A Study on Viscosities of Oxalic Acid and its Salts in Water Rich Binary Aqueous Mixtures of Dioxane

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ABSTRACT: Relative viscosities of oxalic acid and its salts viz. ammonium oxalate, sodium oxalate and potassium oxalate at different concentrations have been determined in different compositions of dioxane (3, 6, 9, 12 and 15% by weight of dioxane) at 298.15 K and 3% (w/w) dioxane + water at five different temperatures. The data have been evaluated using Jones-Dole equation and the obtained parameters have been interpreted in terms of solute-solute and solute-solvent interactions. The activation parameters of viscous flow have been obtained which depicts the mechanism of viscous flow. Oxalic acid and its salts behave as structure breaker in binary aqueous mixture of dioxane.

Keywords: Dioxane; potassium oxalate; viscosity and oxalic acid.

INTRODUCTION: The viscosity of a liquid is a measure of its resistance to flow. Since the flow takes place by displacement of the equilibrium positions of the molecules, studies of viscosity can lead to information about these displacements. The viscosity of electrolyte solutions is usually studied to obtain information of ion solvent interactions. Addition of an electrolyte either breaks or makes the structure of the liquid. The making and breaking the structure of fluids have been considered as a measure of solute-solvent interactions. The solution structure is of great importance in understanding the nature of bioactive molecules in the body system. The survey of literature [1-6] shows that although many studies have been carried out for various electrolytic solutions, little attention have been paid to behavior of oxalic acid and its salts in water and in water rich binary aqueous mixtures of dioxane.

MATERIAL AND METHODS:

Distilled Water: The water used for the calibration of apparatus, for preparing binary mixtures as well as the standard liquid, for preparing various solutions was obtained by distilling the water thrice over alkaline $KMnO_4$, $K_2Cr_2O_7$ and quartz having specific conductance of the order of 10^{-6} $Ohm^{-1}cm^{-1}$. The water was stored in glass bottles.

Reagents: The reagents, oxalic acid [$(COOH)_2 \cdot 2H_2O$, M.W. 126.05 g], ammonium oxalate [$(COONH_4)_2 \cdot H_2O$, M.W. 142.11 g], sodium oxalate [$(COONa)_2$, M.W. 134.00 g] and potassium oxalate [$(COOK)_2 \cdot H_2O$, M.W. 184.23 g], were of AnalaR grade. These reagents were used after drying over anhydrous calcium oxide in a desiccator.

Purification of Dioxane: Dioxane (Analyzed Reagent grade) was purified by refluxing over sodium metal for six hours followed by distillation. Only the middle fraction was used. The physical constants of dioxane used at 298.15 K, such as density and viscosity were 1.0271×10^{-3} kgm^{-3} and 1.191×10^{-3} N sec m^{-2}, respectively and agree with literature values [7] (1.0269×10^{-3} kgm^{-3} and 1.196×10^{-3} N sec m^{-2}). The different compositions of dioxane + water, and solutions of different electrolytes were prepared by weight. The molality (m) of electrolyte was converted into molarity (c) by using the following expression: [8]

$$c = \frac{m.d.1000}{1000 + mM_2}$$

Measurement of Density and Viscosity: The density was measured with the help of an apparatus similar to the one described by the Ward and Millero [9] described elsewhere [10]. The accuracy in density measurement was $\pm$ 1×10^{-5} gcm^{-3}. The relative viscosities were measured at the desired temperature using an Ostwald's suspended level type viscometer with a flow time 375 s for water at 298K. Runs were repeated until three successive determinations were obtained within $\pm$ 0.1 s. since all the flow times were greater than 100 s the kinetic energy correction was not necessary. The relative viscosities of the solutions were calculated by usual procedure [11-12]. The density and viscosity measurements were carried out in water bath ($\pm$ 0.01 ^{0}C)

RESULTS AND DISCUSSION: Viscosities, relative viscosities and densities for the solutions of oxalic acid and its salts viz; ammonium oxalate, sodium oxalate and potassium oxalate in water-rich binary aqueous mixtures of dioxane [3, 6, 9, 12 and 15 weight percent of dioxane] were measured at

