Viscosities of oxalic acid and its salts in water and binary aqueous mixtures of tetrahydrofuran at different temperatures

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Abstract.   Relative viscosities for the solutions of oxalic acid and its salts, viz. ammonium oxalate, sodium oxalate and potassium oxalate, at different concentrations have been determined in water and in binary aqueous mixtures of tetrahydrofuran (THF) [5, 10, 15 and 20% by weight of THF] at 298·15 K, and in water and in 5% (w/w) THF + water at five different temperatures. The data have been evaluated using the 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. The oxalic acid and its salts behave as structure breakers in water and in binary aqueous mixtures of THF.

Keywords.   Viscosities; oxalic acid and its salts; water + THF mixtures; structure-breakers.

1.   Introduction

Studies on viscosities of ionic solutions are of great help in characterizing the structure and properties of solutions. Various types of interactions exist between the ions in the solutions and of these, ion–ion and ion–solvent interactions are of current interest in all the branches of chemistry. These interactions help in better understanding of the nature of solute and solvent, i.e. whether the solute modifies or distorts the structure of the solvent. The solution structure is of great importance in understanding the nature of bioactive molecules in the body system. The survey of literature[1–20] show that although many studies have been carried out for various electrolytic solutions, little attention has been paid to the behaviour of oxalic acid and its salts in water and in water + THF mixtures. Such data are expected to highlight the role of oxalic acid and its salts in influencing the viscosity *B*-coefficient, in water and in mixed solvent systems.

Tetrahydrofuran (THF), commercially known as cellosolves, is a good industrial solvent. It figures prominently in the high energy battery industry and has found its application in the organic syntheses as manifested from physico-chemical studies in this medium.[21] THF + H_2O mixtures are also important

owing to H-bonding between water and tetrahydrofuran. Hence, the present investigation has been undertaken to provide better understanding of the nature of these solutes in water and in THF + water system and to throw light on solute–solvent interactions.

2.   Materials and methods

Oxalic acid, ammonium oxalate, sodium oxalate and potassium oxalate (all of Analytical Reagent grade) were used after drying over P_2O_5 in a desiccator for more than 24 h. The reagents were always placed in the desiccator over P_2O_5 to keep them in dry atmosphere. Freshly distilled conductivity water (sp. cond. $\approx 10^{-6}\,ohm^{-1}\,cm^{-1}$) was used for preparing binary aqueous mixtures of THF as well as standard liquid. Tetrahydrofuran of AnalaR grade was kept over calcium hydride for about 24 h and then decanted and distilled under reduced pressure. The first and last fractions were discarded and only the middle fraction was collected for the present study. Density and viscosity of THF were found to be 0·8810 g cm^{-3} and 0·461 cP respectively at 298 K and are in good agreement with the literature values[22] (0·8811 g cm^{-3} and 0·460 cP).

All the binary aqueous mixtures of THF as well as the solutions of oxalic acid and its salts were made by weight and molalities, *m*, were converted into molarities, *c*, using the standard expression[23]:

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$c = 1000\ d\ m/(1000 + m\ M_2)$, where d is the solution density and M_2 the molecular weight of an solute.

For density measurements, an apparatus similar to the one reported by Ward and Millero[24] and described elsewhere[25] was used. The accuracy in density measurement was of $\pm 1 \cdot 10^{-5}$ g cm^{-3}. The relative viscosities were measured at the desired temperature using Ostwald's suspended level type viscometer with a flow time of 375 s for water at 298 K. Runs were repeated until three successive determinations were obtained within $\pm 0 \cdot 1$ s. Since all the flow times were greater than 100 s, kinetic energy correction was not necessary. The relative viscosities of the solutions ($h_{\rm rel}$) were calculated by the usual procedure.[26,27] Density and viscosity measurements were carried out in a well-stirred water-bath whose temperature was controlled to ± 0.01°C.

