March, 1978] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (3), 783—789 (1978) 783

Experimental Studies of the Liquid Junction Potential between Electrolyte Solutions in Different Solvents. I. Water–Organic Solvent Junctions

Kosuke Izutsu, Toshio Nakamura, Toshihiko Kitano, and Chieko Hirasawa

Department of Chemistry, Faculty of Science, Shinshu University, Asahi, Matsumoto 390

(Received June 6, 1977)

The liquid junction potential (ljp) between water and organic solvents was investigated by measuring the emfs of cells with free-diffusion junctions of various electrolyte solutions. In most experiments, the concentration of the electrolyte on one side of a junction was kept much larger than that on the other side (c MX in S$//c'$ M'X' in S'; S or S' is H_2O and $c \gg c'$); thus the ljp was mainly determined by MX. The ljp may practically be expressed by the sum of $E_{\mathrm{j,ion}}$ (concn)(I), $E_{\mathrm{j,ion}}$ (ion-solv.)(II), and $E_{\mathrm{j,solv.}}$ (III). I and II are contributions from ionic species: I is the concentration term, which can be estimated approximately from the Henderson equation, and II is the term due to the difference in ionic solvations in S and S'. III is the contribution from the transfer of solvent molecules. The sum of II and III for the case in which S=H_2O is approximately equal in absolute value but opposite in sign to that for the case in which S'=H_2O. The change of II with the anion X^- is in linear relation with free energy of transfer of the anion from S to S'. The change of III with the bridge solvent is also a linear function of the heat (or free energy) of solution of S into S'. The rate of the change with the heat of solution can be divided in two classes by the species of the cation M^+: the rate for R_4N^+ ions is just a half of that for such ions as Li^+, Na^+, Mg^{2+}, and Ba^{2+}. The effect of the mixed bridge electrolytes and the mixed bridge solvents was also examined.

Because the problem of the liquid junction potential (abbreviated 'ljp') between electrolyte solutions in different solvents is of considerable importance in the electrochemistry of non-aqueous solvents, many reports have recently appeared concerning this problem.[1—10] According to Alfenaar, DeLigny, and Remijnse,[3] the value of the ljp, E_{j}, at such a junction as (A) can, in principle, be estimated by carrying out the integration of Eq. 1

$$c\,\mathrm{MX}\ \text{in solvent}\ \mathrm{S}\underset{\mathrm{J}}{//}c'\,\mathrm{M'X'}\ \text{in solvent}\ \mathrm{S'} \tag{A}$$

$$E_{\mathrm{j}} = -\frac{1}{F}\int_{\mathrm{S}}^{\mathrm{S'}} \sum_{\mathrm{i}} t_{\mathrm{i}}^{\mathrm{r}} \mathrm{d}\mu(\mathrm{i}), \tag{1}$$

where $t_{\mathrm{i}}^{\mathrm{r}}$ and μ(i) are the reduced transport number[11] and the chemical potential, respectively, of chemical species i, and the sum extends over all species, charged and uncharged, present at the junction. The reduced transport number $t_{\mathrm{i}}^{\mathrm{r}}$ is equal to $t_{\mathrm{i}}/z_{\mathrm{i}}$ for an ion with charge z_{i} and transport number t_{i}, while $t_{\mathrm{i}}^{\mathrm{r}}$ for an uncharged species can be defined by nF/Q, where n is the amount of substance of the uncharged species transported across the junction when a quantity of charge Q flows through the cell. Alfenaar *et al.*[3] considered that E_{j} can be expressed by the sum of two terms, *i.e.*, $E_{\mathrm{j,ion}}$, which is the contribution from ionic species, and $E_{\mathrm{j,solv.}}$, which is the contribution from solvent molecules:

$$E_{\mathrm{j}} = E_{\mathrm{j,ion}} + E_{\mathrm{j,solv.}}, \tag{2}$$

$$E_{\mathrm{j,ion}} = -\frac{1}{F}\int_{\mathrm{S}}^{\mathrm{S'}} \sum_{\mathrm{ions}} \frac{t_{\mathrm{i}}}{z_{\mathrm{i}}} \mathrm{d}\mu(\mathrm{i}), \tag{3}$$

$$E_{\mathrm{j,solv.}} = -\frac{1}{F}\int_{\mathrm{S}}^{\mathrm{S'}} \sum_{\substack{\text{solvent}\\ \text{molecules}}} t_{\mathrm{i}}^{\mathrm{r}} \mathrm{d}\mu(\mathrm{i}). \tag{4}$$

To carry out the above integrations, however, is difficult because of the difficulties in getting enough knowledge concerning $t_{\mathrm{i}}^{\mathrm{r}}$ and dμ(i), which actually determine the ljp between different solvents. Therefore, at the present stage, it seems important to get detailed experimental information about the factors influencing the ljp. An interesting approach from this standpoint has been reported by Cox *et al.*[5] But experimental results are still too scarce to elucidate this problem completely.

