Kinetics of the Alkaline Solvolysis of 3-Chloropropionate Ion in Aquo-Organic Solvents

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The rates of alkaline solvolysis of 3-chloropropionate ion in water-methanol and in water-isopropanol mixtures have been measured over the temperature range 25–55°C. In all cases the rates were first order with respect to both the 3-chloropropionate ion and the total solvoxide ion concentrations. The addition of alcohols to water first causes an increase of rate to a maximum at about 0.8 water mole fraction in the water-methanol solutions and at 0.5 water mole fraction in the water-isopropanol solvent mixtures. Then the rate is decreased on further alcohol addition. The activation parameters E_a, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ show extremum behaviours in each one of the binary solvent mixtures. The results are briefly discussed.

INTRODUCTION

The solvation of molecules and ions in mixed solvents can have a profound influence on many chemical phenomena such as rates of chemical reactions[1], phase separation phenomena in binary mixtures[2], solubilities[3], electrode potentials[4] etc. It has potential technological value.

In aqueous-organic solvents the addition of some organic co-solvents to water may result in a build-up of the water structure which has often been attributed to the formation of fluctuating structures of the clathrate type about the co-solvent molecules[5-8]. The studies of the solvent effects on the chemical reaction rates and on the behaviour of the activation parameters in aquo-organic mixed solvents will yield information on the mechanism of the reaction and on the intermolecular interactions occurring in the solutions. Therefore, we study in this work the solvolysis of 3-chloropropionate ion in water-methanol and in water-isopropanol solutions. This study shows further how far the solvent structure and the internal interactions in aqueous binary mixtures are reflected on the kinetic and the activation parameters.

EXPERIMENTAL

3-chloropropionic acid (Aldrich) was used after further recrystallization from ether. Pure sodium hydroxide, carbonate free, was used without

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further purification. Bi-distilled methanol (C.P. grade), isopropanol (A.R.) and conductivity water were used to make all the solutions.

Reaction mixtures were prepared by mixing known amount of 3-chloropropionic acid, measured volumes of aqueous sodium hydroxide or alcoholic sodium hydroxide (prepared by dissolving sodium metal in absolute methanol) with the proper amounts of bi-distilled water and/or alcohol (methanol or isopropanol) in a volumetric flask. The reactants in the solvent mixtures showed a clear solution when the mole fraction of isopropyl alcohol in the solvent mixture is less than 0.57. While, at higher concentrations of isopropanol the reaction mixture solutions were turbid due to phase separation. Thus, we limited the kinetic runs in the solvent mixtures of the composition range between 0.0 and 0.57 isopropanol mole fraction. Under these conditions the reaction mixtures were clear and the results were reproducible.

The rate of the substitution reaction of chlorine in 3-chloropropionate ion by a hydroxy, methoxy or isopropoxy group was followed in the temperature range 25–55°C using a titrimetric method by following the release of chloride ion according to Volhard's technique[9]. The initial concentrations of each of 3-chloropropionate ion and the base were in the range 0.05–0.10 mole/l. The details of the experimental procedure are similar to those previously outlined[10].

RESULTS AND DISCUSSION

3-chloropropionate ion reacted smoothly with hydroxide or alkoxide ion in both binary solvent mixtures at the desired investigated temperatures 25–55°C. The rate of the alkaline dehydrochlorination was found to be first order with respect to each of the base and the chloropropionate ion concentrations, under all concentrations studied. The total rate of the reaction at all concentrations used covering the whole range of solvent compositions followed the second order till about 80% of the reaction. The specific reaction rate constant k was calculated from the expression:

$$k = \frac{2.303}{(a - b)t} \log \frac{b(a - x)}{a(b - x)},$$

where a = initial concentration of 3-chloropropionate ion, b = initial concentration of base and x = number of moles/litre reacting in time t. Figure 1 shows typical second order plots obtained in water-methanol solutions at 50°C. The rate constants were evaluated from the slopes of such linear plots; data obtained with different solvent compositions and at the several temperatures are listed in Table 1. At least four kinetic runs were performed at each combination of reaction temperature and solvent composition.

