Structural Effects in Solutions of the Alkali-metal Chlorides in Methanol–Water Mixtures from Viscosity Measurements

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As a means of investigating the structural properties of methanol–water mixtures we have measured the relative viscosities of solutions of the alkali-metal chlorides, at various temperatures, in 20% (w/w) and 40% (w/w) methanol–water mixtures, and of LiCl and NaCl in 10% (w/w) methanol-water. We have also made new measurements on RbCl and CsCl in water. The Table gives the B-coefficients of the Jones–Dole equation (1) at 25°,

$$\eta/\eta_0 = 1 + A\sqrt{c} + Bc \qquad (1)$$

and $\Delta B/\Delta T$ for the interval 25°—42·5°. The following points may be noted.

(i) For all salts except LiCl, B decreases from water to 20% methanol, *i.e.* the salts are weaker net structure-makers, or stronger net structure-breakers, in 20% methanol than in water. Because the characteristic structural effects of these ions result from the competition offered by the solvent structure to their own, centrosymmetric ordering tendency, these results mean that the degree of short-range three-dimensional order in 20% methanol is greater than in water.

(ii) Negative B-coefficients seem only to be associated with "three-dimensional" liquids,[1] and particularly with water. That the B-coefficients for KCl, RbCl, and CsCl are more negative in 20% methanol than in water is therefore particularly striking evidence for an enhancement of the three-dimensional order in this mixture over that of water.

(iii) Further evidence for this view is that the discrimination of structural effects between the various electrolytes, particularly the structure-breaking ones, is seen from the B-values to be more marked in this mixture than in water.

Any replacement of water molecules bound more or less firmly by the ions, by methanol molecules, which are of larger volume, should in fact tend to increase B,[1] and offset the structural effect in 20% MeOH. This "volume effect" should be smallest for the largest cations, which bind the fewest solvent molecules; hence the biggest net drop in B from water is found for them. Equally, the "volume effect" is probably large enough for LiCl to offset the negative structural effect for this electrolyte completely, causing B to remain constant from 0—20% MeOH.

All the B-coefficients rise again in the 40% mixture, which is probably therefore of a lower structural order than the 20% mixture, although negative B-values are still found for solutions in it.

These results confirm the view of structure in highly aqueous alcohol–water mixtures taken by Franks and Ives.[2] Enthalpies of transfer[3] and Walden products[2] in methanol–water mixtures have been similarly interpreted. While viscosity measurements have not previously demonstrated points (ii) and (iii), minima in B-coefficients for certain other electrolytes in highly aqueous ethanol- and acetone–water mixtures are implicit in the work of Padova.[4]

The $\Delta B/\Delta T$ values are seen, on the whole, to

Viscosity B-*coefficients* [a] *in the methanol–water system at* 25°

% Methanol (w/w)	0	10	20	40
Mole fraction of methanol				
LiCl	0·143[b]	0·146	0·145	0·25[c]
NaCl	0·079[b]	0·069	0·064	0·111
KCl	−0·014[b]	—	−0·028	−0·002
RbCl	−0·036	—	−0·058	−0·023
CsCl	−0·045	—	−0·070	−0·034

[a] Mean deviation −0·005 except for [b] Kaminsky's[5] values better than ±0·001; [c] ±0·02.

$10^3\Delta B/\Delta T$[d] *for the range* 25°—42·5°.

% Methanol (w/w)	0	10	20	40
LiCl	0·0[e]	−0·4	1·3	−2·4[f]
NaCl	1·1[e]	1·9	1·9	0·9
KCl	2·2[e]	—	2·5	2·4
RbCl	2·3	—	3·7	3·1
CsCl	1·9	—	2·7	3·1

[d] Mean deviation ±0·6, except for [e] Kaminsky's[5] results, better than ±0·1; [f] ±2·1.

vary in the opposite sense with solvent structure to the B-values. This is roughly what would be expected.[5] LiCl now conforms to the general pattern.

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