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Solvolysis Rates of Chloramine-T, Chloramine-B and N-Chlorosuccinimide in Alcohol-Water Mixtures

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معدلات التحلل المذيبى لكلورامين- T وكلورامين- B و N- كلورسكسين اميد في محاليل الماء والكحول

تم دراسة معدلات التحلل المذيبى لكلورامين-T وكلورامين-B وN- كلورسكسين اميد في محاليل الماء/الميثانول ومحاليل الماء/أيزوبروبيل . وقد وجد أن هذه التفاعلات تتبع الرتبه الأولى. ووجد أن الميكانيكية توجد في اتزان معكوس. كما تم دراسة تأثير المذيب على تفاعلات المذاوبة، ووجد ان معدلات التفاعل يتغير بتغير تركيب المذيب حيث أن معدل التفاعل يكون مساويا لمعدل التفاعل المائي ومعدل التفاعل مع المذيب العضوي، ويمر عبر نهايات عظمى مع تغير تركيب المذيب. أيضا تم دراسة تأثير العزل الكهربائي السكوني مع معدلات التفاعل. أخيرا تم حساب معاملات التنشيط ومناقشتها في ضوء تأثير المذيب على معاملات التنشيط المختلفة.

ABSTRACT

Solvolytic stability of the water disinfectants Chloramine-B (CB) Chloramine-T (CT) and N-Chlorosuccinimide (NCS) in methanol/water and isopropyl alcohol/ water mixtures were studied. The values of the hydrolytic first-order rate constants were explained by a mechanism in which the N-chloramine exists in a rapid reversible equilibrium with a heterolytic dissociation products followed by a slow solvent molecule-assisted and proton-assisted rate determining step. The variation of the values of the observed rate constants with solvent composition has been explained in terms of the sum of the two rate constants, a hydrolysis rate constant and an alcoholysis rate constant. The rate of reaction varies in a non-linear manner and shows extremum behavior with changes in solvent composition, which suggest strong dependence of the reaction rate on solvent structure. The enthalpies and entropies of activation of the solvolytic decomposition reactions were calculated as a function of solvent composition and the results were discussed from the viewpoint of the electrostatic theory and the changing of solvent structure.

INTRODUCTION

Studies have been undertaken by several investigators to test for different theories accounting for the effect of solvent on the rates of chemical reactions in aqueous – organic solvent binaries. For many solvolysis reactions carried out in aqueous – organic mixed solvents, the activation enthalpy and entropy pass through an extremum as solvent composition is varied (Diefallah *et.al*.1977 &1978, Espenson 1995, Eyring *et. al*. 1980 &Hynes 1985). The position and depth of the extrema are dependent upon the substrate and the non-aqueous component of the solvent mixture. If the extrema in the various activation parameters are related to the same physical phenomena, it is expected that the variation of these extrema with changes in the organic component of the solvent mixture should parallel one another (Conners 1990). This behaviour is also exhibited by other physical properties related to solvent structure, such as solubility (Deifallah *et.al.* 1989), viscosity (Bertrand *et.al*. 1966), equivalent conductance (Bertrand *et.al*. 1966), apparent acidity function (Arnett *et.al*. 1965) and heats of solution (Deifallah *et.al*. 1976) in aqueous alcohols.

Chlorination is the predominant disinfections method applied in water and wastewater treatment due to its low cost, ease of application, and ability to inactivate a wide variety of pathogenic micro - organisms (Donnermair *et.al*. 2003, Pintar *et.al*. 2003, Kim *et. al*. 2002 & Saldanha *et. al* 2002). In the present work we have studied the hydrolysis and alcoholysis of some useful and novel N-chloramine in water – methanol and water – isopropyl alcohol mixture solutions of different compositions.

