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INFLUENCE OF MONOVALENT CATIONS ON THE RATES OF DIBROMOSUCCINATE AND HYDROXIDE IONS

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ABSTRACT:

The rate constants for the reaction between dibromosuccinate and hydroxide ions have been determined in the presence of lithium and sodium chloride. Effects of temperatures and added electrolytes on this reaction have also been examined. Its has been found that smaller radii have less accelerating effects on the rate of reaction. The activation parameters such as apparent energy of activation (E_a), change in enthalpy of activation ($\Delta H^{\#}$), change in entropy of activation ($\Delta S^{\#}$) and change in free energy of activation ($\Delta G^{\#}$) have been calculated in the absence and presence of lithium and sodium chloride for the reaction and discussed.

INTRODUCTION

The reaction between dibromosuccinate and hydroxide ions is an anion-anion reaction B., Holmberg, 1921 This reaction follows second order kinetics:

$$\frac{dx}{dt} = k\ [(CH\ Br\ COO)e][OH\ J^-] \qquad . \ . \ . \ (1)$$

.

where $\frac{dx}{dt}$ and k represent rate of reaction and rate constant respectively

various workers (B. Holmberg, 1921, F. Ferranti,1970, A., Giacomelli, 1970, F. Ferranti, 1977, M.G. Ahmed 1979, F.Uddin, 1980, 1981, 1985, 1986, F. Uddin & N. Shahid, 1989, F.Uddin, R. Naheed 1989 F.Uddin and N. Shahid, 1996, Fuddin, Z. Khalid, 1996) carried out studies of rate constants of reactions between ions in aqueous solutions. The variation of the rate constant with ionic strength of the solution can be predicted from Bronsted Debye-Huckel theory i.e.

$$\log k = \log k_o + 1.02\ Z_A\ .\ Z_B. \qquad \sqrt{\mu} \quad \text{at } 25° \qquad . \ . \ . \ (2)$$

where $k_\circ$ is the rate constant at zero ionic strength. Z_A and Z_B are the charges of the ions A and B respectively.

In the present work studies are made on the rates of reaction between dibromosuccinate and hydroxide ions in presence of lithium and sodium chlorides in order ^{1}r to find out the dependence of activation parameters as a function of ionic strength.

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EXPERIMENTAL

All the chemicals and salts used were of AR grade. The kinetic measurements were all carried out in electrically operated water bath.

Dibromosuccinate and sodium hydroxide of concentration 1.2 x 10^{-2} mol.dm^{-3} were kept separately in water bath at the required temperature for about half an hour. Equal volumes of both reacting solutions were mixed and the time of mixing was recorded. Concentration of unreacted sodium hydroxide was determined by nitrating 5 mls of reaction mixture against standard hydrochloric solutions at different time intervals using phenolphthalein solution as an indicator. The ionic strength of reaction mixture was 4.8 x 10^{-3}mol.dm^{d}- In order to study the salt effect, ionic strength was varied upto 6.9 x 10^{-2} .mol.dm^{-3} by addition of different salts (lithium chloride, sodium chloride) of different concentrations which were in the range of 2.1 x 10^{-3} to 6.5 x 10^{-3} mol.dm^{-3}. The rates of reaction were measured at various ionic strengths and temperatures in aqueous media.

RESULTS AND DISCUSSION

The rate constants of the reaction between dibromosuccinate and hydroxide ions were calculated using the second order rate equation:

$$K = \frac{1}{T} \frac{x}{a(a-x)} \qquad \ldots (3)$$

where ‘a’ is the initial concentration of both hydroxide and dibromosuccinate ions and ‘x’ is the amount decomposed in time ‘t’.

Rate constants in presence of lithium chloride (LiCl) and sodium chloride (NaCl) salts at different ionic strengths and temperatures are tabulated in table I. It was observed that rate constant increased with the increase of temperature due to increase in effective collision. Moreover, at a particular temperature, there is a gradual increase in rate constant with the increase of ionic strength induced by the addition of salt. It was found that the reaction obeys the following sequence of rate constant.

$$K_{Na}+ \quad > \quad k_{Li}+$$

Less accelerating tendency was observed in LiCl as compared to NaCl salt. This may be related to change in the hydration suggested by Haymann and Stein (BY., Hayman, 1964), and ion pair formation as confirmed by Blandamer, et al (M.J., Blandemer, 1974) and Indelli, et al (A. Indelli, 1960). Ion pair reacts faster and the achieved configuration of the transition state requires less energy to from the products.

