Liquid Junction Potentials Across Aqueous Saturated Calomel Electrode/Some Aquo-organic Solvents Interface

JAYATI DATTA, SUBRATA SINHA & KIRON K KUNDU*

Physical Chemistry Laboratories, Jadavpur University, Calcutta 700 032

The liquid junction potentials (E_j) generated at the boundaries of saturated KCl solution of aqueous saturated calomel electrode [SCE (W)] and mixed aqueous organic solvents have been determined within the framework of tetraphenylarsonium tetraphenylboride (TATB) reference electrolyte extra-thermodynamic assumption. The organic solvents comprise protic methanol (MeOH) and ethanol (EtOH), aprotic dioxane (D) and dipolar aprotic acetonitrile (ACN), N,N-dimethylformamide (DMF) and dimethyl sulphoxide (DMSO). The E_j values increase almost monotonically in the cases of DMF and DMSO and remain almost invariant till 50 wt % MeOH and EtOH, while in ACN and D, the values lie in between. The contribution to E_j values is mainly from difference of ion-solvent interactions in these mixed solvents, which becomes significant only in the organic-rich compositions.

We have recently reported[1] the E_j values across SCE (W)/solvents like protic methanol (MeOH), ethylene glycol (EG) and dipolar aprotic acetonitrile (ACN), N,N-dimethylformamide (DMF), dimethyl sulphoxide (DMSO) and propylene carbonate (PC) employing tetraphenylarsonium tetraphenylboride (TATB) reference electrolyte extra-thermodynamic assumption[2-4]. It was observed that E_j values though fairly small (below 40 mV) in protic solvents, were fairly large (within 100-200 mV) in dipolar aprotic solvents. This was attributed to solvent-solvent interactions across the liquid junctions. In view of extensive applications of SCE (W) in aquo-organic mixtures it was considered worthwhile to extend our studies to some of these mixed solvents. Herein we report E_j values across the interface of aqueous SCE (W)/aquo-organic mixtures of protic MeOH and EtOH, aprotic dioxane and dipolar aprotic ACN, DMF and DMSO of different compositions. The method consisted of emf measurements of the double cell of the type (A)

$$- SCE (W) \| KCl (c), S/AgCl-Ag-AgCl/KCl (c), W \| SCE (W)^+$$

$$(A)$$
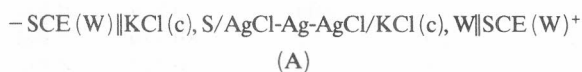
The required ΔG_t^o (Cl^-) values based on TATB assumption are known for these aquo-organic mixtures in literature[5-10].

Materials and Methods

The solvents, other than dioxane (D) were of similar quality and purified by literature procedures[1,9,11]. Dioxane (GR, E Merck) was purified as described earlier[12]. Potassium chloride (AR, BDH) was used after usual pretreatment. Ag-AgCl electrodes were prepared by thermo-electrolytic method as described by Ives and Janz[13]. Aqueous saturated calomel electrodes SCE (W) with porous pin liquid junction were obtained from Elico (India). The bias potentials of the electrodes used were less than ± 0.5 mV. The experimental set up and procedure were similar to those described earlier[1]. The ΔE values of the double cell (A) were measured at 25°C by a digital multimeter (EC, Model M 618, 4B).

Aqueous mixtures of organic solvents of different compositions were prepared by mass dilution. Concentrations of stock solution of KCl in water as well as in each of the solvents were checked by argentometric titration. Solutions of required concentrations in each solvent were prepared by proper dilution.

