Normalization of Potentials in Propylene Carbonate, Ethylene Carbonate, *N,N'*-Dimethylformamide, and Dimethyl Sulfoxide to the Water Scale Studied by Polarographic Method

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The polarographic behavior of alkali metal ions were studied in propylene carbonate(PC), ethylene carbonate(EC), water, *N,N'*-dimethylformamide(DMF), and dimethyl sulfoxide(DMSO). The polarographic half-wave potentials measured in these solvents against an aqueous saturated calomel electrode(SCE) were normalized to the potential of SCE in aqueous system by making corrections of potential required for transfer of rubidium ion from water to these solvents. The free energies of transfer of rubidium ion from water to other solvents were calculated by the application of the modified Born equation. The potential series on the normalized potential scale were given in the order DMSO<DMF<water<PC<EC, indicating that the metal ion-solvent interaction increases with increasing the electron donor property of the solvent. The solvent shifts in potential calculated by the application of the modified Born equation disagreed with the experimental results. In order to fit well the calculated solvent shifts in potential with the experimental results, following values of liquid junction potential must be assumed for these solvents; +0.090 V for DMSO, +0.085 V for DMF, +0.004 V for PC, and −0.064 V for EC against the aqueous phase.

One of the most urgent problems in non-aqueous electrochemistry is to find a way of intercorrelating the potential series measured in different solvents. A direct comparison of electrode potentials measured in various solvents is impossible in the thermodynamic sense. The main difficulty is that the unknown liquid junction potential is inevitably introduced when one attempts to calibrate the potential of a reference electrode in a given solvent against a universal common reference point *viz.* hydrogen electrode or SCE in the aqueous medium. Some efforts have been devoted to estimate the magnitude of the shift in potential for the transfer of a reference redox system from one solvent to another by the application of extrathermodynamic methods.[1,2] In one of these approaches, the standard potentials of redox systems of rubidium,[3,4] ferrocene,[5] cobaltocene,[5] or iron(II–III) complexes of phenanthroline and of its derivatives[6] have been assumed to be respectively constant in various solvents. The ion, constructing each redox system, has been considered to exert a similar type of a weak electrostatic interaction with various solvents, since the ion is symmetrical in shape and slightly polarizable and has large radius but small charge. Accordingly, there should be practically no difference in solvation energies by transfer of these preferred redox systems from one solvent to another. In an alternative way of approach the change in the solvation energy in the process of transferring the ion from one solvent to another was estimated on the assumption of "modified Born equation." The application of the Born equation[7] is in principle seriously limited owing to the ignorance of specific solvation or dielectric saturation effect of solvent towards solute ions. Nevertheless, a consistent value of free energy of solvation has been plausibly obtained, provided a correction term for crystal radius of an ion is introduced in Born equation as effective ionic radius which fits with the radius of a cavity present in the dielectric medium.[8] A similar approximation has been also proposed for Born equation by taking into account the dielectric properties of solvent in the nearest neighborhood of ions.[9] The classical method of Latimer's effective radii of hydrated ions has been recently revalued since there is no other reliable data on the variation of dielectric constant of solvent in the vicinity of solute ions.[10] In this connection, Koepp *et al.*[11] have estimated the solvation energies for rubidium ion in non-aqueous solvents by measuring the solubility products of alkali metal halides in various solvents. Still more, Coetzee *et al.*[12,13] calculated the free energy of transfer for rubidium ion in various nitriles by measuring the polarographic half-wave potentials.

Takaoka[14] proposed an experimental method to refer the polarographic half-wave potentials in DMF to an aqueous SCE. As a reference electrode, he used an aqueous SCE equipped with a non-aqueous salt bridge. He estimated the liquid junction potential at the interphase between the aqueous and the non-aqueous media negligibly small. However, his argument for estimating the liquid junction potential was based on only the transference phenomena of solute ions and the solvent shift in the activity coefficients of ions was not taken into account. Accordingly, his conclusion should be open to further examination.

