Liquid Junction Potentials between Electrolyte Solution in Different Solvents

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Abstract: The factors influencing liquid junction potentials have been investigated. There is a good correlation between the free energy of transfer of solvents across the junctions and the solvent component of the liquid junction potential. The ionic component is a function of the free energy of transfer of the ions and their mobilities and is generally dampened by compensating tendencies of these two factors.

The assumption of negligible liquid junction potential in cell A[1] gives free energies of transfer of silver cation ($\Delta G_{tr}(Ag^+)$) from acetonitrile (AN) to a variety of solvents, S2, which are consistent with those obtained from the application of a number of other popular extrathermodynamic assumptions. In cell A the bridge solvent, S3, is AN or S2, and TEA Pic is tetraethylammonium picrate.

$$\begin{array}{c|c||c||c|c} \mathrm{Ag} & \mathrm{AgClO_4}\ (0.01\ M) & \text{TEA Pic}\ (0.1\ M) & \mathrm{AgClO_4}\ (0.01\ M) & \mathrm{Ag} \\ & \text{acetonitrile, S1} & \text{bridge solvent, S3} & \text{solvent S2} & \end{array}$$

cell A

It was also found that when S2 was dimethyl sulfoxide (DMSO) and the bridge solvent, S3, was varied over a representative group of solvents, the emf of cell A was independent of the bridge solvent to within 5 mV. However, this was not true when the bridge solvent was formamide. The situation where the bridge solvent was water was not tested because of the low solubility of TEA Pic in water. Further it was found that when S2 was formamide, water, or methanol, rather than DMSO, the emf of cell A varied by up to 100 mV as the bridge solvent, S3, was changed, indicating the presence of significant liquid junction potentials in cell A with certain combinations of solvents S2 and S3. This paper presents an investigation into the various factors giving rise to liquid junction potentials in cells, such as cell A, which contain electrolytes in different solvents.

For the emf, E of the general cell B, where the solvent is the same throughout and all ions are univalent, Guggenheim derived[2] expression 1. In this equation

$$\begin{array}{c|c|c|c|} \text{electrode} & \text{solution 1} & \text{transition} & \text{bridge solution} \\ \text{reversible} & \text{containing A} & \text{layer} & 3 \\ \text{to A} & & & \text{(containing RX)} \end{array}$$

$$\begin{array}{c|c|c} \text{transition} & \text{solution 2} & \text{electrode} \\ \text{layer} & \text{containing A} & \text{reversible} \\ & & \text{to A} \end{array}$$

cell B

$$E = \frac{RT}{F}\ln\frac{(a_A)_2}{(a_A)_1} - \frac{1}{F}\int_1^2 \sum t_{R^+}\mathrm{d}\mu_{R^+} + \frac{1}{F}\int_1^2 \sum t_{X^-}\mathrm{d}\mu_{X^-} \qquad (1)$$

$(a_A)_1$ and $(a_A)_2$ are the activities of component A in solutions 1 and 2, respectively, and t_{R^+} and t_{X^-} are transport numbers of any cation R and anion X which moves across the junction. The two integrals of eq 1 represent the liquid junction potential resulting from the chemical potential changes ($\mathrm{d}\mu$) occurring with the passage of ions across the junction through the transition layer. It is important to note that these two integrals are independent of the nature of the bridge solution 3 provided that t_{R^+} and t_{X^-} are constant throughout the cell.

Thus we may write eq 2 for cell B

$$E = E_e + E_{j,ion} \qquad (2A)$$

where $E_e = (RT/F)\ln(a_A)_2/(a_A)_1$ represents the potential difference at the electrodes, and

$$E_{j,ion} = -\frac{1}{F}\int_1^2 \sum t_{R^+}\mathrm{d}\mu_{R^+} + \frac{1}{F}\int_1^2 \sum t_{X^-}\mathrm{d}\mu_{X^-} \qquad (2B)$$

represents the liquid junction potential in cell B.

