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THE INFLUENCE OF SALT CONCENTRATION AND TEMPERATURE ON THE ACTIVATION ENERGY OF AQUEOUS SALT SOLUTIONS BY VISCOSITY METHOD

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The visosity of sodium salts, namely, sodium tartarate and sodium oxalate in acidic aqueous ethanol (10-50% v/v) has been measured at 30°. The viscosities at 30°, 40°, 50°, and 60°C have also been measured at different concentrations of sodium salts in 50% ethanol, for the determination of the energy of activation. The viscosity data were found to fit the Jones-Dole equation. The increase in B-coefficient with an increase in temperature leads to the conclusion that the sodium salts behave as a structure breaker in acidic aqueous ethanol.

INTRODUCTION

To analyse the viscosity data, the Jone – Dole equation[1] is used. The equation is expressed as:

$$\eta/\eta_0 = 1 + A\sqrt{C} + B.C. \dots\dots\dots (1)$$

where η and η_0 are the viscosities of the solution and solvent respectively, C is the molar concentration and A and B are the constants which represent ion-ion interaction and ion-solvent interaction respectively. The B-coefficient is a better measure of the interaction of the added electrolyte in a particular medium. This is in accordance with the views of Gurney[2], Kaminsky[3], Nightingale[4], and Ganapathy[5].

The effect of temperature on viscosity is given by the expression[6]:

$$\eta = A.\,\text{Exp}\,(E/RT) \dots\dots\dots (2)$$

where A is a constant, E is the energy of activation, R is gas constant and T is absolute temperature.

The measurements on activation energy have been reported earlier by Qurashi and *et al.*[7-9], and Lallan Singh [10]. In the present study the viscosities of solutions of sodium tartarate and sodium oxalate in acidic aqueous ethanol have been measured.

EXPERIMENTAL

Sodium tartarate, sodium oxalate, oxalic acid, tartaric acid (Analar grade) were used without further purification. Doubly distilled water was used for preparing stock solutions[11].

To measures the viscosity, an Ostwald viscometer was used and densities were determined using a specific gravity bottle (25 ml capacity). The composition of solvent and the concentration of salts were varied, while the concentrations of tartaric acid and oxalic acid were constant throughout the experiments. The viscosity co-efficients of water used for calculations were 0.995, 0.992, 0.988, and 0.983 millipoise at 30°, 40°, 50°, and 60°C respectively.

RESULTS AND DISCUSSIONS

The viscosities of sodium tartarate in acidic aqueous ethanol at different compositions of solvent and different temperatures are tabulated in Tables 1 and 2. Our results show that there is a regular increment in viscosities of the salt at 30°C with the increase in the composition of the solvent. Viscosities of sodium tartarate increases with the increase in the concentration of salt at 30°C.

The results tabulated in Table 2 indicate that the viscosities of the salt decrease with a rise in temperature

Table 1. Viscosities of sodium tartarate in acidic aqueous Ethanol at 30°C.

[Salt] x 10^2 (mol. dm^{-3})	Viscosities (millipoise)			
	Compositions of solvent (%)			
	10	20	30	40
1.0	0.7225	2.1973	3.8837	9.8529
2.0	0.8801	2.2186	3.9320	10.1344
3.0	0.9845	2.4590	4.0245	11.3211
4.0	0.9931	2.4626	4.7218	11.7350
5.0	1.2944	3.0632	4.8028	12.0925

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(30-60°) at a fixed concentration of the salt. The values of A and B of equation (1) were determined from the intercept and slope of the linear plots of $(\eta/\eta_o - 1) / (C)^{1/2}$ vs $(C)^{1/2}$. The specimen graph for sodium tartarate in acidic 40% aqueous ethanol at 30°C is shown in Fig. 1. A and B values at different composition and different temperatures are summarized in Table 3.

Table 2. Viscosities of sodium tartarate in acidic 50% aqueous ethanol.