3. Results and discussion

The relative viscosities and densities of the solutions of oxalic acid and its salts, viz. ammonium oxalate, sodium oxalate and potassium oxalate in water and in binary aqueous mixtures of THF [5, 10, 15 and 20% by weight of THF] were measured at 298·15 K. The experimental results of relative viscosities of oxalic acid and its salts in water and binary aqueous mixtures of THF have been analysed by the Jones–Dole equation[28]:

$$h_{\rm rel} = h/h_0 = 1 + Ac^{1/2} + Bc, \tag{1}$$

where h and h_0 are the viscosities of the solution and solvent (water, water + THF) respectively, and c is the molar concentration. A and B are the constants characteristic of solute–solute and solute–solvent interactions respectively.

The plots of $[h_r - 1]/\sqrt{c}$ versus $\sqrt{c}$ for oxalic acid and its salts, were found to be linear, with least scatter in water and in different compositions of THF + water reported here. A representative plot for oxalic acid in different compositions of THF + water at 298·15 K is shown in figure 1. The values of A and B parameters have been calculated using the least squares method by fitting the experimental results in the Jones–Dole equation and these values along with standard errors obtained in water and in different mixtures of tetrahydrofuran + water at 298·15 K are recorded in table 1.

A perusal of table 1 shows that the values of A coefficients are positive and large in magnitude in

water but reduce in magnitude considerably just on the addition of a small amount of THF and keep decreasing as the THF content increases and finally become negative, for oxalic acid and its salts at 298·15 K, thereby showing that the solute–solute interactions which were quite strong in water have been reduced to weakened by the addition of THF to water. In other words, these results indicate that oxalic acid and its salts mix more ideally with THF + water as compared to water and there is a perfect solvation of oxalic acid and its salts in higher compositions of THF + water mixtures resulting in weak solute–solute interactions.

It is also evident from table 1 that the *B*-coefficients, are positive for oxalic acid and its salts in water and in binary aqueous mixtures of THF at also increases with the increase in THF composition in water suggesting that the solute–solvent interac-

Table 1. Values of *A* and *B* parameters of Jones–Dole equation for oxalic acid, ammonium oxalate, sodium oxalate and potassium oxalate in water and in different compositions of THF + water at 298·15 K. Standard errors are given in parentheses.

THF + water (% w/w)	A (dm$^{-3/2}$ mol$^{-1/2}$)	B (dm^{3}mol^{-1})
Oxalic acid		
0 (water)	2·840 (0·013)	0·201 (0·001)
5	1·328 (0·015)	0·243 (0·001)
10	0·671 (0·016)	0·258 (0·001)
15	0·014 (0·018)	0·274 (0·001)
20	−0·549 (0·026)	0·287 (0·001)
Ammonium oxalate		
0 (water)	7·720 (0·005)	0·058 (0·001)
5	2·304 (0·015)	0·214 (0·001)
10	1·836 (0·015)	0·225 (0·001)
15	1·410 (0·007)	0·234 (0·002)
20	0·809 (0·021)	0·247 (0·001)
Sodium oxalate		
0 (water)	6·967 (0·032)	0·103 (0·001)
5	1·681 (0·016)	0·308 (0·001)
10	−0·020 (0·036)	0·344 (0·002)
15	−0·362 (0·028)	0·353 (0·001)
20	−0·712 (0·018)	0·364 (0·001)
Potassium oxalate		
0 (water)	10·995 (0·016)	0·177 (0·001)
5	1·414 (0·022)	0·382 (0·001)
10	0·538 (0·025)	0·401 (0·001)
15	−0·405 (0·017)	0·425 (0·001)
20	−2·213 (0·019)	0·468 (0·001)

298·15 K, suggesting the presence of strong solute–solvent interactions. The value of the *B*-coefficient tions increase with the increase of THF in water for oxalic acid and its salts at 298·15 K, which result in the improvement of solute solvation. In other words, preferential solvation by THF molecules would also be expected to reduce the strong interactions of THF molecules with water, resulting in the increase in B values.