If the solvents in solutions 1, 2, and 3 of cell B are different, then there will be an additional contribution to the liquid junction potential resulting from free energy changes associated with the flow of solvent molecules across the boundary. For such a cell, the emf is given by eq 3, where $E_{j,s}$ represents the contribution to the liquid junction potential due to the transport of solvent molecules, S, across the boundary. It should be noted that as the flow of ions and solvent molecules are mutually dependent, the division of the liquid junction potential into $E_{j,ion}$ and $E_{j,s}$ is not strictly justified. Assuming that $E_{j,s}$ results primarily from the change in free energy of any solvent molecules which are carried across the boundary by moving ions, then following Alfenaar, de Ligny, and Remijnse[3] and by analogy with $E_{j,ion}$, $E_{j,s}$ may be of the form shown in eq 4, where for a given part of the junction

$$E = E_e + E_{j,ion} + E_{j,s} \qquad (3)$$

$$E_{j,s} = \frac{1}{F}\int_1^2 \sum t_s'\mathrm{d}\mu_s \qquad (4)$$

$\mathrm{d}\mu_s$ is the change in chemical potential of S on crossing that part of the junction and the coefficient t_s' is related to both the transport numbers and solvation numbers of the ions which carry S in that part of the junction (*i.e.*,

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[1] R. Alexander, A. J. Parker, J. H. Sharp, and W. E. Waghorne, *J. Amer. Chem. Soc.*, 94, 1148 (1972).

[2] E. A. Guggenheim, *J. Phys. Chem.*, 34, 1758 (1930).

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

Table I. Mutual Heats of Solution[a] (ΔH_s, kcal mol^{-1}) of Solvents at 23°

Solute[b]	Solvent MeCN	 MeNO$_2$	 PC	 Me$_2$CO	 DMSO	 DMF	 NMePy	 Form	 MeOH	 H$_2$O
(1) MeCN		−0.01	−0.02	−0.14	+0.02	−0.22	−0.50	+0.45	+1.03	−0.45
(2) MeNO$_2$	−0.06		−0.07	−0.27	−0.20	−0.43	−0.76	+0.80	+1.10	+0.77
(3) PC	−0.03	−0.17		−0.08	+0.39	−0.04	−0.29	+0.59	+1.84	+0.39
(4) Me$_2$CO	−0.06	−0.11	+0.05		+0.36	−0.02	−0.06	−0.42	+0.52	−2.38
(5) DMSO	+0.04	−0.36	+0.35	−0.28		+0.15	+0.13	−1.76	−0.22	−4.61
(6) DMF	−0.13	−0.35	0.00	−0.07	+0.20		−0.02	−1.54	−0.14	−3.92
(7) NMePy	−0.32	−0.52	−0.20	−0.20	+0.13	−0.12		−1.62	−0.78	−5.06
(8) Form	+1.28	+2.25	+1.58	+0.65	−1.46	−1.02	−1.50		+0.56	+0.49
(9) MeOH	+1.10	+2.30	+1.50	+0.79	−0.27	−0.15	−0.52	+0.28		−1.78
(10) H$_2$O	+1.47	+3.47	+2.15	+1.01	−1.28	−0.91	−1.16	+0.32	−0.80	

[a] Estimated uncertainty ±0.03 kcal mol^{-1}. [b] Abbreviations: PC = propylene carbonate; DMSO = dimethyl sulfoxide; DMF = dimethylformamide; NMePy = *N*-methylpyrrolidone; Form = formamide; the numbers refer to points labeled in Figure 1.

t_s' represents the total number of moles of S carried across that part of the junction per Faraday of current passed).

Application of eq 3 to cell A leads to eq 5, assuming

$$E = \frac{RT}{F}\ln\frac{(a_{Ag^+})_s}{(a_{Ag^+})_{AN}} - \frac{1}{F}\int_{AN}^{S2} t_{TEA^+}\,d\mu_{TEA^+} \times \frac{1}{F}\int_{AN}^{S2} t_{Pic^-}\,d\mu_{Pic^-} + E_{j,s} \qquad (5)$$

that all of the current across the junction is carried by tetraethylammonium (TEA$^+$) and picrate (Pic$^-$) ions.