In the present study, we have measured emfs of many cells with liquid junction(s) between different solvents, in order to learn how the ljp is influenced by the solvents and electrolytes present at the junction(s). A simple cell, which was constructed by using a dual four-way stopcock, gave free-diffusion junctions and was convenient for rapid, repeated measurements of the emf. We also tried to correlate the results of these emf measurements with the literature data of ion-solvent and solvent-solvent interactions. For such data, we mainly referred to the report of Parker and his coworkers.[5,12]

If we carry out the integrations in Eqs. 3 and 4 under the following simplifying assumptions

(i) c' is negligibly small compared to c,

(ii) the molar conductivity for each ion and $t_{\mathrm{i}}^{\mathrm{r}}$ for each molecule do not vary throughout the boundary, and

(iii) the concentration of each ion changes linearly at the boundary, then we can get Eqs. 5—8 from Eqs. 2—4

$$E_{\mathrm{j}} = E_{\mathrm{j,ion}}(\text{concn}) + E_{\mathrm{j,ion}}(\text{ion-solv.}) + E_{\mathrm{j,solv.}}, \tag{5}$$

$$E_{\mathrm{j,ion}}(\text{concn}) = \frac{RT}{F}(t_{\mathrm{M^+}} - t_{\mathrm{X^-}})\ln\frac{c\Lambda(\mathrm{MX})}{c'\Lambda(\mathrm{M'X'})}, \tag{6}$$

$$E_{\mathrm{j,ion}}(\text{ion-solv.}) = -\frac{1}{F}[t_{\mathrm{M^+}}{}^{\mathrm{S}}\Delta\mu^{\mathrm{S'}}(\mathrm{M^+}) - t_{\mathrm{X^-}}{}^{\mathrm{S}}\Delta\mu^{\mathrm{S'}}(\mathrm{X^-})], \tag{7}$$

$$E_{\mathrm{j,solv.}} = -\frac{1}{F}t_{\mathrm{S}}^{\mathrm{r}}\,{}^{\mathrm{S}}\Delta\mu^{\mathrm{S'}}(\mathrm{S}), \tag{8}$$

where ${}^{\mathrm{S}}\Delta\mu^{\mathrm{S'}}(\mathrm{M^+})$, ${}^{\mathrm{S}}\Delta\mu^{\mathrm{S'}}(\mathrm{X^-})$, and ${}^{\mathrm{S}}\Delta\mu^{\mathrm{S'}}(\mathrm{S})$ represent changes in standard chemical potentials of M^+, X^-, and S, respectively, on crossing the boundary from S to S' in the process which actually determines the ljp. Equations 6 and 7 are similar to those recently reported by Gaboriaud.[8] In obtaining Eq. 8, we consider that $E_{\mathrm{j,solv.}}$ receives its chief contribution from the solvent molecule S which is transported from S to S′ with the transfer of electrolyte MX. As is apparent from Eqs. 5 to 8, when condition (i) is satisfied, the effect of M′X′ appears only in the term $E_{\mathrm{j,ion}}$(concn) and the ljp should be almost independent of the species of M′X′, provided that c' and Λ(M′X′) are kept constant. In the present study, we carried out most experiments in cells in which condition (i) is satisfied, after confirming experimentally that the above prediction actually holds.*

By the help of the above simplified equations, we could find some correlations between the ljp and the literature data of ion-solvent and solvent-solvent interactions. In this report, we present the results obtained concerning the water-organic solvent junctions. Detailed results concerning the ljp between different organic solvents will be reported elsewhere.

Experimental

Reagents. The preparation and purification of all tetraethylammonium and tetrabutylammonium salts used in this study were carried out by the conventional procedures. Tetramethylammonium perchlorate was obtained from the Nakarai Chemicals Co., Ltd., and was a product for polarographic use. Anhydrous silver perchlorate and lithium perchlorate, both obtained commercially, were used after drying at 70 and 200 °C, respectively, under a vacuum. Anhydrous sodium perchlorate was prepared by recrystallizing from a hot aqueous solution and was dried at 200 °C under a vacuum. All the other reagents were of analytical reagent grade.

Dimethyl sulfoxide (DMSO), *N*,*N*-dimethylformamide (DMF), propylene carbonate (PC), and acetonitrile (AN) were purified following the methods described in Ref. 13. Nitromethane (NM), acetone (Ac), and methanol (MeOH) were of analytical reagent grade and were purified by distillation.

Apparatus. For emf measurements, the cell shown schematically in Fig. 1 was constructed by using a dual four-way stopcock obtained from the Kyowa Seimitsu Co., Ltd. This stopcock is the one used for high speed liquid chromatography; its liquid path is made of Teflon and has a bore of 1 mm. By turning the stopcock to the position of Fig. 1(A), each of the three compartments of the cell is filled with an appropriate solution. The stopcock is then turned to the position of Fig. 1(B), which results in the formation of sharp liquid boundaries (free-diffusion junctions) at J_1 and J_2. The emf of the cell is established soon after turning the stopcock and remains constant within ±1 mV for a few minutes. After the measurement of the emf, the stopcock is turned back to the position of Fig. 1(A) and the solution in each compartment is renewed. Then, by turning the stopcock to the position of Fig. 1(B), the emf can be measured repeatedly. The ljps obtained with this cell were reproducible within ±1 mV. The emf was measured with a voltmeter with an input impedance of 10^{11} ohms. All measurements were carried out in a room thermostated at about 25 °C.

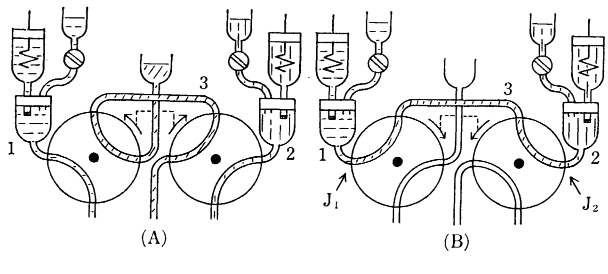

Fig. 1. Cell for emf measurements.

