



Thermodynamic and transport studies of some aluminium salts in water and binary aqueous mixtures of tetrahydrofuran

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Abstract

Viscosities of aluminium chloride, aluminium sulphate and aluminium nitrate have been measured in water and in binary aqueous mixtures of tetrahydrofuran (5, 10, 15, 20% by weight of tetrahydrofuran) at different temperatures (298.15, 303.15, 308.15, 313.15 and 318.15K). Solutions are prepared by using the salts concentrations (0.003, 0.005, 0.007, 0.01, 0.03, 0.05m) in water and THF+water solvents systems. The measured viscosity data has been analysed by using Jones – Dole equation and B-coefficients are also determined. The obtained parameters have been interpreted in terms of ion – ion and ion – solvent interactions. In the present study, all these aluminium salts act as structure breakers in water and in THF+water systems.

Keywords: B - coefficient, relative viscosity and structure breakers.

1. Introduction

The studies on viscosities of electrolyte solutions are usually done to obtain information about structure and properties of solutions [1-4]. Different types of interactions exist between the ions in the electrolytic solutions and of these, ion – ion and ion – solvent interactions are of current interest. These interactions help in understanding the nature of the solvent as it has been found by number of researchers that the addition of an electrolyte either breaks or makes the structure of the liquid. The making and breaking the structure of liquids have been considered as a measure of solute – solvent interactions. The survey of literature [5-16] shows that many studies have been carried out for various electrolytic solutions but little attention has been paid to the behaviour of aluminium salts in water and in different compositions of THF + water. One of the main properties of the THF solvent is that it is completely miscible in water and other organic solvents which led to many applications in organic chemistry. THF has been explored as a water-based co-solvent to aid in the deconstruction and delignification of plant lignocellulosic biomass, which are relevant to the production of renewable platform chemicals and sugars. THF is also used in polymer industry as is used to dissolve polymers prior to determining their molecular mass using gel permeation chromatography. THF dissolves PVC and thus it is the main ingredient in PVC adhesives. Tetrahydrofuran and especially its 2—methyl derivative are also useful solvents for rechargeable high energy density batteries [17]. As a reaction solvent THF plays important role in Grignard reagent and pharmaceutical steroids. All these application of this solvent forms the basis to select THF as a co solvent in the present study. On the other hand in the present study aluminium salts; aluminium chloride, aluminium nitrate and aluminium sulphate were selected as electrolytes because of their wide range of industrial and commercial applications in the manufacture of various consumer products. Aluminium sulphate (or "alum") and aluminium chloride are primarily used in municipal drinking water and wastewater treatment facilities to help remove suspended particles and bacteria from the water and also used in industrial water and wastewater treatment in the pulp and paper industry. These salts are also used as ingredients in drugs, natural health products and cosmetics, such as antiperspirants and topical creams. The primary uses of aluminium chloride are in manufacturing and industry as it is a component in the production of aluminium, in metallurgy, and as an ingredient in aluminium smelting. It's also used in manufacturing petrochemicals like ethyl benzene and alkyl benzene. Aluminium nitrate is used in some fertilizers and as a chemical reagent in various industries. Hence, it

becomes very important to analyse the behaviour of these electrolytes in water and THF+ water solvent system and the present study is an attempt to study the solute-solute and solute-solvent interactions of these solutes in water and THF+ water solvent systems.

