

Relative Solvent Transport of Ion Constituents in Aqueous Organic Solvents

By DAVID FEAKINS,* ROBERT O'NEILL, W. EARLE WAGHORNE, and ANTHONY J. I. WARD
(Department of Chemistry, University College, Belfield, Dublin 4)

Summary In dilute solutions of the organic component the alkali-metal, chloride, and hydrogen ions mostly transport water with respect to raffinose, dioxan, dimethyl sulphoxide, and allyl alcohol, but transport glycine with respect to water.

RECENTLY¹ we showed how the relative solvent transport of individual ions in a binary solvent mixture could be determined unambiguously. For a (1:1) electrolyte at infinite dilution in an aqueous mixture, a transport experiment² gives the Washburn number, w_w^0 , of water W with respect to the co-solvent S [equation (1)]. Erdey-Grúz

$$w_w^0 = (n_w^0)_+ t_+^0 - (n_w^0)_- t_-^0 \quad (1)$$

proposed that diffusion experiments³ could give $\sum n_w^0$ [equation (2)].

$$\sum n_w^0 = (n_w^0)_+ + (n_w^0)_- \quad (2)$$

The numbers of moles of water transported per mole of ions with respect to the co-solvent $(n_w^0)_+$ and $(n_w^0)_-$ then follow from equations (1) and (2).

We have now carried out a substantial programme of measurements of $\sum n_w^0$ using a diffusion cell based on Stokes's⁴ design, and analysis by interferometry, and measurements of w_w^0 .

When we began our own programme of diffusion measurements it became clear that Erdey-Grúz *et al.*³ had not properly corrected their results for the effect of dissolved

electrolyte on the solvent activities, and had thereby seriously overestimated the transport of the non-aqueous component. Thus, as well as a selection of the new data for ionic n_w^0 , the Table shows the corrected data for the system previously reported,¹ 10% (w/w) allyl alcohol.

The values shown for the raffinose system were obtained using Miller's⁵ measurements of diffusion and Longworth's⁶ measurements of transport.

Preferential solvation in these systems is predominantly by water (positive n_w^0). A striking exception is the glycine-water system, which is also interesting because the large negative n_w^0 resolve to very small w_w^0 for the alkali-metal chlorides (0–0.2 mol F⁻¹). These results must be related to the zwitterionic and amphoteric character of glycine.

The corrected values for the allyl alcohol system are now all positive, not negative as stated previously. Now, n_w^0 will be given by equation (3), where N is the total number

$$n_w^0 = N(l - \lambda)/(l + 1) \quad (3)$$

of molecules of water and organic solvent transported by the ion and λ and l respectively are the ratios of number of moles of W to the number of moles of S in the mixture and in the transported solvent respectively.

Where there is strong preferential solvation by water, n_w^0 closely approaches N ; it has been suggested⁷ that this happens in the raffinose-water system. Now that n_w^0 is experimentally accessible, a minimum value of N can be found for any ion; it will be the highest value of n_w^0 found

TABLE. Number of moles of water transported with respect to the organic component at infinite dilution, n_w^0 .^a

	Raffinose 0.75%	Dioxan 5%	Allyl alcohol 10%	Me ₂ SO 5%	Glycine 2.5%
Li ⁺	15	9.5	4.1	0.8	-7.3
Na ⁺	10	8.3	4.6	4.3	-5.0
K ⁺	5.5	4.8	2.8	2.1	-3.5
Rb ⁺	—	1.5	—	3.1	—
Cs ⁺	—	1.3	—	1.8	-3.3
H ⁺	1.5	—	—	-0.9	—
Cl ⁻	4	1.7	0.0	-0.9	-3.6

^a Composition as weight % organic component. Accuracy: raffinose ± 2 ; others better than ± 1 ; relative accuracy in a given system rather better.

in all measurements with various co-solvents at high water concentrations. For the present, therefore, N cannot be less than the n_w° values in the raffinose-water system.

Although these are perhaps the least accurate of any in the Table it is still clear that they are large and that earlier ideas⁷ about shear occurring at the ionic surface for the larger alkali-metal and halide ions must be revised.

The smaller n_w° values in the remaining systems therefore indicate varying degrees of competition by the co-solvent for the solvation of the ion; n_w° for Li^+ shows this particularly well.

Recently Chemla and M'Halla⁸ have analysed the irreversible thermodynamics involved, and have confirmed the possibility of obtaining ionic n_w° . They have obtained a value of $\sum n_w^\circ = 14$ for Na^+Cl^- at infinite dilution of dioxan from a rather different type of diffusion experiment. Extrapolation of our results gives $n_w^\circ = 12 \pm 2$.

(Received, 19th July 1979; Com. 782.)

¹ D. Feakins, E. de Valera, P. J. McCarthy, R. O'Neill, and W. E. Waghorne, *J.C.S. Chem. Comm.*, 1978, 218.

² D. Feakins, *J. Chem. Soc.*, 1961, 5308.

³ T. Erdey-Grúz, A. Hunyár, E. Pogány, and A. Váli, *Acta Chim. Acad. Sci. Hung.*, 1948, **1**, 7; T. Erdey-Grúz, 'Transport Phenomena in Aqueous Solutions,' Hilger, London, 1974, p. 486, and references therein.

⁴ R. H. Stokes, *J. Amer. Chem. Soc.*, 1950, **72**, 763.

⁵ D. G. Miller, *J. Phys. Chem.*, 1959, **63**, 570.

⁶ L. G. Longworth, *J. Amer. Chem. Soc.*, 1947, **69**, 1288.

⁷ D. Feakins, K. H. Khoo, J. P. Lorimer, D. A. O'Shaughnessy, and P. J. Voice, *J.C.S. Faraday I*, 1976, **72**, 2661.

⁸ J. M'Halla and M. Chemla, to be published.