Results and Discussion

Emf Measurements of Cells I and II. Emfs of cells I and II were measured by changing solvents S_1 and S_2 and electrolyte MX:

$$\mathrm{Ag/10^{-3}\,M\ AgClO_4,\ 1M\ NaClO_4(S_1)\underset{j1}{//}1M\ NaClO_4(S_1)\underset{J1}{//}}$$

$$\mathrm{0.1\,M\ MX(S_1)\underset{J2}{//}10^{-3}\,M\ Et_4NClO_4(S_2{=}S_1\ or\ H_2O)\underset{j2}{//}5\times}$$

$$\mathrm{10^{-3}\,M\ AgClO_4,\ 5\times10^{-3}\,M\ Et_4NClO_4(S_2{=}S_1\ or\ H_2O)/Ag} \qquad \text{Cell I**}$$

$$\mathrm{aq\ SCE\underset{j1}{//}3M\ NaCl(S_1{=}H_2O)\underset{J1}{//}0.1\,M\ MX(S_1{=}H_2O)\underset{J2}{//}}$$

$$\mathrm{10^{-3}\,M\ Et_4NClO_4(S_2)\underset{j2}{//}5\times10^{-3}\,M\ AgClO_4,\ 5\times10^{-3}\,M}$$

$$\mathrm{Et_4NClO_4(S_2)/Ag} \qquad \text{Cell II}$$

where S_1 in cell I was MeOH, AN, PC, DMSO, or DMF, S_2 in cell II was H_2O, MeOH, AN, PC, DMSO, or DMF, and MX was Me_4NClO_4, Et_4NClO_4, Pr_4NClO_4, Bu_4NClO_4, $LiClO_4$, $NaClO_4$, $Mg(ClO_4)_2$, $Ba(ClO_4)_2$, Et_4NPic, Et_4NI, Et_4NBr, Et_4NCl, or Et_4NNO_3. The measured emf values were corrected for the ljps at j_1, j_2, and J_1, which were calculated by using the Henderson equation (Eq. 23 in Ref. 14) and the conductivity data.[15] The corrected emf values are shown in Tables 1 and 2. The change in corrected emf values with the change of MX corresponds to the change in the ljp at J_2. In Table 3, the values of $\Delta E(\mathrm{I})=[$corrected emf$(S_2{=}H_2O)-$corrected emf$(S_2{=}S_1)]$ for cell I and $\Delta E(\mathrm{II})=[$corrected emf$(S_2{\neq}H_2O)-$corrected emf$(S_2{=}H_2O)]$ for cell II are tabulated. If we consider that $E_{\mathrm{j,ion}}$(concn) for the case in which $S_2{\neq}S_1$ is nearly equal to that for the case in which $S_2{=}S_1$ (see Eq. 6), then we can think that ΔE(I) and ΔE(II) are nearly equal to $[E_{\mathrm{Ag/Ag^+}}(S_2{=}H_2O)-E_{\mathrm{Ag/Ag^+}}(S_2{=}S_1)+E_{\mathrm{j,ion}}(\text{ion-solv.})+E_{\mathrm{j,solv.}}]$ for cell I and $[E_{\mathrm{Ag/Ag^+}}(S_2\neq H_2O)-E_{\mathrm{Ag/Ag^+}}(S_2=H_2O)+E_{\mathrm{j,ion}}(\text{ion-solv.})+E_{\mathrm{j,solv.}}]$ for cell II, respectively. Though both ΔE(I) and ΔE(II) changed considerably (sometimes by more than 200 mV) with the change of MX, it is interesting to note that, for most kinds of MX used, the absolute values of ΔE(I) and ΔE(II) for the case in which S_1 for cell I and S_2 for cell II were the same organic solvent agreed with each other within several millivolts. Because, in this case, $E_{\mathrm{Ag/Ag^+}}(S_2{=}H_2O)$ and $E_{\mathrm{Ag/Ag^+}}(S_2{=}S_1)$ for cell I should be equal to $E_{\mathrm{Ag/Ag^+}}(S_2{=}H_2O)$ and $E_{\mathrm{Ag/Ag^+}}(S_2{\neq}H_2O)$ for cell II, the

---

* An example of such an experiment was that the emf of the cell, $\mathrm{Ag/0.01\,M\ AgClO_4,\ 0.1\,M\ Et_4NClO_4(AN)//0.1\,M\ Et_4NClO_4(AN)\underset{J1}{//}10^{-3}\,M\ Et_4NX(AN)\underset{J2}{//}0.1\,M\ Et_4NClO_4(H_2O)//0.01\,M\ AgClO_4,\ 0.1\,M\ Et_4NClO_4(H_2O)/Ag}$, was constant within several millivolts even when the anion X^- was changed from Pic^- to Cl^-. When compared with the large emf changes of cell III with the anion X^- (Fig. 4(C)), this result may be regarded as a confirmation of the above prediction.

** M = mol dm^{-3}.

TABLE 1. CORRECTED EMFS OF CELL I (in mV)

MX	S_1					S_1				
	MeOH	AN	PC	DMSO	DMF	MeOH	AN	PC	DMSO	DMF
	$S_2=S_1$					$S_2=H_2O$				
Me_4NClO_4	(−39)	−18	−48	−77	−71	(−131)	173	−246	184	0
Et_4NClO_4	(−38)	−22	−51	−83	−77	(−157)	140	−273	172	−17
Pr_4NClO_4	−47	−31	−63	−95	−85	−191	110	−303	148	−47
Bu_4NClO_4	−54	−37	−70	−103	−91	−213	91	−321	134	−66
$LiClO_4$	−52	−31	−70	−100	−92	−164	179	−227	141	−38
$NaClO_4$	−46	−26	−65	−97	−84	−130	200	−204	155	−16
$Mg(ClO_4)_2$*	−68	−45	−77	−112	100	−176	172	−234	128	−50
$Ba(ClO_4)_2$*	−66	−45	−81	−113	102	−158	181	−234	135	−48
Et_4NCl	−26	−21	−45	−87	−77	−203	17	−427	38	−162
Et_4NBr	−29	−21	−44	−87	−75	−193	46	−397	73	−127
Et_4NI	−33	−22	−50	−88	−76	−173	87	−344	122	−77
Et_4NNO_3	−32	−23	−54	−90	−78	−181	64	−374	97	−103
Et_4NPic	(−23)	−10	−34	−73	−63	(−94)	185	−222	218	32

* The correction was made by assuming that the ljp at J_1 is equal to that for $MX=LiClO_4$. Values in parentheses show that the solubility of MX was less than 0.1 M.