It is also clear from table 1 that the value of the *B*-coefficient is influenced to a considerable extent by the addition of 5% (w/w) THF in water for individual solutes. In other words, the solvation of ions is greatly influenced in the presence of aqueo-organic medium as compared to aqueous medium. Since oxalate ion is common in all the three salts so from the values of B-coefficients it may be inferred that the K^+ ion is preferentially solvated by THF + water medium and the order of solvation is:
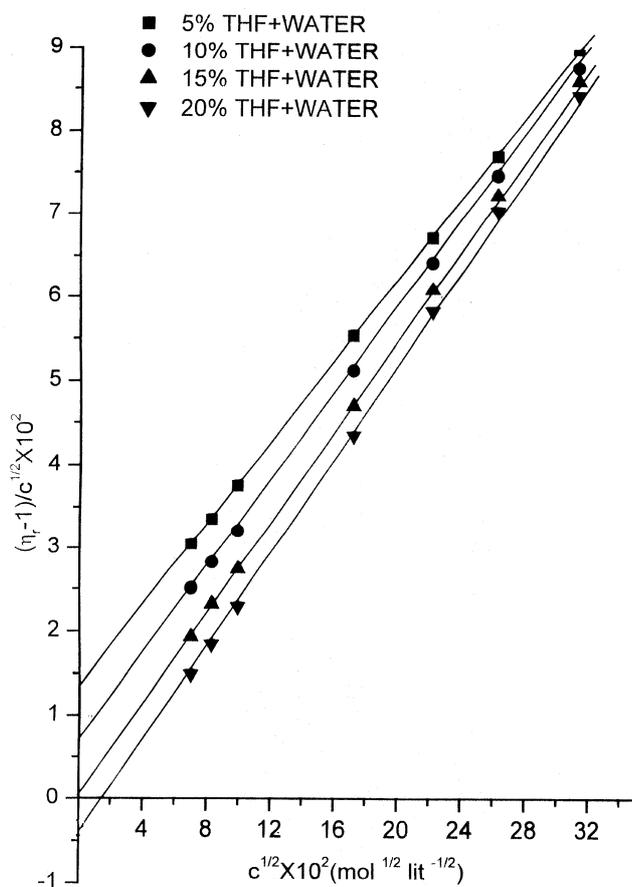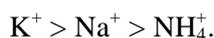
$$K^+ > Na^+ > NH_4^+.$$

Figure 1. Plots of $(\eta_r-1)c^{1/2}$ vs $c^{1/2}$ for oxalic acid in different compositions of THF + water at 298·15 K.

The viscosity data have also been analysed on the basis of transition state treatment of relative viscosity as suggested by Feakins *et al.*[29] The B parameter in terms of this theory is given by the following equation:

$$B = \frac{\bar{V}_1^0 - \bar{V}_2^0}{1000} + \frac{\bar{V}_1^0}{1000}\left[\frac{\Delta m_2^{0*} - \Delta m_1^{0*}}{RT}\right], \quad (2)$$

where $\bar{V}_1^0$ is the mean volume of the solvent and $\bar{V}_2^0$ is the partial molar volume of the solute. The free energy of activation per mole of the pure solvent (Δm_1^{0*}), and the free energy of activation per mole of solute (Δm_2^{0*}) were calculated[30] with the help of (3) and (4) respectively:

$$\Delta m_1^0* = RT \ln (h_0\bar{V}_1^0/hN), \quad (3)$$

and

$$\Delta m_2^0* = \Delta m_1^0* + RT/\bar{V}_1^0 [1000 B - (\bar{V}_1^0 - \bar{V}_2^0)], \quad (4)$$

where h is the Planck constant, N the Avogadro number, h_0 the viscosity of solvent, R the gas con-

Table 2. Values of $\bar{V}_1^0$ (dm³ mol⁻¹), $\bar{V}_2^0$ (dm³ mol⁻¹), Δm_1^0* (kJ mol⁻¹) and Δm_2^0* (kJ mol⁻¹) for oxalic acid, ammonium oxalate, sodium oxalate and potassium oxalate in different compositions of THF + water at 298·15 K.

