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Standard Potentials of Alkali Metals, Silver, and Thallium Metal/Ion Couples in *N,N'*-Dimethylformamide, Dimethyl Sulfoxide, and Propylene Carbonate

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The relative standard potentials of alkali metals, silver, and thallium metal/ion couples in *N,N'*-dimethylformamide(DMF), dimethyl sulfoxide(DMSO), and propylene carbonate(PC) were measured against an aqueous saturated calomel electrode(SCE). These standard potentials of lithium, sodium, potassium, rubidium, caesium, thallium, and silver are −3.237, −2.898, −3.116, −3.079, −3.079, −0.643, and +0.372 V *vs.* SCE respectively in DMSO, and −3.163, −2.830, −3.067, −3.040, −3.048, −0.559, and +0.538 V *vs.* SCE respectively in DMF, and −2.906, −2.691, −3.002, −2.980, −2.986, −0.402, and +0.813 V *vs.* SCE respectively in PC. The thallium electrode was found to be stable enough to be used as a reference electrode in these solvents. For the purpose of examining the Debye-Hückel equation for estimating the activity coefficient, the formal potentials of the thallium electrode were measured at various ionic strengths. The Debye-Hückel equation was confirmed to be applicable in these solvents, provided a proper value was chosen for the ionic radius parameter, *a*, for each solvent—3.6 for DMSO, 5.0 for DMF and 0.0 for PC.

The measurements of the standard potentials of metal/ion couples in non-aqueous media have been made for only a few media, such as alcohols, acetonitrile, and liquid ammonia.[1] In this connection, we have attempted to determine the standard potentials of alkali metals, silver, and thallium metal/ion couples in DMF, DMSO, and PC. The method employed by Lewis and his co-workers[2-4] for the determination of the potentials of alkali metal electrodes in aqueous solutions is applicable for a variety of non-aqueous solvents. According to a modification of Lewis *et al.*'s method, we determined the potential of a dilute metal amalgam electrode against aqueous SCE equipped with a specially-constructed non-aqueous salt bridge. After correcting the difference in potential between the metal amalgam and the pure metal electrode, a relative potential series was determined for each solvent. The purpose of determining the potential of an electrode in a non-aqueous solvent is to find a stable electrode which can be used as a reference electrode in the solvent. For this purpose we studied the stability of alkali metal, silver, and thallium electrodes and found the potential of the thallium electrode to be very stable in these solvents. It is also important to confirm the applicability of the Debye-Hückel equation for calculating the activity coefficient in these solvents. In order to examine the applicability of the Debye-Hückel equation, the shifts of the formal potentials of the thallium amalgam electrodes were determined at various ionic strengths.

Experimental

Solvents and Electrolytes. The purification of DMF, DMSO, and PC, as well as the preparation and purification of tetraethylammonium perchlorate (TEAP) and perchlorates of alkali metals and thallium, have been described elsewhere.[5] The silver perchlorate was obtained commercially. The electrolytes were dried in a vacuum oven for several tens of hours at 70—100 °C.

Preparation of Metal Amalgams. The alkali metal amalgams were prepared by electrolysis; the aqueous solution of alkali metal chloride or nitrate was electrolyzed with a mercury cathode and a plutinum anode. The thallium amalgam was prepared by adding pure thallium metal to distilled mercury, heating them with an infrared lamp under a nitrogen atmosphere. The metal contents in the amalgams were determined by acidimetric titration;[6] the amalgams were decomposed in a 0.01 M H_2SO_4 solution, and then the excess acid was titrated with a standard NaOH solution. A pure silver rod was used as the silver electrode. The silver rod was polished well with fine emery paper and then with filter paper until a stable potential was obtained. The silver electrode was kept immersed in the solvent for several hours before use.