TABLE 2. CORRECTED EMFS OF CELL II (in mV)

MX	S_2					
	H_2O	MeOH	AN	PC	DMSO	DMF
Me_4NClO_4	378	471	186	572	117	307
Et_4NClO_4	361	480	196	585	104	298
$LiClO_4$	372	477	158	526	127	316
$NaClO_4$	386	467	154	530	138	320
$Mg(ClO_4)_2$*	359	462	138	524	117	305
$Ba(ClO_4)_2$*	363	455	136	520	119	308
Et_4NCl	355	525	323	734	226	434
Et_4NBr	353	512	288	704	189	398
Et_4NI	354	488	248	653	142	348
Et_4NNO_3	359	506	272	682	167	376

* The correction was made by assuming that the ljp at J_1 is equal to that for $MX=LiClO_4$.

TABLE 3. ΔE(I) AND ΔE(II) (in mV)*

MX	Organic solvent									
	MeOH		AN		PC		DMSO		DMF	
	ΔE(I)	ΔE(II)	ΔE(I)	ΔE(II)	ΔE(I)	ΔE(II)	ΔE(I)	ΔE(II)	ΔE(I)	ΔE(II)
Me_4NClO_4	(−92)	+93	+191	−192	−198	+194	+261	−261	+71	−71
Et_4NClO_4	(−119)	+119	+162	−165	−222	+224	+255	−257	+60	−63
Pr_4NClO_4	−144	—	+141	—	−240	—	+243	—	+38	—
Bu_4NClO_4	−159	—	+128	—	−251	—	+237	—	+25	—
$LiClO_4$	−112	+105	+210	−214	−157	+154	+241	−245	+54	−56
$NaClO_4$	−84	+81	+226	−232	−139	+144	+252	−248	+68	−66
$Mg(ClO_4)_2$	−108	+103	+217	−221	−157	+165	+240	−242	+50	−54
$Ba(ClO_4)_2$	−92	+92	+226	−227	−153	+157	+248	−244	+54	−55
Et_4NCl	−177	+170	+38	−32	−382	+379	+125	−129	−85	+79
Et_4NBr	−164	+159	+67	−65	−353	+351	+160	−164	−52	+45
Et_4NI	−140	+134	+109	−106	−294	+299	+210	−212	−1	+6
Et_4NNO_3	−149	+147	+87	−87	−320	+323	+187	−192	−25	+17
Et_4NPic	(−71)	—	+195	—	−188	—	+291	—	+95	—

* ΔE(I) = [corrected emf($S_2=H_2O$) − corrected emf($S_2=S_1$)] for cell I and ΔE(II) = [corrected emf($S_2 \neq H_2O$) − corrected emf($S_2=H_2O$)] for cell II.

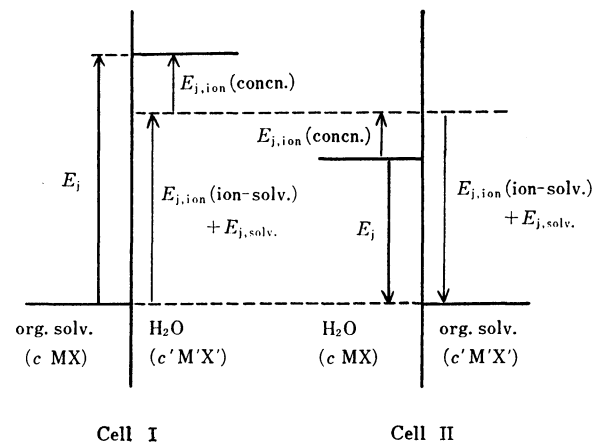

Fig. 2. Schematic representation of the ljp at J_2 in cells I and II ($c \gg c'$).

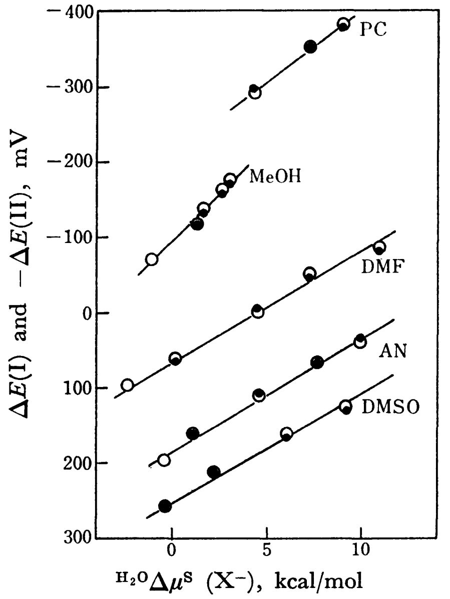

Fig. 3. ΔE(I) (○) and $-\Delta E$(II) (●) as the function of $^{H_2O}\Delta\mu^S(X^-)$. Organic solvent is given along each line. X^- on each line are, from right to left, Cl^- Br^-, I^-, ClO_4^-, and Pic^-. (Plots for ClO_4^- and Pic^- are not given when the values of $^{H_2O}\Delta\mu^S(X^-)$ are not available.)

above results seem to show that the absolute values of $E_{j,\mathrm{ion}}$(ion-solv.)$+E_{j,\mathrm{solv.}}$ for cells I and II agree with each other within several millivolts. (We found that similar relations can be obtained at any junctions possible between such organic solvents as MeOH, AN, DMSO, and DMF.[16]) This situation is illustrated schematically in Fig. 2. Probably it would be reasonable to consider that the above statement holds for each $E_{j,\mathrm{ion}}$(ion-solv.) and $E_{j,\mathrm{solv.}}$.