Parameter	THF + water (% w/w)			
	5	10	15	20
$\bar{V}_1^0$	18·80	19·61	20·46	21·44
Δm_1^0*	21·08	21·48	21·88	22·20
Oxalic acid				
$\bar{V}_2^0$	103·45	109·58	115·89	124·98
Δm_2^0*	64·28	65·47	66·64	67·35
Ammonium oxalate				
$\bar{V}_2^0$	95·23	110·76	117·04	125·85
Δm_2^0*	59·37	61·44	61·93	62·83
Sodium oxalate				
$\bar{V}_2^0$	71·23	81·36	89·53	100·73
Δm_2^0*	68·60	72·77	73·02	73·45
Potassium oxalate				
$\bar{V}_2^0$	67·83	79·10	88·41	98·60
Δm_2^0*	78·18	79·69	81·60	85·23

Table 3. Values of parameters A ($dm^{3/2} mol^{-1/2}$) and B ($dm^3 mol^{-1}$) of Jones–Dole equation for oxalic acid, ammonium oxalate, sodium oxalate and potassium oxalate in water and in THF + water (5% w/w) at different temperatures. Standard errors are given in parentheses.

Parameters	Temperature (K)				
	298·15	303·15	308·15	313·15	318·15
Water					
Oxalic acid					
A	2·840	2·211	1·296	0·159	–0·325
	(0·013)	(0·011)	(0·023)	(0·028)	(0·019)
B	0·201	0·218	0·241	0·277	0·286
	(0·001)	(0·001)	(0·001)	(0·001)	(0·002)
Ammonium oxalate					
A	7·720	6·469	5·616	4·188	3·361
	(0·005)	(0·026)	(0·015)	(0·031)	(0·016)
B	0·058	0·090	0·112	0·154	0·177
	(0·001)	(0·001)	(0·001)	(0·002)	(0·001)
Sodium oxalate					
A	6·967	5·301	4·618	4·035	3·039
	(0·032)	(0·019)	(0·019)	(0·019)	(0·015)
B	0·103	0·152	0·171	0·187	0·214
	(0·001)	(0·001)	(0·001)	(0·001)	(0·002)
Potassium oxalate					
A	10·995	9·938	9·448	6·850	6·248
	(0·016)	(0·023)	(0·042)	(0·027)	(0·045)
B	0·177	0·206	0·251	0·289	0·305
	(0·001)	(0·001)	(0·002)	(0·001)	(0·002)
5% (w/w) THF + water					
Oxalic acid					
A	1·328	0·829	0·239	–0·056	–0·913
	(0·015)	(0·019)	(0·024)	(0·013)	(0·015)
B	0·243	0·255	0·270	0·277	0·304
	(0·001)	(0·001)	(0·002)	(0·001)	(0·001)
Ammonium oxalate					
A	2·304	1·773	0·283	–0·165	–0·462
	(0·015)	(0·018)	(0·017)	(0·020)	(0·028)
B	0·214	0·229	0·271	0·284	0·290
	(0·001)	(0·001)	(0·001)	(0·002)	(0·001)
Sodium oxalate					
A	1·681	1·196	0·396	–0·344	–1·272
	(0·016)	(0·020)	(0·024)	(0·008)	(0·016)
B	0·308	0·320	0·341	0·362	0·376
	(0·001)	(0·001)	(0·001)	(0·001)	(0·002)
Potassium oxalate					
A	1·414	0·973	0·050	–0·425	–3·268
	(0·022)	(0·035)	(0·021)	(0·024)	(0·030)
B	0·383	0·389	0·413	0·425	0·512
	(0·001)	(0·002)	(0·001)	(0·001)	(0·002)

stant and T the absolute temperature. The values of $\ddot{A}m_1^0*$ calculated from (3) are given in table 2.