$E_{j,s}$. It has been observed that the mobility of TEA$^+$ is approximately equal to that of Pic$^-$ in a number of solvents,[4] including some of those studied here. If this behavior extends to the remainder of the solvents studied here, then the transport numbers can be taken as 0.5 for TEA$^+$ and Pic$^-$ throughout the cell, irrespective of the bridge solvent S3. In this case the emf of cell A will be given by eq 6, where $\Delta\mu_{TEA^+}$

$$E = \frac{RT}{F}\ln\frac{(a_{Ag^+})_2}{(a_{Ag^+})_{AN}} - \frac{0.5}{F}\Delta\mu_{TEA^+} + \frac{0.5}{F}\Delta\mu_{Pic^-} + E_{j,s} \qquad (6)$$

and $\Delta\mu_{Pic^-}$ represent the change in chemical potential of TEA$^+$ and Pic$^-$ on crossing from acetonitrile to solvent S2. Thus if solvent S2 is kept constant while the bridge solvent S3 is varied in cell A, then the first three terms on the right of eq 6 will not change and any variation in E results from variation in $E_{j,s}$. Evaluation of $E_{j,s}$ requires a knowledge of $d\mu_s$ at all points in the junction between acetonitrile and S3 and between S3 and S2 as well as the solvation numbers of TEA$^+$ and Pic$^-$ which cross these junctions (eq 4). However, neither of these ions have strong specific interactions with the solvents studied here, and so the solvation numbers of TEA$^+$ and Pic$^-$ may be constant and approximately equal for the various solvents studied. If this is the case, $E_{j,s}$ will be given by eq 7,

$$E_{j,s} = \frac{t'_s}{F}\sum\Delta\mu_s \qquad (7)$$

where $\Sigma\Delta\mu_s$ for cell A is defined in eq 8.

$$\Sigma\Delta\mu_s = {}^{AN}\Delta\mu_k{}^{S3}(AN) + {}^{S3}\Delta^{S2}\mu_s(S3) + {}^{S2}\Delta\mu_s{}^{S3}(S2) + {}^{S3}\Delta\mu_s{}^{AN}(S3) \qquad (8)$$

In eq 8 $^{AN}\Delta\mu_s{}^{S3}$(AN) represents the free energy per mole of transfer of AN from AN to S3 (*i.e.*, the free energy per mole of solution of AN in S3), $^{S3}\Delta\mu_s{}^{S2}$ (S3) is the free energy of solution per mole of S3 in S2, and so on. Under these conditions then, one would expect a simple relationship between the measured emf, E, of cell A and $\Sigma\Delta\mu_s$. Because of the difficulty of obtaining sufficient data for the free energies of transfer of the various solvents, it was decided to study the relationship between E of cell A and the corresponding total heats of transfer, $\Sigma\Delta H_s$, as defined in eq 9. The various

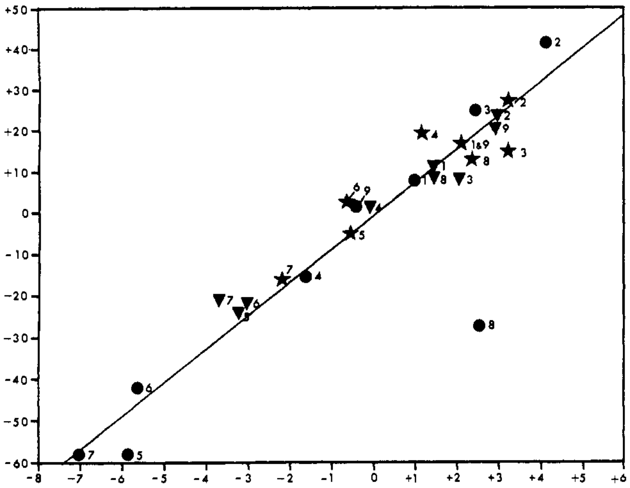

Figure 1. Plot of E' against $\Sigma\Delta H_s$ for cell A with solvent S2 as water (●), formamide (▼), and methanol (⋆). The numbers correspond to the numbers in Table I and refer to the bridge solvent, S3. Ordinate: E', mV. Abscissa: $\Sigma\Delta H_s$, kcal mol^{-1}.

$$\Sigma\Delta H_s = {}^{AN}\Delta H_s{}^{S3}(AN) + {}^{S3}\Delta H_s{}^{S2}(S3) + {}^{S2}\Delta H_s{}^{S3}(S2) + {}^{S3}\Delta H_s{}^{AN}(S3) \qquad (9)$$

terms in eq 9 are defined in an analogous manner to those in eq 8.