EXPERIMENTAL

Chloramine-T (CT), Chloramine-B (CB) and N-Chlorosuccinimide (NCS) of the purest grade available were used in all experiments. Conductivity water and purified organic solvents were used to prepare all solutions. The solvolysis reactions were carried out in organic – aqueous solvent mixtures containing the following water mole fractions: 1.00, 0.88, 0.77, 0.64, 0.48 and 0.31 for methanol – aqueous solvent mixtures and 1.00, 0.97, 0.93, 0.88, 0.83, 0.77 and 0.69 for isopropyl alcohol – aqueous solvent mixtures. The reactant in the solvent mixture lead to a clear solution when the mole fraction of water was higher than 0.67 and 0.3 in isopropyl alcohol and methanol solution mixtures, respectively. At higher alcohol concentrations, the reaction mixture solutions were turbid due to phase separation. Thus we limited our kinetic runs to solvent mixtures containing higher than about 0.69 and 0.31 water mole fraction in isopropyl alcohol and methanol reaction mixtures, respectively. In the isopropyl alcohol – aqueous and methanol – aqueous solutions, the experiments were carried out in the temperature range 40.0 to 60.0^{o}C. In all experiments the solvent mixtures were prepared by mixing the appropriate amounts of the organic solvent in water.

The rate of the decomposition of the chloramines in solutions was followed iodometrically. The N-halamine librated iodine in the acidified test solution containing potassium iodide, the librated iodine was titrated with a standard sodium thiosulphate solutions to a starch end point (ASTM 1973).

Reaction mixtures used for all kinetic experiments were prepared by the dissolution of a known amount of halamine in appropriate solvent mixture pre-thermostated at the desired temperature.

Under these conditions the reaction mixtures were clear and the results were reproducible giving rise to pseudo- first order behaviour.

Results and Discussion:

The rate of reaction in a series of water – methanol and water – isopropyl alcohol mixture solutions followed a pseudo – first order law. Figures (1 and 2) showed a typical first – order plots in water-methanol and water – isopropyl alcohol mixture solutions, respectively, obtained at 50^{o}C for N-halamine. The rate constants were evaluated from the slope of the straight lines of such plots. The data obtained in the different temperatures and different N-halamine compounds in the water-methanol and water-isopropyl alcohol mixtures are listed in tables (1 and 2). The rate constants are the average of at least three determinations. It can be seen that the rate of the hydrolysis reaction is relatively slow in pure water, increases in a nonlinear manner by increasing the amount of organic solvent in solutions and passes through a maximum for a water mole fraction of about 0.3 –0.9 for the three N-halamine in the two solution mixtures. Figures (3 and 4) show how the first order rate constants for the reaction vary with solvent composition for N-halamine in water-methanol and water-isopropyl alcohol mixtures respectively.

Figures (5 and 6) show the plots of ln *k* versus 1/D for N-halamine in methanol-water and isopropyl alcohol-water mixture solutions, respectively. It can be showed that there is an increase in the reaction rate constants passing through a maximum at about 0.5 and 0.8 water mole fraction for methanol and isopropyl alcohol solutions in a nonlinear manner. Values for the dielectric constant at 50.0^{o}C were interpolated from the data of Åkerlöf (Åkerlöf 1932). These results show that there is no simple correlation between the dielectric constant D and the rate constant k and that the values are not even in the same order predicted by simple electrostatic theory (Laidler *et. al*. 1956). The prediction of the dielectric theory of the medium effects sometimes fits and sometimes fails to fit the actual behavieour of polar reactions (Leffler 1955). This failure of the electrostatic picture might be because its general postulates are too simplified and because solvation effects other than those describable in terms of the dielectric constant can be expected to be of similar importance.