Table-I

Rate Measurements Data

Ionic strength	**rate constant 10^2k (dm$^{'}$ /moist at temp.°C**					
10^3 p (mol / dm$^{'}$)	**20°**	**25°**	**30°**	**35°**	**40°**	**45°**
		in presence of LiC1				
6.9	1.99	2.63	4.78	6.76	9.55	14.71
9.5	2.39	3.63	5.24	7.94	10.96	15.84
15.0	2.88	4.26	6.02	8.91	12.58	17.37
34.8	3.46	5.01	7.24	10.96	14.45	20.41
69.8	4.46	6.30	8.70	12.58	17.37	22.90
Zero	1.42	2.02	3.56	5.22	7.44	11.85
		in presence of NaCl				
6.9	2.88	4.50	7.14	10.08	14.26	20.12
9.5	3.46	5.28	7.83	11.90	16.36	21.56
15.0	2.17	6.22	9.00	13.35	18.79	23.29
34.8	5.08	7.30	10.83	16.42	21.58	25.50
69.8	6.56	9.20	13.02	18.84	25.90	30.00
Zero	2.03	3.33	5.30	7.79	11.11	16.59

Kilpatrick equation (M. Kilpatrick, 1934) given as below was used to determine the values of $Z_A.Z_B$ at different temperatures:

$$\ln k = \ln k_o + e^3 \frac{(8\pi N/1000)^{1/2}}{(\epsilon \mathbf{K} T)^{3/2}}. \quad Z_A.Z_B \quad \left(\frac{\sqrt{\mu}}{1+\sqrt{\mu}}\right) \qquad \ldots. \ (4)$$

where e is electronic charge, N is Avogadro number, ϵ , **K** and T represent dielectric constent of the medium, Boltzmann's constant and absolute temperature respectively.

Bronsted-Kilpatrick's plots of log k against $(\sqrt{\mu}/1+\sqrt{\mu})$ were drawn and shown in figures 1 and 2 for salts LiCl and NaCl respectively.

The positive slopes of straight line led to the conclusion that the reaction is occurring between ions of similar charges. The average value of $Z_A.Z_B$ obtained from the above data as 1.88 is in agreement with the theoretical value ($Z_A.A_B$ =2). The values of rate constants at zero ionic strength (k_o) were obtained from the extrapolation of plots and also tabulated in table I.

From the rate measurements data, the Arrhenius plots i.e. log k versus reciprocal of the absolute temperature (l/T) were drawn and shown in figures 3 and 4, for LiC1 and NaCl salts respectively. The values of activation energy against corresponding ionic strengths were obtained from the negative slopes of the Arrhenius plots and tabulated in table II. Results show that activation energy decreases with the increase in ionic strength and with the increase in the size of the cation of the added salt due to change in configuration of activated complex. The results are in accordance with the theory.

The plots of energy of activation (E_a) against square root of the ionic strength ($\sqrt{\mu}$) drawn for lithium chloride and sodium chloride salts are shown in figures. 5 & 6 respectively. Straight-line graphs having negative slopes were obtained. This is in accordance with the theoretical equation (F. Uddin, 1980). This value of energy of activation at zero ionic strength obtained from extrapolation of E_a vs $\sqrt{\mu}$ plots are also tabulated in table II.

Activation parameters i.e. $\Delta H^{\#}$, $\Delta S^{\#}$ and $\Delta G^{\#}$ were calculated using the following expressions (J. L., Latham, 1962)

$$\Delta H^{\#} = E_a - RT \qquad (5)$$

$$A = \frac{KT}{H} . e^{\Delta S^{\#}/R} \ \ldots\ldots\ldots\ldots\ldots\ldots \ (6)$$

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#} \qquad \ldots. \qquad (7)$$