Measurement of the Potential with an Amalgam Electrode. The apparatus for storing the amalgam and measuring the potential was a modification of Lewis *et al.*'s cell. The cell equipment is given in Fig. 1. The reservoir (B) was evacuated first. The amalgam was introduced into the com-

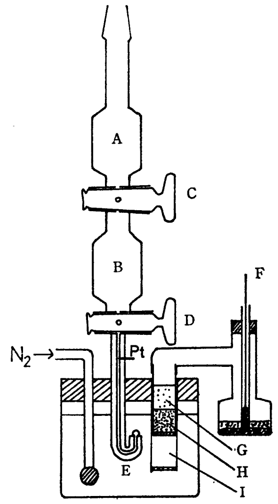

Fig. 1. Cell equipment for measurement of the potential of amalgam electrode.
A, B: amalgam reservoir. C, D: stopcock. E: capillary electrode. F: aqueous SCE. G: agar salt bridge composed of DMF-water mixture containing 0.05 M TEAP. H: agar salt bridge composed of aqueous solution containing 0.1 M NaCl. I: non-aqueous salt bridge containing 0.01 M TEAP.

partment (A) and then evacuated in order to remove the trace of water and oxygen, after which the amalgam was filtered into the reservoir (B) through the stopcock (C) by opening the stopcock (C) slightly with great caution. The prospect of the amalgam in the reservoir was the same as with pure mercury. Before measurement, the reservoir (B) was filled with pure nitrogen gas at a pressure of about 1.5 atm. Nitrogen gas was bubbled through the solution for 30 min, and an atmosphere of nitrogen was maintained during the measurement. The amalgam was admitted to the capillary electrode (E) from the reservoir (B) through the stopcock (D). The potential of the amalgam electrode was measured against an aqueous SCE equipped with a non-aqueous salt bridge.[7)] The potential of the electrode was measured at various concentrations of electroactive species, ranging from 1×10^{-4} to 2×10^{-3} M, under a constant ionic strength kept by TEAP. During the measurements, the cell was thermostated at 25.0±0.05 °C. The potential measurement was made with Yokogawa Hewlett-Paccard Model 2727 potentiometer.

Results and Discussion

The cell arrangement is as follows:

$$\begin{array}{c|c|c|cr} \text{SCE} & \text{TEAP } 0.01\text{ M} & \begin{array}{c}\text{TEAP } 0.01\text{ M}\\ \text{MClO}_4\ C\ \text{M}\end{array} & \text{M(Hg)} & (1) \\ & \text{(I)} & \text{(II)} & & \end{array}$$

Phase (I) is a salt bridge consisting of the same solvent as Phase (II). The electromotive force (e.m.f.) of this combination changed slowly on standing. A little more amalgam was admitted into the capillary electrode (E), thus effecting a removal of the electrode surface. When the surface was removed, the e.m.f. almost always returned to a given constant value, although occasionally it deviated from this value by several milli-volts. This was the case for alkali metal amalgams, especially when the concentration of the electroactive species was lower than 5×10^{-4} M. The potential was continuously monitered for a few hours. The total potential drift during this time was typically of the order of a few milli-volts for alkali metal amalgams and of several milli-volts for the silver electrode. The potential drift of the thallium amalgam was of the order of one to two milli-volts. The thallium amalgam electrode was very stable, especially when the concentration of Tl^+ in the solution was greater than 1×10^{-3} M, the potential drift did not exceed one milli-volt.

The overall potential of Cell (1) is given by;

$$E_{\text{cell}} = E_{\text{M}^+/\text{M(Hg)}} - E_{\text{SCE}} - E_{\text{LJ1}} - E_{\text{LJ2}} \qquad (2)$$

where E_{LJ1} and E_{LJ2} represent the liquid junction potentials of the left- and the right-hand junctions of the salt bridge respectively. By defining E'_{SCE} as $E'_{\text{SCE}}=E_{\text{SCE}}+E_{\text{LJ1}}$, and by assuming initially that the liquid junction potential, E_{LJ2}, is negligible and that the Debye-Hückel equation applies, the following relations can be written:

$$E'_{\text{cell}} = E_{\text{cell}} - 0.0591 \log C \qquad (3)$$

$$E'_{\text{cell}} = E^{\circ\prime}_{\text{M}^+/\text{M(Hg)}} - E'_{\text{SCE}} - (0.0591)\frac{A\sqrt{\mu}}{1+Ba\sqrt{\mu}} \qquad (4)$$