298.15 K. The concentration dependence of relative viscosity (η_r) for oxalic acid and its salts in present systems can be represented by Jones-Dole equation[13]

$$\eta_r = \eta/\eta_o = 1 + Ac^{1/2} + Bc \qquad (1)$$

where η and η_o are the viscosity coefficients of the solution and solvent (water and water + dioxane) respectively, and c is the molar concentration . A and B are the constants characteristic of solute-solute and solute- solvent interactions respectively. Linear plots have been obtained between (η_r-1)/$\sqrt{c}$ vs $\sqrt{c}$ for oxalic acid and its salts in different compositions of aqueous mixtures of dioxane at 298.15 K. A sample plot for potassium oxalate is shown in Figure 1.
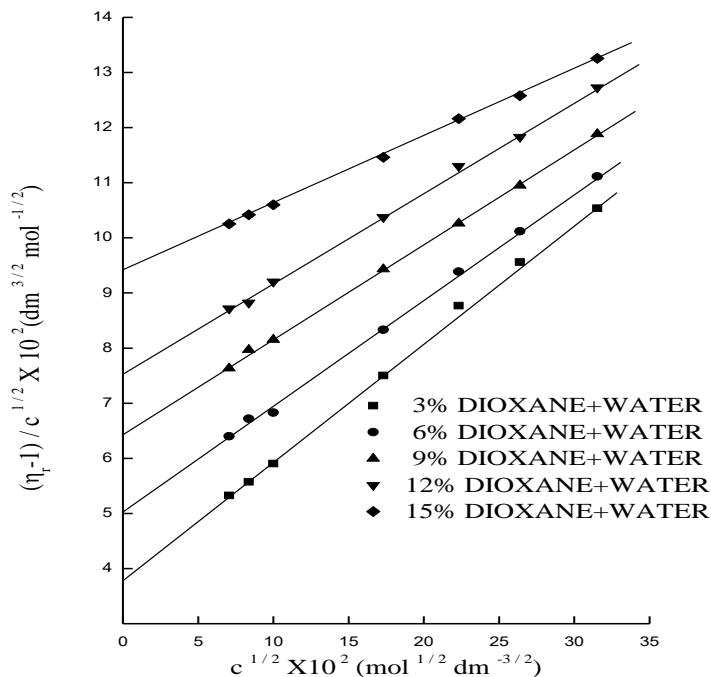

Fig.1. PLOTS OF (η_r-1)/$c^{1/2}$ vs $c^{1/2}$ FOR POTASSIUM OXALATE IN DIFFERENT COMPOSITIONS OF DIOXANE+WATER AT 298.15K.

The values of parameters A and B of Jones-Dole equation have been calculated by applying the method of least-squares to linear plots of (η_r-1)/$\sqrt{c}$ vs $\sqrt{c}$ and the corresponding values, along with their standard errors, are recorded in Table – I. It is evident from this table, the values of parameter A are positive in the entire composition range of dioxane + water for an individual solute at 298.15 K, showing the existence of specific ion-ion interactions. It is also clear from this table-I, the value of A-parameter for each solute continuously increases with the increase of dioxane content in water at 298.15 K, suggesting that ion-ion interactions are further strengthened with the increase of dioxane in water, which may be attributed to the decrease in ion-solvation. In other words, the solvation of so lutes decreases with the increase of dioxane in water, which may be attributed to increase in solvent-solvent interactions i.e. dioxane has more affinity for water than the added solute.

It is also clear from Table 1, the values of B-parameter, for oxalic acid and its salts are positive in the entire composition range of dioxane + water at 298.15 K, showing the presence of strong ion-solvent interactions. Further, the value of B-parameter decreases with the increase of dioxane composition in water at 298.15 K, for an individual solute, shows that ion-solvent interactions are weakened with the increase of dioxane content in water. In other words, ion-solvation is further reduced as the composition of dioxane in water increases or it may be said that dioxane has more affinity for water than the added solute.