In this work, polarographic behaviors of alkali metal ions in several selected organic solvents were studied for examining the reversibility of the electrode process. The free energy changes in transfer of rubidium ion from water to other solvents were evaluated from the reversible polarographic half-wave potentials by using the modified Born equation. The liquid junction potentials of the interphase between water and non-aqueous solvent were estimated by comparing the calculated solvent shift in potentials with the experimental results.

Experimental

Solvent. DMF was dehydrated over oven-dried potassium carbonate and DMSO was freed from impurities with activated alumina prior to distillation. PC and EC were treated with *p*-toluenesulfonic acid for the removal of basic contaminants.[15] All these solvents were distilled twice in a current of dry nitrogen gas at a reduced pressure of about 20 Torr. The water content of the middle fraction of the distillates was always less than 0.01%, as determined by the Karl-Fischer titration. Triply distilled water was used throughout the runs for the measurement in aqueous medium.

Electrolyte. Tetraethylammonium perchlorate(TEAP) was prepared by the double decomposition of tetraethylammonium iodide with sodium perchlorate.[16] The starting material, tetraethylammonium iodide, was synthesized by heating an equimolar mixture of triethylamine and ethyliodide at 80 °C for two hours in nitrobenzene.[17] Tetrabutylammonium perchlorate(TBAP) was prepared in a similar way as TEAP from tetrabutylammonium bromide which was synthesized by refluxing an equimolar mixture of tributylamine and butyl bromide in acetonitrile for 36 hours.[18] TEAP was recrystallized from hot water for five times. TBAP was purified by dissolving it in hot ethyl alcohol followed by precipitation with the addition of water, and this treatment was repeated for five times. Conversions into perchlorate of potassium, rubidium, caesium and thallium were made by the double decomposition of their chlorides or nitrates with perchloric acid. Zinc perchlorate was prepared by heating zinc metal to dryness with an excess of perchloric acid. Lithium and sodium perchlorates were obtained commercially. All these perchlorates were recrystallized from water for several times. The G. R. grade barium and silver perchlorates, and cadmium nitrate were used without further purification. All these electrolytes were kept over phosphorus pentoxide, and before use TEAP and TBAP were dried at 70 °C and other perchlorates at 100 °C in vacuum-oven.

Polarography. The polarographic measurement was made by using an H-type cell with compartments A and B separated by a sintered glass diaphragm. The dropping mercury electrode(DME) was inserted into compartment A and an agar salt bridge into compartment B. The salt bridge was prepared as follows: the lower half portion of a glass tubing sealed with a fine porosity sintered glass at one end was filled with agar solution composed of 70% DMF-30% water mixture containing 0.5 M TEAP, and then the upper half portion with aqueous agar solution containing 1.0 M sodium chloride. The potential drift caused by the salt bridge amounts to several tens of milli-volts immediately after the preparation of the salt bridge, while it fell to minimum after several tens of days of aging by immersing it in DMF. The potential of the SCE with the salt bridge was calibrated against an auxiliary aqueous SCE of common type. As the SCE of the former special type being kept in compartment B of the H-type cell, the DME in compartment A was replaced with another SCE of common type. Potential measurement between these two SCE was performed by allowing the KCl solution to flow out slightly from the latter aqueous SCE through a sintered glass.[14] Polarogram was recorded after the passage of nitrogen gas for 20 min. The potential was supplied manually with an accuracy of ±0.1 mV and iR drop was corrected. During the runs the temperature was kept at 40 °C for EC and at 25 °C for all other solvents. The DME has following characteristics; m=0.620 mg/s and t=4.0 s for water, m=0.764 mg/s and t=3.9 s in DMSO and m=0.727 mg/s and t=4.0 s in PC.