Results have been obtained for cell A with S2 as water, formamide or methanol, and with the bridge solvent, S3, as one of a variety of solvents. The heats of solution required for the calculation of $\Sigma\Delta H_s$ from eq 9 in the various cells are given in Table I.

To enable results for cells with S2 as water, formamide, or methanol to be included on the same plot, $E' = E - E_0$ has been plotted against $\Sigma\Delta H_s$ in Figure 1, where E is the measured emf of cell A obtained from ref 1, and E_0 is the emf corresponding to cell A in which $\Sigma\Delta H_s = 0$. Values of E_0 were obtained from plots of E against $\Sigma\Delta H_s$. The values of E_0 obtained were

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(4) A. J. Parker, *J. Chem. Soc. A*, 220 (1966).

Table II. Free Energies of Solution (ΔG_s, kcal mol^{-1}) of Solvents in Other Solvents at 25°

No.[a]	Solute[a]	Solvent[a]	h[b]	ΔG_s[c]	No.[a]	Solute[a]	Solvent[a]	h[b]	ΔG_s[c]
1	MeCN	DMSO	5.3	−0.13	15	H_2O	Form	1.3	−0.19
2	$MeNO_2$	DMSO	3.2	+0.17	16	Me_2CO	Form	8.2	+0.30
3	H_2O	DMSO	0.53	−0.70	17	MeCN	MeOH	29.0	+0.68
4	MeOH	DMSO	5.0	−0.49	18	H_2O	PC	16.1	+1.18
5	Me_2CO	DMSO	31.0	+0.40	19	H_2O	C_6H_6		+3.2[d]
6	MeCN	$MeNO_2$	3.7	−0.19	20	H_2O	EtOAc[g]		+1.2[d]
7	H_2O	$MeNO_2$	25.4	+1.77	21	DMSO	H_2O		−1.3[e]
8	H_2O	MeCN	8.9	+1.15	22	MeOH	H_2O	4.0	+0.3
9	MeOH	MeCN	19.1	+0.62	23	Me_2CO	H_2O	33.8	+1.2
10	Me_2CO	MeCN	10.5	−0.07	24	MeCN	H_2O	21.0	+1.5
11	MeCN	DMF	7.3	−0.09	25	$MeNO_2$	H_2O	21.5	+2.1
12	H_2O	DMF	1.6	−0.20	26	P.C.	H_2O		+1.9[f]
13	MeCN	Form	11.7	+0.30					
14	$MeNO_2$	Form	6.2	+0.46					

[a] Abbreviations as in Table I; the numbers are used in Figure 2. [b] Henry's law constants in mm mol^{-1} l. [c] From eq 10. [d] From solubility data: A. Weissberger, "Techniques of Organic Chemistry," Vol. VII, Interscience, New York, N. Y., 1955. [e] From vapor pressure data at 70°: J. Kenttamaa and J. Lindberg, *Suom. Kemistilehti B*, **33**, 98 (1960). [f] From measured solubility of PC in H_2O, solubility = 1.76 *M*. [g] Ethyl acetate.

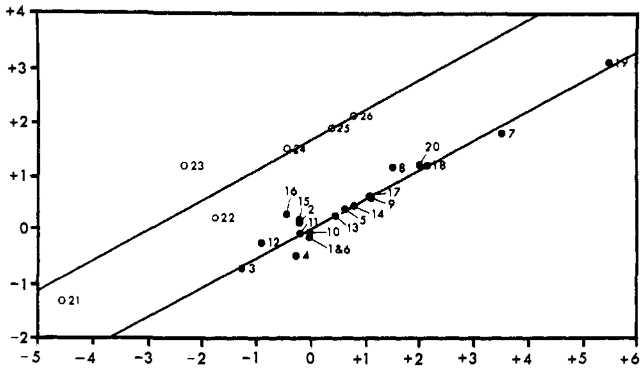

Figure 2. Plot of the free energy of solution (ΔG_s) against the enthalpy of solution (ΔH_s) of solvents into water (○) and nonaqueous solvents (●). The numbers correspond to those in Table II. Ordinate: ΔG_s, kcal mol^{-1}. Abscissa: ΔH_s, kcal mol^{-1}.