Table 1:Values of a and b parameters of the Jones-Dole equation for oxalic acid, ammonium oxalate, sodium oxalate and potassium oxalate in different compositions of dioxane + water at 298.15 K

Composition of dioxane + water [(w/w) %]	A $(dm^{3/2} mol^{-1/2})$	B $(dm^3 mol^{-1})$
OXALIC ACID		
3	4.99 (±0.04)*	0.098 (±0.002)
6	5.73 (±0.04)	0.090 (±0.002)
9	6.87(±0.02)	0.069 (±0.001)
12	8.23 (±0.01)	0.032 (±0.001)
15	9.39 (±0.01)	0.012 (±0.001)
AMMONIUM OXALATE		
3	3.68 (±0.07)	0.253 (±0.004)
6	4.40 (±0.03)	0.238 (±0.002)
9	5.06 (±0.04)	0.227 (±0.002)
12	6.41 (±0.05)	0.204 (±0.002)
15	7.16 (±0.05)	0.201 (±0.002)
SODIUM OXALATE		
3	4.49 (±0.07)	0.390 (±0.003)
6	6.03 (±0.06)	0.354 (±0.003)
9	7.09 (±0.07)	0.352 (±0.004)
12	8.14 (±0.06)	0.340 (±0.003)
15	8.93 (±0.08)	0.334 (±0.004)
POTASSIUM OXALATE		
3	3.77 (±0.07)	0.218 (±0.003)
6	5.01 (±0.06)	0.194 (±0.003)
9	6.46 (±0.04)	0.170 (±0.002)
12	7.52 (±0.05)	0.165 (±0.003)
15	9.38 (±0.03)	0.122 (±0.001)

*standard errors are given in parentheses.

The viscosity data can also be analysed on the basis of transition state theory of relative viscosity of electrolytic solution as suggested by Feakins et al.[14] The B coefficient in the light of this theory can be related by the equation:

$$B = \frac{\overline{V}_1^0 - \overline{V}_2^0}{1000} + \frac{\overline{V}_1^0}{1000} \left[\frac{\Delta\mu_2^{0*} - \Delta\mu_1^{0*}}{RT} \right] \quad (2)$$

here $\overline{V}_1^0$ and $\overline{V}_2^0$ are the partial molar volumes of the solvent and solute (at infinite dilution) respectively, $\Delta\mu_2^{0*}$ is the contribution per mole of the solute to the free energy of activation for the viscous flow of solution, $\Delta\mu_1^{0*}$ is the free energy of activation per mole of pure solvent and is given by the following expressions[15]:

$$\Delta\mu_1^{0*} = \Delta G_1^{0*} = RT \ln (\eta_o \overline{V}_1^0 /Nh) \quad (3)$$

The equation (3.2) may also be rearranged as follows:

$$\Delta\mu_2^{0*} = \Delta\mu_1^{0*} + \frac{RT}{\overline{V}_1^0} [1000 B - (\overline{V}_1^0 - \overline{V}_2^0)] \quad (4)$$

where h is the Planck's constant and N is the Avogadro's number, η_o is the viscosity of the solvent, R is the gas constant and T is the absolute temperature. The values of $\Delta\mu_1^{0*}$ calculated from equation (3) are given in Table 2. For mixed solvents each solvent mixture was treated as pure and molar volume was taken as a mean volume defined as:

$$\overline{V}_1^0 = [x_1M_1 + x_2M_2]/d_1 \quad (5)$$

where x_1, M_1 and x_2, M_2 are the mole fractions and molecular weights of water and dioxane, respectively, and d_1 is the density of solvent mixture (dioxane + H_2O).

Table 2: Values of $\overline{V}_1{}^0$, $\overline{V}_2{}^0$, $\Delta\mu_1{}^0*$ and $\Delta\mu_2{}^0*$ for oxalic acid, ammonium oxalate, sodium oxalate and potassium oxalate in different compositions of dioxane + water at 298.15 K

Composition of dioxane + water [(w/w)%]	$\overline{V}_1{}^0 \times 10^{-6}$ (m^{3}mol^{-1})	$\overline{V}_2{}^0 \times 10^{-6}$ (m^{3}mol^{-1})	$\Delta\mu_1{}^0*$ (kJmol^{-1})	$\Delta\mu_2{}^0*$ (kJmol^{-1})
OXALIC ACID				
3	18.43	87.64	60.74	83.22
6	18.85	79.14	60.93	80.70
9	19.27	71.93	61.13	76.78
12	19.71	65.96	61.33	71.17
15	20.21	57.58	61.52	67.57
AMMONIUM OXALATE				
3	18.43	100.21	60.74	105.76
6	18.85	96.87	60.93	102.50
9	19.27	89.86	61.13	99.40
12	19.71	83.66	61.33	95.02
15	20.21	74.68	61.52	92.86
SODIUM OXALATE				
3	18.43	74.82	60.74	120.76
6	18.85	68.36	60.93	114.00
9	19.27	58.86	61.13	111.49
12	19.71	52.41	61.33	108.19
15	20.21	45.32	61.52	105.57
POTASSIUM OXALATE				
3	18.43	108.70	60.74	102.19
6	18.85	102.02	60.93	97.39
9	19.27	96.69	61.13	92.95
12	19.71	92.92	61.33	91.28
15	20.21	88.54	61.52	84.86

