A New Method for determining Ionic Solvent Transport Numbers and Free Energy of Transfer of Electrolytes from Water to Mixed Aqueous Solvents

Robert D. O'Neill,* Lobna Sheiha,† W. Earle Waghorne, and David Feakins

Chemistry Department, University College, Belfield, Dublin 4, Ireland

By combining data from electrochemical cells with transport and coupled diffusion measurements, the free energy of transfer of an electrolyte, together with ionic relative solvent transport numbers, has been determined accurately without the use of electrodes reversible to both ions.

The free energy of transfer, ΔG_t, of an electrolyte from water (W) to a mixed aqueous solvent (S) can be determined using e.m.f. data from electrochemical cells without transport, if electrodes reversible to both the cation and anion are available.[1] Thus the standard e.m.f.s of cell (I), E°_w, and cell (II), E°_s, are related to the free energy of transfer of the electrolyte at infinite dilution, ΔG°_t by equation (1). A cell with transport can be constructed with electrodes reversible to one of the ions. The e.m.f. of cell (III) with transport E_T, is given[1] by equation (2). Here m is the molal concentration of the salt, MCl, in moles per kilogram of mixed solvent (S) or of water (W); $a_\pm$ is the mean ion activity of the electrolyte referred to the molal standard state in pure water; a_w is the activity of water referred to the standard state of pure water; and w_w is the average Washburn number of water in the interval W to S (*e.g.*, 2.5% if the mixed solvent composition is 5%). The concentration of MCl on the two sides of cell (III) can be adjusted so that $(a_\pm)_w \approx (a_\pm)_s$; the value of the cationic transport number, t_+, under these conditions can be treated as a constant, and equal to the average value on the two sides of the cell.[2] This is achieved when $E_T \approx 0$, since the second integral in equation (2) is small compared with the first. Equation (2) therefore becomes equation (3) with χ given in equation (4).

$$\text{Glass(M)}|\text{M}^+\ \text{Cl}^-\ (m_w),\ \text{W}|\text{AgCl}|\text{Ag} \qquad \text{(I)}$$

$$\text{Glass(M)}|\text{M}^+\ \text{Cl}^-\ (m_s),\ \text{S}|\text{AgCl}|\text{Ag} \qquad \text{(II)}$$

$$E^\circ_s - E^\circ_w = \Delta E^\circ = \frac{\Delta G^\circ_t}{F} \qquad (1)$$

$$\text{Ag}|\text{AgCl}|\text{M}^+\ \text{Cl}^-\ (m_w),\ \text{W}\vdots\text{M}^+\ \text{Cl}^-\ (m_s),\ \text{S}|\text{AgCl}|\text{Ag} \qquad \text{(III)}$$

$$E_T = \frac{2RT}{F}\int_s^w t_+ \mathrm{dln}\,(a_\pm) + \frac{RT}{F}\int_s^w w_w \mathrm{dln}\,(a_w) \qquad (2)$$

$$E_T = t_+ \frac{2RT}{F}\int_s^w \mathrm{dln}\,(a_\pm) + \chi \qquad (3)$$

$$\chi = \frac{RT}{F}\int_s^w \omega_w \mathrm{dln}\,(a_w) \qquad (4)$$

$$E^\circ_T = -t_+\,\Delta E^\circ + \chi^\circ = -t_+\,\frac{\Delta G^\circ_t}{F} + \chi^\circ \qquad (5)$$

$$w^\circ_w = t_+\,(n^\circ_w)_+ - t_-(n^\circ_w)_- \qquad (6)$$

$$\Sigma n^\circ_w = (n^\circ_w)_+ + (n^\circ_w)_- \qquad (7)$$

$$\text{W(1); co-solvent (2), M}_2\text{; salt (3), M}_3\ |\ \text{W(1); co-solvent (2), (M}_2)_\text{B} \qquad \text{(IV)}$$

At infinite dilution of the electrolyte equation (3) becomes equation (5). It is possible, therefore, to determine ΔG°_t from cells with transport if the χ term in equation (5) is calculable using equation (4).

The Washburn number of water, defined by equation (6) can be determined accurately[2] using data from electrochemical cells (I), (II), and (III). The $(n^\circ_w)_+$ and $(n^\circ_w)_-$ are the number of moles of water transported to the cathode with respect to the co-solvent per Faraday of charge passed in a hypothetical Hittorf experiment[2] by the cation and anion at infinite dilution, and $t_\pm$ are the ionic transport numbers. To obtain the individual ionic relative solvent transport numbers, n°_w, the Erdey–Gruz number of water (equation 7), can be measured in a diffusion experiment[3,4] represented by diffusion cell (IV), where W is component 1; the co-solvent is component 2; the electrolyte is component 3; and M is the aquamolal concentration scale. If the solvent composition in electrochemical cell (III) is $2X$% mixed aqueous solvent, then the composition in diffusion cell (IV) is X% mixed solvent. Combining equations (6) and (7) yields the individual ionic n°_w unambiguously. The Erdey-Gruz number is determined from the ratio of the fluxes, J_2/J_3, after J_2 is adjusted for the movement of component 2 due to the chemical potential

Table 1. Thermodynamic and solvent transport data obtained using cells (I)—(V). The free energy of transfer is for 0 to 5% t-butanol/water, whereas the relative solvent transport numbers are for the 2.5% t-butanol/water system.