$$E^{\circ\prime}_{\text{M}^+/\text{M(Hg)}} = E^{\circ}_{\text{M}^+/\text{M}} + E_{\text{A}} \qquad (5)$$

where E'_{cell} is the formal potential of Cell (1) and where $E^{\circ\prime}_{\text{M}^+/\text{M(Hg)}}$ is the potential of the amalgam electrode when the activity of the metal ion in the solution is unity; $E^{\circ}_{\text{M}^+/\text{M}}$ is the standard potential of the metal/ion couple, and E_{A}, the e.m.f. of the following cell:

$$\text{M}|\text{M}^+|\text{M(Hg)} \qquad (6)$$

viz. the difference between the potentials of the metal and the amalgam electrode. The other terms have their usual meanings.

The E_{A} values of our amalgam electrodes were calculated from the literature values of the potential of Cell (6), in which the concentration of metal in the amalgam is different from ours. The concentrations of metal in our amalgams are given in Table 1, along with those in the amalgams used for the direct measurement of the potential of Cell (6) in the literature. The concentration of metal in the amalgams used in this work does not greatly differ from that used in the literature. Accordingly, the activity coefficients of metal in the two amalgams can reasonably be assumed to be equal. The potential of our amalgam electrode against the metal electrode can, therefore, be calculated from the following equation:

$$E_{\text{A2}} = E_{\text{A1}} - 0.0591 \log\frac{x_2}{x_1} \qquad (7)$$

where E_{A1} and E_{A2} indicate the e.m.f. of Cell (6), consisting of amalgam electrode used in the literature and in this work respectively, and where x_1 and x_2 are, respectively, the mole fraction of metal in each amalgam. The values of E_{A2} thus calculated are given in Table 1, along with the values of E_{A1}. The potential of the

TABLE 1. THE POTENTIAL OF AMALGAM ELECTRODE AGAINST METAL ELFCTRODE

	Concentration of metal in amalgam (mole fraction)		Potential of amalgam *vs.* metal electrode (V)	
	Amalgam given in literature	Amalgam used in this work	Amalgam given in literature	Amalgam used in this work
Lithium	0.01002[a)]	0.00212	0.9502[a)]	0.990
Sodium	0.01834[b)]	0.0168	0.8456[b)]	0.848
Potassium	0.01127[c)]	0.0176	1.0481[c)]	1.037
Rubidium	0.00540[d)]	0.00384	1.0745[d)]	1.083
Caesium	0.002827[e)]	0.00438	1.119[e)]	1.108
Thallium		0.00750		0.154

a) Ref. 3b. b) Ref. 2. c) Ref. 3a. d) Ref. 4. e) H. E. Bent, G. S. Forbes, and A. F. Forziati, *J. Amer. Chem. Soc.*, **61**, 709 (1939).

thallium amalgam electrode against the metallic thallium electrode was calculated by using Lewis and Randlall's results, which give the relation among the concentration of thallium in the amalgam, the activity coefficient of thallium, and the potential of the amalgam electrode against the matallic thallium electrode.[8] The potential of the thallium electrode thus estimated is also given in Table 1.

The equilibrium potential of Cell (1) was measured at various concentrations of electroactive species by maintaining the concentration of TEAP at 0.01 M. The values of the cell potential, E_{cell}, and the formal potential, E'_{cell}, are given in Tables 2—4. As the concentrations of electroactive species approach zero, the contents of bothphases, (I) and (II), in Cell (1) approach an identical solution of TEAP. Upon extrapolation to zero concentration of electroactive species, a potential, E'_{cell}, is obtained at a fixed ionic strength from which the liquid junction potential, E_{LJ2}, has been eliminated. For this purpose, the data were analyzed by the method of least squares; the results are also given in Tables 2, 3, and 4.