Results

Since the double cell (A) was formed by coupling of the cell in water (W) and that in solvent (S) in opposition, the measured emf (ΔE) of the cell (A), at any molarity (C) of the electrolyte KCl is given by Eq. (1)

$$\Delta E = {}_w E - {}_s E$$
$$= ({}_w E_{cal} - {}_w E^o_{Ag-AgCl} + k \log {}_w a_{Cl^-})$$
$$- ({}_w E_{cal} - E_j - {}_s E^o_{Ag-AgCl} + k \log {}_s a_{Cl^-})$$
$$= E_j - \Delta G_t^o(Cl^-)/F + k \log ({}_w C_{Cl^-}/{}_s C_{Cl^-})$$
$$+ k \log ({}_w \gamma_{Cl^-}/{}_s \gamma_{Cl^-}) \quad \cdots (1)$$

where k = 2.303 RT/F, subscripts s and w refer to the solvent and water respectively and E_j is the liquid junction potential across saturated aqueous KCl/aquo-organic mixture at zero ionic strength relative to that in water. If the concentrations of KCl in the

two cells were the same, say C and the activity coefficient term is expressed in Debye-Huckel form (2)

$$\log \gamma_{Cl^-} = -S_f c^{1/2} + bc$$
$$- \log (d_s - 0.001 Mc + 0.002 M_s c) \ldots (2)$$

where the terms have usual significance, we have an extrapolation function $\Delta E'$ defined by Eq. (3)

$$\Delta E' = \Delta E + \Delta G_t^o (Cl^-)/F - k_{\,w}\Delta_s S_f c^{1/2}$$
$$- k_{\,w}\Delta_s \log (d_s - 0.001 Mc + 0.002 M_s c)$$
$$= E_j + k_{\,w}\Delta_s bc \qquad \ldots (3)$$

where $_w\Delta_s$ denotes the difference of the quantities in the solvent from that in water. Evidently, the plot of $\Delta E'$ against c on extrapolation to c = 0 would yield E_j on the molar scale.

The ΔE values and the corresponding values of the extrapolation function $\Delta E'$ at different concentrations in the respective solvents are given in Table 1. $\Delta G_t^0 (Cl^-)$ values in different solvents required for the computation of E_j values as per Eq. (2), obtained from literature[14-19], are also given in Table 1. The plots of $\Delta E'$ against c are linear, which

Table 1—Values of ΔE and $\Delta E'$ (in volts) at Various Concentrations

20 wt % $[\Delta G_t^{o^c} (Cl^-) = 1.05$ kJ mol$^{-1}]$			50 wt % $[\Delta G_t^{o^c} (Cl^-) = 3.80$ kJ mol$^{-1}]$			70 wt % $[\Delta G_t^{o^c} (Cl^-) = 6.60$ kJ mol$^{-1}]$		
c (mol dm^{-3})	ΔE	$\Delta E'$	c (mol dm^{-3})	ΔE	$\Delta E'$	c (mol dm^{-3})	ΔE	$\Delta E'$
				MeOH − H$_2$O				
0.10	− 0.014	− 0.004	0.10	− 0.041	− 0.004	0.10	− 0.060	0.001
0.08	− 0.014	− 0.004	0.08	− 0.040	− 0.003	0.08	− 0.060	0.002
0.06	− 0.014	− 0.004	0.06	− 0.040	− 0.003	0.06	− 0.060	0.003
0.04	− 0.013	− 0.003	0.04	− 0.040	− 0.002	0.04	− 0.061	0.004
0.02	− 0.013	− 0.002	0.02	− 0.039	0.000	0.02	− 0.060	0.007
0.01	− 0.012	0.000	0.01	− 0.038	0.002	0.01	− 0.061	0.007

10 wt % $[\Delta G_t^{o^c} (Cl^-) = 0.532$ kJ mol$^{-1}]$			30 wt % $[\Delta G_t^{o^c} (Cl^-) = 1.895$ kJ mol$^{-1}]$			50 wt % $[\Delta G_t^{o^c} (Cl^-) = 5.075$ kJ mol$^{-1}]$		
c (mol dm^{-3})	ΔE	$\Delta E'$	c (mol dm^{-3})	ΔE	$\Delta E'$	c (mol dm^{-3})	ΔE	$\Delta E'$
				EtOH − H$_2$O				
0.10	− 0.007	− 0.003	0.10	− 0.024	− 0.008	0.10	− 0.045	0.000
0.08	− 0.008	− 0.002	0.08	− 0.025	− 0.008	0.08	− 0.045	0.001
0.07	− 0.008	− 0.002	0.06	− 0.024	− 0.007	0.07	− 0.046	0.001
0.06	− 0.007	− 0.002	0.04	− 0.024	− 0.005	0.06	− 0.045	0.002
0.04	− 0.008	− 0.001	0.02	− 0.024	− 0.004	0.04	− 0.046	0.003
0.02	− 0.006	0.000	0.01	− 0.023	− 0.004	0.02	− 0.046	0.004