177, 54, and 248 mV for S2 as water, formamide, and methanol, respectively.

It can be seen from Figure 1 that there is an excellent linear correlation between E' and $\Sigma\Delta H_s$ for cells with S2 as water, formamide, or methanol, with the exception of the value for the cell with S3 as formamide and S2 as water. This relationship would be expected from eq 7 if there is a linear relationship between $\Sigma\Delta\mu_s$ and $\Sigma\Delta H_s$. To see if this is the case, the free energies of solution of a number of solvents in other solvents calculated from Henry's law constants and solubility data as recorded in Table II, are compared with the corresponding heats of solution in Figure 2. The required heats of solution are taken from data in Table I, with the exception of $\Delta H_s(H_2O) = +5.6$ and $+2.0$ kcal mol^{-1} for solution in benzene and ethyl acetate, respectively.

There is a good linear correlation between $\Delta\mu_s$ and ΔH_s for solution of solvents in all solvents, other than water, and there is a separate but relatively poor correlation between ΔH_s and $\Delta\mu_s$ in water. For solution in solvents other than water, the line in Figure 2 corresponds to $\Delta\mu_s = 0.5\Delta H_s$. As $\Delta\mu_s$ and ΔH_s are related by $\Delta\mu_s = \Delta H_s - T\Delta S_s$, this means that $T\Delta S_s = 0.5\Delta H_s$; *i.e.*, there is a corresponding variation of ΔH_s and ΔS_s. It is known that solution of nonelectrolytes in water often leads to large decreases in entropy, and this is also clearly the case with the results in Figure 2. While there is a rough correlation between $\Delta\mu_s$ and ΔH_s for solution of the solvents shown into water, the scatter indicates that the entropy changes are not simply a linear function of the enthalpy changes. This scatter may not have a large effect on the points in Figure 1 as transfers into water involve only one of four interactions involved in any cell with S2 as water. The large deviation of the point corresponding to cell A with S3 as formamide and S2 as water may result from large differences between $\Sigma\Delta H_s$ and $\Sigma\Delta\mu_s$ for this cell. This is not unreasonable as both water and formamide are highly structured and large entropy changes may be involved on mixing.

The results shown in Figures 1 and 2 indicate that eq 4 is a reasonable representation of $E_{j,s}$. It should be noted from Table I that all heats of solution other than those involving water, formamide, and methanol are small and so any $E_{j,s}$ terms should be small for cells A not containing these solvents. This is consistent with the constant emf's observed for cells with S2 as DMSO for a variety of bridge solvents.[1]

$E_{j,\text{ion}}$. In cell A where the bridge electrolyte is R^+X^-, $E_{j,\text{ion}}$ as defined by eq 2B will be small if $\int_1^2 t_{R^+}\,d\mu_{R^+} \simeq \int_1^2 t_{X^-}\,d\mu_{X^-}$. Originally tetraethylammonium picrate was chosen as the bridge electrolyte in cell A primarily because of the approximate equality of t_{TEA^+} and t_{Pic^-} in several solvents, thus minimizing any terms dependent on the concentration of the bridge electrolyte. An alternative approach is to select an electrolyte RX for which one would expect $\Delta\mu_{R^+} \simeq \Delta\mu_{X^-}$. For this reason, cells with NBu_4BPh_4 as bridge electrolyte were studied. NBu_4^+ and BPh_4^- are both large, with charge buried under hydrocarbon ligands. This bridge electrolyte closely resembles triisoamyl-*N*-butylammonium (TAB^+) tetraphenylboride for which Popovych has assumed $\Delta G_{tr}(TAB^+) = \Delta G_{tr}(BPh_4^-)$ for transfer between solvents.[5] Table III shows a comparison of results obtained with TEA Pic and NBu_4BPh_4 as bridge electrolytes in cell A. Within experimental error, the emf's of the cells are independent of the bridge electrolyte. The results in Table III together with the previously observed close correspondence between the values for a variety of assump-

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(5) O. Popovych, *Crit. Rev. Anal. Chem.*, **1**, 73 (1970).