Results and Discussion

Reversibility. The DC and AC polarograms of alkali metal perchlorated indicated that the electrode process is one electron reduction process not only in aqueous medium but also in the non-aqueous solvents. The DC polarographic waves were diffusion-controlled as evidenced by the limiting currents proportional to the square root of the height of mercury head. The peak current of the AC polarogram was independent of the height of mercury head. A trace of water left unremoved in the non-aqueous media, if it is less than 0.1%, did not affect the half wave potential $E_{1/2}$ and the peak potential E_p. The reversibility of the electrode reaction was examined from the slope of $\log(i_d-i)/i$ *vs.* E plots, the half-width of E_p peak ($\delta E_{p/2}$) and the reversibility factor defined by the current ratio $i_p/i_d\tau^{1/2}$.[19] All these data are represented together with the potential values in Table 1. The observed waves were all reversible or quasi-reversible except for a few example, particularly for lithium ion.

Potentials in Aqueous Medium. In Table 1(a) the half wave potentials and the peak potentials of alkali metal ions at a fixed concentration of 1×10^{-3} M in 0.1 M TEAP aqueous solution are represented. The values of half-wave potential for alkali metal ions are in good agreement with those given in literatures.[4,20] The reversibilities were shown excellent as examined from the slope of log-plots, $\delta E_{p/2}$, $i_p/i_d\tau^{1/2}$ ratio and ($E_p-E_{1/2}$) by comparing them with the referred values of thallium(I) ion whose reversibility in perchlorate solution is well accepted.[21] By varing the concentration of supporting electrolyte in the range between 0.025 and 0.25 M, the $E_{1/2}$ values differed less than several milli-volts. Consequently, it is possible to assume that there is no association between the alkali metal cations and the perchlorate anion, at least in a TEAP concentration range cited above.[22–24]

Potentials in PC and EC. The results in Tables 1(b) and (c) for the potentials of alkali metal ions in PC and EC can be regarded as potential values of reversible process except for caesium in EC and lithium in both PC and EC. Despite of reversibility, an unusual form of polarogram was obtained in PC, showing an appreciable deviation of slope of log-plots, depending on whether a maximum or an average current is taken for DC ploarogram. The values in parentheses in Table 1(b) for the slope of log-plot made with the average current showed deviation from values of reversible wave. A correct analysis of DC polarogram in solvent of high viscosity,[13] PC, must be made with the maximum current polarogram.

Potentials in DMF and DMSO. The results in Tables 1(d) and (e) show that all the alkali metal ions except for lithium ion gave reversible wave in DMF and DMSO containing 0.1 M TEAP. The irreversibility of the polarographic wave of lithium ion was improved by using TBAP in place of TEAP as supporting electrolyte. However, in this time, there appeared a polarographic maximum, which made the accurate determination of the half-wave potential difficult. Since there was found no effective suppressor for the maximum in these solvents, the obtained potentials were less accurate for lithium. For this reason, with the exception for lithium, all the potential measurements were made by the use of TEAP. The half-

TABLE 1. POLAROGRAPHIC RESULTS OF ALKALI METAL IONS IN (a) WATER, (b) PC, (c) EC, (d) DMF AND (e) DMSO[a]