20 wt % $[\Delta G_t^{o^c} (Cl^-) = 4.787$ kJ mol$^{-1}]$			30 wt % $[\Delta G_t^{o^c} (Cl^-) = 7.815$ kJ mol$^{-1}]$			50 wt % $[\Delta G_t^{o^c} (Cl^-) = 9.869$ kJ mol$^{-1}]$		
c (mol dm^{-3})	ΔE	$\Delta E'$	c (mol dm^{-3})	ΔE	$\Delta E'$	c (mol dm^{-3})	ΔE	$\Delta E'$
				Dioxane − H$_2$O				
0.10	− 0.013	0.037	0.10	− 0.022	0.056	0.08	− 0.046	0.105
0.08	− 0.013	0.037	0.08	− 0.022	0.055	0.07	− 0.046	0.105
0.06	− 0.014	0.039	0.06	− 0.022	0.054	0.06	− 0.048	0.104
0.04	− 0.014	0.036	0.04	− 0.022	0.054	0.04	− 0.049	0.104
0.02	− 0.014	0.036	0.02	− 0.021	0.055	0.02	− 0.050	0.103
0.01	− 0.012	0.038	0.01	− 0.022	0.054	0.01	− 0.052	0.102

20 wt % $[\Delta G_t^{o^c} (Cl^-) = 3.962$ kJ mol$^{-1}]$			50 wt % $[\Delta G_t^{o^c} (Cl^-) = 8.798$ kJ mol$^{-1}]$			60 wt % $[\Delta G_t^{o^c} (Cl^-) = 10.233$ kJ mol$^{-1}]$		
c (mol dm^{-3})	ΔE	$\Delta E'$	c (mol dm^{-3})	ΔE	$\Delta E'$	c (mol dm^{-3})	ΔE	$\Delta E'$
				ACN − H$_2$O				
0.10	− 0.009	0.031	0.10	− 0.032	0.056	0.0635	− 0.044	0.059
0.08	− 0.008	0.032	0.08	− 0.032	0.057	0.0500	− 0.044	0.059
0.06	− 0.009	0.032	0.06	− 0.032	0.057	0.0400	− 0.043	0.061
0.04	− 0.008	0.033	0.04	− 0.032	0.058	0.0200	− 0.043	0.063
0.02	− 0.005	0.036	0.02	− 0.031	0.060	0.0100	− 0.041	0.066
0.01	− 0.003	0.038	0.01	− 0.031	0.061	0.0050	− 0.043	0.065

(Contd.)

Table 1—Values of ΔE and $\Delta E'$ (in volts) at Various Concentrations—(*Contd*)

20 wt % [$\Delta G_t^{o\,c}$ (Cl$^-$) = 2.514 kJ mol^{-1}]			50 wt % [$\Delta G_t^{o\,c}$ (Cl$^-$) = 12.166 kJ mol^{-1}]			70 wt % [$\Delta G_t^{o\,c}$ (Cl$^-$) = 18.866 kJ mol^{-1}]		
c (mol dm^{-3})	ΔE	$\Delta E'$	c (mol dm^{-3})	ΔE	$\Delta E'$	c (mol dm^{-3})	ΔE	$\Delta E'$
			DMF − H$_2$O					
0.10	− 0.011	0.015	0.10	− 0.066	0.056	0.0884	− 0.069	0.119
0.08	− 0.010	0.016	0.08	− 0.066	0.057	0.0700	− 0.070	0.119
0.06	− 0.007	0.018	0.06	− 0.067	0.056	0.0638	− 0.070	0.119
0.04	− 0.009	0.016	0.04	− 0.067	0.057	0.0500	− 0.071	0.119
0.02	− 0.007	0.019	0.02	− 0.065	0.059	0.0300	− 0.071	0.120
0.01	− 0.006	0.020	0.01	− 0.064	0.061	0.0100	− 0.067	0.126

