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Note

THERMODYNAMICS OF ELECTROLYTES IN DIOXANE—WATER MIXTURES FROM CONDUCTANCE DATA

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Water at ordinary temperature has a quasicrystalline structure [1—5]. A dynamic equilibrium seems to exist between the three-dimensional hydrogen bonded clusters and the denser monomers [5]

$$(H_2O)_c \rightleftharpoons (H_2O)_d$$

Electrolytes which dissolve in water have been classified as structure makers or structure breakers, depending on whether the above equilibrium is shifted to the left or right. Frank and Wen [3] gave a picture in which an ion is surrounded by concentric regions of water molecules polarised, immobilised and electrostricted by the ion, analogous to a kind of freezing; this they called region A. The water molecules in region C have the normal three-dimensional network as stated above. The centrosymmetric structure imposed by the ion in region A is incompatible with the normal structure in region C and there is a tendency to resist such order and balance between the two competing forces, giving rise to region B. Ions with a low charge density have a smaller width of region A and larger width of region B and are net structure breakers. On the other hand, ions with a high charge density show an opposite behaviour and are net structure makers.

Dioxane and water are miscible at all solvent compositions and some of their physical properties, such as boiling point, vapour pressure and density, are identical but their dielectric constants and dipole moments are very different. Dioxane is an aprotic solvent, whereas water is both an electron donor and an acceptor. These and several other properties make studies of their aqueous mixtures interesting, particularly the ionic processes accompanying the solution of electrolytes.

In the present communication, attempts have been made to evaluate the dissociation constants of the ion pairs of ternary salts and of bibivalent salts and hence the change in free energy (ΔG^0), which would give information concerning whether dioxane—water mixtures will resist the centrosymmetric ordering of the ion more or less than pure water.

MATERIALS AND METHODS

The salts and dioxane used were of E. Merck extra pure grade. Purification of dioxane, preparation of solvents, solutions and conductance measurements have been reported earlier [6]. The conductance measurement was of an accuracy of ±2 in 1000. The concentration range was 0.02—0.002 mole^{-1}. The temperature of investigation was 35° C.

DISCUSSION

The dissociation constants of ternary salts were obtained by the method of Das et al. [7], whereas those for bibivalent salts were determined by the method of Fuoss and Krauss [8] and that of Shedlovsky [9]. From these values (Table 1) the changes in free energy (ΔG^0) have been calculated by the equation

$$\Delta G^0 = -RT \ln K$$

and are recorded in Table 2. It is seen that the ΔG^0 values decrease with increase in dioxane content, which shows that ion pair formation is thermodynamically favourable. The ΔG^0 values indicate that the ion—solvent interaction differs with increase in dioxane content, which can be explained as follows.

Dioxane is more basic and less acidic than that of water because of the electron releasing tendency of the methylene group in the molecule. A water molecule which is hydrogen bonded to the oxygen atom of a dioxane molecule also becomes more basic and less acidic than pure water. A cation will interact more strongly with the oxygen atoms of dioxane—water mixtures. An anion will react more strongly with hydrogen atoms. This type of ion—solvent interaction is in the primary solvation sheath.

The addition of small amounts of dioxane to water may give rise to two effects: if the dioxane is accommodated in the solvent structure, it may

TABLE 1

Dissociation constants ($K \times 10^2$)

Ion pair on salt	Mass fraction of dioxane		
	10%	20%	30%
$MgCl^+$		4.96	3.06
$MgBr^+$		51.93	11.69
$Mg(ClO_4)^+$	14.39	5.42	2.51
$Mg(NO_3)^+$	9.31	6.42	3.32
$BaCl^+$	10 35	5.71	2.73
$BaBr^+$	23.06	10.76	8.20
$Ba(ClO_4)^+$	11.14	4.06	1.46
$Ba(NO_3)^+$	9.42	6.52	4.31
$SrCl^+$	8.71	2.69	1.95
$Sr(NO_3)^+$	6.43	5.42	3.78
$CaCl^+$	4.07	2.40	0.89
$Ca(NO_3)^+$	5 87	4.98	3.42
$MgSO_4$	0.640	0.420	0.300
$ZnSO_4$	0.470	0.188	0.113
$NiSO_4$	0.490	0.350	0.32

TABLE 2

Change in free energy (ΔG^0)(kJ mole^{-1})

Ion pair on salt	Mass fraction of dioxane		
	10%	20%	30%
$MgCl^+$		8.189	3.700
$MgBr^+$		20 224	12 588
$Mg(ClO_4)^+$	13.645	8.653	4.718
$Mg(NO_3)^+$	11.422	9 520	6.143
$BaCl^+$	11.963	8.920	5.142
$BaBr^+$	16.064	12.159	10 772
$Ba(ClO_4)^+$	12.341	7.088	1.938
$Ba(NO_3)^+$	11.484	9.589	7.480
$SrCl^+$	11.435	5 067	3.419
$Sr(NO_3)^+$	10.384	9.878	7.832
$CaCl^+$	7.188	4 482	1.679
$Ca(NO_3)^+$	9.752	8.463	6.456
$MgSO_4$	14.256	11.020	8.437
$ZnSO_4$	11.285	4.849	0 839
$NiSO_4$	12.205	9.622	8.832

strengthen the water structure because dioxane is a better proton acceptor; if it cannot be accommodated because of its bulky size, then it may cause a breakdown in the three-dimensional water structure. The ΔG^0 value decreases with increase in dioxane content, but the changes are not regular, i.e. it changes with the cation. This indicates that dioxane is not accommodated in the solvent structure and hence it breaks down the three-dimensional water structure, therefore the order of ion—solvent interaction with respect to anion or cation is not consistent.

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