2. Materials and methods

Aluminium salts, viz., aluminium chloride, aluminium sulphate and aluminium nitrate all were of Analytical grade used after drying them over calcium P₂O₅ desiccator. Double distilled water was used for the preparation of binary mixtures of THF with water as a standard solvent. The binary aqueous mixtures of THF as well as the solutions of all aluminium salts of concentration 0.003m,0.005m,0.007m,0.01m,0.03m,0.05m has been prepared by weight and the conversion of molal solutions (m) into molar solution (C) were made by using the following expression:

$$C = \frac{1000 dm}{1000 + mM_2} \quad (1)$$

where d and M₂ is the density and molecular weight of the each of the aluminium salt. The densities of solutions of aluminium salts, viz., aluminium chloride, aluminium sulphate and aluminium nitrate were measured with the help of an apparatus as described by the Ward and Millero [18].The glass sample cell had a Bakelite top with a hole in the centre and was placed in a water bath (±0.01°C).The glass float weighed 33.813 g and had a volume 25.066 cm³ (±0.0001) at 303.15K.Density was calculated using the relation $d = d_0 + (W_0 - W)/V_f$ where d and d₀ are densities of sample solution and pure water respectively, W and W₀ are the weights of float in in the sample solution and water, and V_f is float volume. The accuracy in the measurement of solutions densities was found to be 1 x 10⁻⁴ gcm⁻³.The relative viscosities of the solutions of aluminium salts were determined with the help of Ostwald viscometer with the flow time of 164 seconds for water at 303.15K. Process was repeated until three successive determinations were obtained with in ±0.1 seconds. No kinetic energy correction required, as the flow time was greater than 100 seconds. The relative viscosities of the solutions were determined by usual procedure [19-20].The density and viscosity studies were carried out in water thermostat (± 0.01K) in order to study the effect of temperature.

3. Results and Discussions

3.1 Effect of Concentration

The relative viscosities and densities of the solutions of aluminium salts, viz., aluminium chloride, aluminium sulphate and aluminium nitrate in water and in THF + water systems of four different compositions 5%, 10%, 15%, and 20% (w/w) were determined at 303.15K.The relative viscosity data has been analysed with Jones Dole equation [21].

$$\eta_{rel} = \frac{\eta}{\eta_0} = 1 + AC^{1/2} + BC \quad (2)$$

where, η and η_0 are the viscosities of solutions and solvent respectively. A and B are two constants parameters. A coefficient corresponds to ion- ion interactions and parameter B coefficient corresponds to ion – solvent interactions. These parameters A and B have been obtained by plotting a graph between $(\eta_r - 1)/\sqrt{C}$ verses \sqrt{C} for all the aluminium salts in water as well as in all the prepared compositions of THF + water at one temperature i.e 303.15 K. All these obtained values of A and B parameters were recorded in Table 1 and a sample plot of $(\eta_r - 1)/\sqrt{C}$ verses \sqrt{C} shown in fig1 for Aluminium sulphate.

Table 1 : Values of A and B coefficients of the Jones – Dole equation for Aluminium sulphate , Aluminium nitrate and Aluminium chloride in water and in different composition of THF+Water at 303.15K.

THF+ WATER [(w/w)%]	Aluminium sulphate		Aluminium nitrate		Aluminium chloride	
	A (dm ^{3/2} mol ^{-1/2})	B (dm ³ mol ⁻¹)	A (dm ^{3/2} mol ^{-1/2})	B (dm ³ mol ⁻¹)	A (dm ^{3/2} mol ^{-1/2})	B (dm ³ mol ⁻¹)
0	30.130	3.324	41.877	2.947	9.933	3.620
5	30.329	4.079	17.645	4.519	13.005	4.626
10	18.356	4.473	6.870	4.942	- 0.272	5.226
15	8.562	5.012	- 5.1612	5.395	- 9.247	5.483
20	- 4.448	5.605	- 12.543	5.662	- 20.912	5.933

It is clear from, Table - 1 that the values of A decreases with the increase in the content of THF in water indicating that ion- ion interactions are weakened with the increase in the content of THF in water. It is also clear from Table - 1 that the values of B-coefficient for aluminium sulphate, aluminium nitrate and aluminium

chloride are positive, in the entire composition range of binary aqueous mixtures of THF at 303.15K, thereby showing the presence of strong ion –solvent interactions, which dominate over the ion –ion interactions. This may be attributed to the strong solvation of these ions by the binary mixtures of THF +water. Further it is also clear from Table-1 that the value of B –coefficient increases with the increase of THF content in water at 303.15K, for an individual salt, thereby showing that ion – solvent interactions are further strengthened with the increase of THF content in water. In other words the ion –solvation is further enhanced as the composition of THF in water increases, or it may be said that THF has more affinity for an electrolyte than that for water.