For mixed solvents, each solvent mixture was treated as pure and the molar volume taken as a mean volume defined[12] as:

$$\bar{V}_1^0 = [x_1 M_1 + x_2 M_2]/d_1, \tag{5}$$

where x_1, M_1 and x_2, M_2 are the mole fractions, and molecular weights of water and THF respectively, and d_1 is the density of solvent (THF + water). The values of $\bar{V}_2^0$, the partial molar volumes at infinite dilution for oxalic acid and its salts, determined from density data, are also recorded in table 2. The values of $\ddot{A}m_2^0*$ and $\bar{V}_1^0$, calculated with the help of (4) and (5) respectively, are also recorded in table 2.

It is evident from the data (table 2) that $\ddot{A}m_1^0*$ is practically constant at all solvent compositions implying that $\ddot{A}m_2^0*$ is dependent mainly on B coefficient and $(\bar{V}_1^0-\bar{V}_2^0)$ terms. It is also clear from table 2 that the values of $\ddot{A}m_2^0*$ are positive and larger than $\ddot{A}m_1^0*$ which suggest that the formation of the transition state is less favoured in the presence of oxalic acid and its salts, meaning thereby that the formation of transition state is accompanied by the breaking and distortion of the intermolecular bonds between THF and water, i.e. solvent.

Recently, it has been emphasized by many workers that dB/dT is a better criterion[31] for determining the structure making/breaking nature of any solute than simply the B coefficient. So this means that in order to follow this criterion, the temperature effect must be studied.

3.1 *Effect of temperature*

Because of the identical behaviour of oxalic acid and an individual salt in different compositions of THF + water at 298·15 K, the effect of temperature has been studied in water and only in 5% (w/w) THF + water. The plots of $[h_r–1]/\sqrt{c}$ versus $\sqrt{c}$ have been found to be linear at 298·15, 303·15, 308·15, 313·15 and 318·15 K in accordance with the Jones–Dole equation, (1), for oxalic acid, ammonium oxalate, sodium oxalate and potassium oxalate. A sample plot for oxalic acid is shown in figure 2 at different temperatures. Values of A and B parameters have been calculated using the least squares method and these values, along with standard errors, are recorded in table 3.

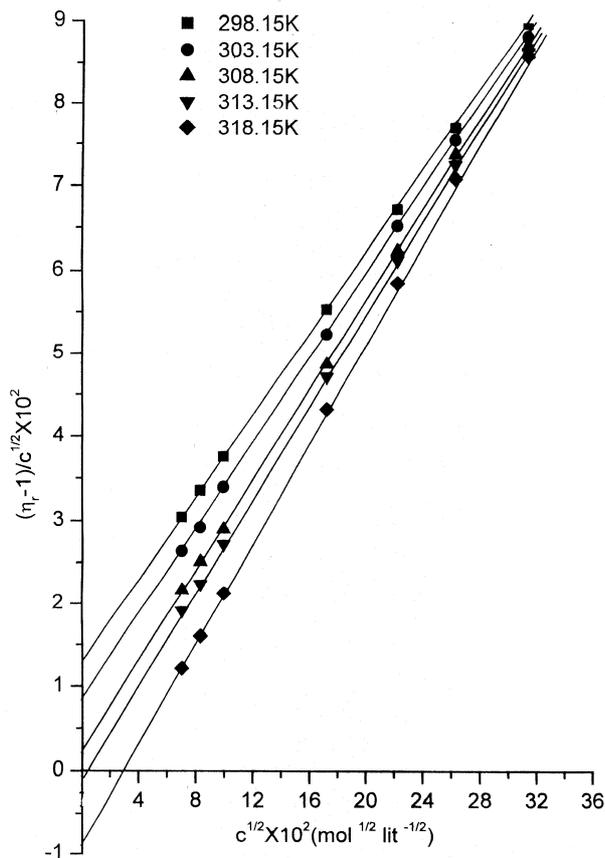It is evident from table 3 that the values of A coefficient are either positive or negative for oxalic