From the values of E'_{cell} at a fixed ionic strength, $E^{\circ\prime}_{\mathrm{M^+/M(Hg)}}-E'_{\mathrm{SCE}}$ can be calculated from Eq. (4) if we know the radius parameter, a, in the Debye-Hückel equation. The radius parameter, a, was determined as follows.

Table 2. Data from cell 1 in DMSO
(Potential: V *vs.* aq. SCE, *C*: mol l^{-1})

Lithium			Caesium		
$C\times10^3$	$-E_{\mathrm{cell}}$	$-E'_{\mathrm{cell}}$	$C\times10^3$	$-E_{\mathrm{cell}}$	$-E'_{\mathrm{cell}}$
0.298	2.454	2.248	0.302	2.184	1.976
0.680	2.447	2.260	0.690	2.170	1.983
1.047	2.437	2.261	1.063	2.164	1.988
2.312	2.424	2.258	2.346	2.148	1.992
$E'_{\mathrm{cell}}=-2.253\pm0.004$ at $\mu=0.01$			$E'_{\mathrm{cell}}=-1.977\pm0.002$ at $\mu=0.01$		
Sodium			Thallium		
$C\times10^3$	$-E_{\mathrm{cell}}$	$-E'_{\mathrm{cell}}$	$C\times10^3$	$-E_{\mathrm{cell}}$	$-E'_{\mathrm{cell}}$
0.295	2.262	2.054	0.145	0.723	0.496
0.673	2.247	2.060	0.332	0.705	0.486
1.037	2.237	2.061	0.512	0.694	0.499
2.289	2.219	2.063	1.130	0.675	0.502
$E'_{\mathrm{cell}}=-2.056\pm0.002$ at $\mu=0.01$			$E'_{\mathrm{cell}}=-0.495\pm0.001$ at $\mu=0.01$		
Potassium			Silver		
$C\times10^3$	$-E_{\mathrm{cell}}$	$-E'_{\mathrm{cell}}$	$C\times10^3$	$+E_{\mathrm{cell}}$	$+E'_{\mathrm{cell}}$
0.303	2.294	2.086	0.215	0.136	0.364
0.693	2.272	2.085	0.308	0.163	0.370
1.068	2.263	2.087	0.472	0.175	0.372
2.358	2.244	2.088	1.050	0.196	0.372
$E'_{\mathrm{cell}}=-2.085\pm0.001$ at $\mu=0.01$			$E'_{\mathrm{cell}}=+0.366\pm0.002$ at $\mu=0.01$		
Rubidium					
$C\times10^3$	$-E_{\mathrm{cell}}$	$-E'_{\mathrm{cell}}$			
0.298	2.210	2.002			
0.679	2.191	2.004			
1.047	2.182	2.006			
2.312	2.164	2.008			
$E'_{\mathrm{cell}}=-2.002\pm0.001$ at $\mu=0.01$					

Table 3. Data from cell (1) in DMF
(Potential: V *vs.* aq. SCE, *C*: mole l^{-1})

