

The E.m.f. Method for studying the Transport of Non-electrolytes in Electrolytic Solutions; Results for the Methanol- and Dioxan-Water Systems

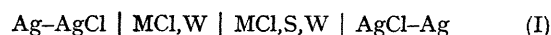
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Summary An e.m.f. method has been used for the first time to study the transport of water in solutions of the alkali-metal chlorides in methanol- and dioxan-water mixtures; in some cases the transport, or Washburn number of water, w_w is inflected at the highly aqueous end of the composition range.

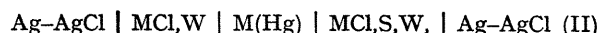
If a current is passed through the solution of an electrolyte in a binary solvent mixture, a movement of one component of the solvent relative to the other is expected. For aqueous mixtures the number of mols of water per Faraday transported towards the cathode relative to the second non-electrolytic component, or the Washburn number of water, w_w ,¹ was first determined by the Hittorf² and moving boundary³ methods.

more rapid than either classical method, and also readily yields results at high concentrations of the non-aqueous non-electrolytic component and at infinite dilution of the electrolyte. The e.m.f. of cell (I) is given by



$$E = 2k \int_{s,w}^w t_+ d \log a_{\pm} - k \int_{s,w}^{s,w} w_w d \log a_w \quad (\text{I})$$

where $k = 2.3026 RT/F$ and the activities of the electrolyte



(a_{\pm}) in the mixed solvent (S,W) relative to a standard state in water (W) are obtained by measurements on the cell

TABLE

Average Washburn numbers of water w_w (mols F^{-1}) in the intervals shown. Non-aqueous concentration in % (w/w)

		(a) Variation with cation					
		HCl ⁴	LiCl	NaCl	KCl	RbCl	CsCl
0—20% methanol	0.21	1.29	1.62	1.23	1.16	0.95
0—20% dioxan	—	1.65	1.71	1.49	—	1.10
		(b) Variation with solvent composition					
		0—5%	0—10%	5—10%	10—20%	20—40%	40—60%
<i>Methanolic systems</i>							
NaCl	1.41	—	1.79	1.63	1.38	1.10
KCl	—	1.10	—	1.36	1.16	—
RbCl	—	1.19	—	1.14	0.94	—
CsCl	—	1.00	—	0.90	0.89	—
<i>Dioxan system</i>							
NaCl	—	2.42	—	1.14	1.15	—

w_w can also be determined by an e.m.f. method,⁴ which works for those binary electrolytes to whose ions there exist reversible electrodes. Advances in the use of alkali-metal amalgam electrodes⁵ have now enabled us to extend this method to solutions of the alkali-metal chlorides. The e.m.f. method is at least as precise as, and far easier and

(II). If a_{\pm} is the same on both sides of cell (I), then the first term in equation (I) normally vanishes within experimental error.⁴ The second term, $\chi = -k \int_s^{s,w} w_w d \log a_w$, is extrapolated to zero concentration of the electrolyte, and,

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the activities, a_w , of water being known, an average value of w_w in the interval between pure water and the mixed solvent may be calculated. The results are also readily treated to give average values of w_w between various mixed solvents. The Table shows the results obtained by this method so far. These values are strikingly similar to those found by the earlier workers. Although some dependence on the nature and concentration of the organic non-electrolyte is expected and found, all methods yield w_w of the order of 1—2 for the alkali-metal chlorides and an order of magnitude less for hydrochloric acid, at least in these predominantly aqueous solvents.

In the case of sodium and potassium chlorides in the methanol-water system, the average Washburn numbers pass through maxima in the highly aqueous region of solvent composition, that is, that in which the mixed solvent is believed to be more structured than water itself.⁶ (This does not arise from a mere inflexion in the

ionic transport numbers in this region.) If χ is known as a

$$d\chi/d\log a_w = -kw_w \quad (2)$$

function of $\log a_w$, w_w may be found for a particular mixed solvent. Values of w_w from equation (2), not shown here, exhibit more pronounced maxima than the average values and thus confirm the effect. For sodium chloride in the dioxan-water system, equation (2) yields values of w_w which by contrast show a pronounced minimum at 20% dioxan.

Although we are satisfied that these effects are outside experimental error, it would be desirable to have them confirmed by measurements at closer intervals of non-electrolyte concentration, particularly if equation (2) is to be applied.

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¹ J. N. Agar, in "The Structure of Electrolytic Solutions," ed. W. J. Hamer, John Wiley and Sons, New York, 1959, p. 218.

² E. W. Washburn, *J. Amer. Chem. Soc.*, 1909, **31**, 322.

³ L. G. Longworth, *J. Amer. Chem. Soc.*, 1947, **69**, 1288.

⁴ D. Feakins, *J. Chem. Soc.*, 1961, 5308.

⁵ H. P. Bennetto, D. Feakins, and K. G. Lawrence, *J. Chem. Soc. (A)*, 1968, 1493.

⁶ F. Franks and D. J. G. Ives, *Quart. Rev.*, 1966, **20**, 1.