In Fig. 3, the values of ΔE(I) and ΔE(II) at various water-organic solvent junctions with Et_4NX as MX are plotted as functions of the free energies of transfer of X^- from H_2O to organic solvent S, $^{H_2O}\Delta\mu^S(X^-)$. For $^{H_2O}\Delta\mu^S(X^-)$, we referred to the values of Ref. 12 which were obtained under the extrathermodynamic assumption of $^{H_2O}\Delta\mu^S(Ph_4As^+) = {}^{H_2O}\Delta\mu^S(Ph_4B^-)$. Excellent linear correlations are always obtained between ΔE and $^{H_2O}\Delta\mu^S(X^-)$, as can be expected from Eq. 7. (If $E_{j,\mathrm{solv.}}$ is independent of X^-, the change in ΔE can be considered to correspond to that in $E_{j,\mathrm{ion}}$(ion-solv.). Because the molar ion conductivities of the anions other than picrate are nearly equal to each other,[15] t_{M^+} and t_{X^-} in the present case may be considered to remain approximately constant, irrespective of the species of X^-.) The slopes, however, change with the organic solvents: the slopes are between 14 and 15 mV/(kcal/mol) for AN, DMSO, and DMF, but *ca.* 17 mV/(kcal/mol) for PC and *ca.* 25 mV/(kcal/mol) for MeOH. According to Eq. 7, the slopes in Fig. 3 for such organic solvents as AN, DMSO, and DMF correspond to t_{X^-} of about 0.3_5, which seems to be smaller than that expected from the conductivity data ($t_{X^-} > 0.6$).[15] Therefore, the linear correlation in Fig. 3 cannot be regarded as in quantitative agreement with Eq. 7. The larger slopes for PC and MeOH cannot be explained from the conductivity data. Though the mechanism determining these slopes cannot be elucidated from the present study, it may be that $\Delta\mu(X^-)$ and/or t_{X^-} expected from the literature data are effective only partially in the processes which determine the ljp.

The change in E_j with the cations of MX is somewhat more complicated and will be discussed in the next section.

Emf Measurements of Cell III. The emf of cell III was measured by changing the bridge electrolytes and solvents:

$$\mathrm{Ag/5\times10^{-3}\,M\ AgClO_4,\ 5\times10^{-3}\,M\ Et_4NClO_4(S_1{=}AN)}\underset{j1}{//}$$
$$\mathrm{10^{-3}\,M\ Et_4NClO_4(S_1{=}AN)}\underset{J1}{//}\mathrm{0.1\,M\ MX(S_3)}\underset{J2}{//}\mathrm{10^{-3}\,M}$$
$$\mathrm{Et_4NClO_4(S_2{=}H_2O)}\underset{j2}{//}\mathrm{5\times10^{-3}\,M\ AgClO_4,\ 5\times10^{-3}\,M}$$
$$\mathrm{Et_4NClO_4(S_2{=}H_2O)/Ag} \qquad \text{Cell III}$$

where S_3 was AN, PC, NM, Ac, DMSO, or DMF, and MX was Et_4NClO_4, Me_4NClO_4, Pr_4NClO_4, Bu_4NClO_4, $LiClO_4$, $NaClO_4$, $Mg(ClO_4)_2$, $Ba(ClO_4)_2$, Et_4NPic, Et_4NBF_4, Et_4NI, Et_4NBr, Et_4NCl, or Et_4NNO_3. The results are summarized in Fig. 4. Solvents S_3 are designated on the abscissa at the corresponding emfs of cell III, in which the bridge electrolyte is 0.1 M Et_4NClO_4.

Figures 4(A) and 4(B) show that the emf for each bridge electrolyte changes approximately linearly against the abscissa, and that the slopes of these straight lines can be classified according to the bridge cations in two groups, *i.e.*, one for tetraalkylammonium ions and the other for such cations as Li^+, Na^+, Mg^{2+}, and Ba^{2+}. The slope of the second group is just twice that of the first group.*** In Fig. 4(A) the values of $\Delta\Delta H_s = {}^{S3}\Delta H^{S1}(S_3) - {}^{S3}\Delta H^{S2}(S_3)$ obtained from Table I in Ref. 5 are also plotted against a similar abscissa (here, $^{S3}\Delta H^{S1}(S_3)$ represents the heat per mole of transfer of S_3 from S_3 to S_1). A good linear relation is observed for all aprotic solvents used as S_3 (*cf.* Ref. 5).

When the bridge solvent S_3 in cell III changes, the ljps at both J_1 and J_2 may change. From Eqs. 6 to 8,