Lithium			Caesium		
$C\times10^3$	$-E_{\mathrm{cell}}$	$-E'_{\mathrm{cell}}$	$C\times10^3$	$-E_{\mathrm{cell}}$	$-E'_{\mathrm{cell}}$
0.298	2.388	2.179	0.299	2.155	1.947
0.679	2.371	2.183	0.683	2.139	1.952
1.047	2.360	2.183	1.052	2.119	1.950
2.312	2.339	2.182	2.323	2.108	1.952
$E'_{\mathrm{cell}}=-2.181\pm0.001$ at $\mu=0.01$			$E'_{\mathrm{cell}}=-1.948\pm0.001$ at $\mu=0.01$		
Sodium			Thallium		
$C\times10^3$	$-E_{\mathrm{cell}}$	$-E'_{\mathrm{cell}}$	$C\times10^3$	$-E_{\mathrm{cell}}$	$-E'_{\mathrm{cell}}$
0.303	2.199	1.989	0.146	0.638	0.412
0.693	2.182	1.994	0.333	0.620	0.413
1.068	2.173	1.995	0.514	0.610	0.416
2.358	2.155	1.997	1.133	0.590	0.410
			1.676	0.577	0.413
$E'_{\mathrm{cell}}=-1.990\pm0.001$ at $\mu=0.01$			$E'_{\mathrm{cell}}=-0.413\pm0.001$ at $\mu=0.01$		
Potassium			Silver		
$C\times10^3$	$-E_{\mathrm{cell}}$	$-E'_{\mathrm{cell}}$	$C\times10^3$	$+E_{\mathrm{cell}}$	$+E'_{\mathrm{cell}}$
0.306	2.246	2.038	0.151	0.301	0.527
0.699	2.229	2.042	0.345	0.326	0.531
1.078	2.221	2.045	0.532	0.336	0.529
2.381	2.204	2.048	1.173	0.355	0.528
			1.735	0.363	0.526
$E_{\mathrm{cell}}=-2.038\pm0.001$ at $\mu=0.01$			$E'_{\mathrm{cell}}=+0.530\pm0.001$ at $\mu=0.01$		
Rubidium					
$C\times10^3$	$-E_{\mathrm{cell}}$	$-E'_{\mathrm{cell}}$			
0.303	2.171	1.963			
0.693	2.156	1.969			
1.068	2.144	1.968			
2.358	2.126	1.970			
$E'_{\mathrm{cell}}=-1.965\pm0.002$ at $\mu=0.01$					

From Eq. (4) a plot of the formal potential of the cell against the $\sqrt{\mu}/(1+Ba\sqrt{\mu})$ term should be a straight line with the slope of $-0.0591\,A$. In DMSO, DMF, and PC at 25 °C, A and B are calculated to be 1.18 and 0.435 for DMSO, 1.73 and 0.493 for DMF, 0.717 and 0.363 for PC, respectively. The a term can be varied to give the best fit.

For the purpose of examining this relation, the formal potentials of the thallium amalgam electrode were measured at various concentrations of TEAP in the right-hand-half cell of Cell (1) by maintaining the concentration of TEAP in the Phase (I) at 0.01 M. This time, the measured formal potentials include the liquid junction potential, E_{LJ2}. In this case, the liquid interphase between Phases (I) and (II) is composed of the same solvent; only the concentrations of the same electrolyte TEAP differ from each other. For such a simple liquid interphase, Henderson equation for estimating the liquid junction potential can be used with sufficient accuracy. E_{LJ2} was calculated by the following Henderson equation:

$$E_{\mathrm{LJ2}} = 0.0591\frac{u_+-u_-}{u_++u_-}\log\frac{a_{\mathrm{II}}}{a_{\mathrm{I}}} \qquad (8)$$

Table 4. Data from cell (1) in PC
(Potential: V *vs.* aq. SCE, C: mol l^{-1})

Lithium

$C\times10^3$	$-E_{\text{cell}}$	$-E'_{\text{cell}}$
0.307	2.128	1.920
0.703	2.112	1.925
1.084	2.102	1.926
2.393	2.087	1.932

$E'_{\text{cell}}=-1.920\pm0.001$
at $\mu=0.01$

Sodium

$C\times10^3$	$-E_{\text{cell}}$	$-E'_{\text{cell}}$
0.306	2.054	1.846
0.700	2.040	1.853
1.078	2.029	1.854
2.381	2.014	1.858

$E'_{\text{cell}}=-1.847\pm0.002$
at $\mu=0.01$

Potassium

$C\times10^3$	$-E_{\text{cell}}$	$-E'_{\text{cell}}$
0.299	2.177	1.969
0.683	2.162	1.975
1.052	2.154	1.978
2.323	2.140	1.984

$E'_{\text{cell}}=-1.969\pm0.001$
at $\mu=0.01$

Rubidium

$C\times10^3$	$-E_{\text{cell}}$	$-E'_{\text{cell}}$
0.305	2.107	1.899
0.696	2.095	1.908
1.073	2.084	1.908
2.369	2.069	1.913