Table III. Emf of the Cell

$$\mathrm{Ag}\left|\begin{array}{c}\mathrm{AgClO_4}\ (0.01\ M)\\ \mathrm{AN\ (S1)}\end{array}\right\|\begin{array}{c}\mathrm{A^+B^-}\ (0.1\ M)\\ \mathrm{AN\ (S3)}\end{array}\left\|\begin{array}{c}\mathrm{AgClO_4}\ (0.01\ M)\\ \text{solvent S2}\end{array}\right|\mathrm{Ag}$$

Solvent[a] S2	ΔE, V A$^+$ B$^-$ NBu$_4$BPh$_4$	A$^+$ B$^-$ NEt$_4$ Pic
MeNO$_2$	+0.521	+0.520
PC	+0.411	+0.414
Me$_2$CO	+0.307	+0.308
DMSO	−0.149	−0.152
DMF	+0.042	+0.040
NMePy	−0.029	−0.028
Form	+0.063	+0.065
MeOH	+0.272	+0.270
H$_2$O	+0.183	+0.185

[a] Abbreviations as in Table I.

tions of $\Delta G_{tr}(Ag^+)$ and the values from the assumption of negligible liquid junction potential in cell A for those junctions, where $\Sigma\Delta H_s$ of the solvents (and hence $E_{j,s}$) is negligible, indicate that $E_{j,ion}$ is small with both TEA Pic and NBu$_4$BPh$_4$ as bridge electrolyte.

Finally it should be pointed out that small values of $E_{j,ion}$ require $\int_1^2 t_i d\mu_i$ to be approximately equal for the various ions in the bridge solution and transition layers. In general, one might expect that the more highly solvated an ion is in a given solvent the lower will be its mobility. Thus changes in $\int_1^2 t_i d\mu_i$ should be dampened, helping to minimize $E_{j,ion}$ even for very different bridge electrolytes in a variety of solvents. A notable exception to such dampening should be observed with bridges involving the proton in water, which although heavily solvated, has a very high mobility.

Table IV lists the results of some measurements on cells designed to find evidence for such a trend. Measurements were carried out on cell A with S3 as acetonitrile and S2 as propylene carbonate and with S3 as water and S2 as water. The bridge electrolytes had the same anion (ClO$_4^-$) and a variety of cations whose solvation energies are known to vary considerably in the solvents chosen.

Table IV. Emf (E) of the Cell

$$\mathrm{Ag}\left|\begin{array}{c}\mathrm{AgClO_4}\ (0.01\ M)\\ \mathrm{AN\ (S1)}\end{array}\right\|\begin{array}{c}\mathrm{M^+\ ClO_4^-}\ (0.1\ M)\\ \text{solvent S3}\end{array}\left\|\begin{array}{c}\mathrm{AgClO_4}\ (0.01\ M)\\ \text{solvent S2}\end{array}\right|\mathrm{Ag}$$

Solvent S2[a]	Bridge solvent S3	M$^+$	E, mV	$\Delta G_{tr}(M^+)$,[b] kcal mol^{-1}
(a) With TEA Pic in Cell A, E = 414 mV				
PC	CH$_3$CN	Ag$^+$	400	+9.4
		NEt$_4^+$	414	
		Na$^+$	419	−0.3[c]
(b) With TEA Pic in Cell A, E = 185 mV				
Water	Water	Ag$^+$	162	+5.2
		NEt$_4^+$	180	
		K$^+$	213	−1.9
		Na$^+$	217	−4.0
		Li$^+$	214	−6.5
		H$^+$	277	−8.1 (−11.0)[d]

[a] PC = propylene carbonate, AN = acetonitrile. [b] Values obtained from ref 1, or I. M. Kolthoff and M. K. Chantooni, private communication. [c] Assuming $^{AN}\Delta G_{tr}{}^{PC}(Na^+) = {}^{AN}\Delta G_{tr}{}^{PC}(K^+)$. [d] The proton will presumably remain as H_3O^+ in the cell on transfer from H_2O to AN; −8.1 kcal mol^{-1} is the value obtained from measurements in AN containing 0.07% H_2O (C. Papon and J. Jacq, *Bull. Chim. Soc. Fr.*, 13 (1965)); −11.0 is the value quoted for transfer of H^+ to dry AN (I. M. Kolthoff, private communication).