	DC polarography			AC polarography			
	$-E_{1/2}$ (V)	I_d	slope (mV)	$-E_p$ (V)	$\delta E_{p/2}$ (mV)	$i_p/i_d\tau^{1/2}$	$E_p-E_{1/2}$ (V)
(a) water							
Li+	2.332	2.38	56	2.339	105	38	−0.007
Na+	2.113	3.02	62	2.114	105	40	−0.001
K+	2.136	3.44	61	2.140	135	35	−0.004
Rb+	2.131	3.66	62	2.140	138	35	−0.009
Cs+	2.108	3.77	65	2.128	140	39	−0.020
(b) PC							
Li+	2.001	0.94	77[1] (82)[2]	2.039	155	11	−0.038
Na+	1.848	1.08	65 (65)	1.854	120	44	−0.006
K+	1.965	1.11	63 (62)	1.970	110	45	−0.005
Rb+	1.989	1.16	63 (67)	1.991	120	42	−0.002
Cs+	1.981	1.22	60 (72)	1.982	125	43	−0.001
(c) EC							
Li+	2.009	1.27	73	2.046	140	10	−0.037
Na+	1.861	1.28	70	1.862	150	29	−0.001
K+	1.986	1.45	70	1.986	130	33	0.000
Rb+	2.009	1.60	75	2.009	135	29	0.000
Cs+	2.011	1.59	77	2.046	170	27	−0.035
(d) DMF							
Li+	2.385[b]	1.65	91	2.425	170	2	−0.040
Na+	2.035	1.83	62	2.035	105	34	0.000
K+	2.055	1.84	63	2.060	108	35	−0.005
Rb+	2.045	1.91	62	2.050	105	42	−0.005
Cs+	2.011	2.04	58	2.013	98	39	−0.002
(e) DMSO							
Li+	2.578[b]	0.93	90	2.688	260	2	−0.110
Na+	2.075	1.24	60	2.075	120	38	0.000
K+	2.093	1.34	63	2.095	115	45	−0.002
Rb+	2.075	1.33	60	2.075	120	46	0.000
Cs+	2.047	1.46	61	2.050	120	49	−0.003

1) Values obtained from maximum current polarogram.
2) Values obtained from mean current polarogram.

a) $E_{1/2}$ and E_p are half-wave and peak potentials directly measured against aq. SCE. I_d is polargraphic diffusion current constant; $i_d/Cm^{2/3}t^{1/6}$. $\delta E_{p/2}$ is the half width of AC current peak. $i_p/i_d\tau^{1/2}$ is the reversibility factor, τ is the drop time at AC peak, in s. b) The half-wave potentials of lithium ion in DMF and DMSO are 2.308 and 2.461, respectively when TBAP was used as supporting electrolyte.

wave potentials of alkali metal ions showed a good internal consistency with those given in literatures.[25,26]

The shifts in half-wave potentials with increasing the concentration of TEAP are shown in Fig. 1. The shift in the half wave potential of lithium ion was found to be abnormally large to an extent of exceeding the usual effect of increasing ionic strength. The unusual behavior of lithium ion has not been clearly explained. As the reversibility was found to be recovered for lithium ion by the use of TBAP, the ion-pair formation of lithium ion with perchlorate anion in TEAP solution is not the primary reason for the unusually large negative shift of the half-wave potential. It is worthy to note the similar observation made by Izutsu *et al.*, *i. e.* an unexpectedly large negative values of the half-wave potential of alkali metal ions of small radius with TEAP or TMAP(tetramethylammonium perchlorate) in hexamethylphosphoramide, but a small shift with TPAP(tetrapropylammonium perchlorate) or TBAP.[27]

Significance of Half-Wave Potential. A systematic survey on the reversible polarograhpic half-wave potentials for a group of cations provides data for evaluating the free energy of solvation of the cations. An approach for obtaining a common potential scale in various solvents is undertaken by evaluating the free energy of transfer of cation from one solvent to another. The evaluation of transfer free energy is based on the assumption that the standard potential of metal-ion system can be obtained by Born-Haber cycle, involving the free energies of sublimation ΔG°(sub), ionization ΔG°(ion), photoelectric work function ΔG°(w). The thermodynamic expression for standard potential E° in absolute scale is given by Eq. (1).

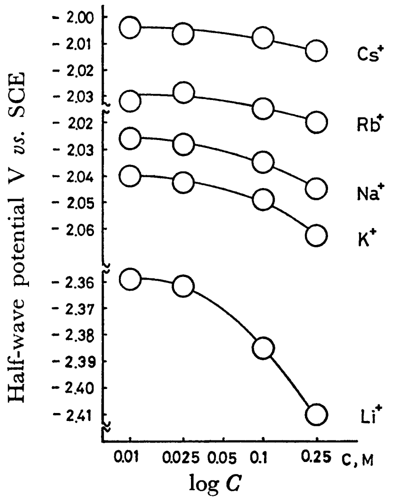

Fig. 1. Half-wave potentials of alkali metal ions in DMF at various concentration of TEAP (A similar result was obtained for DMSO).