$E'_{\text{cell}}=-1.901\pm0.002$
at $\mu=0.01$

Caesium

$C\times10^3$	$-E_{\text{cell}}$	$-E'_{\text{cell}}$
0.296	2.090	1.882
0.676	2.076	1.889
1.042	2.070	1.894
2.300	2.057	1.901

$E'_{\text{cell}}=-1.882\pm0.002$
at $\mu=0.01$

Thallium

$C\times10^3$	$-E_{\text{cell}}$	$-E'_{\text{cell}}$
0.148	0.477	0.251
0.340	0.458	0.253
0.523	0.448	0.254
1.155	0.429	0.254
1.708	0.420	0.256

$E'_{\text{cell}}=-0.252\pm0.001$
at $\mu=0.01$

Silver

$C\times10^3$	$+E_{\text{cell}}$	$+E'_{\text{cell}}$
0.144	0.581	0.808
0.330	0.606	0.810
0.509	0.618	0.813
1.124	0.639	0.813
1.664	0.652	0.816

$E'_{\text{cell}}=+0.809\pm0.001$
at $\mu=0.01$

where a_{I} and a_{II} are the mean activities of ions in the Phases (I) and (II) respectively, and where u_+ and u_- are the ionic mobilities of the tetraethylammonium cation and the perchlorate anion respectively, which were obtained from conductance measeurments as 16.8 and 24.6 ohm^{-1} cm^2 in DMSO, as 36.9 and 50.6 ohm^{-1} cm^2 in DMF, and as 13.8 and 18.3 ohm^{-1} cm^2 in PC, respectively.[9] The contribution of the small amount of thallium perchlorate in the right-hand-half cell was neglected in this calculation. Plot of E'_{cell} against $\sqrt{\mu}/(1+Ba\sqrt{\mu})$ should, then, give a straight line with a slope of $-0.0591A\ \{1-(u_+-u_-)/(u_++u_-)\}$, again, a was used as a fitting parameter to obtain the best fit to the straight line. By means of this method we have determined the values of a for the solvents to be 3.6, 5.0, and 0.0 for DMSO, DMF, and PC respectively. The results, the plots of E'_{cell} corrected for the liquid junction potentials E_{LJ2} from Eq. (8) by the use of estimated a values, are shown in Fig. 2.

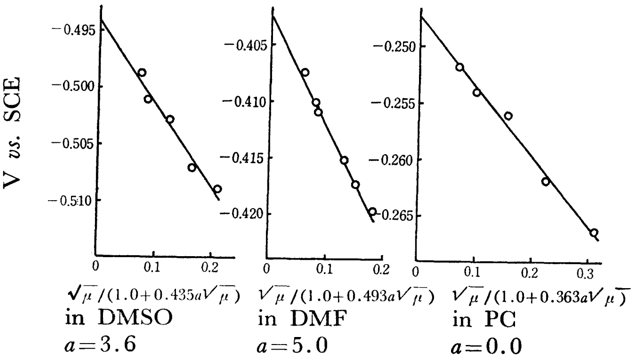

Fig. 2. Formal potential of thallium amalgam electrode as a function of ionic strength.

A satisfactory best fit was obtained for each solvent; these best fits indicate that the slopes of the straight lines are −0.073, −0.10, and −0.060 for DMSO, DMF, and PC respectively. For DMSO and DMF the experimentally-determined slopes are nearly equal to the theoretical values, −0.070 for DMSO and −0.102 for DMF, but for PC the experimental value is slightly different from the theoretical value, −0.042. In order to obtain the theoretical slope for PC, a value of −2.0 must be estimated for a. However, in this case the best fit to the straight line is not obtained; moreover, the negative value of a is not understandable. Accordingly, we tentatively estimate the value of a for PC to be 0.0. With the use of these values of a, small corrections in the potential due to the activity coefficient were calculated, and the values of $E^{\circ\prime}_{\text{M}^+/\text{M(Hg)}}-E'_{\text{SCE}}$ were obtained from Eq. (4). Then, the standard potentials, relative to the aqueous SCE, were calculated from Eq. (5); they are given in Table 5.