[salt] x 10^2 (mol.dm^{-3})	Viscosities (millipoise)			
	Temperature °C			
	30	40	50	60
1.0	11.6973	10.6091	8.7124	3.4355
2.0	13.4021	10.9906	9.0605	4.4094
3.0	12.8071	11.6559	8.6340	6.6206
4.0	12.4140	12.1502	9.8734	6.9426
5.0	12.3046	12.1015	9.6006	7.3433

Table 3. The values of the parameters A & B of Jone – Dole equation

Comp. of ehtanol (%)		Sodium Tartarate A	Sodium Tartarate B	Sodium Oxalate A	Sodium Oxalate B
10	(a)	–6.4	25.88	–4.35	9.67
20	(a)	–7.1	24.28	–4.54	6.66
30	(a)	–7.54	23.55	–3.76	7.74
40	(a)	–6.3	21.17	–6.15	19.20
50	(a)	–4.9	21.03	–4.82	19.31
	(b)	–4.59	12.72	–3.79	14.62
	(c)	–5.58	16.00	–5.99	15.65
	(d)	–5.88	17.14	–7.5	22.60

a denotes 30°C; b denotes 40°C; c denotes 50°C; d denotes 60°C.

To understand the irregular variation in A, the solvent structure must be taken into account. Variation in A is attributed to the size of the tartarate and sodium ions which differ in their degree of hydration. Low values of A at lower ethanol content of the solvent leads to the conclusion that the hydration is greater and solvent – solvent interaction is small. Increase in ethanol content results in lesser degree of hydration and increase in the value of A, at higher temperatures. Ions escape from the surrounding sheath and get a chance to interact with each other.

The β-coefficient can be discussed in terms of viscosity effects at a particular concentration, according to the Stokes equation[12]:

$$\eta^E + \eta^A + \eta^D = \eta^\circ . B.C \ldots\ldots\ldots (3)$$

where η^E is the viscosity increment due to the size and shape of the ion, η^A is viscosity increment due to the orientation of solvent molecules around the ion and η^D is the viscosity decrement as a result of distortion of solvent structure.

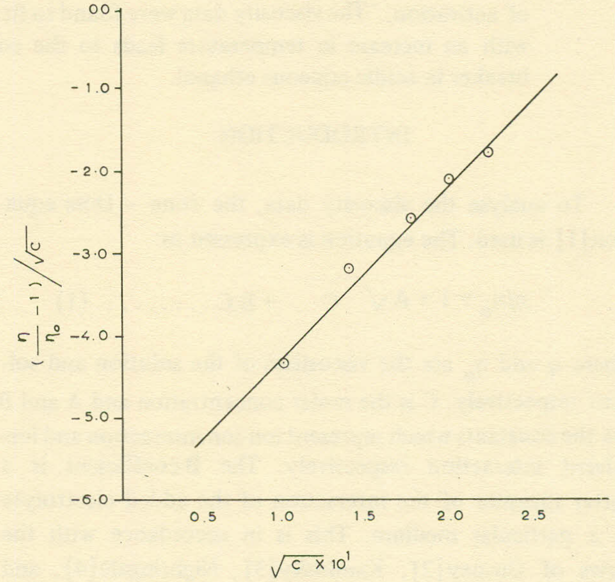

Fig. 1. Plot of $(\eta/\eta_o - 1)/(C)^{1/2}$ vs $(C)^{1/2}$ for sodium tartarate in acidic aqueous ethanol (40%) at 30°C.

Decrease in β-coefficient may be explained by the consideration of the fact that this effect may be due to the formation of mixed solvent clusters, which are more strongly bonded with each other, become bulkier and are therefore unable to interact with ions for the lack of proper orientation around the ion. Although the high positive values of B-coefficients reveal that sodium tartarate behaves as a structure breaker, the decrease is attributed to the increase in solvent-solvent interactions, with increase in ethanol content of the solvent. Also at high temperature, the surrounding sheath of the solvent molecule around the ion is broken and ion-solvent interaction weakens. Under such circumstances, ions may get a chance to interact with each other.

The activation energy of viscous flow can be related to the work needed to form vacant sites in the solvent matrix and may be regarded as the measure of the structure of solvent. A plot of log η vs reciprocal of the absolute temperature (I/T) gives a straight line whose slope is E/2.303R. The values of the energy of activation for sodium tartarate in 50% acidic ethanol are given in Table 4. Energy of activation for the viscous flow was found to be increasing with the increase in salt concentration. At higher concentration, greater number of ions will be present which will hinder the ionic mobility and will make it difficult to produce vacant sites in the solvent matrix resulting in high energy of activation.

Tables 5 and 6 show the values of the viscosities of sodium oxalate in acidic aqueous ethanol at various compositions of solvent and different temperatures for different concentrations of the salt. Our results indicate that the viscosities of the salt solution at 30°C increase with the increase in the composition of the solvent as well as salt, and decrease with a rise in temp (30-60°C) except at 40°C, at a fixed concentration of the salt solution.