$$nE^\circ F = \Delta G^\circ(\text{sub}) - \Delta G^\circ(\text{ion}) - \Delta G^\circ(\text{w}) + \Delta G^\circ(\text{solv}) \quad (1)$$

The reversible polarographic half-wave potentials are related to the standard potential of amalgam electrode by Eq. (2),

$$E_{1/2} = E^\circ_{\text{amalgam}} - \frac{RT}{nF}\ln\frac{f'}{f} - \frac{RT}{nF}\ln\frac{\sqrt{D}}{\sqrt{D'}} \quad (2)$$

where f and f' are activity coefficients, and D and D' are diffusion coefficients respectively, the values being concerned with metallic ion in solution and metal in amalgam. The second and third terms of Eq. (2) make a very small contribution to $E_{1/2}$, since the ratio f'/f and D/D' deviate not largely from unity. The reversible polarographic half-wave potential is regarded as a good approximation of standard amalgam potential.[29] The difference between the standard electrode potential and the standard amalgam electrode potential is given by the free energy of amalgamation. In as much as the calculation of the transfer free energy of ions between solvents is concerned, the free energy of amalgamation can be out of consideration, because of the cancellation of this free energy term by computing the potential difference of identical amalgam electrode in two different solvents.

The ambiguity involved in the evaluation of transfer free energy of ions from the observed polarographic half wave potential data is due to the undetermined activity coefficients and diffusion coefficients in Eq. (2). However, these ambiguous terms can be excluded from consideration by taking the potential difference between a pair of cations i_+ and j_+, $\underset{i_+-j_+}{\Delta} E_{1/2}$, for each solvent and then by taking the difference of this difference in two solvents k and l, $\underset{k-l}{\Delta}\,\underset{i_+-j_+}{\Delta} E_{1/2}$. The ratio of the activity coefficients as well as the ratio of the diffusion coefficients for a pair of ions, appearing in the double comparison cited above, are nearly constant irrespective of the kind of solvent, as being evidenced from Eq. (2) by calculating the activity coefficient with the Debye-Hückel equation and by replacing the diffusion coefficient with the polarographic diffusion current constant given in Table 1. Accordingly, by taking the solvation energy difference between a pair of ions $\Delta\Delta G^\circ(\text{solv})$ from Eq. (1), the expression for the transfer free energy is written as

$$nF\,\underset{k-l}{\Delta}\;\underset{i_+-j_+}{\Delta}\;\Delta E_{1/2} = (\Delta\Delta G^\circ{}_{i_+,j_+}(\text{solv}))_k - (\Delta\Delta G^\circ{}_{i_+,j_+}(\text{solv}))_l \quad (3)$$

Effective Radii of Solvated Ions by the Application of Born Equation. The free energy change in electrostatic work for transfering a pair of gaseous ions, with diameters r_+ and r_- and charges z^+ and z^-, to a medium of dielectric constant ε is given by the modified Born equation.

$$\Delta G_\pm{}^\circ(\text{solv}) = -(Ne^2/2)\left(1-\frac{1}{\varepsilon}\right) \times \{z_+{}^2/(r_+ + R_+') + z_-{}^2/(r_- + R_-')\} \quad (4)$$

In Eq. (4) R_+' and R_-' are empirical correction terms for solvated cations and anions, respectively, and N denotes Avogadro's number. There are two most basic assumptions in Eq. (4); first, the interaction of alkali metal ions with solvent is predominantly electrostatic in nature, and second, the contribution of the neutral part of solvation energy is to the same extent for all the solvents according to the zero energy assumption.[9]

In this work the perchlorate salts were employed as common anion and the specific interaction between alkali metal cations and perchlorate anion is unimportant even at 0.1 M of TEAP concentration as evidenced by the concentration dependence of half-wave potentials on TEAP (Fig. 1). Consequently, the contribution of anionic species to the solvation energy can be discounted because of its invariant values for any couple of the ion pairs. On this ground the double comparison procedure in Eq. (3) is a reasonable way of calculation for relative values of cationic solvation energy by eliminating the contribution from the anionic part.