The dependence of rate constant on solvent compositions is shown in Figs. 2 and 3. The plots in these figures show the appearance of maxima

in the rate constants with the change in the solvent compositions. This behaviour was reported for many water-organic solvent mixtures[11-14]. In
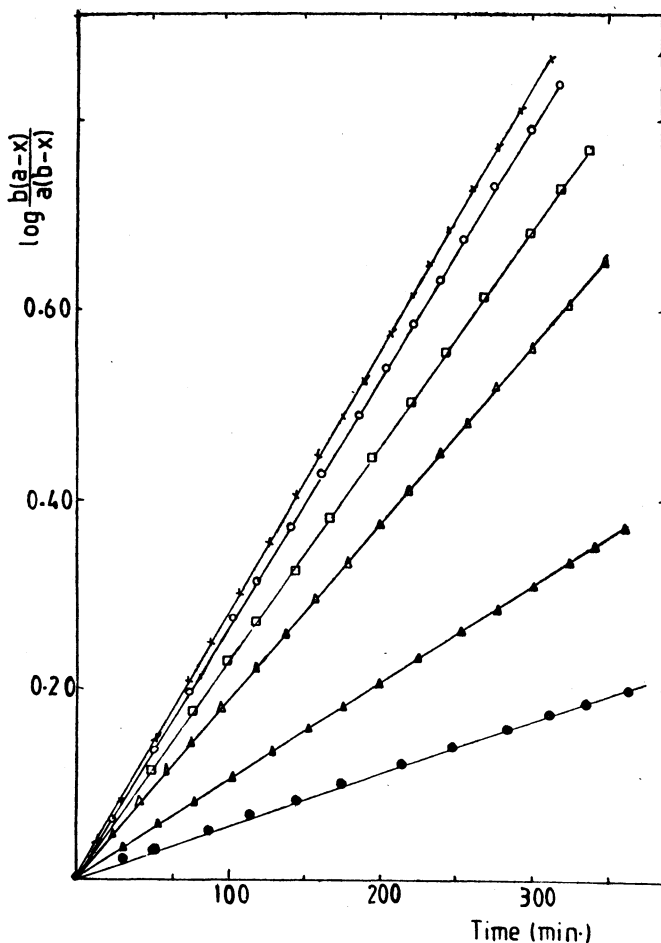

Fig. 1. Second-order plots at 50°C in water-methanol solutions. Water mol fraction: ●, 0.0; ▲, 0.1; □, 0.5; ○, 0.7; × 0.8; △, 1.0.

case of water-methanol solutions, Fig. 2, the maximum in rate constant is shown at about 0.8 water mole fraction. While this maximum appears at 0.5 water mole fraction in the binary mixtures of water-isopropanol solvents, Fig. 3. These extremum behaviours were also observed for the alkaline solvolysis of monochloroacetate ion in water-methanol and in water-isopropanol solutions at about 0.85 and 0.9 water mole fraction respectively[15, 16].

