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Note

THERMODYNAMICS OF SALTS IN DIOXANE—WATER MIXTURES FROM VISCOSITY MEASUREMENTS

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The interpretation of ionic processes in solutions has been the subject of many discussions. Several recent monographs summarise previous works [1—4]. One of the most difficult aspects is the nature of the ion—solvent interaction and the interpretation of the thermodynamic parameters which appropriately describe the interactions. In the present communication the energies and entropies of activation for viscous at 35°C have been calculated from the B values of KCl, KBr, KNO_3, $KBrO_3$, KIO_3, K_2SO_4, NaCl, NaBr, $NaNO_3$, $NaBrO_3$, $NaIO_3$, and Na_2SO_4 at various mass fractions of dioxane + water mixtures (10, 20 and 30%).

MATERIALS AND METHODS

All the salts used were of E. Merck "extra pure" varieties. The preparation of solvents and solutions, and viscometric techniques were the same as described by Das [5]. All kinds of precautions were taken to check the evaporation [5]. The time of flow did not exceed 0.2 sec, with an error of ±0.04 to ±0.08%. Density readings were precise up to 0.0002 g cm^{-3}, i.e. an error of 4 in 10^6. The concentration range was 0.1—0.001 mole l^{-1}. The temperatures used for the investigation were 30, 35, 40 and 45 ± 0.01°C.

RESULTS AND DISCUSSION

The viscosities of the mixed solvents as well as those of the salt solutions under study were measured and the results have been analysed in terms of the Jones—Dole equation, as the plot of $\eta_r - 1/C^{1/2}$ vs. $C^{1/2}$ is linear. The intercept and slope of the plot give the coefficients A and B, respectively. Coefficient A is due to the contribution from interionic forces and coefficient B is a manifestation of ion—solvent interaction, both have been published previously [6,7].

Eyring et al. [8] applied the theory of absolute reaction rate to interpret

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TABLE 1

Activation parameters

	10% D			20% D			30% D		
	ΔE (kJ mole^{-1})	ΔG (kJ mole^{-1})	ΔS (J mole^{-1} K^{-1})	ΔE (kJ mole^{-1})	ΔG (kJ mole^{-1})	ΔS (J mole^{-1} K^{-1})	ΔE (kJ mole^{-1})	ΔG (kJ mole^{-1})	ΔS (J mole^{-1} K^{-1})
Solvent	17.071	9.572	24.33	17.380	10.412	22.61	16.812	10.784	19.56
KCl	18.062	10.082	25.92	18.676	11.211	24.24	18.191	11.829	20.65
KBr	16.599	9.510	23.03	17.088	10.003	19.19	16.770	10.429	20.61
KNO_3	16.758	9.647	23.07	17.217	10.801	20.82	16.720	11.244	20.61
$KBrO_3$	16.139	9.455	21.69	16.770	10.032	21.86	16.645	10.784	19.02
KIO_3	16.720	9.572	23.20	17.180	10.216	22.61	16.745	10.492	20.31
K_2SO_4	18.438	10.500	25.79	19.270	11.622	24.70	18.731	12.164	21.32
NaCl	17.644	9.647	25.96	18.216	10.747	24.24	17.941	11.328	21.44
NaBr	16.101	9.447	21.61	16.921	9.869	23.03	16.277	10.270	19.52
$NaNO_3$	16.298	9.459	19.48	17.079	9.911	23.28	16.348	10.475	19.06
$NaBrO_3$	16.650	9.413	20.23	16.896	9.823	22.95	16.289	10.391	18.18
$NaIO_3$	16.172	9.455	21.82	16.979	9.886	23.03	16.319	10.396	19.23
Na_2SO_4	18.104	10.070	26.08	19.094	11.595	24.33	18.212	11.871	20.61

the viscosity of liquids by calculating the energy, free energy and entropy of activation. Nightingale and Benck [9] and Feakins et al. [10] have shown that this theory of reaction rate can be successfully applied to electrolytic solutions.

Proceeding along similar lines, the authors have calculated ΔE (which does not differ appreciably from ΔH), ΔG and ΔS for the solvent and the salts at mass fractions of dioxane (10, 20 and 30%) + water mixtures at 35°C. The results are recorded in Table 1. It is observed that ΔE, ΔG and ΔS values for viscous flow are greater than those of the solvent in the case of KCl, NaCl, K_2SO_4 and Na_2SO_4, where, as in the case of KBr, NaBr, KNO_3, $NaNO_3$, $KBrO_3$, $NaBrO_3$, KIO_3 and $NaIO_3$, it is less than that of the solvent, indicating a structure breaking effect. The order is $BrO_3^- > IO_3^- > Br^- > NO_3^- > Cl^- > SO_4^{2-}$ and is in accordance with apparent molar volume and conductivity data [11].

The addition of a small amount of dioxane to water may give rise to two effects: if the dioxane is accommodated in the solvent structure it may strengthen the water structure because dioxane is a proton acceptor. If it cannot be accommodated because of its bulky size then it may cause a breakdown in the three-dimensional water structure. Several authors [12—15] have observed that a dioxane—water mixture is less ordered than pure water. It is observed from Table 1 that ΔE and ΔG increase with increase in dioxane content, which indicates that disorderliness increases with increase in dioxane content and the three-dimensional water structure is broken down.

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