Figure 2. Plots of $(h_r-1)c^{1/2}$ vs $c^{1/2}$ for oxalic acid in 5% (w/w) THF + water at different temperatures.

acid and its individual salt in water as well as in THF + water (5% w/w) mixture and continuously decrease with rise in temperature, thereby suggesting that solute–solute interactions are weakened with increase of temperature. In other words it may be said that with rise in temperature the solvation of oxalic acid and an individual salt is enhanced.

The values of B coefficient are positive for oxalic acid and its salts in water and in THF + water (5% w/w) at all temperatures, showing the presence of strong solute–solvent interactions. Further, the value of the B coefficient increases with rise in temperature which suggests that solute–solvent interactions are strengthened with rise in temperature for oxalic acid and its salts in water and THF + water.

The value of dB/dT is positive for oxalic acid, ammonium oxalate, sodium oxalate and potassium oxalate in water as well as in THF + water showing that oxalic acid and its salts act as structure breakers in both the systems.

The data for viscosity B coefficient at different temperatures have also been analysed by applying the transition state theory. The values of $\ddot{A}m_1^0*$ and $\ddot{A}m_2^0*$ have been calculated with the help of (3) and (4) respectively, and are recorded in table 4.

According to Feakins model,[29] $\ddot{A}m_2^0*$ increases with temperature for solutes having positive values of dB/dT. This is nicely shown by oxalic acid and its

Table 4. Values of $\bar{V}_1^0$ (dm^3 mol^{-1}), $\bar{V}_2^0$ (dm^3 mol^{-1}), $\ddot{A}m_1^0*$ (kJ mol^{-1}) and $\ddot{A}m_2^0*$ (kJ mol^{-1}) for oxalic acid, ammonium oxalate, sodium oxalate and potassium oxalate in THF + water (5% w/w) at different temperatures.

Parameters	Temperature (K)				
	298·15	303·15	308·15	313·15	318·15
$\bar{V}_1^0$	18·80	18·83	18·87	18·91	18·92
$\ddot{A}m_1^0*$	21·08	21·09	21·16	21·13	21·29
Oxalic acid					
$\bar{V}_2^0$	103·45	111·44	117·05	120·85	128·09
$\ddot{A}m_2^0*$	64·28	67·62	71·14	73·40	79·05
Ammonium oxalate					
$\bar{V}_2^0$	95·23	102·42	108·39	114·74	123·51
$\ddot{A}m_2^0*$	59·37	62·93	70·10	73·52	76·74
Sodium oxalate					
$\bar{V}_2^0$	71·23	80·17	86·40	93·45	104·41
$\ddot{A}m_2^0*$	68·60	72·13	76·63	81·33	86·09
Potassium oxalate					
$\bar{V}_2^0$	68·85	75·03	81·35	88·02	97·12
$\ddot{A}m_2^0*$	78·18	80·68	85·71	89·26	92·60

Table 5. Entropy, $T\ddot{A}S_2^0*$ (kJ mol^{-1}) and enthalpy, $\ddot{A}H_2^0*$ (kJ mol^{-1}) of activation for viscous flow of oxalic acid, ammonium oxalate, sodium oxalate and potassium oxalate in THF + water (5% w/w) at different temperatures.