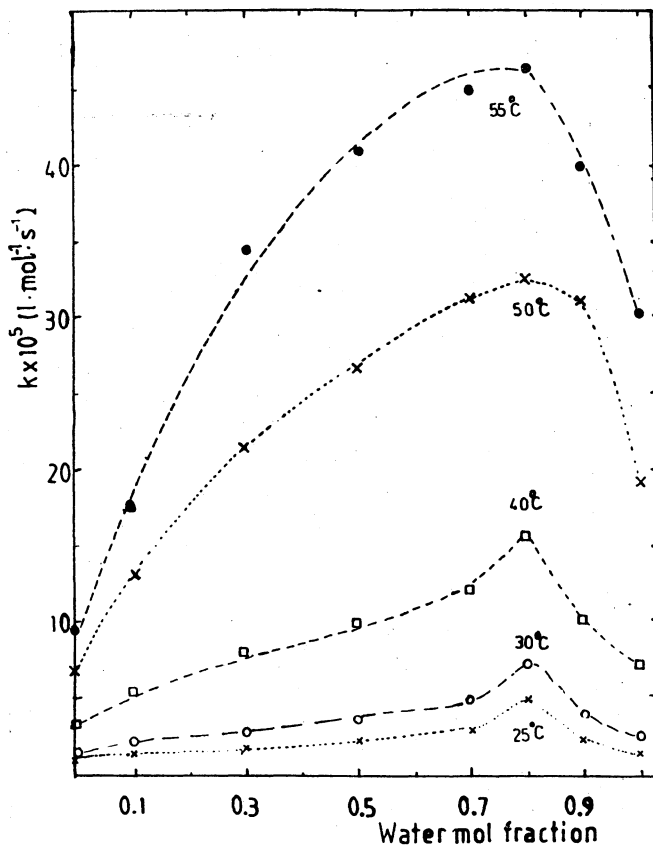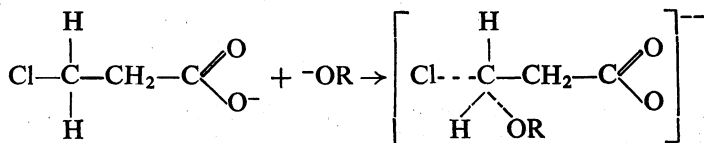The kinetics of the reaction suggest a mechanism in which the rate-

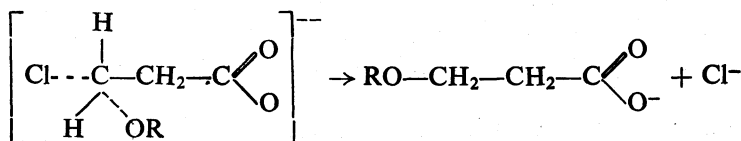Fig. 2. Dependence of the second-order rate constants in water-methanol solutions on solvent composition.

determining step is the formation of the following unstable intermediate:

$$\text{Cl}-\underset{\underset{\text{H}}{|}}{\overset{\overset{\text{H}}{|}}{\text{C}}}-\text{CH}_2-\text{C}\overset{O}{\underset{O^-}{}} + {}^-\text{OR} \rightarrow \left[\text{Cl}--\underset{\underset{\text{H}}{|}}{\overset{\overset{\text{H}}{|}}{\text{C}}}-\text{CH}_2-\text{C}\overset{O}{\underset{O}{}}\right]^{--}$$

where R=H or $\text{CH}_3-\underset{\underset{\text{H}}{|}}{\text{C}}-\text{CH}_3$.

This is followed by the fast releasing of Cl⁻-ion

$$\left[\text{Cl}--\underset{\underset{\text{H}}{|}}{\overset{\overset{\text{H}}{|}}{\text{C}}}-\text{CH}_2-\text{C}\overset{O}{\underset{O}{}}\right]^{--} \rightarrow \text{RO}-\text{CH}_2-\text{CH}_2-\text{C}\overset{O}{\underset{O^-}{}} + \text{Cl}^-$$
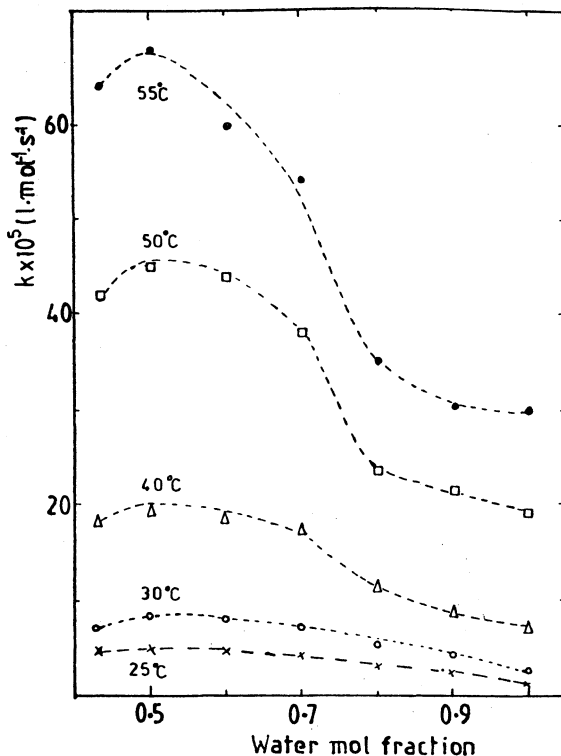
Fig. 3. Dependence of the second-order rate constants in water-isopropanol solutions on solvent composition.