ΔG°_t (0—5%) J mol_3^{-1}	Σn°_w (2.5%) $\text{mol}_1\ \text{mol}_3^{-1}$	w°_w (2.5%) $\text{mol}_1\ \text{mol}_3^{-1}$	$(n^\circ_w)_+$ (2.5%) $\text{mol}_1\ \text{mol}_3^{-1}$	$(n^\circ_w)_-$ (2.5%) $\text{mol}_1\ \text{mol}_3^{-1}$
1111 ± 5	11.1 ± 0.5	2.1 ± 0.1	8.7 ± 0.5	2.4 ± 0.2

Table 2. Thermodynamic and solvent transport data obtained by an iterative method using data from cells (III)—(V) and $(n^\circ_w)^-$ as input. The output values of ΔG°_t and $(n^\circ_w)_+$ agree well with those given in Table 1.

	Input		Output	
	$(n^\circ_w)_-$ (2.5%) $\text{mol}_1\ \text{mol}_3^{-1}$	Number of iterations	ΔG°_t (0—5%) J mol_3^{-1}	$(n^\circ_w)_+$ (2.5%) $\text{mol}_1\ \text{mol}_3^{-1}$
	2.2	18	1365	11.5
	2.4	16	1131	9.2
	2.6	12	1041	6.8
Average:	2.4 ± 0.2	15	1129 ± 50	9.2 ± 1.3
Measured:	2.4 ± 0.2	—	1111 ± 5	8.7 ± 0.5

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† *Present address*: Chemistry Department, Garunise University, P.O. Box 1803, Benghazi, Libya.

gradient, $\Delta\mu_2$, induced by the presence of electrolyte.[3] This correction is achieved by measuring the flux in diffusion cell (V) where the compositions of the mixed solvent on the two sides of the cell are such that $\Delta\mu_2$ is equal to that in cell (IV), and are calculated using ΔG°_t.

$$\text{W (1); co-solvent (2), } (m_2)_A \mid \text{W (1); co-solvent (2), } (m_2)_B \qquad \text{(V)}$$

We have measured ΔG°_t, $(n^\circ_w)_+$, and $(n^\circ_w)_-$ for Na^+Cl^- in the 2.5% t-butanol/water system (Table 1) using cells (I)—(V) as described previously[3,5] in order to test the following suggestion. If $(n^\circ_w)_-$ is known for a particular system, say C^+A^- in X% mixed solvent, from measurements described above, then ΔG°_t for M^+A^- from water to $2X$% mixed solvent, and $(n^\circ_w)_+$ for M^+ in X% mixed solvent can be determined using only cells (III), (IV), and (V), *i.e.*, an electrode reversible to M^+ is unnecessary.

The principle is simple, although the detailed calculations are complex and will be described fully in a later paper. The value of χ° (equation 5) is initially set to zero, and E_T used to obtain a first estimate of ΔG°_t using equation (5). This is used to calculate an approximation to $\Delta\mu_2$ in cell (IV). The value of $\Delta\mu_2$ is used either to calculate the concentrations needed to set up a new cell (V), or to adjust the flux in the existing cell if the experimental concentrations are close to those calculated. The first estimate of Σn°_w obtained from cells (IV) and (V) gives a value of $(n^\circ_w)_+$ which is combined with the known value of $(n^\circ_w)_-$ to give the first approximation to w°_w (equation 6). The improved χ°, calculated using equation (4), is substituted into equation (3) to give the first improved estimate of ΔG°_t. This iterative method is continued until successive values of ΔG°_t differ by less than any preset tolerance. We have checked this procedure by using the data from cells (III), (IV), and (V) for the NaCl in a 2.5% t-butanol/water system to calculate ΔG°_t and $(n^\circ_w)_+$ without using cells (I) and (II). The results for $(n^\circ_w)_- = 2.4 \pm 0.2$ (Table 1) are given in Table 2 for 0.20 mol l^{-1} NaCl in cell (IV).

The value of ΔG°_t obtained by the iterative method is within its experimental error of that measured using cells without transport. The number iterations given refer to the number of computational cycles needed; experimentally, cell (V) needs to be adjusted only once or twice to give a flux of sufficient accuracy. The value of ΔG_t at infinite dilution of the electrolyte is used throughout the calculations although the diffusion experiments were performed at 0.2 mol l^{-1} NaCl. The difference in ΔG_t at the two concentrations is of the order of the experimental error,[3] and the use of ΔG°_t greatly simplifies the calculations. This method provides a relatively simple and reliable way of determining free energies of transfer and solvent transport numbers for strong electrolytes for which electrodes reversible to only one of its ions are available. It is essential, however, to measure the relative solvent transport numbers accurately since the ΔG°_t obtained is quite sensitive to the value of n_w used (see Table 2). The way is now open to study thermodynamic and solvent transport properties of electrolyte solutions containing constituents for which reversible electrodes are not available, such as the tetra-alkylammonium cation and tetraphenylborate anion.

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