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Solvolysis Rates in Aqueous–Organic Mixed Solvents: Part II — Kinetics of Alkaline Solvolysis of Monochloroacetate Ion in Water–Ethanol Solutions

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The second-order rate constants of the alkaline solvolysis of monochloroacetate ion in water-ethanol solutions have been determined. The reactivity is enhanced by increasing the amount of ethanol in the water-ethanol solvent mixtures and the rate of reaction varies with ethanol concentration in a non-linear manner. The activation parameters show an extremum at about 0·8 water mole fraction.

IN a previous study[1] the alkaline solvolysis of monochloroacetate ion in water-methanol solutions was investigated. It was found that the rate constants exhibit a maximum at about 0·85 water mole fraction and the entropy and enthalpy of activation exhibit a minimum at 0·7 water mole fraction. It has long been realized that there is a considerable diversity of behaviour of the thermodynamic activation parameters toward solvent composition of various binary solvent systems[2]. In the present study the alkaline solvolysis of monochloroacetate ion was investigated in water-ethanol solutions to learn more about the behaviour of rate constants and of ΔH^* and ΔS^* toward solvent composition.

Details of the experimental methods are similar to those outlined in the previous paper[1].

The reaction rates in a series of water-ethanol solutions covering a wide range of solvent compositions and reactant concentrations were found to follow the second-order rate law, being first-order

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TABLE 1 — EFFECT OF TEMPERATURE AND SOLVENT COMPOSITION ON THE RATE CONSTANTS OF ALKALINE SOLVOLYSIS OF SODIUM MONOCHLOROACETATE IN WATER-ETHANOL SOLUTIONS

Ethanol (% by wt)	Temp. °C	Dielectric constant	$k \times 10^5$ (litre mole^{-1} sec^{-1})
0	38·7	73·6	0·567 ± 0·025
	48·2	70·6	1·66 ± 0·05
	55·0	68·3	3·36 ± 0·05
	63·0	65·6	7·83 ± 0·1
20·8	38·7	63·0	0·74 ± 0·03
	48·2	60·5	1·76 ± 0·07
	55·0	58·3	3·70 ± 0·1
	63·0	56·0	9·32 ± 0·25
38·6	38·7	53·7	0·83 ± 0·04
	48·2	51·7	2·00 ± 0·1
	55·0	50·0	3·96 ± 0·1
	63·0	47·6	9·34 ± 0·25
52·0	38·7	47·0	0·97 ± 0·03
	48·2	45·0	2·35 ± 0·05
	55·0	43·4	4·70 ± 0·1
	63·0	41·5	13·00 ± 0·5
69·5	38·7	38·2	1·43 ± 0·05
	48·2	36·5	3·78 ± 0·1
	55·0	35·0	7·86 ± 0·1
	63·0	35·5	18·4 ± 0·5
83·9	38·7	30·5	2·50 ± 0·05
	48·2	29·0	7·02 ± 0·2
	55·0	28·0	15·4 ± 0·1
	63·0	26·5	45·6 ± 0·1
95·5	38·7	24·5	3·26 ± 0·06
	48·2	23·2	8·65 ± 0·3
	55·0	22·4	19·2 ± 0·2
	63·0	21·2	50·0 ± 0·3

in each of the monochloroacetate ion and the solvoxide ion. There is an increase in the specific rate constant with increasing the amount of ethanol in the solvent mixtures and the rate of reaction increases first slowly up to about 60% by weight ethanol and then more rapidly with increase in ethanol content of the medium on further ethanol addition. The results, listed in Table 1, show that as the solvent polarity increases the reaction rate decreases. This is not in agreement with electrostatic consideration which require $d \ln k/d \, (1/D)$ to be negative if the ions have the same charge[3,4]. It is probable that in a mixture of water and an organic solvent with low dielectric constant, the molecules of water will be preferentially oriented around the ions; the dielectric constant in the vicinity of the ions will thus be different from that in the bulk. In such a case, the interaction between the water molecules and the reactant ions, and the degree of orientation of these molecules around the ions increase as the amount of ethanol in the solvent mixture increases.