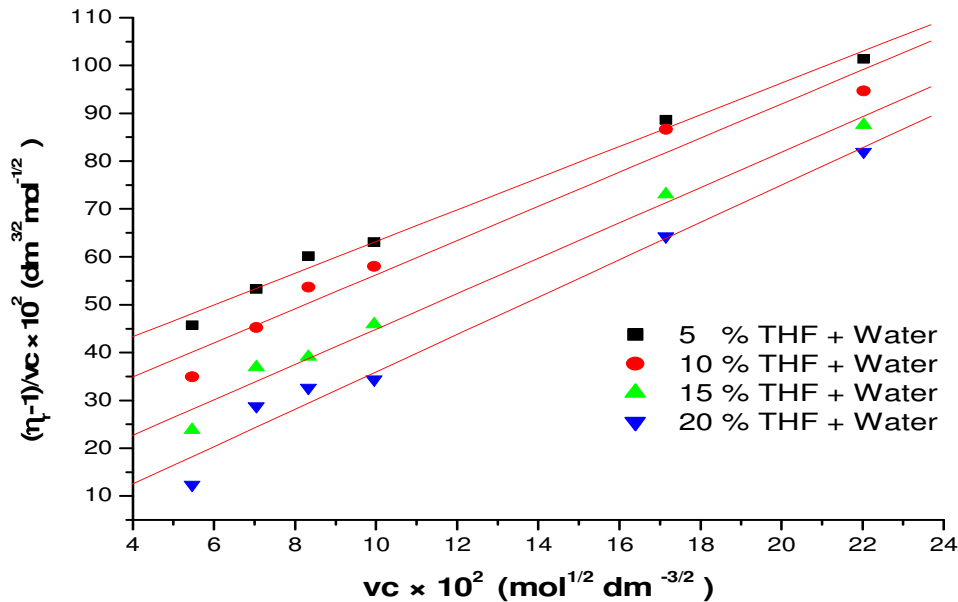


Figure 1: Plots of $(\eta_r-1)/\sqrt{c}$ vs \sqrt{c} for Aluminium sulphate in different composition of THF+ Water at 303.15K.

The viscosity data has also been analysed on the basis of transition state treatment of relative viscosity as proposed by Feakins [22]. The parameter B in terms of transition state theory is given by the following relation:

$$B = \frac{\overline{V}_1^0 - \overline{V}_2^0}{1000} + \frac{\overline{V}_1^0}{1000} \left[\frac{\Delta\mu_2^{0*} - \Delta\mu_1^{0*}}{RT} \right] \quad (3)$$

Where, \overline{V}_1^0 is mean volume of the solvent \overline{V}_2^0 is the partial molar volume of the aluminium salts, $\Delta\mu_1^{0*}$ and $\Delta\mu_2^{0*}$ are the free energies of activations per mole of pure solvent and aluminium salts respectively:

$$\Delta\mu_1^{0*} = RT \ln \left(\eta_0 \overline{V}_1^0 / hN \right) \quad (4)$$

$$\Delta\mu_2^{0*} = \Delta\mu_1^{0*} + RT / \overline{V}_1^0 \left[1000B - \left(\overline{V}_1^0 - \overline{V}_2^0 \right) \right] \quad (5)$$

Where R is the gas constant, T is the absolute temperature, η_0 is the viscosity of the solvent, h is the Planck's constant and N is the Avogadro number.