The values of $\Delta\mu_2{}^{0*}$ and $\overline{V}_1{}^0$, for different dioxane + water mixtures, have been calculated with the help of relations (4) and (5), respectively, and the corresponding values are recorded in Table 2. It is clear from Table 2, the value of $\Delta\mu_1{}^{0*}$ does not change appreciably with the change in composition of dioxane + water mixture at 298.15 K. In other words, it may be said that $\Delta\mu_1{}^{0*}$ is practically held constant. It is also clear from this table that the value of $\Delta\mu_2{}^{0*}$ changes with the change in composition of dioxane + water at 298.15 K. The positive values of $\Delta\mu_2{}^{0*}$ suggest that the formation of transition state is less favoured in the presence of oxalic acid and its salts or it may be said that the formation of transition state is accompanied by breaking/distortion of intermolecular bonds. Recently it has been emphasized by many workers that dB/dT is a better criterion[16] for determining the structure making or breaking nature

of any solute, so in order to follow this criterion the effect of temperature must be studied.

Since the behaviour of oxalic acid and its salts have been found to be identical in different compositions of dioxane + water at 298.15 K, only 3 weight percent composition of dioxane + water has been selected to study the effect of temperature .

The plots of $(\eta_r - 1)/\sqrt{c}$ vs $\sqrt{c}$, for oxalic acid and its slats in 3% (w/w) dioxane + water mixture have been found to be linear in accordance with Jones-Dole equation (1). A sample plot for oxalic acid is shown in Figure 2. The values of A and B parameters of Jones-Dole equation have been computed by using least-squares method and the corresponding values, along with their standard errors, are recorded in Table 3. It is evident from Table 3, the values of parameter A are in general positive but small in magnitude, in the entire temperature range, studied here, for oxalic acid and its salts in 3% (w/w) dioxane +

water mixture, showing the existence of specific/weak ion-ion interactions. It is also clear from this table, the value of parameter– A, for individual solute, in 3% (w/w) dioxane + water mixture decreases with the rise in temperature, suggesting that ion-ion interactions are further weakened with the increase of temperature. This may be attributed to the increase in solvation of ions with the increase of temperature. It is also clear from Table -3, the values of parameter-B are positive for the solutions of oxalic acid and its salts in 3% (w/w) dioxane + water mixture at different temperatures, suggesting the presence of strong ion-solvent interactions. The value of B-parameter increases with the rise in temperature, for an individual solute, in 3% (w/w) dioxane + water mixture, showing that ion-solvent interactions are strengthened with the increase of temperature, which may be attributed to increase in solvation of ions
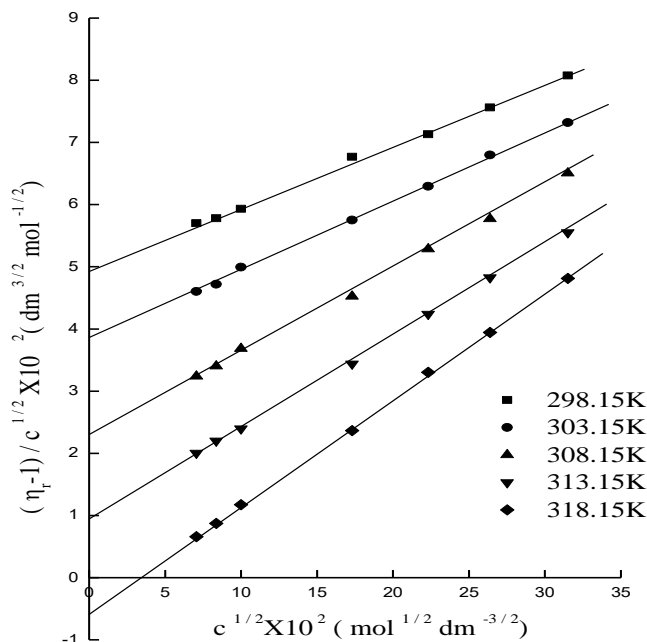

Fig.2. PLOTS OF $(\eta_r-1)/c^{1/2}$ vs $c^{1/2}$ FOR OXALIC IN 3% (W/W) DIOXANE+WATER AT DIFFERENT TEMPERATURES.