Since the transition state of the solvolysis reaction bears a double negative charge, it is expected that as the solvent polarity increases the reaction rate increases[17]. However our results show that it is not true in all solvent compositions.

According to the electrostatic theory the dependence of reaction rate on the dielectric rate constant (D) of the medium was governed by the equation[18]:

$$\ln k = \ln k_0 + \frac{Z^2 e^2}{k_b D T} \left[(1/r) - (1/r^{**}) \right]$$

which predict a linear plot between $\ln k$ and $1/D$ with a negative slope for negatively charged ion-molecule reactions. In fact such linear plots have not been obtained as must be expected for both investigated binary solvents in the present study. It indicates that the polarity of the medium is not the major factor which affects the reactivity of the reaction, but other factors should influence the reaction rate.

In the temperature range 25–55°C, the rate of the reaction in both binary mixed solvents was found to follow the Arrhenius equation[19]. The

activation energies (E_a) were calculated by applying the least squares method[20]. Activation enthalpies (ΔH^{**}), entropies (ΔS^{**}) and free energies (ΔG^{**}) were calculated from the respective rate constants according to the absolute rate theory equations[19]. Table 2 lists the thermodynamic parameters at 30°C. The variation in the thermodynamic parameters E_a, ΔH^{**} and ΔS^{**} with the change in the solvent composition are represented in Figs. 4 and 5 for water-methanol and water-isopropanol respectively. These figures show that the activation parameters appreciably change with the change in the solvent composition of the medium. In the solutions of water-methanol (Fig. 4), the effect of solvent composition on the activation
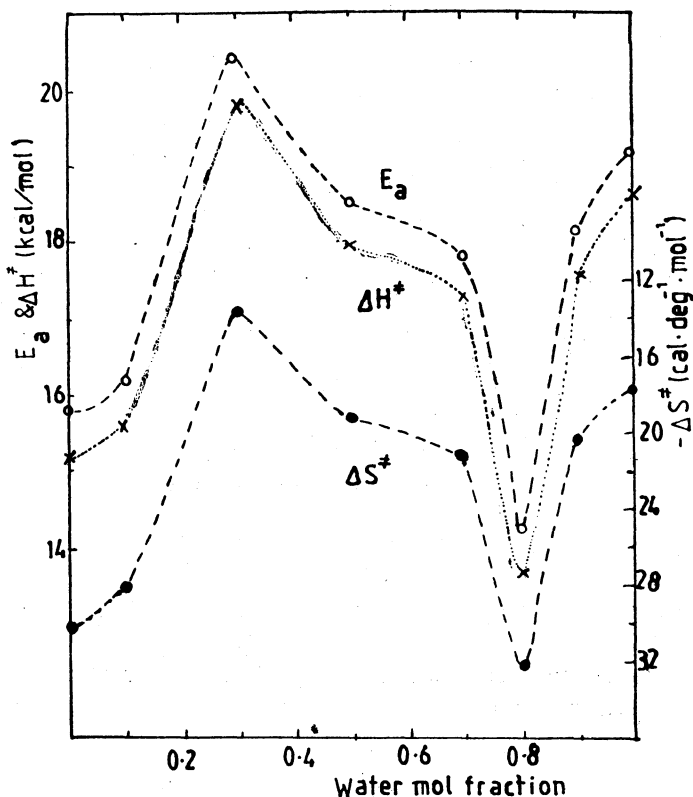

Fig. 4. Dependence of the activation parameters on solvent composition in water-methanol solutions (at 30°C).