A plot of ln *k* against 1/T for the reactions in all the mixed solvents investigated produced straight lines, indicating that the data closely follow the Arrhenius equation. The values of the activation energy (ΔE_a), evaluated by using the least square method computerized, are listed in tables (3 and 4) for all N-chloramine and all solvent mixtures. The enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) of activation for the reaction were calculated making use of the transition state theory (Laidler 1985) and the results, together with the free energy of activation ($\Delta G^{\ddagger}$), are given in Tables (3 and 4). The trend in the values of enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) for chloramines-T in methanol are characterized by a maximum at a mole fraction of about 0.6 water mole fraction and a minimum at a water mole fraction of 0.49, while in isopropyl alcohol-water mixtures shows a maximum at about 0.88 water mole fraction and a minimum at 0.93 and 0.83 water mole fraction. The data for chloramines-B show a maximum at 0.88 and a minimum at 0.49 water mole fractions for methanol - water mixtures, while in the case of isopropyl alcohol mixtures a minimum occurs at 0.77 water mole fractions. In the case of N-chlorosuccinimide a minimum in the enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) values at a mole fraction of 0.3 water for the water-methanol mixtures was observed, while for isopropyl alcohol –water mixtures a minimum at about 0.97 and a minimum at about 0.83 water mole fractions. The extrema in enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) with the change in water mole fraction (Figures 7 and 8) are similar to those found for many of the solvolysis reactions (Deifallah *et. al.* 1977, 1978, 1987, 1989 &1976) previously studied.

Also, these extrema of Figures 7 and 8 correlate with several of physical properties of water – alcohol mixtures, such as the structural contribution to the change in the temperature of maximum density (Wada *et. al*. 1962), the depth of the minimum in the variation of relative partial molar volume of the alcohol with solvent composition (Nakanishi 1960), the deviation of the minimum in the excess enthalpy of mixing, (ΔH^{E}_{mix}), from the mole fraction of 0.5 (Lama *et. al.* 1965 and Kettama *et. al.* 1959), and the size of the maximum in the variation of the ultrasonic absorption with solvent composition (Andrae et.al. 1965 and Blandamer 1973), all suggest that the additions of methanol to water produce less structural change in the solvent than when branched – chain alcohol, such as isopropyl alcohol, is added.

Such extrema are thought to reflect corresponding structural changes in binary mixtures (Deifallah *et. al*. 1976, 1978, 1977, 1987 & 1989). The changes in structural features in the solvent zones surrounding the reactants in their transition state as well as structural effects in the transition state are specifically influential in controlling the magnitude of the enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) for the overall process.

The free energy of activation ($\Delta G^{\ddagger}$), shows, within experimental errors, little changes with solvent composition and a plot of the enthalpy ($\Delta H^{\ddagger}$) against

the entropy ($\Delta S^{\ddagger}$) Figure (9) is approximately a straight lines. This compensation effect is frequently the case for a given reaction investigated in a series of solvents and is possible because there is a general tendency in solution for enthalpy and entropy to compensate for each other, so that the changes in the free energy of activation are much smaller (Laidler 1985).

N-Halamine	Water mole fraction	kx10^5 (s^{-1})		
CT		40°C	50C	55°C
	0.877	1.3 ±0.1	2.03 ±0.08	2.5 ±0.3
	0.768	1.5 ±0.1	2.6 ±0.2	3.5 ±0.6
	0.640	1.75 ±0.06	3.8 ±0.2	6.0 ±0.3
	0.489	2.6 ±0.1	5.7 ±0.4	7.3 ±0.7
	0.308	1.4 ±0.1	3.9 ±0.4	6.7 ±0.7
CB	1.00	1.0 ±0.2	1.2 ±0.2	1.5 ±0.1
	0.877	1.7 ±0.1	2.5 ±0.2	3.3 ±0.5
	0.768	1.7 ±0.2	2.5 ±0.3	3.3 ±0.3
	0.640	2.3 ±0.2	3.1 ±0.1	3.4 ±0.4
	0.489	2.0 ±0.4	2.6 ±0.2	2.9 ±0.2
	0.308	0.75 ±0.05	1.8 ±0.1	2.2 ±0.2
NCS	1.00	1.23 ±0.05	2.12 ±0.1	4.5 ±0.2
	0.877	1.06 ±0.04	1.75 ±0.08	3.5 ±0.2
	0.768	1.4 ±0.01	2.1 ±0.3	3.8 ±0.1
	0.640	1.06 ±0.06	1.5 ±0.2	3.81 ±0.09
	0.489	1.55 ±0.10	2.4 ±0.2	3.1 ±0.2
	0.308	1.9 ±0.1	2.5 ±0.1	3.5 ±0.1
	0.165	1.2 ±0.2	1.9 ±0.2	2.4 ±0.3