The expression for $\Delta\Delta G^\circ{}_{i_+,j_+}$ (solv) is, then, given by Eq. (5), showing the solvation energy difference between a couple of cations i_+ and j_+ in each solvent. For simplification, $\Delta\Delta G^\circ{}_{i_+,j_+}$ (solv) is denoted by $\Delta\Delta G^\circ{}_{i_+,j_+}$ in the following discussion.

$$\Delta\Delta G^\circ{}_{i_+,j_+} = -(Ne/2)(1-1/\varepsilon)\{1/(r_{i_+} + R_+') - 1/(r_{j_+} + R_+')\} \quad (5)$$

The expression for calculating the transference free energy between non-aqueous solvent S and aqueous solution is given by Eq. (6).

$$(\Delta\Delta G^\circ{}_{i_+,j_+})_{\text{aq}} - (\Delta\Delta G^\circ{}_{i_+,j_+})_{\text{S}} = -(Ne^2/2)[(1-1/78.5) \times \{1/(r_{i_+} + R'_{+\text{aq}}) - 1/(r_{j_+} + R'_{+\text{aq}})\} - (1-1/\varepsilon_{\text{S}})\{1/(r_{i_+} + R'_{+\text{S}}) - 1/(r_{j_+} + R'_{+\text{S}})\}] \quad (6)$$

The value for dielectric constant for aqueous solution ε_{aq} is taken as 78.5 esu at 25 °C and for radius correction term the value of 0.72 Å was tentatively assigned to $R'_{+\text{aq}}$ in Eq. (6). All values except for $R'_{+\text{S}}$ have been found; r_+ from crystal data, ε_{S} from dielectric data and $\Delta\Delta G^\circ$ from our potential data. The values of radius correction term $R'_{+\text{S}}$ were obtained from Eq. (6) and the results are shown in Table 2. A comparison was made in Table 2 with the published data for the solvents other than our's. In the solvent system so far investigated, there exists a

TABLE 2. ESTIMATION OF THE RADIUS CORRECTION TERM R_+'

	Donor number[a)]	R_+' (Å)	ε[b)]
Benzonitrile	11.9	0.83[c)]	25.2
Acetonitrile	14.1	0.82[c)]	38.0
Sulpholane	14.8	0.80[c)]	43.0
Propylene carbonate	15.1	0.82	65.1
Iso-butyronitrile	15.4	0.79[c)]	20.2
Propionitrile	16.1	0.80[c)]	26.1
Ethylene carbonate	16.4	0.86	89.6 (40 °C)
Acetone	17.0	0.74[c)]	20.7
Water	18.0	0.72[d)]	78.5
N,N'-Dimethylformamide	26.6	0.69	36.7
Dimethyl sulfoxide	29.8	0.68	46.4

a) Taken from V. Gutmann and E. Wychera, *Inorg. Nucl. Lett.*, **2**, 257 (1966). b) Dielectric constant at 25 °C. c) Taken from Ref. 13. d) Taken from Ref. 9.

close relation with the donor number rather than the dielectric constant of the solvent for the radius correction term. The value R_+' decreases with increasing value of the donor number. This means that a solvent of large donor number shows a strong interaction with the solute cation. The theoretical values of $\Delta\Delta E_{1/2}$ were calculated by the use of R_+' given in Table 2. A comparison was made for $\Delta\Delta E_{1/2}$ between experimental and the theoretical values in Table 3. The agreement is reasonablly good except for lithium ion, indicating that the radius correction term is a convenient and very useful parameter for computing the solvation energy of free ions in these solvents.