Table 3: Values of A and B parameters of the jones-dole equation for oxalic acid, ammonium oxalate, sodium oxalate and potassium oxalate in 3% (w/w) of dioxane + water at different temperatures

Temperature (K)	A ($dm^{3/2} mol^{-1/2}$)	B ($dm^3 mol^{-1}$)
OXALIC ACID		
298.15	4.99 ($\pm$0.04)[*]	0.098 ($\pm$0.002)
303.15	3.83 ($\pm$0.03)	0.112 ($\pm$0.002)
308.15	2.30 ($\pm$0.04)	0.132 ($\pm$0.002)
313.15	0.96 ($\pm$0.02)	0.146 ($\pm$0.001)
318.15	-0.55 ($\pm$0.02)	0.171 ($\pm$0.001)
AMMONIUM OXALATE		
298.15	3.68 ($\pm$0.07)	0.253 ($\pm$0.004)
303.15	1.85 ($\pm$0.06)	0.266 ($\pm$0.003)
308.15	0.81 ($\pm$0.02)	0.292 ($\pm$0.001)
313.15	-1.08 ($\pm$0.06)	0.311 ($\pm$0.003)
318.15	-2.07 ($\pm$0.08)	0.335 ($\pm$0.004)
SODIUM OXALATE		

298.15	4.49 (±0.07)	0.390 (±0.003)
303.15	2.92 (±0.08)	0.428 (±0.004)
308.15	1.08 (±0.07)	0.463 (±0.003)
313.15	-0.32 (±0.05)	0.479 (±0.002)
318.15	-2.65 (±0.05)	0.532 (±0.003)
POTASSIUM OXALATE		
298.15	3.77 (±0.07)	0.218 (±0.004)
303.15	2.43 (±0.03)	0.227 (±0.002)
308.15	0.88 (±0.07)	0.253 (±0.003)
313.15	-0.71 (±0.05)	0.280 (±0.002)
318.15	-1.45 (±0.06)	0.291 (±0.003)

*standard errors are given in parentheses.

The values of dB/dT are positive, for the solutions of oxalic acid and its salts in 3% (w/w) dioxane + water mixture, suggesting that oxalic acid and its salts act as structure breakers. The data of viscosity B-coefficient, at different temperatures, have also been analyzed in terms of transition state theory. The values of $\Delta\mu_1^{0*}$,- the free energy of activation per mole of solvent (dioxane + water), and $\Delta\mu_2^{0*}$, the contribution per mole of solute to the free energy of activation for viscous flow of various solutes in dioxane + water, have been determined at different temperatures with the help of relations (3) and (4), respectively, and are given in Table 4. The corresponding values of $\overline{V}_1^0$ and $\overline{V}_2^0$ required for the calculation of $\Delta\mu_1^{0*}$ and $\Delta\mu_2^{0*}$ are also recorded in Table 4. According to Feakins[14] model, $\Delta\mu_2^{0*}$ increases with temperature for solutes having positive value of dB/dT. This is nicely shown by oxalic acid and its salts which act as structure breakers in water as well as in dioxane+water. The values of $\Delta\mu_2^{0*}$ at various temperatures can be used to calculate the activation entropy for oxalic acid and its salts with the help of following relation[14]:

$$d\left(\Delta\mu_2^{0*}\right)/dT = -\Delta S_2^{0*} \tag{6}$$

Table 4: Values of $\overline{V}_1^0$, $\overline{V}_2^0$, $\Delta\mu_1^{0*}$ and $\Delta\mu_2^{0*}$ for oxalic acid, ammonium oxalate, sodium oxalate and potassium oxalate in 3% (w/w) dioxane + water at different temperatures