Table - II

Activation Parameters at 25°C

$10^3\mu$	Electrolyte	E_a (KJ/mol)	$\Delta H^{\#}$ (KJ/mol)	$\Delta S^{\#}$ (J/deg.mol)	$\Delta G^{\#}$ (KJ/mol)
6.9	LiCl	62.07	59.56	-64.83	78.91
6.9	NaCl	58.93	56.43	-71.68	77.83
9.5	LiCl	57.47	55.00	-78.54	78.41
9.5	NaCl	56.64	54.17	78.16	77.45
15.0	LiCl	55.09	52.62	-85.23	77.99
15.0	NaCl	53.88	51.41	-85.98	77.03
34.8	LiCl	54.38	51.95	-86.02	77.58
34.8	NaCl	51.45	48.98	-92.67	77.66
69.8	LiCl	53.81	48.07	-97.06	77.03
69.8	NaCl	51.02	48.52	-100.56	76.49
Zero	LiCl	65.45	63.53	-56.22	80.67
Zero	NaCl	64.79	62.32	-56.59	79.29

where ‘A’is frequency factor obtained from the intercept of Arrhenius plots, and ‘h’ is Planck’s constants, Calculated values of $\Delta H^{\#}$, $\Delta S^{\#}$ and $\Delta G^{\#}$ as a function of ionic strength are also summarized in Table II. The values of $AS^{\#}$ are negative which indicate a loss of entropy as a consequence of the increased charge on the activated complex with respect to the charge of the separated ions. It was observed that as the ionic strength increases, the formation of activated complex is accompanied by a large decrease in entropy. This is due to the conversion of some translational and rotational degree of freedom of the reactants to vibrational degree of freedoms of the activated complex. Positive values of $\Delta G^{\#}$ show that the formation of activated complex is a non-spontaneous process.

Temperature coefficient of rate constants per five degree rise in temperature were also evaluated and summarized in table. III. Data show that the temperature coefficients are almost unaffected by change in ionic strength as reported earlier for an anion-anion reaction (M. Kilpatrick, 1934).

Table – III

Temperature Coefficients in Presence of Electrolytes

$10^2 \sqrt{\mu}$ (mol.dm-3)	K_{25}/k_{20}	k_{30}/k_{25}	k_{35}/k_{30}	k_{40}/k_{35}	k_{45}/k_{40}	Average
			In presence of LiC1			
8.30	1.32	1.82	1.41	1.41	1.55	1.50
9.70	1.51	1.44	1.51	1.38	1.44	1.45
12.24	1.48	1.41	1.47	1.41	1.38	1.43
18.65	1.44	1.44	1.51	1.31	1.41	1.42
26.41	1.41	1.38	1.44	1.38	1.32	1.38
			in presence of NaCl			
8.30	1.56	1.58	1.41	1.41	1.41	1.48
9.70	1.52	1.48	1.52	1.37	1.31	1.47
12.24	1.49	1.45	1.48	1.40	1.24	1.42
18.65	1.44	1.48	1.51	1.31	1.18	1.38
26.41	1.41	1.41	1.45	1.37	1.15	1.36

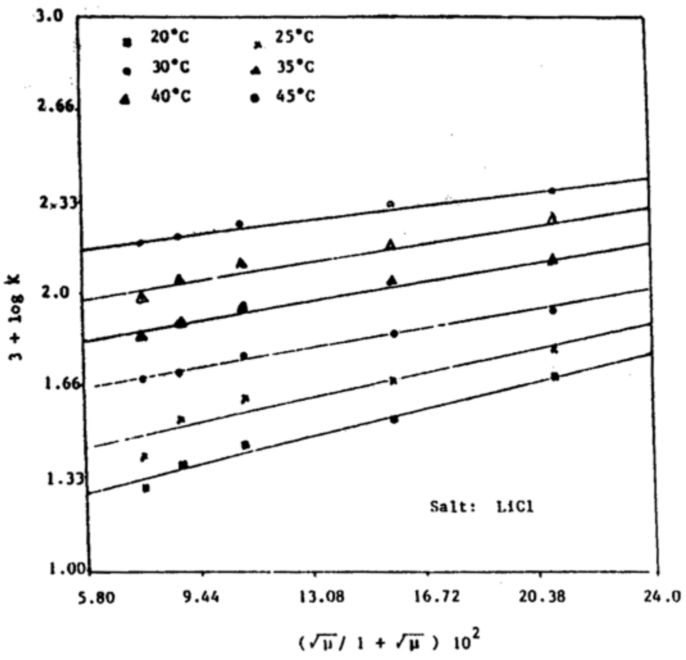

Fig. 1: Plots of log k vs $(\sqrt{\mu}/1+\sqrt{\mu})$ at various temperatures in presence of LiCl.