The values of $\Delta\mu_1^{0*}$ were calculated with the help of relation (4) are given in Table 2 for mixed solvents, each solvent mixture was treated as pure and the molar volume taken as a mean volume given as:

$$\overline{V}_1^0 = (x_1M_1 + x_2M_2) / d_1 \quad (6)$$

where x_1, M_1 and x_2, M_2 are the mole fractions and molecular weights of the water and THF respectively and d_1 is the density of (THF + water) as solvent. The values of \overline{V}_2^0 for the selected aluminium salts calculated with the help of the density data and are recorded in Table 2. The values of $\Delta\mu_2^{0*}$ and \overline{V}_1^0 calculated with the help of relations (5) and (6) and are also recorded in Table 2. It is clear from the table that the values of $\Delta\mu_1^{0*}$ and \overline{V}_1^0 are practically constant in all solvent compositions.

Table 2: Values of \bar{V}_1° , \bar{V}_2° , $\Delta\mu_1^{0*}$ and $\Delta\mu_2^{0*}$ for Aluminium sulphate , Aluminium nitrate and Aluminium chloride indifferent composition of THF + water at 303.15 K.

THF + Water (w/w %)	Aluminium sulphate				Aluminium nitrate				Aluminium chloride			
	\bar{V}_1° (dm ³ mol ⁻¹)	\bar{V}_2° (dm ³ mol ⁻¹)	$\Delta\mu_1^{0*}$ (Kj mol ⁻¹)	$\Delta\mu_2^{0*}$ (kJ mol ⁻¹)	\bar{V}_1° (dm ³ mol ⁻¹)	\bar{V}_2° (dm ³ mol ⁻¹)	$\Delta\mu_1^{0*}$ (kJ mol ⁻¹)	$\Delta\mu_2^{0*}$ (kJ mol ⁻¹)	\bar{V}_1° (dm ³ mol ⁻¹)	\bar{V}_2° (dm ³ mol ⁻¹)	$\Delta\mu_1^{0*}$ (kJ mol ⁻¹)	$\Delta\mu_2^{0*}$ (kJ mol ⁻¹)
5	18.84	610.8	61.41	624.78	18.84	316.22	61.41	644.23	18.84	179.10	61.41	640.20
10	19.64	617.92	61.54	650.7	19.64	335.75	61.54	674.67	19.64	184.81	61.54	691.74
15	20.52	633.6	61.68	690.9	20.52	355.80	61.68	703.82	20.52	196.03	61.68	695.00
20	21.49	644.32	61.81	730.41	21.49	366.20	61.81	698.15	21.49	202.09	61.81	717.02

It is clear from table 2, that the values of $\Delta\mu_2^{0*}$ are positive and more in magnitude than $\Delta\mu_1^{0*}$ values which suggests that the transition state formation is less favoured in the presence of the selected aluminium salts. This indicates that the formation of transition state is followed by the breaking and distortions of the intermolecular bonds between THF and water. Many workers [23] intensified that instead of parameter B, $\frac{dB}{dT}$ is a better criterion for determining the structure making/breaking nature of any solute. In order to analyse $\frac{dB}{dT}$ parameter, the effect of temperature must be studied.

3.2 Effect of temperature

Since the behaviour of all selected aluminium salts in different compositions 5%,10%,15% and 20% (w/w) of THF + water was found to be linear and identical at 303.15 K. So, only 5% (w/w) THF + water system have been selected for studying the effect of temperatures 298.15,303.15,308.15,313.15 and 318.15 K. The plot of $(\eta_r - 1)/\sqrt{C}$ versus \sqrt{C} has been found to be linear for all the selected aluminium salts at four temperatures (298.15K to 318.15K). A sample plot for aluminium sulphate in 5% w/w THF + water system is shown in fig.2 at different temperatures. This is in accordance to the Jones – Doles equation. The plot of $(\eta_r - 1)/\sqrt{C}$ versus \sqrt{C} has been fitted to least square fit method to obtain the values of A and B parameters.