---

*** A similar phenomenon was also observed when picrates, instead of perchlorates, were used as MX.

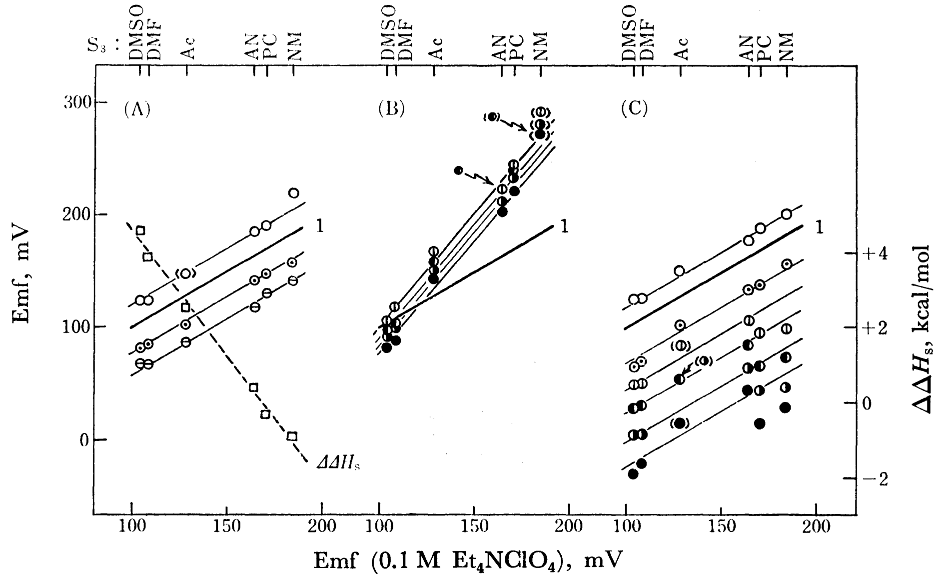

Fig. 4. Emf of cell III and $\Delta\Delta H_s$ (see text).
(A) and (B) for $MX = MClO_4$. M^+: 1 Et_4N^+; ○ Me_4N^+; ⊙ Pr_4N^+; ⊖ Bu_4N^+; ⦶ Na^+; ◑ Li^+; ◐ Ba^{2+}; and ● Mg^{2+}. (C) for $MX = Et_4NX$. X^-: 1 ClO_4^-; ○ Pic^-; ⊙ BF_4^-; ⦶ I^-; ◐ NO_3^-; ◑ Br^-; and ● Cl^-.

the sum of the ljps at J_1 and J_2 can be expressed by the sum of the following three terms:

$$E_{j,\mathrm{ion}}(\mathrm{concn})_{(J1+J2)} \approx 0, \tag{9}$$

$$E_{j,\mathrm{ion}}(\text{ion-solv.})_{(J1+J2)} = -\frac{1}{F}[t_{M^+}{}^{S1}\Delta\mu^{S2}(M^+) - t_{X^-}{}^{S1}\Delta\mu^{S2}(X^-)], \tag{10}$$

$$E_{j,\mathrm{solv.}(J1+J2)} = \frac{1}{F}t^r_{S3}[{}^{S3}\Delta\mu^{S1}(S_3) - {}^{S3}\Delta\mu^{S2}(S_3)] = \frac{1}{F}t^r_{S3}\Delta\Delta\mu_s. \tag{11}$$

If these simplified equations may be assumed to hold in cell III, the change of the bridge solvent (S_3) affects only the term of $E_{j,\mathrm{solv.}(J1+J2)}$, and the emf of cell III is expected to change linearly with the change of $\Delta\Delta\mu_s = [{}^{S3}\Delta\mu^{S1}(S_3) - {}^{S3}\Delta\mu^{S2}(S_3)]$. Here, the following relations have been found by Cox *et al.*:[5] ${}^S\Delta\mu^{H_2O}(S) \approx ({}^S\Delta H^{H_2O}(S) + 3\ \mathrm{kcal\ mol^{-1}})/2$ and ${}^S\Delta\mu^{AN}(S) \approx {}^S\Delta H^{AN}(S)/2$, where S denotes an organic solvent. Therefore, the good linear correlations in Figs. 4(A) and 4(B) between $\Delta\Delta H_s$ and the change in emf indicate that Eq. 11 is, at least qualitatively, a reasonable representation.† Here we must point out that, as was found by Cox *et al.*,[5] the change in ${}^S\Delta\mu^{H_2O}(S)$ is generally much larger than the change in ${}^S\Delta\mu^{AN}(S)$. Thus, most of the change in emf of cell III with the bridge solvent should be attributed to the change in $E_{j,\mathrm{solv.}}$ at J_2 (water–organic solvent junction). This has been confirmed experimentally from the investigation of the ljp between different aprotic solvents.[16]

In deriving Eq. 8, we assumed that solvent molecules which are transferred across the boundary with the bridge electrolyte determine $E_{j,\mathrm{solv}}$. The fact that two classes of straight lines with a simple slope ratio (1 : 2) are obtained might be an indication that solvent molecules are really carried across the junction with the bridge electrolyte and that the number of the solvent molecules determines the ljp. It is difficult, however, to understand why the slopes are the same for all tetraalkylammonium perchlorates, on one hand, and for the perchlorates of Li^+, Na^+, Mg^{2+}, and Ba^{2+}, on the other hand, even though there exist considerable differences in ionic mobilities and solvations among the cations in each group.

We showed in Table 3 that the difference of ΔE between such bridge cations as Li^+, Na^+, Mg^{2+}, and Ba^{2+} is relatively small. The results in Fig. 4(B) also show that these cations behave in approximately the same way. Similar phenomena have also been observed at junctions between different organic solvents.[16] Cox *et al.*[5] tried to attribute this small difference in ljp among these cations to the compensating effect of two factors, the free energies of transfer of cations and their mobilities. We would rather consider, however, that it is because the contribution from these cations to $E_{j,\mathrm{ion}}$(ion-solv.) is actually relatively small. This can be supported by the following reasoning: Parker and his coworkers[4,5] considered that, when the bridge electrolyte is 0.1 M Et_4NPic, the value of $E_{j,\mathrm{ion}}$(ion-solv.) is generally small. If this is correct, the ljp of cell III with 0.1 M Et_4NPic as the bridge electrolyte may be considered to be small when $\Delta\Delta H_s$ becomes +3 kcal/mol, because $\Delta\Delta\mu_s$ is then approximately zero and $E_{j,\mathrm{solv.}}$ may also be expected to be small. From Fig. 4(C), the emf of cell III with 0.1 M Et_4NPic bridge electrolyte is *ca.* 140 mV at 123 mV of the abscissa at which $\Delta\Delta H_s = +3$ kcal/mol. We find from Fig. 4(B) that the emfs of cell III with such bridge cations as Li^+, Na^+, Mg^{2+}, and Ba^{2+} are also near 140 (±15) mV at $\Delta\Delta H_s = +3$ kcal/mol, a good coincidence with the above emf value (here the contribution from the perchlorate ion may be considered to be relatively

---

† The results in Fig 4 show that t^r_{S3} in Eq. 11 has negative values.