20 wt % [$\Delta G_t^{o\,c}$ (Cl$^-$) = 2.859 kJ mol^{-1}]			40 wt % [$\Delta G_t^{o\,c}$ (Cl$^-$) = 7.885 kJ mol^{-1}]			60 wt % [$\Delta G_t^{o\,c}$ (Cl$^-$) = 15.961 kJ mol^{-1}]		
c (mol dm^{-3})	ΔE	$\Delta E'$	c (mol dm^{-3})	ΔE	$\Delta E'$	c (mol dm^{-3})	ΔE	$\Delta E'$
			DMSO − H$_2$O					
0.10	− 0.012	0.017	0.142	− 0.023	0.057	0.0642	− 0.045	0.117
0.08	− 0.008	0.021	0.100	− 0.024	0.056	0.06	− 0.045	0.117
0.06	− 0.008	0.021	0.080	− 0.022	0.058	0.05	− 0.046	0.116
0.04	− 0.008	0.021	0.060	− 0.021	0.059	0.04	− 0.045	0.118
0.03	− 0.009	0.020	0.040	− 0.021	0.059	0.03	− 0.045	0.118
0.02	− 0.007	0.023	0.020	− 0.020	0.060	0.02	− 0.042	0.120

Table 2—Values of E_j at SCE (W)/Aquo-Organic Mixtures Interface and Involved ΔG_t^o (K$^+$), ΔG_t^o (Cl$^-$), E_j (γ_i − solv) and E_j (solv) in Various Aquo-Organic Solvents at 25°C

Cosolvent	wt % cosolvent	$\Delta G_t^{o\,c}$(K$^+$) (kJ mol^{-1})	$\Delta G_t^{o\,c}$(Cl$^-$) (kJ mol^{-1})	E_j (mV)	E_j (γ_i − solv) (mV)	E_j (solv) (mV)
MeOH[a]	20	2.6	1.1	− 1	− 8	7
	50	5.8	3.8	1	− 10	11
	70	7.9	6.6	8	− 7	15
	100	9.6[g]	13.2[g]	30[h]	38	− 8
EtOH[b]	10	0.8	0.5	1	− 1	2
	30	1.9	1.9	− 3	0	− 3
	50	3.1	5.1	6	10	− 4
	100	16.4[g]	20.2[g]	37[h]	39	− 2
D[c]	20	− 1.8	4.8	36	34	2
	30	− 2.7	7.8	45	55	− 10
	50	− 0.8	9.9	48	56	− 8
ACN[d]	20	1.6	4.0	37	28	9
	50	− 0.7	8.8	61	49	12
	60	− 0.4	10.2	66	55	11
	100	8.1[g]	42.1[g]	95[h]	176	− 81
DMF[e]	20	− 0.2	2.5	20	14	6
	50	− 3.3	12.2	60	81	− 21
	70	− 5.2	18.9	120	125	− 5
	100	− 10.3[g]	48.3[g]	199[h]	304	− 105
DMSO[f]	20	− 0.5	2.9	23	18	5
	40	− 1.7	7.9	61	50	11
	60	− 5.4	16.0	119	111	8
	100	− 13.0[g]	40.3[g]	182[h]	277	− 95