parameters is too high, where one maximum and one minimum were observed for each one of the activation parameters at 0.3 and 0.8 water mole fraction respectively. These irregularities in the activation parameters indicate that the orientation of the solvent molecules in the mixed solvent of the investigated system having no longer any orientation with each other or with the reactants as well as with the activated complex. These

orientations break down quickly with little change in the solvent composition. The irregularity in the activation parameters with the change in the solvent composition was also observed in case of binary water-isopropanol solvent mixtures (Fig. 5), where one minimum for each one of the activation parameters could be observed at 0.9 water mole fraction. In the
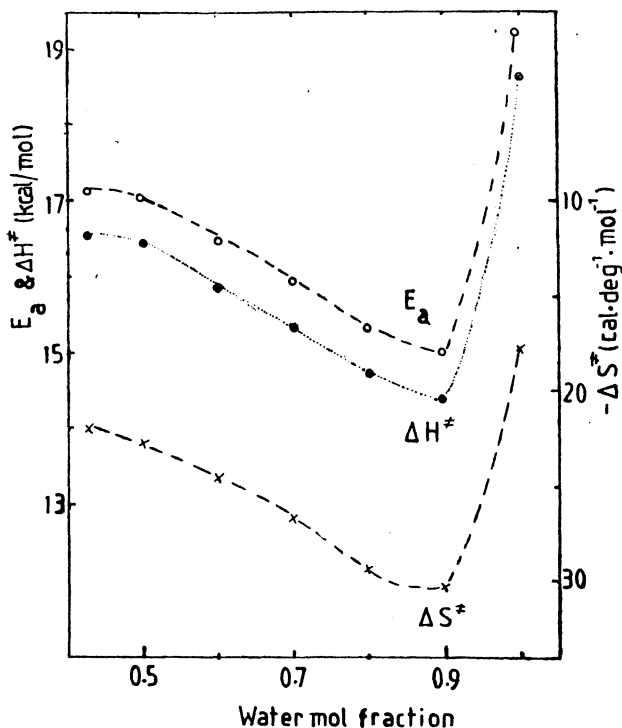

Fig. 5. Dependence of the activation parameters on solvent composition in water-isopropanol solutions (at 30°C).

isopropanol-water solutions the depth of $\Delta H^{\ast}$ minimum relative to the pure water is about 4.24 kcal/mol and that for $\Delta S^{\ast}$ is 12.64 cal deg^{-1} mol^{-1}. This compares with 5.01 kcal/mol for $\Delta H^{\ast}$ and 14.59 cal deg^{-1} mol^{-1} for $\Delta S^{\ast}$ for the methanol-water solutions. These results (number of extremum behaviours and the depth of $\Delta H^{\ast}$ and $\Delta S^{\ast}$) indicate that in isopropanol-water solvent mixtures the activation parameters show relatively little variation with changes in solvent composition. It means that the reorganization of solvent molecules during the activation process has relatively less effect on the alkaline solvolysis of 3-chloropropionate ion in isopropanol-water system than that in the methanol-water system. This result has also been found in the solvolysis of monochloroacetate ion in water-methanol[15] and in water-isopropanol solutions[16]. It indicates

that the change in the solvent structure with the change in the solvent composition of the investigated solvents and the rearrangement of the solvent molecules around the reactants and the transition state has not been affected with changing the substrates.

The extremum behaviour of the activation parameters reflects a common solvent behaviour[11-13, 21, 22] which has occurred on the solvent reorganization accompanying the activation process in many water-organic binary solvents[21]. It can be deduced that the reduction in $\Delta H^{\neq}$-values on the addition of small increments of alcohols to water is a consequence of compensating changes in the solvation of the initial state[23]. Each added increment of alcohol appears to move the initial state solvation shell closer to that of the transition state.

Water is regarded as a highly structured liquid, made of a mixture of fluctuating regions of three-dimensional hydrogen-bonded polymers in equilibrium with randomly arranged monomer molecules of water. The addition of alcohol molecules to water increases the structuredness of the solution in the water-rich concentration range and that the extremum behaviour may be related to the accompanying solvent reorganization attending the activation process for solvolysis in binary alcohol-water systems[25].