It is clear from Table 3, that the values of A parameter decreases with the rise in temperature in 5% w/w THF + water for all the aluminium salts. So, it suggests that ion- ion interactions further weakened with the rise of temperature. In order words, the presence of weak ion – ion interactions may attributes to increase in the solvation of aluminium salt in THF + water system. From Table 3, the values of B-coefficient are positive for all aluminium salts in 5% w/w THF + water at all temperatures. These positive values indicate the presence of strong ion – solvent interactions. Further the values of B-coefficient increases with the rise in temperature which suggests that ion-solvent interaction are enhanced with rise in temperature for all these aluminium salts. The value of $\frac{dB}{dT}$ is positive for all the aluminium salts both in water and in 5% w/w THF + water. This indicates the structure breaking nature of aluminium sulphate, aluminium nitrate and aluminium chloride in water and THF + water system.

Table 3: Values of A and B coefficients of the Jones – Dole equation for Aluminium sulphate, Aluminium nitrate and Aluminium chloride in 5% THF+ water at different temperatures.

Temp (K)	Aluminium sulphate		Aluminium nitrate		Aluminium chloride	
	A (dm ^{3/2} mol ^{-1/2})	B (dm ³ mol ⁻¹)	A (dm ^{3/2} mol ^{-1/2})	B (dm ³ mol ⁻¹)	A (dm ^{3/2} mol ^{-1/2})	B (dm ³ mol ⁻¹)
298.15	36.880	3.982	26.241	4.356	20.705	4.421
303.15	30.329	4.079	17.645	4.519	13.005	4.626
308.15	21.260	4.351	6.140	4.813	04.672	4.761
313.15	8.738	4.689	- 3.252	5.054	-04.708	5.007
318.15	1.093	4.749	- 13.169	5.314	-14.753	5.275

The data of viscosity B-coefficients at 298.15K, 303.15K, 308.15K, 313.15K and 318.15 K has also been interpreted by applying the transition state theory. The values of $\Delta\mu_1^{0*}$ and $\Delta\mu_2^{0*}$ have been recorded in Table 4. Also, It is clear from Table 5, that the quantity $(\Delta\mu_2^{0*} - \Delta\mu_1^{0*})$, the change in activation energy per mole of solute on replacing one mole of solute by one more mole of solute at infinite dilution is positive and large for all aluminium salts in 5% (w/w) THF + water at different temperatures. Therefore from Table 5, it is clear that the formation of the transition state is followed by breakage of the intermolecular bonds of the solvent. That is, the formation of transition state is less favoured in the presence of aluminium salts in the selected temperature range.

The entropy of activation ΔS_2^{0*} for all aluminium salts has been calculated from the following equations:

$$\frac{d(\Delta\mu_2^{0*})}{dT} = -\Delta S_2^{0*} \quad (7)$$

The values of ΔS_2^{0*} have been calculated from the slopes of linear plot of $\Delta\mu_2^{0*}$ verses T. The enthalpy of activation ΔH_2^{0*} has been calculated with the help of relationship:

$$\Delta H_2^{0*} = \Delta\mu_2^{0*} + T\Delta S_2^{0*} \quad (8)$$

A sample plot has been shown for aluminium sulphate is shown in fig 3. The $T\Delta S_2^{0*}$ and ΔH_2^{0*} values at different temperatures are recorded in Table 5.

It is clear from Table 5 that both parameters enthalpy and entropy of activation are negative for the aluminium salts taken in the present study. These negative values of ΔH_2^{0*} and $T\Delta S_2^{0*}$ parameters indicates that the transition state is associated with bond making and increase in order [24].

Table 4: Values of \overline{V}_1^0 , \overline{V}_2^0 , $\Delta\mu_1^{0*}$ and $\Delta\mu_2^{0*}$ for Aluminium sulphate, Aluminium nitrate and Aluminium chloride in 5% THF+ water at different temperatures.