Table(1) Effects of temperature and solvent composition on the rate constants in the solvolysis of N-halamine in water-methanol mixtures

N-Halamine	Water mole fraction	$kx10^5$ (s^{-1})			
		40ºC	50C	55ºC	60ºC
CT	0.968	1.7 ±0.1	1.4 ±0.1	2.9 ±0.2	4.2 ±0.3
	0.930	1.18 ±0.05	2.4 ±0.2	4.5 ±0.2	5.2 ±0.6
	0.886	1.25 ±0.06	3.5 ±0.1	6.7 ±0.3	7.1 ±0.4
	0.833	1.8 ±0.1	4.33 ±0.08	6.8 ±0.2	7.9 ±0.6
	0.769	1.8 ±0.07	3.9 ±0.4	6.6 ±0.7	8.6 ±0.5
	0.690	0.95 ±0.02	3.7 ±0.3	5.5 ±0.3	8.3 ±0.3
CB	1.00	1.0 ±0.2	1.2 ±0.2	1.5 ±0.1	
	0.968	1.9 ±0.2	2.4 ±0.1	2.6 ±0.1	
	0.930	1.01 ±0.04	1.32 ±0.05	1.38 ±0.04	
	0.886	1.39 ±0.07	1.9 ±0.1	2.3 ±0.1	
	0.833	1.42 ±0.08	2.16 ±0.09	2.7 ±0.3	
	0.769	1.47 ±0.09	2.41 ±0.06	3.5 ±0.2	
	0.690	1.60 ±0.05	2.7 ±0.2	3.7 ±0.2	
NCS	1.00	1.23 ±0.05	2.12 ±0.1	4.5 ±0.2	5.1 ±0.1
	0.968	2.7 ±0.1	3.5 ±0.2	5.0 ±0.4	5.7 ±0.2
	0.930	3.8 ±0.2	6.0 ±0.3	9.2 ±0.3	13.3 ±0.7
	0.886	3.1 ±0.1	3.5 ±0.2	7.5 ±0.3	9.4 ±0.6
	0.833	1.4 ±0.3	2.9 ±0.2	5.6 ±0.1	7.8 ±0.9
	0.769	1.2 ±0.2	2.7 ±0.3	4.4 ±0.2	7.2 ±0.5
	0.690	1.0 ±0.2	2.3 ±0.2	3.3 ±0.2	6.7 ±0.2

Table(2) Effects of temperature and solvent composition on the rate constants in the solvolysis of N-halamine in water-isopropyl alcohol mixtures.