(a-f) ΔG_t^o (K$^+$) and ΔG_t^o (Cl$^-$) values for the aqueous mixtures were obtained from (a) ref. 5; (b) ref. 6; (c) ref. 7; (d) ref. 8; (e) ref. 9; (f) ref. 10.
(g) ΔG_t^o (K$^+$) and ΔG_t^o (Cl$^-$) values for the pure solvents have been taken from ref. 3.
(h) E_j values in pure solvents are taken from ref. 1.

on extrapolation to c = 0 yield the desired E_j values, which are given in Table 2. The values are correct to within ± 2 mV. The extrapolated E_j values being at infinite dilution of the test solution, are independent of ion-ion interactions. However, the effect on E_j of the concentration of the test electrolyte in the solvent side, which are usually small, could be accounted for by limiting or extended form of Debye-Huckel equation. The E_j values thus obtained are plotted against wt % of the cosolvent in Fig. 1.

Discussion

It is evident from Table 1 and Fig. 1 that E_j values are by no means a linear function of the wt % of the cosolvents. Thus while E_j values in the aqueous mixtures of dipolar aprotic DMF and DMSO show a more or less monotonic increase with increase in organic solvent proportion, in protic EtOH and MeOH, E_j values are nearly invariant till 50 wt % cosolvent. The junction potentials generated in ACN- and dioxane-H_2O systems on the other hand attain values nearly in between.

For a better understanding of the nature of E_j-composition profiles in these solvent systems, analysis of the overall E_j values in terms of the individual components [vide Eq. (1)] should be of interest. As indicated by Senanayake and Muir[14], current theories[14-17] on the origin and formation of E_j relate that the magnitudes of E_j for the junction (B)

$$AX \text{ in } S_1 (c_1 \text{ mol dm}^{-3})/MZ \text{ in } S_2 (c_2 \text{ mol dm}^{-3})$$
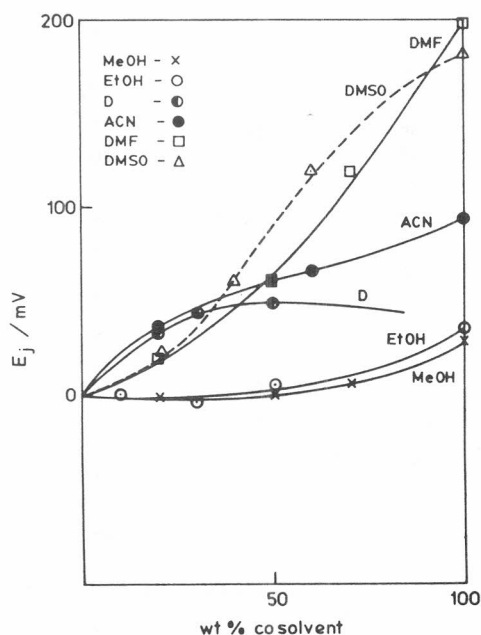$$\dots (B)$$

Fig. 1—Variation of E_j with wt % of organic cosolvent in some aquo-organic solvents.

where $c_1 \gg c_2$ are given by the relation (4)

$$E_j = -(t_A - t_X) \frac{RT}{F} \ln \frac{(c \gamma \lambda)_{AX}}{(c \gamma \lambda)_{MZ}} - \frac{1}{F}[t_A \Delta G_t^o(A)$$
$$- t_X \Delta G_t^o(X)] + E_j \text{(solv)} \qquad \dots (4)$$

The terms γ and λ in Eq. (4) represent the activity coefficients due to Debye-Hückel-type interactions and molar conductivity respectively. Thus the first term in Eq. (4) corresponds to $E_j(\gamma_i)$ and $E_j(\lambda_i)$ of Eq. (5) due to Senanayake and Muir[14]

$$E_j = E_j(\lambda_i) + E_j(\gamma_i) + E_j(\gamma_i - solv) + E_j(solv) \dots (5)$$