Temp. (K)	Aluminium sulphate				Aluminium nitrate				Aluminium chloride			
	\overline{V}_1^0 (dm ³ mol ⁻¹)	\overline{V}_2^0 (dm ³ mol ⁻¹)	$\Delta\mu_1^{0*}$ (kJ mol ⁻¹)	$\Delta\mu_2^{0*}$ (kJ mol ⁻¹)	\overline{V}_1^0 (dm ³ mol ⁻¹)	\overline{V}_2^0 (dm ³ mol ⁻¹)	$\Delta\mu_1^{0*}$ (kJ mol ⁻¹)	$\Delta\mu_2^{0*}$ (kJ mol ⁻¹)	\overline{V}_1^0 (dm ³ mol ⁻¹)	\overline{V}_2^0 (dm ³ mol ⁻¹)	$\Delta\mu_1^{0*}$ (kJ mol ⁻¹)	$\Delta\mu_2^{0*}$ (kJ mol ⁻¹)
298.15	18.83	606.80	60.66	601.59	18.83	303.46	60.66	610.89	18.83	165.03	60.66	601.22
303.15	18.84	610.80	61.41	624.79	18.84	316.22	61.41	644.24	18.84	179.10	61.41	640.21
308.15	18.87	617.06	62.16	671.77	18.87	329.25	62.16	695.41	18.87	184.24	62.16	668.67
313.15	18.88	631.49	62.91	730.94	18.88	351.34	62.91	742.63	18.88	195.54	62.91	714.68
318.15	18.91	638.37	63.68	750.91	18.91	361.39	63.68	791.19	18.91	207.79	63.68	764.26

Table 5: Values of $(\Delta\mu_2^{0*} - \Delta\mu_1^{0*})$, $T\Delta S_2^{0*}$ and ΔH_2^{0*} for Aluminium sulphate, Aluminium nitrate and Aluminium chloride in 5% (THF+ water) at different temperatures.

Temp (K)	Aluminium sulphate			Aluminium nitrate			Aluminium chloride		
	$(\Delta\mu_2^{0*} - \Delta\mu_1^{0*})$ (kJ mol ⁻¹)	$T\Delta S_2^{0*}$ (kJ mol ⁻¹)	ΔH_2^{0*} (kJ mol ⁻¹)	$(\Delta\mu_2^{0*} - \Delta\mu_1^{0*})$ (kJ mol ⁻¹)	$T\Delta S_2^{0*}$ (kJ mol ⁻¹)	ΔH_2^{0*} (kJ mol ⁻¹)	$(\Delta\mu_2^{0*} - \Delta\mu_1^{0*})$ (kJ mol ⁻¹)	$T\Delta S_2^{0*}$ (kJ mol ⁻¹)	ΔH_2^{0*} (kJ mol ⁻¹)
298.15	540.02	-2424.52	-3025.21	550.22	-2737.01	-3347.91	540.56	-2388.36	-2989.59
303.15	563.38	-2465.18	-3089.98	582.83	-2782.91	-3427.16	578.81	-2428.41	-3068.63
308.15	609.60	-2505.84	-3177.61	633.25	-2828.81	-3524.23	606.51	-2468.47	-3137.14
313.15	668.03	-2546.50	-3277.44	679.72	-2874.71	-3617.35	651.77	-2508.52	-3223.20
318.15	687.23	-2587.16	-3338.07	727.51	-2920.61	-3711.81	700.58	-2548.57	-3312.83