The values in Table IV, while not conclusive, seem to provide some evidence for opposing effects of t_{R^+} and $d\mu_{R^+}$, so that $\int t_{R^+} d\mu_{R^+}$ is dampened. Thus Ag^+ which is very well solvated by acetonitrile has a large positive free energy of transfer from acetonitrile to propylene carbonate, but presumably because of a correspondingly low mobility of Ag^+ in acetonitrile relative to Na^+, the measured emf of cell A with $AgClO_4$ as bridge electrolyte and S2 as propylene carbonate differs by only 19 mV from that with $NaClO_4$ as bridge electrolyte. Similarly for the cells with S2 and S3 as water, the series Li^+, Na^+, and K^+ perchlorates gives virtually constant emf's, despite the much greater $\Delta G_{tr}(Li^+)$ than $\Delta G_{tr}(K^+)$ for transfer from water to acetonitrile. The fact that $u_{K^+} > u_{Na^+} > u_{Li^+}$ in water,[6] where u is the ionic mobility, may account for this behavior. The much greater emf of cell A when $HClO_4$ is the bridge electrolyte relative to other perchlorates is consistent with the high mobility yet strong solvation of the proton in water.

Since the interactions between acetonitrile and propylene carbonate are small (Table I), $E_{j,s}$ is expected to be negligible. However, $E_{j,s}$ may be significant in cells with S2 as water since the interactions are larger. The much lower emf of cell A when $AgClO_4$ is the bridge electrolyte relative to other metal perchlorates may at least be partly due to an $E_{j,s}$ term, because Ag^+ is more strongly solvated by acetonitrile than by water and so will tend to transport acetonitrile into water (ΔH_s = −0.45 kcal mol^{-1}) whereas Li^+, Na^+, and K^+ being much more strongly solvated by water will tend to transport water into acetonitrile (ΔH_s = +1.47 kcal mol^{-1}). However, in the absence of mobility data for the ions concerned in actonitrile and propylene carbonate, it is impossible to make quantitative estimates of the various effects.

Experimental Section

The preparation (where necessary) and purification of the various solvents and chemicals used in this study have been described previously[1] or were carried out by standard procedures.

Heats of solution were determined by conventional methods of calorimetry using a Gould Solution Calorimeter Model 400, the design of which is essentially that of the calorimeter described by Arnett and coworkers.[7]

All emf measurements were made on a Radiometer expanded scale pH meter 26.

Henry's law constants for solutions of some volatile solvents in other less volatile solvents were measured as described previously.[8] Solubilities were also measured in some cases. These values were used to estimate free energies of solution as recorded in Table II. The free energies of solution of solvents A (ΔG_s(A)) in solvent B are based on the mole fraction scale and are obtained from eq 10, where

$$\Delta G_s(A) = 2.303RT \log f_A \qquad (10)$$

f_A is defined by eq 11 and is the activity coefficient of A in B referred

$$f_A = h_A 1000 d_B / P_A{}^0 M_B \qquad (11)$$

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(6) G. M. Barrow, "Physical Chemistry," 2nd ed, McGraw-Hill, Toronto, Ontario, Canada, 1966, p 677.

(7) E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. McC. Duggleby, *J. Amer. Chem. Soc.*, 87, 1541 (1965).

(8) E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, 70, 846 (1948).

to pure A as the reference state. In (11), h_A (mm mol^{-1} l.) is the measured Henry's law constant, P_A^0 is the vapor pressure of pure solvent A at 25°, d_B is the density of solvent B, and M_B is the molecular weight of solvent B. Equation 11 follows from the relationship

$$f_A = \frac{P_A}{P_A^0 X_A} = \frac{h_A}{P_A^0}\frac{d_B 1000}{M_B}$$

since

$$h_A = \frac{P_A}{C_A} = \frac{P_A}{X_A}\frac{M_B}{d_B 1000}$$

where P_A is the vapor pressure of A at concentration C_A mol l.$^{-1}$ in B and X_A is the corresponding mole fraction of A in B.