In aqueous-alcohol solvent mixtures, the OH-group of the alcohol is visualized as fitting into the hydrogen-bonded network of the water structure while the water forms a continuous hydrogen-bonded shell about the alkyl group[23]. The relative amount of alcohol compatible with a three-dimensional quasi-aqueous structure is directly dependent on the volume of the alkyl group[23, 25]. Figs. 4 and 5 show that the observed minima in the activation parameters are shifted from 0.8 water mole fraction in methanol-water mixtures to 0.9 water mole fraction in isopropanol-water mixtures. This goes in the same trend as that found in the basic hydrolysis of monochloroacetate ion in water-methanol[15] and in water-isopropanol[16] solutions.

Table 2 shows higher negative entropy values $\Delta S^{\neq}$ for each of the hydrolysis and alcoholysis reactions. It indicates that the degree of freedom of the system as a whole decreases when the reactants pass into the transition state and most probably it is due to the freezing of solvent molecules strongly oriented around the high negative charged transition state. The orientation of methanol molecules is higher than the orientation of water molecules around the transition state. However, the addition of alcohol to water will lead to reinforce the solvation structure around the transition state, as shown from increasing the negative values of $\Delta S^{\neq}$. On further addition of the alcohols the solvation shell around the transition state begins breaking, i.e. the orientation of solvent molecules becomes relatively more random than before as mentioned above.

The $\Delta G^{\neq}$-values (Table 2) do not change much with solvent composi-

TABLE 1

EFFECT OF TEMPERATURE AND SOLVENT COMPOSITION ON THE
RATE CONSTANT OF THE ALKALINE SOLVOLYSIS OF 3-CHLORO-
PROPIONATE ION IN AQUEOUS ORGANIC SOLVENTS

Solvent composition	Water mol fraction	Rate constant, $k \times 10^5$ (l mol^{-1} s^{-1})				
		25.0°C	30.0°C	40.0°C	50.0°C	55.0°C
Water-methanol	0.00	0.94 ± 0.01	1.40 ± 0.02	3.10 ± 0.02	6.63 ± 0.04	9.51 ± 0.05
	0.10	1.47 ± 0.01	2.20 ± 0.02	5.39 ± 0.03	12.68 ± 0.05	17.99 ± 0.05
	0.30	1.52 ± 0.02	2.75 ± 0.02	8.01 ± 0.03	21.78 ± 0.07	34.81 ± 0.07
	0.50	2.27 ± 0.03	3.72 ± 0.04	10.10 ± 0.05	26.92 ± 0.07	41.02 ± 0.09
	0.70	2.93 ± 0.02	4.83 ± 0.04	12.30 ± 0.05	30.91 ± 0.10	45.00 ± 0.13
	0.80	5.11 ± 0.03	7.50 ± 0.04	15.84 ± 0.07	32.55 ± 0.09	46.19 ± 0.14
	0.90	2.34 ± 0.03	4.05 ± 0.04	10.33 ± 0.06	31.07 ± 0.09	39.96 ± 0.13
	1.00	1.44 ± 0.01	2.62 ± 0.02	7.26 ± 0.04	19.35 ± 0.10	30.35 ± 0.09
Water-isopropyl alcohol	0.43	4.53 ± 0.03	7.01 ± 0.05	18.40 ± 0.09	42.00 ± 0.11	63.97 ± 0.13
	0.50	5.02 ± 0.02	8.00 ± 0.04	19.60 ± 0.06	45.00 ± 0.12	67.90 ± 0.11
	0.60	4.84 ± 0.03	7.71 ± 0.05	18.41 ± 0.04	42.22 ± 0.13	59.91 ± 0.15
	0.70	4.67 ± 0.03	7.16 ± 0.04	17.59 ± 0.06	38.20 ± 0.05	54.69 ± 0.08
	0.80	3.13 ± 0.02	4.61 ± 0.02	11.16 ± 0.04	23.63 ± 0.06	35.25 ± 0.08
	0.90	2.90 ± 0.01	4.48 ± 0.02	10.10 ± 0.04	21.05 ± 0.04	30.50 ± 0.07
	1.00	1.44 ± 0.01	2.62 ± 0.02	7.26 ± 0.04	19.35 ± 0.10	30.35 ± 0.09