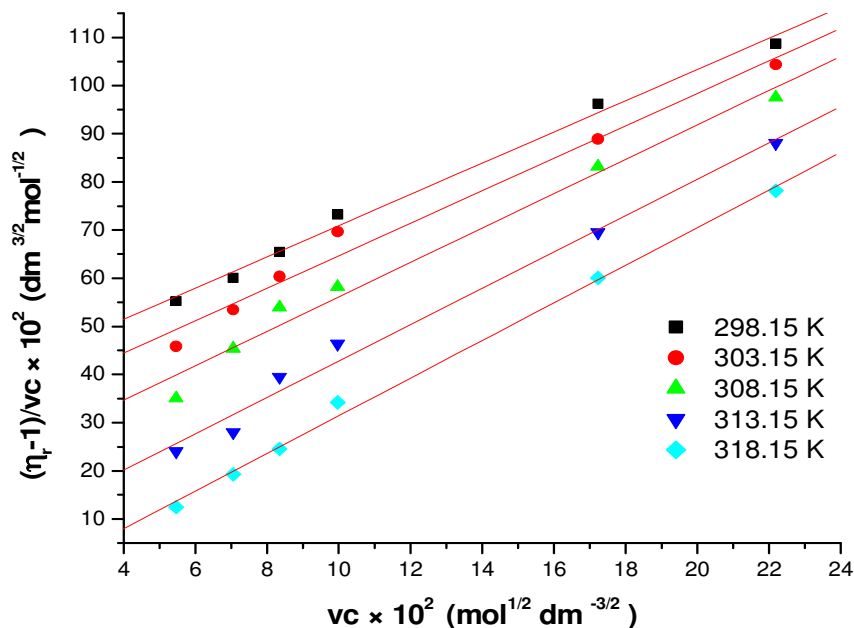


Figure 2: Plots of $(\eta_r-1)/\sqrt{c}$ vs \sqrt{c} for Aluminium nitrate in 5% THF+ Water at different temperatures.

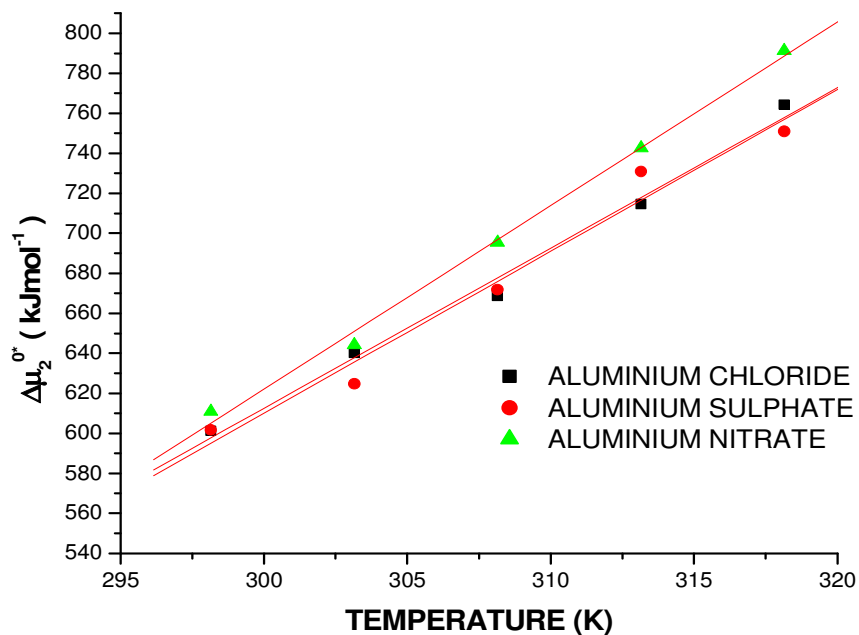


Figure 3: Variation of $\Delta\mu_2^{0*}$ with temperature for Aluminium sulphate, Aluminium nitrate and Aluminium chloride in 5% THF + Water

Conclusion:

As the value of $\frac{dB}{dT}$ is positive for all the aluminium salts taken here both in water and in 5% w/w THF + water. This indicates the structure breaking nature of aluminium sulphate, aluminium nitrate and aluminium chloride in water and THF + water system. Since the data of viscosity B-coefficients at different temperatures have also been analysed by applying the transition state theory and from this analysis it is clear that the formation of the

transition state is followed by breakage of the intermolecular bonds of the solvent i.e. the formation of transition state is less favoured in the presence of aluminium salts in the selected temperature range.

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