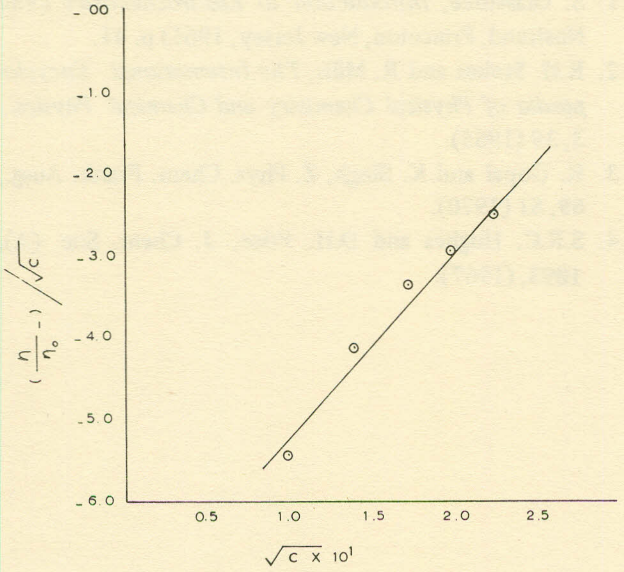

Fig. 2. Plot of $(\eta/\eta_o - 1)/(C)^{1/2}$ vs $(C)^{1/2}$ for sodium oxalate in acidic aqueous ethanol (50%) at 60°C.

The linear plots for sodium oxalate were obtained when$(\eta/\eta_o - 1) / (C)^{1/2}$ was plotted against the square root of the concentration of the salt $(C)^{1/2}$. A specimen graph for sodium oxalate in acidic 50% aqueous ethanol at 60°C is shown in Fig. 2. It can be seen from Table 3 that the values of A and B are not regular. This indicates that the behaviour of solvent in acidic medium with salt is not regular. A value should decrease with the rise in temperature. It was seen that it did decrease with the rise in temperature except at the temperature of 40°C, where it was increased. This may be due to the interpenetration effect (cation-cation [13], or cation-anion[14].

Table 4. Energy of activation for sodium tartarate and sodium oxalate in 50% acidic ethanol.

$[Salt] \times 10^2$ $(mol. dm^{-3})$	$E_\eta \times 10^{-3}$ $J.mol^{-1})$	
	Sodium Tartarate	Sodium Oxalate
1.0	19.13	04.02
2.0	20.62	19.13
3.0	21.50	20.20
4.0	21.87	27.74
5.0	26.09	09.46

Table 5. Viscosities of sodium oxalate in acidic aqueous ethanol at 30°C.

$[Salt] \times 10^2$ $(mol.dm^{-3})$	Viscosities (millipoise)			
	Composition of solvent (%)			
	10	20	30	40
1.0	0.7409	1.8227	3.8868	5.3631
2.0	0.7553	2.0404	4.2380	6.0689
3.0	0.9615	2.2259	5.1547	6.2240
4.0	1.0315	2.3992	5.2865	6.8708
5.0	1.2316	2.7636	5.3674	7.2389

Table 6. Viscosities of sodium oxalate in acidic 50% aqueous ethanol.

$[Salt] \times 10^2$ $(mol. dm^{-3})$	Viscosities (millipoise)			
	Temperature in °C			
	30	40	50	60
1.0	9.0844	14.7361	8.2778	7.9598
2.0	8.7784	11.0553	11.5070	7.2079
3.0	12.0468	13.2693	08.7604	7.2872
4.0	8.9172	13.1168	08.6970	6.9831
5.0	9.5172	10.5519	09.1154	8.7272

The β-coefficient increases with a slight irregularity with the increase in temperature. This shows that the salt behaves as a structure breaker in acidic ethanol medium.

The regular arrangement of solvent molecules must have broken down due to the dipole interaction with salt. These results are in well comparison with the results obtained by Ganapathy and *et al.* [5].

The values of E for sodium oxalate are given in Table 4. A regular increase in E is observed with the increase in salt concentration except at the concentration of 5.0 x 10^{-2} mol.dm $^{-3}$, where E suddenly drops to a lower value. The values of constant A obtained from viscosity – temperature equation are 7.943, 7.079, 7.413, 6.988. and 8.70 at the concentration of 1.0, 2.0, 3.0, 4.0, 5.0 x 10^{-2} mol. dm $^{-3}$ for salts respectively. Higher value of A indicates that the solution becomes more stable and hence significant decrease in viscosity is observed.

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