Transfer Energy of Rubidium Ion. The estimation of the potential shift caused by changing the solvent for rubidium ion was made by use of the R_+' values in Table 2. The results are given in Table 4, along with the experimental potential shifts. If the liquid junction potentials were properly calibrated the calculated values of solvent shift in potential should coincide with the experimental values. The data represented in Table 4 show poor agreements between the theoretically expected values and the experimentally obtained ones. The deviations shown in fourth row of Table 4 are far greater than a limit of 10 mV expected inevitably for the difference in salt activity coefficient and diffusion coefficient in Eq. (2). This discrepancy can mainly be attributed to the liquid junction potential appeared in the interface between the aqueous SCE and applied organic solvent containing 0.1 M of TEAP. The liquid junction potentials shown in the fifth row of Table 4 are the average values for the difference of half-wave potentials of alkali metal ions between the theoretically computed and experimentally obtained data. These liquid junction potentials must be reduced from the experimentally obtained half-wave potentials for the purpose to intercorrelate the potentials in different solvents on the common potential scale (Corrected Rubidium Scale). The half-wave potential series of cations on the common potential scale are alined in the order DMSO<DMF<water<PC<EC, the more negative value indicating the stronger solvation, showing a good agreement with the cationic solvation property of these solvents.[30,31]

Comment to the Ferrocene Scale and the Rubidium Scale. Half-wave potentials of cations referred to those of ferrocene and rubidium are given in Table 5. A con-

TABLE 3. COMPARISON OF THE CALCULATED AND THE OBSERVED $\Delta\Delta E_{1/2}$ BY TAKING RUBIDIUM AS REFERENCE[a)]

	DMSO		DMF		PC		EC	
	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd
Li^+	−0.185[b)]	−0.075	−0.062[b)]	−0.038	+0.189	+0.203	+0.201	+0.266
Na^+	−0.018	−0.034	−0.008	−0.015	+0.123	+0.094	+0.129	+0.124
K^+	−0.013	−0.008	−0.005	−0.004	+0.029	+0.022	+0.028	+0.028
Rb^+	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Cs^+	+0.005	+0.007	+0.011	+0.003	−0.015	−0.023	−0.025	−0.031

a) $\Delta\Delta E_{1/2}=(\Delta E_{1/2})_S-(\Delta E_{1/2})_W$: $(\Delta E_{1/2})_S$ is the difference of the half-wave potential of metal ions with respect to that of rubidium ion in solvent S, and $(\Delta E_{1/2})_W$ is that in water. b) Half-wave potential obtained by using TBAP as supporting electrolyte.

TABLE 4. ESTIMATION OF THE SOLVENT SHIFT OF RUBIDIUM STANDARD POTENTIAL AND OF LIQUID JUNCTION POTENTIAL *vs.* THE AQUEOUS SATURATED CALOMEL ELECTRODE

	DMSO	DMF	PC	EC
$E_{tr}(Rb)$[a)]	−0.069	−0.029	+0.109	+0.155
$E_{tr}(Rb)_{obsd}$[b)]	+0.056	+0.086	+0.142	+0.122
$E_{s,m}$[c)]	−0.035	−0.034	−0.040	−0.034
$E_{LJ}(Rb)$[d)]	+0.090	+0.081	−0.007	−0.067
E_{LJ}[e)]	+0.090	+0.085	+0.004	−0.064

a) Calculated solvent shift of rubidium standard potential. Correction for the solvent molality is included. b) Observed solvent shift of the half-wave potential of rubidium. c) Correction for the solvent molality on the solvent shift of the standard potential. d) Estimated liquid junction potential. The value of b)-a)-c). e) Average value of the estimated liquid junction potentials for all alkali metals.