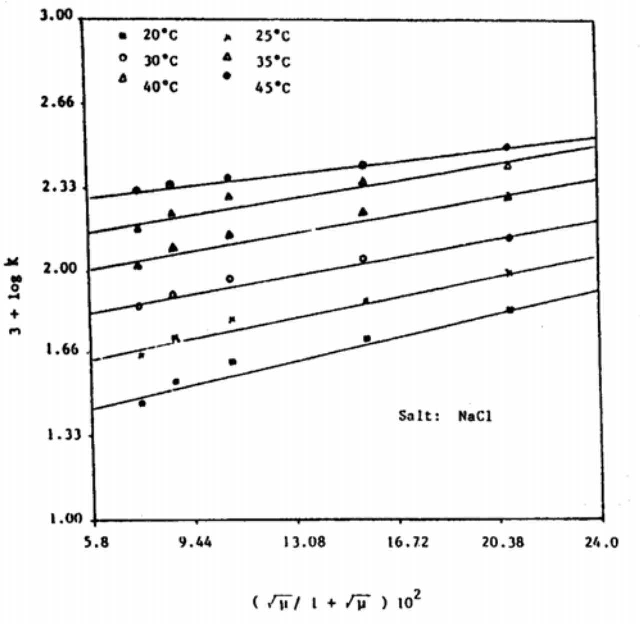

Fig. 2: Plots of log k vs $(\sqrt{\mu}/1+\sqrt{\mu})$ at various temperatures in presence of NaCl.

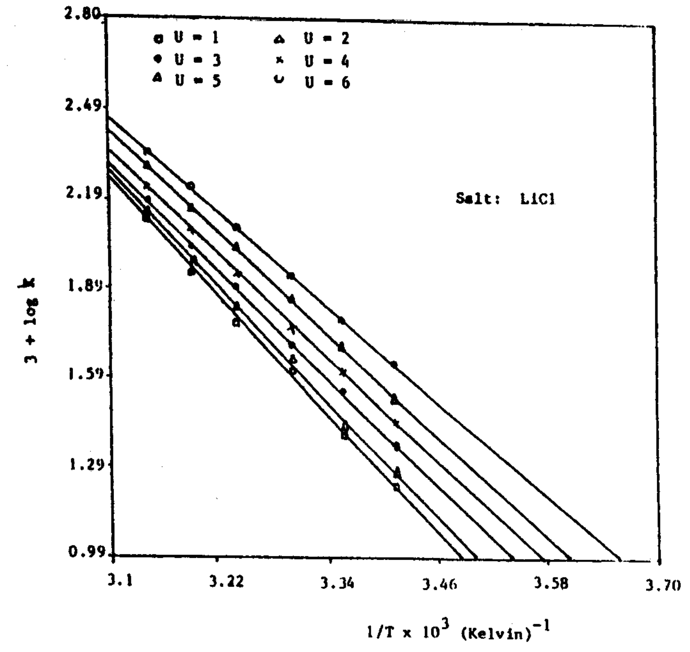

Fig. 3: Plots of log k vs 1/T at various ionic Strengths in presence of LiCl.