Conclusions

(1) It has been shown that contributions to the liquid junction potentials from the free energy changes associated with the transport of solvent molecules across the junction ($E_{j,s}$) may be as high as 100 mV in cell A. For cells A in which solvent S2 is water, formamide, or methanol and the bridge solvent S3 is any one of a variety of solvents, an excellent linear correlation has been found between the observed emf and the mutual heats of solution of the various solvents in the cell.

(2) The contribution to the liquid junction potential from the free energy changes associated with the passage of ions across the boundary ($E_{j,ion}$) depends upon $\int_1^2 t_i d\mu_i$, where t_i is the transport number of ion i in a given region, across which there is a free energy change of $d\mu_i$. $E_{j,ion}$ will be zero if $\int_1^2 t_i d\mu_i$ is equal for all ions crossing the junction. It is suggested that because of a general tendency of an ion to have a low mobility in a solvent where it is heavily solvated, $\int_1^2 t_i d\mu_i$ may remain fairly constant (and hence $E_{j,ion}$ small) even for ions involving quite large changes in free energy on crossing the boundary.

(3) It is possible to reduce the liquid junction potentials in cells between different solvents by careful selection of bridge solvents and electrolytes. In order to minimize the liquid junction potential between two different solvents (as in cell A), it is necessary for the bridge solvent to be such that it does not strongly interact with either of the other solvents and the bridge electrolyte should be such that the transport numbers of the cation and anion and their free energy changes on crossing the junction should be equal. The choice of either tetraethylammonium picrate or tetrabutylammonium tetraphenylboride as bridge electrolytes seems reasonable.

On the Relation between Surface Tension and Dielectric Constant

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Abstract: Recently an empirical relation between surface tension and dielectric constant has appeared in the literature [H. A. Papazian, *J. Amer. Chem. Soc.*, **93**, 5634 (1971)]. Theoretical reasons behind this correlation are examined in this paper. It is found that the Lifshitz theory of macroscopic forces can be used to treat a previously proposed model for calculation of surface tension. Theoretical expressions are demonstrated which imply a correlation between surface tension and dielectric constant, and these expressions are compared with experimental data.

In a recent article Papazian[1] has noted a correlation between the surface tension (γ) and the function $(\epsilon_0 - 1)/(2\epsilon_0 + 1)$, where ϵ_0 is the static dielectric constant, for nonpolar liquids. For polar liquids he finds that γ correlates with $(n^2 - 1)/(2n^2 + 1)$, where n is the index of refraction. It is the purpose of this paper to discuss theoretical relationships between γ and ϵ_0 (or n^2) and to offer some comments on the relationship of dispersion forces to the surface tension. A more detailed analysis of the experimental correlation between γ and functions of ϵ_0 for nonpolar liquids will also be offered.

Our analysis is based on a model proposed in 1968 by Padday and Uffindell.[2] Their approximate theory for calculation of surface tensions of hydrocarbons calculated the interaction energy due to van der Waals forces at the surface of a liquid. For nonpolar liquids this energy consists solely of a dispersion term. Consider the formation of two unit areas of surface from bulk liquid. Thermodynamically the increase in energy per unit area of surface formed is

$$E = W/2 + Q/2 = \gamma + TS \tag{1}$$

where W is the work done on the system, Q is the heat required to obtain equilibrium, T is the temperature, and S is the entropy of surface formation. Padday and Uffindell obtain W by calculating the decrease in potential energy occurring when two semiinfinite surfaces of a liquid are brought together from an infinite distance to a distance at which the surface region is indistinguishable from the bulk liquid. They then make the assumption, justified *a posteriori*, that TS

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[1] H. A. Papazian, *J. Amer. Chem. Soc.*, 93, 5634 (1971).

[2] J. F. Padday and N. D. Uffindell, *J. Phys. Chem.*, 72, 1407 (1968).