The energies of activation were calculated from the temperature coefficient of the rate constants. The enthalpy and entropy of activation for the solvolysis reaction were calculated from the rate constants using the absolute rate theory equations[4] and the results, together with ΔG^*, the free energy

TABLE 2 — ACTIVATION PARAMETERS (AT 48·2°) FOR THE SOLVOLYSIS OF SODIUM MONOCHLOROACETATE IN WATER-ETHANOL SOLUTIONS

Ethanol (% by wt)	Mole fr. of water	E_a kcal mole^{-1}	ΔH^* kcal mole^{-1}	ΔS^* cal deg^{-1} mole^{-1}	ΔG^* kcal mole^{-1}
0	1·000	22·52	21·88	12·53	17·85
20·8	0·907	22·00	21·36	14·28	16·77
38·6	0·803	21·05	20·41	16·68	15·05
52·0	0·703	21·40	20·76	15·27	15·85
69·5	0·530	22·55	21·91	10·75	18·46
83·9	0·330	24·10	23·46	4·70	21·95
95·5	0·105	24·70	24·06	2·42	23·28

of activation, are listed in Table 2. It can be seen that the activation parameters pass through a minimum at about 0·8 water mole fraction. The positions of the ΔH^* and ΔS^* minima appear to coincide, which is characteristic of binary solvent mixtures in which both components are hydroxylic[1,2]. The results for methanol-water[1] and ethanol-water are quite similar. The decrease in ΔH^* at higher mole fraction of water simulates the behaviour observed in the case of methanol as the co-solvent. The solvolysis of monochloroacetate ion in water-ethanol solutions produces a decrease of 4 cal/deg mole in ΔS^* between water mole fractions of 1 and 0·8 water corresponding to a change in ΔH^* of about 1·5 kcal/mole for the same composition range. Here, the principal contribution toward increasing rate over the range 0 to 40% by weight ethanol (1·0 to 0·8 water mole fraction) is from the decrease in ΔH^*. In contrast, at water mole fraction of < 0·8 ΔS^* decreases by more than 12 cal/deg mole and its effect becomes increasingly important, sufficiently so as to outweigh by far the actual reversal of the trend in ΔH^*. For solvolysis in water-methanol solutions, the ΔH^*-ΔS^* minimum is located at about 0·7 water mole fraction. Moreover, the depth of the minimum relative to pure water amounts to 12 cal/deg mole for ΔS^* and 4 kcal/mole for ΔH^*. These results are in agreement with observations[5-7] that the extrema in ΔH^* and ΔS^* shift to lower concentration in the case of alcohol of ethanol with bulky group. The results are in conformity with the conclusion that the relative amount of alcohol compatible with a three-dimensional quasi-aqueous structure is directly dependent on the bulk of the group[5,6]. Furthermore, the extremum behaviour in ΔH^* and ΔS^* in aquo-organic solvent mixtures was observed for many solvolysis reactions[1,2,5-9]. This behaviour has been interpreted on the basis that the breakdown of solvent structure as a consequence of charge separation in the activation process parallels the sensitivity to changes in the solvent composition[6,10].

The experimentally calculated values of the free energies of activation (Table 2) do not change much with solvent composition, due mainly to the linear compensation between ΔH^* and ΔS^*. This behaviour is similar to that reported for many solvolysis reactions[1,6] and is to be expected if the solvents in a series perform closely similar roles in the reaction.

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A Study of Ion-Solvent Interaction in Propylene Carbonate from Viscosity Data

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Interaction of the common and tetraalkylammonium (R_4N^+) ions in propylene carbonate has been examined from the viscosity point of view, using the dependence of coefficient B of the Jones and Dole viscosity equation, on temperature and radius of the cation. While the temperature coefficient dB/dt fails to indicate any interaction in this solvent, the variation of B with radius reveals that smaller common cations are solvated but not the larger R_4N^+ ions.

A STUDY of solute-solvent interaction in propylene carbonate (PC) from electrical conductance measurements[1] indicates that the ionic Walden product is almost temperature independent and hence fails to give any indication about the nature of ion-solvent interaction. A closer look on the values of ionic conductivities and the derived Walden products shows that while the conductivity of the R_4N^+ ions decreases with the increase in the radius of the ion, opposite is the case with the small alkali metal ions for which conductivity increases, although slowly, with the increase in the ionic radius. These observations suggest that the R_4N^+ ions remain almost bare (unsolvated) in solution but the small alkali metal ions are associated with the solvent molecules (i.e. solvated), their number varying inversely as the radius of the ion in question. It appears, therefore, worth while to examine this problem from the viscosity point of view since this property of salt solutions has been used as an effective tool for studying solute-solvent interaction[2-10]. Although viscosity of some salt solutions in PC has been reported recently[12,13], the studies have been confined to one temperature and hence the data inadequate. This prompted us to measure the viscosity of the solutions of some alkali metal and tetraalkylammonium iodides in PC at 30°, 35°, 40°, 45° and 50° and the results obtained are reported in this note.