Since in the present case AX is KCl, S_1 is water and $t_{K^+} \approx t_{Cl^-} \approx 0.5$ in aqueous solutions even at high concentrations, for $dt_+/d\sqrt{c} \approx 0$ in the case of $t_+ \approx 0.5^{18}$, the first term of Eq. (4) can be tentatively taken to be zero and the component $E_j(\gamma_i - solv)$ of Eq. (5) being equal to the second term of Eq. (4), therefore

$$E_j(\gamma_i - solv) = 0.5/F[\Delta G_t^o(K^+) - \Delta G_t^o(Cl^-)] \dots (6)$$

Taking the required values of $\Delta G_t^o(K^+)$ and $\Delta G_t^o(Cl^-)$ from literature[5-10] (vide Table 2) $E_j(\gamma_i - solv)$ values were computed for the solvents and are given in Table 2. Subtraction of these values from the experimentally observed E_j values yielded the values of E_j (solv) for all the solvents, which are presented in Table 2.

It is clear from the data in Table 2, that the term $E_j(\gamma_i - solv)$ which stands for the difference of ion-solvent interactions of K^+ and Cl^- in the respective solvents relative to that in water, contributes largely to the overall E_j value. Thus the nature of the $E_j(\gamma_i - solv)$-composition profiles (vide Fig. 2a) greatly resembles the corresponding E_j-composition profiles (vide Fig. 1) for the respective solvent systems. On the other hand, the contributions of E_j (solv) which stem from the solvent-solvent interactions as a result of mixing of the solvents across the phase boundary, are found to be fairly small in most of the cases. Moreover, their contributions being bereft of any simple correlation (vide Table 2 and Fig. 2b) with the protic or aprotic nature of the cosolvents especially for their aqueous mixtures, preclude any significant effect of the possible interactions between protic-protic and protic-aprotic cosolvent mixtures across the phase boundaries. In the case of pure solvents however, despite very large contributions of $E_j(\gamma_i - solv)$, E_j (solv) values are also fairly significant, as is expected from the possible non-ideal mixing of the hetero-solvent components at the respective phase boundaries.

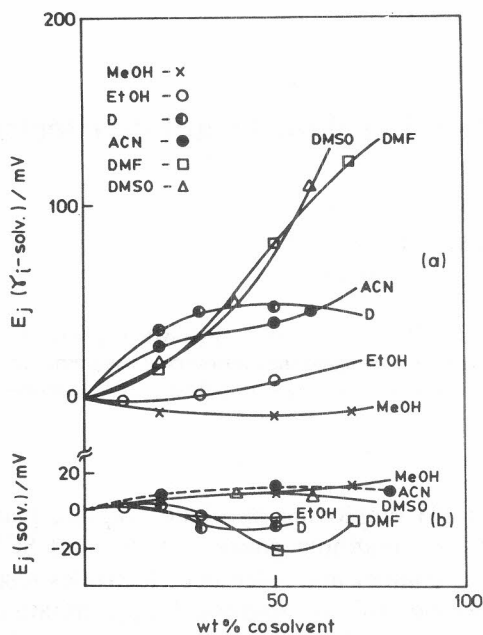Hence, it may be concluded that the liquid junction potentials at the hetero-solvent bondaries are

Fig. 2—Variation of (a) E_j (γ_i − solv), (b) E_j (solv) with wt % cosolvent in some aquo-organic solvents.

largely determined by the differences of free energies of transfer of the involved ions at the boundaries. Effects of solvent mixing at the boundaries lower the values than what are expected from ion-solvent interactions only or in other words E_j (solv) serves as a correction factor for E_j (γ_i − solv) term, which is obtained with the help of TATB assumption. These observations are in conformity with those of Senanayake and Muir[14] who used a host of other salt bridges in some of these aquo-organic solvents. Furthermore, the results of the present study reveal that the use of the SCE (W) with saturated KCl as the bridge electrolyte should be preferable to other electrolytes as the first term in Eq. (4) seems to contribute little to E_j values. And thus it should rightly serve as a convenient reference electrode for various electrochemical measurements in different aquo-organic solvents, provided the E_j values are determined for the respective solvent systems on TATB assumption.

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