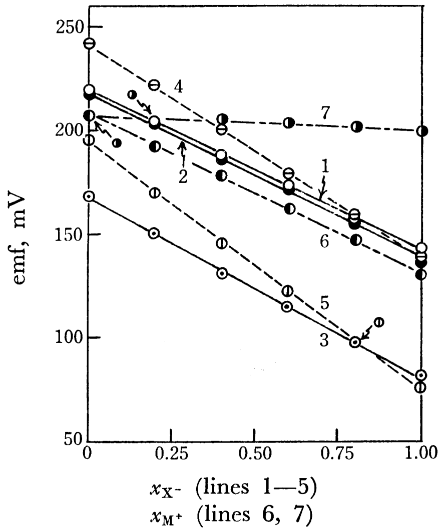

Fig. 5. Changes of emfs of cells IV and IV′ with the molar ratios of the mixed bridge electrolytes.
Lines 1—5 are for cell IV and lines 6 and 7 for cell IV′. $X^-=Br^-$ and $Y^-=ClO_4^-$ for lines 1(○), 2(●), and 3(⊙), $X^-=Br^-$ and $Y^-=Pic^-$ for lines 4(⊖) and 5(⦶), $M^+=Bu_4N^+$ and $N^+=Na^+$ for line 6(◐), and $M^+=Li^+$ and $N^+=Na^+$ for line 7(◑). Solvent S_3 is AN for lines 2, 4, 6, and 7, H_2O for line 1, and DMF for lines 3 and 5.

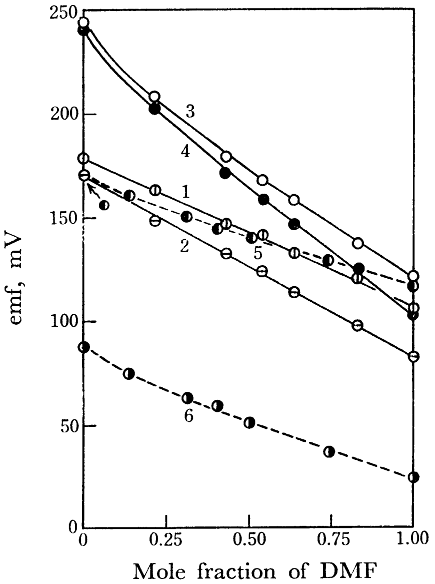

Fig. 6. Changes of emfs of cells V and V′ with the mole fractions of mixed bridge solvents.
Lines 1—4 for cell V′. M^+: 1(⦶) Et_4N^+; 2(⊖) Bu_4N^+; 3(○) Na^+; and 4(●) Li^+. Lines 5 and 6 for cell V. X^-: 5(◐) ClO_4^-; and 6(◑) Br^-.

small). A similar coincidence between the emf of the cell with 0.1 M Et_4NPic bridge electrolyte and those with 0.1 M bridge electrolytes of the perchlorates of these cations was observed at $\Delta\Delta\mu_s \approx 0$ also in the case in which MeOH, instead of H_2O, was used as S_2 in cell III.[16]

The effect of tetraalkylammonium ions on the ljp at water–organic solvent junctions was considerable, as is shown in Table 3. When these ions were used as the bridge cations in cell III, the emf decreased with the increase of the cationic size, as can be expected from Eq. 10 (Fig. 4(A)). But quantitative study is difficult because the available data concerning the free energy of transfer of these ions is insufficient.

Figure 4(C) shows that the effect of bridge anions on the emf of cell III is quite large. If we consider the emfs of the cell in which the bridge solvents are AN, DMSO, and DMF, we find that the emf changes linearly with the bridge solvents, with slopes approximately equal for all bridge anions, and the lines shift to smaller emf values from picrate to chloride ions. Because ${}^{S}\Delta\mu^{AN}(X^-)$ is smaller than ${}^{S}\Delta\mu^{H_2O}(X^-)$, most of the change in the emf with the bridge anions corresponds to the change in ljp at J_2 (see Fig. 3). When the bridge solvent was PC or NM, however, deviations from linearity occurred, especially with halogenide and nitrate ions, as can also be expected from the results in Fig. 3.

Use of a Salt Bridge Consisting of Mixed Electrolytes or Mixed Solvents. Salt Bridge Consisting of Mixed Electrolytes: The emfs of cells IV and IV′ were measured by changing the ratio of the mixed electrolytes in the salt bridge. The results are represented in Fig. 5.

$$Ag/5\times10^{-3}\,M\ AgClO_4,\ 10^{-2}\,M\ Et_4NClO_4(AN)\underset{j1}{//}10^{-2}\,M$$

$$Et_4NClO_4(AN)\underset{J1}{//}0.1x M\ Et_4NX\text{-}0.1(1-x)M\ Et_4NY(S_3)\underset{J2}{//}$$

$$10^{-2}\,M\ Et_4NClO_4(H_2O)\underset{j2}{//}5\times10^{-3}\,M\ AgClO_4,\ 10^{-2}\,M$$

$$Et_4NClO_4(H_2O)/Ag \qquad \text{Cell IV}$$

$$Ag/10^{-2}\,M\ AgClO_4(AN)\underset{J1}{//}0.1x M\ MClO_4\text{-}0.1(1-x)M$$

$$NClO_4(S_3)\underset{J2}{//}10^{-2}\,M\ AgClO_4(H_2O)/Ag \qquad \text{Cell IV}'$$