Temperature (K)	$\overline{V}_1^0$ x 10^{-6} (m^3mol^{-1})	$\overline{V}_2^0$ x 10^{-6} (m^3mol^{-1})	$\Delta\mu_1^{0*}$ ($kJmol^{-1}$)	$\Delta\mu_2^{0*}$ ($kJmol^{-1}$)
OXALIC ACID				
298.15	18.43	87.64	60.74	83.22
303.15	18.48	93.24	61.48	86.96
308.15	18.51	99.66	62.23	91.73
313.15	18.55	105.21	62.99	95.65
318.15	18.58	110.29	63.77	101.16
AMMONIUM OXALATE				
298.15	18.43	100.21	60.74	105.76
303.15	18.48	103.94	61.48	109.43
308.15	18.51	109.27	62.23	115.20
313.15	18.55	116.72	62.99	120.42
318.15	18.58	119.80	63.77	125.85
SODIUM OXALATE				
298.15	18.43	74.82	60.74	120.76
303.15	18.48	82.90	61.48	128.66
308.15	18.51	88.24	62.23	135.95
313.15	18.55	94.83	62.99	140.93

318.15	18.58	98.55	63.77	150.87
POTASSIUM OXALATE				
298.15	18.43	108.70	60.74	102.19
303.15	18.48	117.40	61.48	105.94
308.15	18.51	123.17	62.23	111.72
313.15	18.55	131.65	62.99	118.17
318.15	18.58	136.65	63.77	121.99

The values of ΔS_2^{0*} have been calculated from the slopes of linear plots of $\Delta\mu_2^{0*}$ vs T. The activation enthalpy (ΔH_2^{0*}) has been calculated with the help of relation[14] (7):

$$\Delta H_2^{0*} = \Delta\mu_2^{0*} + T\Delta S_2^{0*} \qquad (7)$$

and the values of ΔH_2^{0*} are also given in Table 5.

Table 5: Values of ($\Delta\mu_2^{0*} - \Delta\mu_1^{0*}$), $T\Delta S_2^{0*}$ and $\Delta\mu_2^{0*}$ for oxalic acid, ammonium oxalate, sodium oxalate and potassium oxalate in 3% (w/w) dioxane + water at different temperatures

Temperature (K)	($\Delta\mu_2^{0*}-\Delta\mu_1^{0*}$) (kJmol^{-1})	$T\Delta S_2^{0*}$ (kJmol^{-1})	ΔH_2^{0*} (kJmol^{-1})
OXALIC ACID			
298.15	22.48	-265.85	-182.63
303.15	25.48	-270.31	-183.35
308.15	29.50	-274.77	-183.05
313.15	32.66	-279.23	-183.58
318.15	37.39	-283.69	-182.53
AMMONIUM OXALATE			
298.15	45.02	-305.24	-199.49
303.15	47.95	-310.36	-200.94
308.15	52.97	-315.48	-200.28
313.15	57.43	-320.60	-200.18
318.15	62.08	-325.72	-199.87
SODIUM OXALATE			
298.15	60.02	-432.20	-311.44
303.15	67.18	-439.45	-310.80
308.15	73.72	-446.70	-310.75
313.15	77.94	-453.95	-313.02
318.15	87.10	-461.20	-310.33
POTASSIUM OXALATE			
298.15	41.45	-309.00	-206.81
303.15	44.46	-314.18	-208.24
308.15	49.49	-319.36	-207.64
313.15	55.18	-324.55	-206.38
318.15	58.22	-329.73	-207.74

It is evident from Table 5 that both enthalpy and entropy of activation are negative for oxalic acid and its salts viz; ammonium oxalate, sodium oxalate and potassium oxalate, in 3% (w/w) dioxane + water mixture at different temperatures, which suggest that the transition state is associated with bond-breaking and increase in order. Although a detailed mechanism for this cannot be easily advanced, it may be suggested that the slip-plane is in the disordered state.

CONCLUSIONS: Ion-ion interactions though weak improve as the dioxane content in water increases and strong ion-solvent interactions decreases on more addition of dioxane to water.

Ion-ion interactions are further weakened with the increase of temperature. This may be attributed to the increase in solvation of ions with the increase of temperature. Oxalic acid and its salts modifies the structure of the mixed solvent systems i.e. dioxane +water as all act as structure breakers.

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