These standard potentials include the liquid junction potential between the aqueous and non-aqueous interphase, E_{LJ1}. The estimation of the liquid junction potential is made by comparing the experimentally-determined potential scale with the common potential scale established in a previous work.[5] The solvent shifts in the potential of rubidium by the transfer of the rubidium ion from water to these solvents have been estimated as −0.034 V for DMSO, +0.005 V for DMF, and +0.149 V for PC. Accordingly, the standard potentials of rubidium should be −3.200, −3.161, and −3.017 V *vs.* SCE in DMSO, DMF, and PC respectively, since the standard potential of rubidium in an aqueous solution has been given as −3.166 V *vs.* SCE.[10] By comparing these potentials of rubidium with the experimental values, the liquid junction potentials of aqueous and non-aqueous interphases were estimated as +0.121 V for DMSO, +0.121 V for DMF, and +0.037 V for PC against the aqueous phase. By correcting these liquid junction potentials, the standard potentials on the common potential scale—Corrected Rubidium Scale—were obtained; these values are shown in Table 5.

The liquid junction potentials estimated in this work are different from the values previously estimated from the polarographic half-wave potentials by +0.031 V for DMSO, by +0.036 V for DMF, and by +0.033 V for PC. These differences may be attributed partly to the different concentration of electrolyte in the non-aqueous phase in the two experiments: in present work the non-aqueous phase includes 0.01 M TEAP, while in the previous polarographic study it included 0.1 M TEAP. Moreover, these differences

Table 5. Standard potentials of metal/ion couples on the corrected rubidium scale and estimation of the liquid junction potential *vs.* the aqueous saturated calomel electrode

	DMSO		DMF		PC		Water[d)]
	$E^{\circ\mathrm{a)}}$	$E^{\circ\mathrm{b)}}$	$E^{\circ\mathrm{a)}}$	$E^{\circ\mathrm{b)}}$	$E^{\circ\mathrm{a)}}$	$E^{\circ\mathrm{b)}}$	E°
Lithium	−3.237	−3.358	−3.163	−3.284	−2.906	−2.943	−3.27
Sodium	−2.898	−3.019	−2.830	−2.951	−2.691	−2.728	−2.954
Potassium	−3.116	−3.237	−3.067	−3.188	−3.002	−3.039	−3.166
Rubidium	−3.079	−3.200	−3.040	−3.161	−2.980	−3.017	−3.166
Caesium	−3.079	−3.200	−3.048	−3.169	−2.986	−3.023	−3.164
Thallium	−0.643	−0.764	−0.559	−0.680	−0.402	−0·439	−0.577
Silver	+0.372	+0.251	+0.538	+0.417	+0.813	+0.776	+0.553
$E_{\mathrm{LJ1}}{}^{\mathrm{c)}}$		+0.121		+0.121		+0.037	

a) Standard potential measured directly against aqueous SCE. b) Standard potential on the corrected rubidium scale. Solvent shift in rubidium standard potential is −0.034 V for DMSO, +0.005 V for DMF and +0.149 V for PC by transfer of rubidium ion from water to these solvents as determined in Ref. 5. c) Estimated liquid junction potential against aqueous phase. d) Ref. 10.

may also be due to the solvent shift in the polarographic half-wave potentials caused by the variation in the diffusion constants and the salt activity coefficients of ions for changing the solvent.

At first, the present authors intended to estimate the solvent shift in the potential of rubidium by the application of the modified Born equation by the use of the standard potential series determined in this work. However, this attempt was unsuccessful, because the accuracy of the determined standard potentials was not good enough to be used for this purpose. The authors found that the potentials of an amalgam measured with different capillary electrodes showed a deviation of several milli-volts among them, although the potential of each electrode was stable by itself. The potential of the amalgam electrode must be affected by the structure of the capillary electrode. In this connection, for the purpose of obtaining more accurate and reproducible potentials, it would be worth-while to examine the utility of the dropping amalgam electrode used by Ulich and Spiegel.[11)]

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