Lines 1—3 were obtained for cell IV in which $X^-=Br^-$, $Y^-=ClO_4^-$, and solvent S_3 was AN, H_2O, and DMF, respectively. All these lines were straight. Because the molar conductivities of Br^- and ClO_4^- are approximately equal in all the solvents concerned, this linear relation is what can be expected. If $X^-=Br^-$ and $Y^-=Pic^-$ in cell IV or $M^+=Bu_4N^+$ or Li^+ and $N^+=Na^+$ in cell IV′, there exist some differences between the molar conductivities of X^- and Y^- or M^+ and N^+.[15] But the changes of emfs with the molar ratio of the mixed electrolyte were also almost linear, as shown by lines 4 to 7. This can be understood if we consider that the relations $x\Lambda_{Et_4NX}/[x\Lambda_{Et_4NX}+(1-x)\Lambda_{Et_4NY}]$ *vs.* x and $x\Lambda_{MClO_4}/[x\Lambda_{MClO_4}+(1-x)\Lambda_{NClO_4}]$ *vs.* x are almost linear even when there exist some differences in molar conductivities.

Salt Bridge Consisting of Mixed Solvents: The results in Fig. 6 were obtained by measuring emfs of cells V and V′ for various ratios of the mixed bridge solvents.

$$Ag/5\times10^{-3}\,M\ AgClO_4,\ 10^{-2}\,M\ Et_4NClO_4(AN)\underset{j1}{//}10^{-2}\,M$$

$$Et_4NClO_4(AN)\underset{J1}{//}0.1\,M\ Et_4NX(AN+DMF)\underset{J2}{//}10^{-2}\,M$$

$$Et_4NClO_4(H_2O)\underset{j2}{//}5\times10^{-3}\,M\ AgClO_4,\ 10^{-2}\,M$$

$$Et_4NClO_4(H_2O)/Ag \qquad \text{Cell V}$$

$$Ag/10^{-2}\,M\ AgClO_4(AN)\underset{J1}{//}0.1\,M\ MClO_4(PC+DMF)\underset{J2}{//}$$

$$10^{-2}\,M\ AgClO_4(H_2O)/Ag \qquad \text{Cell V}'$$

When M^+ in cell V′ was Et_4N^+ or Bu_4N^+, the emfs changed almost linearly with the mole fraction of the solvents. But deviations from linearity occurred when M^+ in cell V′ was Na^+ or Li^+, and X^- in cell V was Br^- or ClO_4^-. To predict the effect of the mixed solvents is rather difficult. Besides the effect to the solvent component of the ljp, $E_{j,\mathrm{solv.}}$, the effect of the preferential ionic solvation by one of the mixed solvents must be taken into account. In the cases of Fig. 6, lines 3 and 4, the deviation from linearity seems to be due to the preferential solvation of DMF to the bridge cations (Na^+ and Li^+).

In the present report, we have examined in detail how the ljps between water and organic solvents are influenced by the solvents and electrolytes present at the junctions and found that some of the influence can be correlated, at least qualitatively, with the literature data concerning ion-solvent and solvent-solvent interactions. The influence at the junctions between water and organic solvents is much larger than that at any junctions possible between such organic solvents as MeOH, AN, PC, DMF, and DMSO.[16] Therefore, we must take this influence carefully into account when we measure emfs of cells involving water-organic solvent junctions. The results in the present report will be of use in such cases.

References

1) I. M. Kolthoff, *J. Polarogr. Soc.*, **10**, 22 (1964).

2) J. F. Coetzee and J. J. Campion, *J. Am. Chem. Soc.*, **89**, 2513, 2517 (1967).

3) M. Alfenaar, C. L. DeLigny, and A. G. Remijnse, *Recl. Trav. Chim. Pays-Bas*, **86**, 986 (1967).

4) R. Alexander, A. J. Parker, J. H. Sharp, and W. E. Waghorne, *J. Am. Chim. Soc.*, **94**, 1148 (1972).

5) B. G. Cox, A. J. Parker, and W. E. Waghorne, *J. Am. Chem. Soc.*, **95**, 1010 (1973).

6) N. Matsuura and K. Umemoto, *Bull. Chem. Soc. Jpn.*, **47**, 806, 813, 1334 (1974).

7) J. W. Diggle and A. J. Parker, *Aust. J. Chem.*, **27**, 1617 (1974).

8) R. Gaboriaud, *J. Chim Phys.*, **72**, 347 (1975).

9) R. C. Murray, Jr., and D. A. Aikens, *Electrochim. Acta*, **21**, 1045 (1976).

10) M. Cappelletti, P. Longhi, and T. Mussini, *Gazz. Chem. Ital.*, **106**, 241 (1976).

11) A. J. Staverman, *Trans. Faraday Soc.*, **48**, 176 (1952).

12) B. G. Cox, G. R. Hedwig, A. J. Parker, and D. W. Watts, *Aust. J. Chem.*, **27**, 477 (1974).

13) K. Izutsu, "Denkyoku-hanno no Kiso," ed by T. Osa, Kyoritsu Shuppan, Tokyo (1973), Chap. 2.

14) D. A. MacInnes, "The Principles of Electrochemistry," Dover Publications, New York (1961), p. 232.

15) M. Spiro, "Physical Chemistry of Organic Solvent Systems," ed by A. K. Covington and T. Dickinson, Plenum Press, New York (1973), pp. 673—680; M. L. Jansen and H. L. Yeager, *J. Phys. Chem.*, **77**, 3089 (1973).

16) K. Izutsu, unpublished results.