

Effect of Solvent Structure on the Transport of Water in Methanol–Water–Alkali-metal Halide Systems

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Summary In the methanol–water system, the Washburn number of water, w_w , in alkali-metal halide solutions is inflected with respect to solvent composition; particularly pronounced maxima are observed for sodium iodide at *ca.* 15 and 40% (w/w) methanol.

For binary aqueous mixtures w_w is the number of moles of water transported per Faraday towards the cathode in an electrolysis, relative to the cosolvent. An e.m.f. method gives w_w at infinite dilution of the electrolyte.¹

Equation (1) relates w_w to the transport numbers t of, and numbers of moles of water n transported by the ions.

$$w_w = n_+t_+ - n_-t_- \quad (1)$$

Plots of w_w against solvent composition for the alkali-metal chlorides in the range 0–30% (w/w) methanol are little differentiated (Figure, a). The curves for lithium, sodium, and potassium chlorides do, however, show maxima at *ca.* 15% methanol (w/w); there is no extremum for rubidium chloride and a shallow minimum for caesium chloride.

In contrast, a remarkable and progressive enhancement of the peak at 15% methanol is observed when for the sodium salts we change the anion from chloride through bromide to iodide (Figure, b). Further, in the region 35–45% (w/w) methanol there is a second peak for sodium iodide, a less pronounced maximum for sodium chloride, and evidence of at least weak inflections for sodium bromide.

We have found that t_- for any of the sodium halides changes very little, and is uninflected, over the range 0–60% (w/w) methanol, and, at a particular solvent composition varies little from halide to halide.

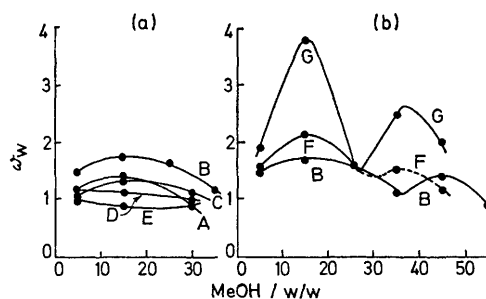


FIGURE. A, LiCl; B, NaCl; C, KCl; D, RbCl; E, CsCl; F, NaBr; G, NaI.

In (b) the point at 25% methanol is common, within the accuracy of drawing the graphs, to each of the curves B, F, and G.

The effects observed have therefore to be explained in terms of n , whose value is probably dominated by near-neighbour interactions of the ion.

Although methanol is expected to be the more 'basic' and less 'acidic' of the two components,² any tendency to preferential primary solvation of cations by methanol or of anions by water (i) is reduced by the averaging of the

'acidic' and 'basic' properties over both solvent components³ and (ii) must be over-ridden by some other factor if the positive Washburn numbers found here are to result. For ions of either sign this is probably a steric preference for water over methanol.

On steric and energetic grounds n_- should fall from chloride to iodide, and, with a common cation, w_w should increase. A clear differentiation in this sense is only observed at 15% methanol (Figure, b). Here the structure of the solvent is probably maximal,³ and molecules of either kind are least readily yielded to the centrosymmetric arrangement around the ion. Thus at this solvent composition n_- is a minimum, and w_w a maximum; the most

pronounced maximum is for the ion least able to create structure, namely iodide.

The development of a maximum in w_w as anionic size increases and n_- falls is paralleled by extinction of the maximum and development of a minimum as cationic size increases and n_+ falls.

As the concentration of methanol is increased past the point of maximum solvent structure, the disordered region around an ion should gradually disappear and n increase accordingly. The extrema in w_w at the higher methanol concentrations could arise from different rates of increase in n_+ and n_- over particular ranges of solvent composition.

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¹ D. Feakins, *J. Chem. Soc.*, 1961, 5308; D. Feakins and J. P. Lorimer, *Chem. Comm.*, 1971, 646.

² D. Feakins and P. Watson, *J. Chem. Soc.*, 1963, 4734.

³ F. Franks and D. J. G. Ives, *Quart. Rev.*, 1966, 20, 1.