N-Halamine	Water mole fraction	E_a (kJ mol^{-1})	$\Delta H^{\ddagger}$ (50°C) (kJ mol^{-1})	$-\Delta S^{\ddagger}$ (50°C) (J mol^{-1} K^{-1})	$\Delta G^{\ddagger}$ (50°C) (kJ mol^{-1})
CT	0.877	36.2 ±0.2	33.6 ±0.2	232 ±1	108.4 ±0.5
	0.768	47.2 ±2	44.5 ±2	195 ±6	107.7 ±4
	0.640	69.3 ±3	66.7 ±3	124 ±10	106.6 ±6
	0.489	58.6 ±5	55.9 ±5	154 ±18	105.8 ±10
	0.308	90.7 ±1	88.0 ±1	57 ±3	106.6 ±2
CB	1.00	17.9 ±3	15.3 ±3	292 ±10	109.7 ±6
	0.877	38.0 ±3	35.3 ±3	224 ±10	107.8 ±6
	0.768	37.0 ±2	34.3 ±2	227 ±6	107.7 ±4
	0.640	21.7 ±1	19.1 ±1	273 ±3	107.3 ±2
	0.489	19.8 ±0.3	17.1 ±0.3	281 ±1	107.8 ±0.7
	0.308	65.8 ±8	63.1 ±8	142 ±21	109.0 ±15
NCS	1.00	69.7 ±2	67.0 ±2	126 ±6	107.7 ±4
	0.877	64.5 ±2	61.8 ±2	144 ±6	108.2 ±4
	0.768	52.2 ±2	49.6 ±2	180 ±7	107.8 ±5
	0.640	38.5 ±1	35.8 ±1	227 ±3	109.0 ±2
	0.489	39.6 ±2	36.9 ±2	220 ±7	107.9 ±4
	0.308	33.6 ±1	30.9 ±1	237 ±3	107.6 ±2
	0.165	38.4 ±1	35.7 ±2	225 ±6	108.5 ±4

Table(3) Activation parameters for the solvolysis of N-halamine in water-methanol mixtures.

N-Halamine	Water mole fraction	E_a (kJ mol^{-1})	$\Delta H^{\ddagger}$ (50°C) (kJ mol^{-1})	$\Delta S^{\ddagger}$ (50°C) (J mol^{-1} K^{-1})	$\Delta G^{\ddagger}$ (50°C) (kJ mol^{-1})
CT	0.968	79.5 ±8	76.8 ±8	99 ±21	108.9 ±15
	0.930	67.6 ±1	64.9 ±1	132 ±3	107.7 ±2
	0.886	79.9 ±3	77.2 ±3	92 ±10	107.0 ±6

	0.833	66.8 ±3	64.1 ±3	131 ±10	106.5 ±6
	0.769	88.0 ±4	85.3 ±4	67 ±12	106.8 ±8
	0.690	94.7 ±5	92.0 ±5	47 ±14	107.2 ±10
CB	1.00	17.9 ±3	15.2 ±3	293 ±10	109.7 ±6
	0.968	18.4 ±2	15.8 ±2	285 ±7	108.0 ±4
	0.930	28.1 ±4	25.4 ±4	260 ±12	109.4 ±8
	0.886	28.1 ±2	25.4 ±2	254 ±6	107.5 ±4
	0.833	36.5 ±1	33.8 ±1	230 ±3	108.2 ±2
	0.769	48.9 ±6	46.2 ±8	190 ±23	107.8 ±15
	0.690	46.6 ±2	44.0 ±2	197 ±7	107.6 ±4
NCS	1.00	65.7 ±5	63.0 ±5	139 ±15	107.8 ±10
	0.968	32.8 ±2	30.2 ±2	237 ±7	106.6 ±5
	0.930	54.5 ±3	51.8 ±3	165 ±10	105.2 ±6
	0.886	48.8 ±2	46.1 ±2	184 ±6	105.6 ±4
	0.833	76.8 ±6	74.1 ±6	102 ±17	107.1 ±12
	0.769	75.6 ±4	72.9 ±4	107 ±12	107.4 ±8
	0.690	79.2 ±5	76.6 ±5	97 ±15	108 ±10

Table(4) Activation parameters for the solvolysis of N-halamine in water-isopropy alcohol mixtures.

List of Figures:

Figure 1. First order plots at 50°C in water - methanol mixtures. Water mole fraction . 1.0, ס 0.877, **o** 0.768, **x** 0.640, **ж** 0.489, O 0.308 and **θ** 0.165

Figure 2. First order plots at 50°C in water isopropyl alcohol mixtures. Water mole fraction . 1.0, ס 0.968, **o** 0.93, **x** 0.886, **ж** 0.883, O 0.769 and **θ** 0.69

Figure 3. Dependence of the first order rate constants on the solvent composition in water - methanol mixtures.