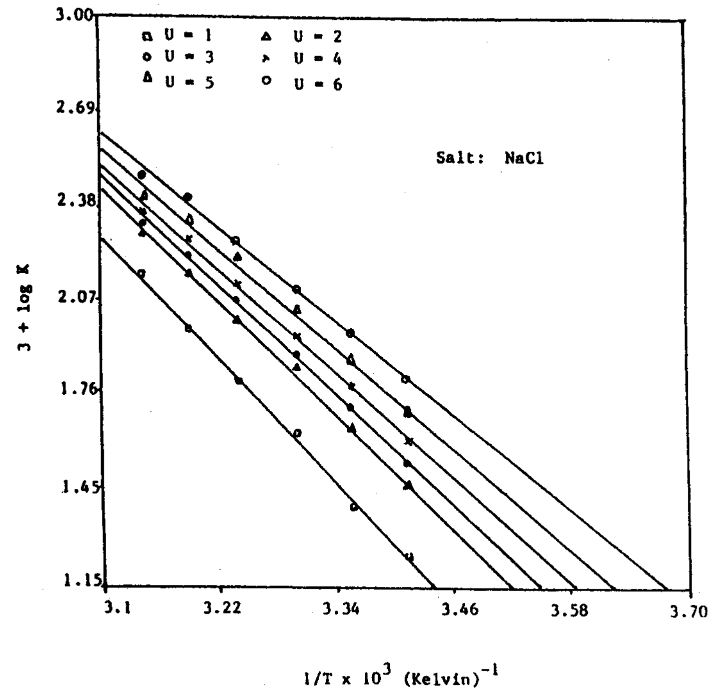

Fig. 4: Plots of log k vs 1/T at various ionic Strengths in presence of NaCl.

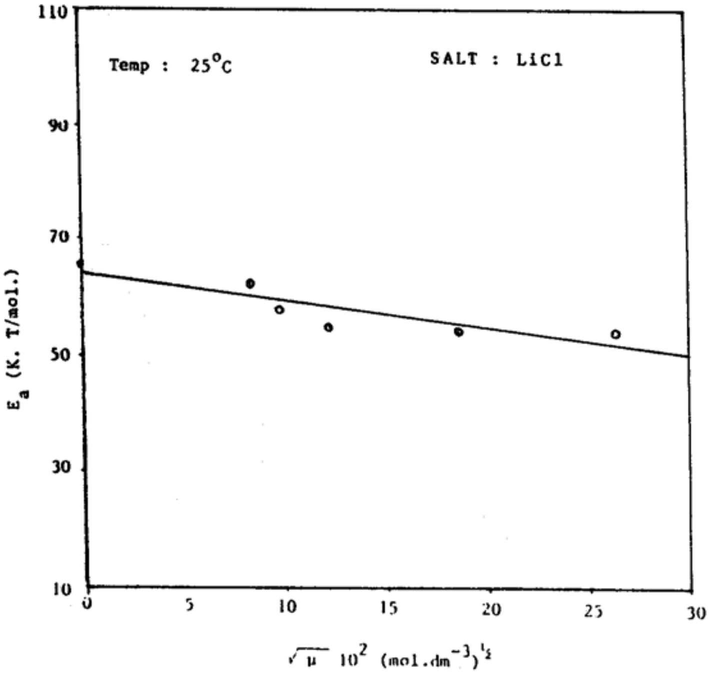

Fig. 5: Plots of E_a vs $\sqrt{\mu}$ in presence of LiCl.

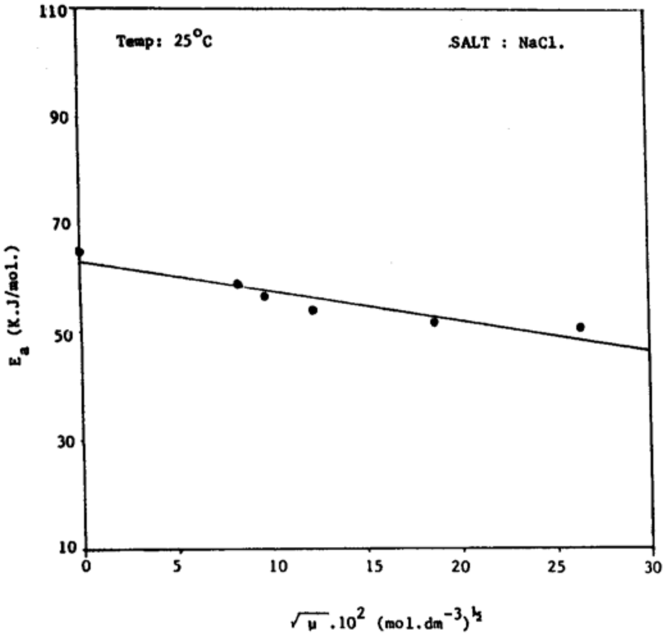

Fig. 6: Plots of E_a vs $\sqrt{\mu}$ in presence of NaCl.

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