TABLE 5. COMPARISON OF HALF WAVE POTENTIALS IN VARIOUS SOLVENTS ON THE RUBIDIUM SCALE, USING 0.1 M TEAP AS THE SUPPORTING ELECTROLYTE[a)]

	DMSO	DMF	Water	PC	EC	ACN[b)]
Li^+	−0.386[c)]	−0.263[c)]	−0.201	−0.012	0.000	+0.03
	(−0.297)	(−2.83)	(−2.47)	(−2.36)		(−2.36)
Na^+	0.000	+0.010	+0.018	+0.141	+0.147	+0.13
	(−2.55)	(−2.52)	(−2.27)	(−2.22)		(−2.25)
K^+	−0.018	−0.010	−0.005	+0.024	+0.023	+0.02
	(−2.53)	(−2.52)	(−2.28)	(−2.32)		(−2.34)
Rb^+	0.000	0.000	0.000	0.000	0.000	0.000
Cs^+	+0.028	+0.034	+0.023	+0.008	−0.002	+0.01
Tl^+	+1.557	+1.566	+1.676	+1.722	d)	+1.71
Zn^{2+}	+1.003	+1.060	+1.147	+1.722	d)	+1.71
	(−1.50)	(−1.43)	(−1.14)	(−1.02)		(−1.03)
Cd^{2+}	+1.388	+1.471	+1.569	+1.697	d)	+1.72
Ba^{2+}	+0.024	+0.004	+0.094	+0.203	d)	+0.35
Ag^+	+2.387	e)	e)	e)	d)	+2.40

a) The values given in parentheses are the half-wave potentials on the ferrocene scale cited in T. Fujinaga and K. Izutsu, *Kagaku to Kogyo*, **23**, 117 (1970). b) Data from Ref. 4. The other data were determined in this work. c) Half-wave potential obtained by using TBAP as supporting electrolyte. d) Not measured. e) Immeasurable.

tradictory behavior is noticed between the rubidium and the ferrocene scale for the transfer of potassium ion from water to acetonitrile(ACN). On the ferrocene scale, the shift in the half-wave potential of potassium for the transfer of potassium ion from water to ACN, $\underset{\text{A-W}}{\Delta}\ \underset{\text{K}^+\text{-Fe}}{\Delta}\ E_{1/2}$, is given as −0.06 V, whereas on the rubidium scale, $\underset{\text{A-W}}{\Delta}\ \underset{\text{K}^+\text{-Rb}^+}{\Delta}\ E_{1/2}$ is given as +0.03 V; opposite signs of $\Delta\Delta E_{1/2}$ were obtained whether the half-wave potential of potassium was referred to the ferrocene scale or to the rubidium scale. Suzuki *et al.*[32)] have reported a similar observation; the half-wave potentials of thallium and cadmium referred to the ferrocene scale shifted to more negative with increasing content of ACN in ACN–water mixture, while half-wave potentials referred to the rubidium scale shifted to less negative.

ACN is a poor solvent for inorganic electrolyte and yields a smaller solvation energy for inorganic ions. Accordingly, the free energy in transfer of ions from water to ACN is positive, resulting in a positive value of $\Delta\Delta E_{1/2}$. The observed contradiction in $\Delta\Delta E_{1/2}$ is probably due to the inaccuracy of the ferrocene scale. The solubility of ferrocene in ACN is greater than in water by a factor of 10^4.[6,12)] A large increase of the ferrocene solubility in ACN results in a large shift of the redox potential of ferrocene-ferricinium couple to less negative side by the change of solvent from water to ACN. Accordingly, it is quite probable that such a potential shift to the negative direction is expected by the transfer of ions from water to a solvent of high ferrocene solubility, when ferrocene is chosen as reference. In fact, it can be seen from the potential data in Table 5 that the ferrocene scale gives about 0.1 V more negative shift of potential in transfer of cations from water to ACN than the rubidium scale does.

Furthermore, it would be worthy to give a comment to the method employed by Strehlow and his coworkers to correct the ferrocene scale. They calculated the electrostatic free energy change in transfer of ferricinium ion from water to ACN by the modified Born equation with a radius correction term R_+' which was obtained for alkali metal cations. It should be noticed that the radius correction term is very sensitive to the specific interaction between solute ion and solvent molecules, and accordingly, a value of R_+' obtained for a series of alkali metal ions, whose interaction with solvent is similar among them, should not be applied for ferricinium ion whose interaction with solvent is quite different from that of alkali metal ions.

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