| Parameters	Temperature (K)				
	298·15	303·15	308·15	313·15	318·15
Oxalic acid					
$T\ddot{A}S_2^0*$	−210·49	−214·02	−217·55	−221·08	−224·61
$\ddot{A}H_2^0*$	−146·21	−146·40	−146·41	−147·68	−145·56
Ammonium oxalate					
$T\ddot{A}S_2^0*$	−270·42	−274·96	−279·49	−284·03	−288·56
$\ddot{A}H_2^0*$	−211·05	−212·03	−209·39	−210·51	−211·82
Sodium oxalate					
$T\ddot{A}S_2^0*$	−263·56	−267·98	−272·40	−276·82	−281·24
$\ddot{A}H_2^0*$	−194·96	−195·85	−195·77	−195·49	−195·15
Potassium oxalate					
$T\ddot{A}S_2^0*$	−360·17	−366·21	−372·25	−378·29	−384·33
$\ddot{A}H_2^0*$	−281·99	−285·53	−286·54	−289·03	−280·25
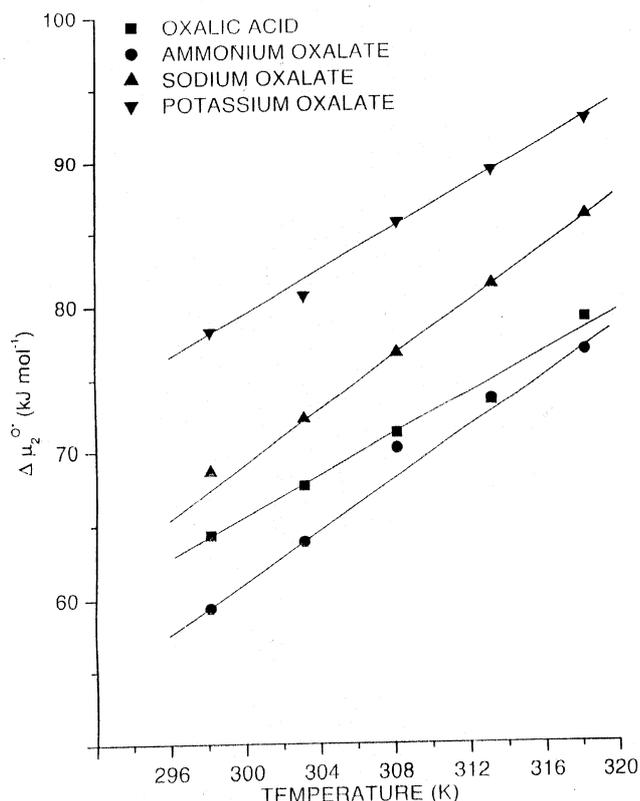
Figure 3. Variation of $\ddot{A}\mu_2^0*$ with temperature for oxalic acid, ammonium oxalate, sodium oxalate and potassium oxalate in 5% (w/w) THF + water.

salts, which act as structure breakers in water as well as in THF + water.

It is also evident from table 4 that the quantity ($\ddot{A}\mu_2^0*-\ddot{A}\mu_1^0*$), the change in activation energy per mole of solute on replacing one mole of solvent by one mole of solute at infinite dilution, is positive and large for oxalic acid and its salts studied in 5% (w/w) THF + water at different temperatures, therefore it may be concluded from these data that the formation of the transition state is accompanied by breaking/distortion of the intermolecular bonds of the solvent. In other words, the formation of the transition state is less favoured in the presence of oxalic acid and its salts in the entire temperature range.

The activation entropy for oxalic acid and its salts has also been calculated from the following relation[29]:

$$d(\ddot{A}\mu_2^0*)/dT = -\ddot{A}S_2^0*. \tag{6}$$

The values of $\ddot{A}S_2^0*$ have been calculated from the slopes of linear plots of $\ddot{A}\mu_2^0*$ versus T, shown in figure 3, by using the least squares method. The values of $T\ddot{A}S_2^0*$ at different temperatures are listed

in table 5. The activation enthalpy ($\ddot{A}H_2^0*$) has been calculated with the help of following expression[29]:

$$\ddot{A}H_2^0* = \ddot{A}\mu_2^0* + T\ddot{A}S_2^0*, \tag{7}$$

and the values are also recorded in table 5.

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 5% (w/w) THF + 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.

Acknowledgement

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