Figure 4. Dependence of the first order rate constants on the solvent composition in water - isopropyl alcohol mixtures.

Figure 5. Dependence of the first order rate constants on the dielectric constant of the medium in water - methanol mixtures.

Figure 6. Dependence of the first order rate constants on the dielectric constant of the medium in water - isopropyl alcohol mixtures.

Figure 7. Dependence of the activation parameters on the solvent composition in water - methanol solutions (- - - $\Delta S^{\ddagger}$ and — $\Delta H^{\ddagger}$).

Figure 8. Dependence of the activation parameters on the solvent composition in water - isopropyl alcohol mixtures (- -- - $\Delta S^{\ddagger}$ and — $\Delta H^{\ddagger}$).

Figure 9. a plot of $\Delta S^{\ddagger}$ vs. $\Delta H^{\ddagger}$ for the solvolysis of N-halamine in (A) water methanol solutions and (B) water isopropyl solutions.

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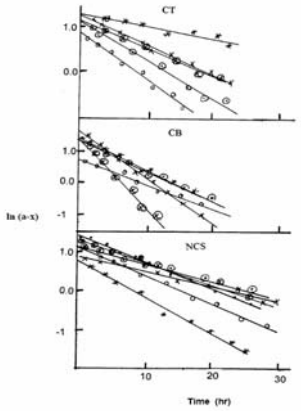

Figure 1. First plots at 50°C in water methanol solutions. Water mole fraction • 1.0, ⊙ 0.877, ○ 0.768, x 0.640, × 0.489, ⊙ 0.308 and ⊖ 0.165

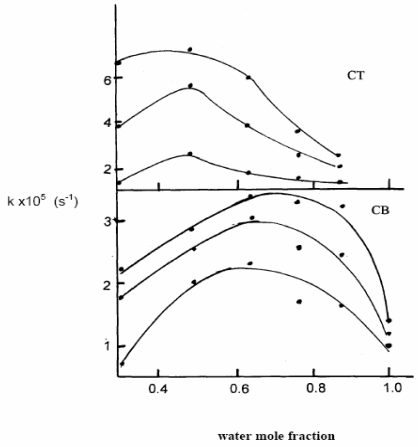

Figure 3 . Dependence of the first order rate constants on the solvent composition in water methanol solutions

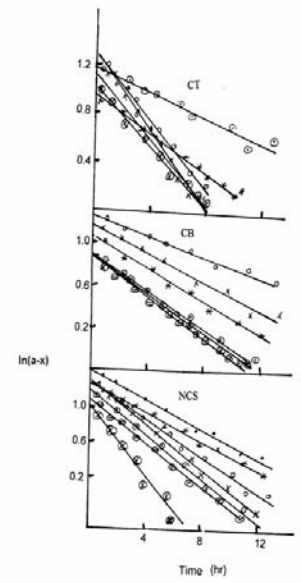

Figure 2. First plots at 50°C in water isopropyl solutions. Water mole fraction • 1.0, ⊙ 0.968, ○ 0.93, x 0.886, × 0.883, ⊙ 0.769 and ⊖ 0.69

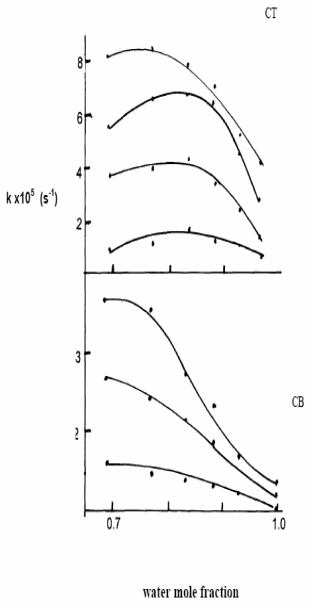

Figure 4 . Dependence of the first order rate contants on the solvent composition in water isopropyl solutions

