Relative Solvent Transport of Ions in Binary Aqueous Mixtures: an Unambiguous Assignment to Ionic Constituents

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Summary Using a method suggested by Erdey-Grúz, the number of moles of water transported by an ion with respect to the co-solvent in a binary aqueous mixture has been unambiguously determined for the first time.

AN ion moving through a binary solvent mixture will in general transport one solvent component with respect to the other because of preferential solvation effects.[1] For aqueous mixtures, for example, one mol of ions will carry n_W mol of water (W) relative to the second component (S) *e.g.* an alcohol, across a plane normal to its direction of movement. n_W is given by equation (1),[2] where N is the

$$n_W = N[(l - \lambda)/(l + 1)] \qquad (1)$$

total number of molecules of both solvent components carried by a given ion, λ is the ratio of the number of moles of W to the number of moles of S in the mixture as a whole, and l is the corresponding ratio in the transported solvent. Only if $l >> \lambda$, is $n_W = N$.

The Washburn[1] or transport number, w_W, of water is defined for a (1,1) electrolyte as in equation (2).

$$w_W = (n_W)_+t_+ - (n_W)_-t_- \qquad (2)$$

Early measurements[3] of w_W had the object of studying 'hydration numbers' by adding to water an 'inert' second component which would not move with the ions. Then $n_W = N$ [equation (1)]. It was later realised that w_W varies with S;[4] it could be difficult to find an 'inert' substance.

Erdey-Grúz,[5] however, proceeded on the assumption than an 'inert' substance could be found. He suggested that while transport experiments gave the difference between the 'hydration numbers' of the two ions, measurement of the diffusion of water with respect to such a substance would give the sum. Thus enough information would be available to determine 'hydration numbers' for individual ions rather as individual ionic conductances are determined.

Accordingly he and his co-workers conducted a series of diffusion experiments using mixtures of water with allyl alcohol, sucrose, and various carboxylic acids. Erdey-Grúz, however, abandoned this important enterprise when he found that in most cases a net transport of the non-aqueous component occurred in diffusion. In fact Erdey-Grúz's method leads to $(n_W)_+$ and $(n_W)_-$ which, though not 'hydration numbers,' are important because they give unambiguous experimental information about the preferential solvation of individual ion constituents in mixed aqueous solvents.

We decided to complete Erdey-Grúz's work by measuring w_W. Because of analytical difficulties most of his diffusion experiments relate to concentrated electrolyte solutions. The most suitable system for comparison was 1·0 molal KCl + 10%(w/w) allyl alcohol + water. The e.m.f. method[5] was used to determine w_W. (Solvent activities at high electrolyte concentrations were found much as suggested by Ortmanns.[6])

For K^+Cl^- Erdey-Grúz found the value given in equation (3). We find $w_W = 1{\cdot}0$; in equation (2) with $t_+ = t_- = 0{\cdot}5$,

$$(n_W)_+ + (n_W)_- = -3{\cdot}8 \qquad (3)$$

the relationship (4) is obtained.

$$0{\cdot}5(n_W)_+ - 0{\cdot}5(n_W)_- = 1{\cdot}0 \qquad (4)$$

Thus $n_W(K^+) = -0{\cdot}9$ and $n_W(Cl^-) = -2{\cdot}9$; from values of w_W for Li^+Cl^- and Na^+Cl^- we obtain the values given in the Table by difference.

TABLE

Number of moles of water transported with respect to allyl alcohol n_W, by 1 mol of ions in 1·0 molal solution in the system 10% allyl alcohol (w/w) + water.

	Li^+	Na^+	K^+	Cl^-
n_W	−5·6	−2·7	−0·9	−2·9

The results are striking. Whilst (a) the n_W values correspond to relatively weak specific solvation, their negative values indicate that both (b) the cations and (c) the anion are specifically solvated by allyl alcohol. (d) In the case of the cations, the 'acid–base' interaction,[3] favouring solvation by allyl alcohol, thus competes significantly with the ions' steric preference for water, even for Li^+.

Conclusions (a), (c), and (d) had already been tentatively reached, in the absence of a method for separating w_W, in the similar methanol + water system.[2]

The pattern should not be too different at infinite dilution of the electrolyte, where $w_W = 1 \cdot 4$ as against 1·0 at 1 M KCl.

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[3] E. W. Washburn, *J. Amer. Chem. Soc.*, 1909, **31**, 322.

[4] See *e.g.* L. G. Longsworth, *J. Amer. Chem. Soc.*, 1947, **69**, 1288.

[5] T. Erdey-Grúz, A. Hunyár, E. Pogány, and A. Váli, *Hungarica Acta Chimica*, 1948, **1**, 7; T. Erdey-Grúz, 'Transport Phenomena in Aqueous Solutions,' Adam Hilger, London, 1974, p. 468; and references therein.

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