0} should be larger in the Li$^+$ medium, and this is observed, but the effect of higher ionic strength may offset the ion pairing effect somewhat. K_{s1} should be independent of the ionic medium to a first approximation, but the discrepancies between the two results for this constant may be a reflection of experimental and theoretical errors.

Iodide-Selective Electrodes in Reacting and in Equilibrium Systems

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WHEN H$_2$O$_2$ is added to iodate in acid solution, iodine and reactive intermediate compounds—e.g., HIO, HIO$_2$, H$_2$I$_2$O$_3$—thereof are formed, a complex reaction system results, and hydrogen peroxide is catalytically decomposed (1). Earlier investigations of this system (2) are being continued with major emphasis at present on measurements of the iodide activity, [I$^-$], long recognized as a crucial variable and thought at times to be below $10^{-6}M$. The usual Ag/AgI electrode could not be trusted in this reactive system. Of much greater promise are the iodide-selective electrodes (3) now available, in which crystalline silver iodide is interposed as a membrane between the unknown [I$^-$] solution (here, the reaction mixture) and presumably an Ag/AgI electrode in contact with aqueous silver nitrate. When such an electrode is used in a reaction mixture, the membrane is a possible reactant. For example, if the mixture contains no silver ion, the reaction

$$\text{AgI (c, membrane)} = \text{Ag}^+ \text{(aq)} + \text{I}^- \text{(aq)} \qquad (1)$$
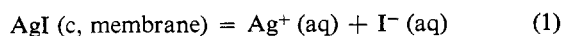
will proceed to establishment of the solubility equilibrium

$$\text{AgI (c)} \overset{K_2}{\rightleftarrows} \text{Ag}^+ \text{(aq)} + \text{I}^- \text{(aq)} \qquad (2)$$
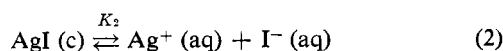
The iodide produced in Reaction 1 of course influences the electrode reading. When this iodide is at least comparable with the iodide to be measured, the electrode reading will be too large. It will approach $\sqrt{K_2}$ as a limit (the solubility limit of the electrode) as the initial [I$^-$] approaches zero.

Fluoride-selective electrodes in equilibrium systems (4, 5)

and others (6) have been shown to behave in accord with the discussion just given. In reacting systems, fluoride-selective electrodes have been used successfully (7) to follow [F$^-$] at activities (about $10^{-4}M$) so far above the solubility limit that calibration presented no serious problems (8). In the present investigation, [I$^-$] values near and below the solubility limit proved of concern.

EXPERIMENTAL

Analytical Reagent or C.P. grade chemicals were used as purchased. The 30% H$_2$O$_2$ contained no preservative. An Orion iodide-selective electrode was used and its potential measured with an Orion 801 Digital pH/mV meter and recorded by a Hewlett-Packard 7100B recorder with a 17500A input module. Measured potentials were precise to 0.2 mV and recorded to 1 mV. The Ag/AgI electrode was made by electrolyzing a silver billet electrode (L&N #117226) in $1M$ HI for several minutes at low (5–10 mA/cm^2) current density and was aged several days before use. Its potential was measured directly with a 17500A input module on the same (two-channel) recorder. The reference electrode (Orion 90-02, double junction) contained a $1N$ Na$_2$SO$_4$ solution as salt bridge between the reacting system and the calomel reference electrode; this salt solution is compatible with the reacting system, which contained perchloric acid. In the longer experiments, some of which extended to several days, the sleeve-junction end of the reference electrode was covered with a collodion film (9) to retard flow of the bridging solution into the reaction mixture. The collodion had no significant disturbing effect. All [I$^-$] measurements were performed in a borosilicate beaker at constant (± 0.02 °C.) temperature in a water bath on solutions stirred magnetically with a Teflon-coated stirring bar. The rubber stopper closing the beaker and holding the electrodes was protected by a film of collodion to prevent serious attack by iodine vapor. The iodide-

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(2) H. A. Liebhafsky, unpublished work, University of California, Berkeley, 1928.
(3) G. A. Rechnitz, *Chem. Eng. News*, **43**, (25), 146 (1967).
(4) M. S. Frant and J. W. Ross, Jr., *Science*, **154**, 1553 (1966).
(5) J. J. Lingane, ANAL. CHEM., **40**, 935 (1968).

(6) R. P. Buck, ANAL CHEM., **40**, 1432, 1439 (1968).
(7) K. Srinivasian and G. A. Rechnitz, *ibid.*, p 1955.
(8) *Ibid.*, p 509.
(9) H. A. Fales and M. J. Stammelman, *J. Amer. Chem. Soc.*, **95**, 1272 (1923).