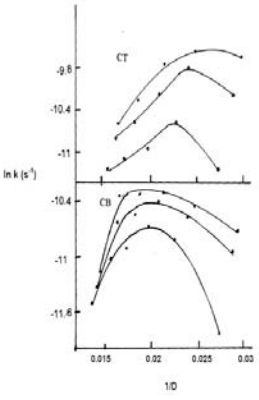

Figure 5. Dependence of the first order rate constants on the dielectric constant of the medium in water methanol solutions

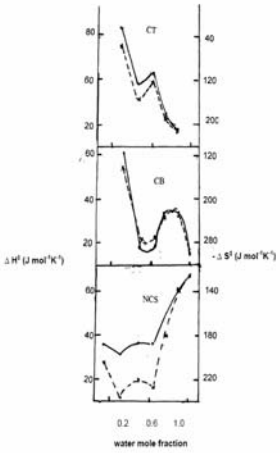

Figure 7. Dependence of the activation parameters on the solvent composition in water methanol solutions (- - - $\Delta S^{\neq}$ and — $\Delta H^{\neq}$)

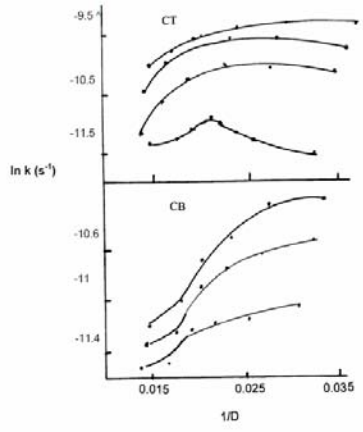

Figure 6. Dependence of the first order rate constants on the dielectric constant of the medium in water isopropyi solutions

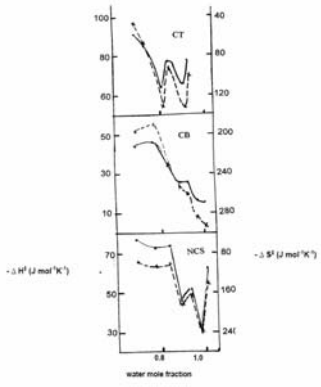

Figure 8. Dependence of the activation parameters on the solvent composition in water isopropyl solutions (- - - $\Delta S^{\neq}$ and — $\Delta H^{\neq}$)

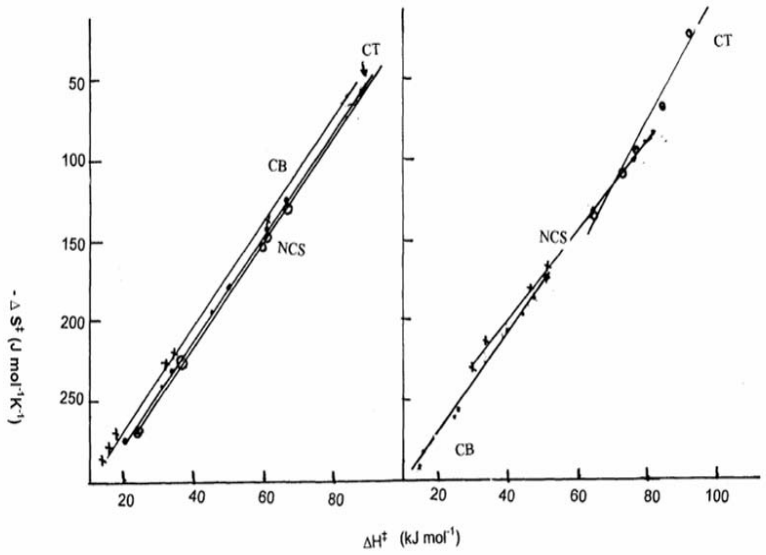

Figure 9. Aplot of $\Delta S^{\ddagger}$ vs. $\Delta H^{\ddagger}$ for the Solvolysis of N-halamine in (A) water methanol solutions and (b) water isopropyl solutions

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