TABLE 2

ACTIVATION PARAMETERS (AT 30°C) FOR THE SOLVOLYSIS OF
3-CHLOROPROPIONATE ION IN AQUEOUS ORGANIC SOLVENTS

Solvent composition	Water mol fraction	E_a (kcal/mol)	$\Delta H^{\neq}$ (kcal/mol)	$-\Delta S^{\neq}$ (cal deg^{-1} mol^{-1})	$\Delta G^{\neq}$ (kcal/mol)
Water-methanol	0.00	15.80 ± 0.05	15.20 ± 0.05	30.29 ± 0.20	24.37 ± 0.11
	0.10	16.19 ± 0.06	15.58 ± 0.06	28.13 ± 0.20	24.10 ± 0.12
	0.30	20.43 ± 0.04	19.82 ± 0.04	13.69 ± 0.16	23.96 ± 0.09
	0.50	18.54 ± 0.08	17.94 ± 0.08	19.34 ± 0.28	23.80 ± 0.17
	0.70	17.88 ± 0.08	17.28 ± 0.08	21.00 ± 0.28	23.64 ± 0.17
	0.80	14.24 ± 0.10	13.64 ± 0.10	32.27 ± 0.35	23.41 ± 0.21
	0.90	18.17 ± 0.08	17.56 ± 0.08	20.39 ± 0.29	23.73 ± 0.17
	1.00	19.25 ± 0.10	18.65 ± 0.10	17.68 ± 0.37	24.00 ± 0.21
Water-isopropyl alcohol	0.43	17.14 ± 0.07	16.54 ± 0.07	22.04 ± 0.23	23.21 ± 0.14
	0.50	17.05 ± 0.05	16.45 ± 0.05	22.73 ± 0.18	23.33 ± 0.11
	0.60	16.50 ± 0.06	15.90 ± 0.06	24.62 ± 0.22	23.36 ± 0.12
	0.70	15.94 ± 0.06	15.34 ± 0.06	26.62 ± 0.21	23.40 ± 0.12
	0.80	15.35 ± 0.07	14.75 ± 0.07	29.44 ± 0.24	23.67 ± 0.14
	0.90	15.01 ± 0.08	14.41 ± 0.08	30.32 ± 0.29	24.03 ± 0.17
	1.00	19.25 ± 0.10	18.65 ± 0.10	17.68 ± 0.37	24.00 ± 0.21

tion, which is mainly due to the linear compensation between ΔH^{**} and ΔS_i^{**}. Fig. 6 shows the plots of ΔH_i^{**} versus ΔS^{**} which is a straight line for each one of the binary mixtures.
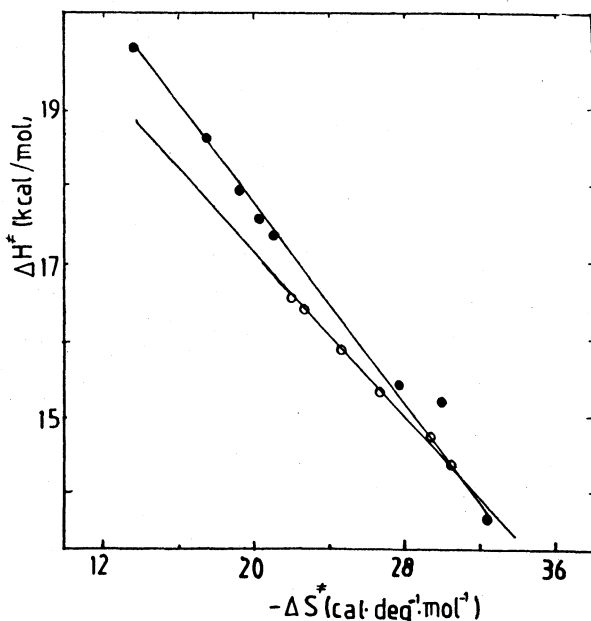

Fig. 6. A plot of ΔH^{**} vs. ΔS^{**} for the alkaline solvolysis of 3-chloropropionate ion in water-methanol (●) and in water-isopropanol (○) solutions.

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