Molecular Behaviour of Aluminium Chloride In Binary Aqueous Mixture of Acetonitrile

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Abstract:

The present study is conducted to analyze the molecular properties of aluminium chloride in binary aqueous solution of acetonitrile. Density and viscosity of the salt has been obtained at different temperatures and different compositions of acetonitrile where were further used to obtain the PMV, viscosity B - coefficient and other activation parameters. The parameters were analyzed in terms of structure making behaviour.

*Keywords***:**Partial molar volume, viscosity B – coefficient and structure maker.

1. Introduction

Thermodynamic properties are considered as strong evidence to analyze the molecular behaviour of solute in different solvent systems. The partial molar volumes, partial molar expansibilities etc. are calculated by measuring solute-solute as well as solute-solvent interactions[1-5].

Aluminium chloride is mostcommonly used for making pure aluminum metal.The salt has a role in deodorants also as it works on the sweat glands and closes the pores and for preventing from sweat. Parallely, acetonitrile is the commonly used polar aprotic solvent which is usedto make, rubber products, pesticides, acrylic nail removers, pharmaceuticals, perfumes and batteries. The literature is available on molecular behaviour of aluminium chloride in different solvent systems but there is no data available on the molecular behaviour of aluminium chloride in acetonitrile and its binary mixtures [6-11]. Hence, the present study is an approach to analyze the molecular behaviour ofaluminium chloride in binary aqueous mixtures of acetonitrile.

2. Experimental

2.1 Material

The reagents, aluminium chloride and acetonitrile were taken of AR grade and were obtained from S.D Fine-Chem. Limited.The chemicals are used as such without purifying further; the aluminium chloride was dried in desiccator in the presence of anhydrous calcium chloride forapproximately 48 hours.

2.2 Methods

All the solutions used in the experiments were prepared using the triple distilled deionized water having conductivity value of order1-2 µs-cm^{-1}anda pH value of 7.1.
Molar concentration (C) were derived from molal concentrations, (m) with the help of following equation

$$C = \frac{m\rho 1000}{1000 + mM} \tag{1}$$

Here, M and are molecular weight and the density of the acetonitrile. The densities (ρ) of the solutions were obtained using Anton Paar DSA 5000 instrument. Calibration of the instrument with triple distilled water was done at the temperature range of the experiments before the start of each measurement [12]. The standard uncertainties for the values of density were found to be $\pm 3\times10^{-3}$ kg.m^{-3}

3. Results and Discussion

The study has been conducted in two phases. In first phase the effect of composition has been analyzed where the solution of aluminium chloride are prepared in different compositions of acetonitrile (5%, 10%, 15% and 20%) at 303.15 K. In the second phase the effect of temperature has been analyzed for the solution of aluminium chloride in the lowest compositions of acetonitrile i.e. 5% acetonitrile + water.

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The representative equation are used for the determination of the apparent molar volumes form the densities obtained from the instrument:

$$\phi_v = \frac{M}{\rho} - \frac{1000(\rho - \rho_0)}{c\rho_0} \quad (2)$$

Where*m* defines the molality, *C* represents the molarity of solution whereas, *M* defines the molecular mass of solute, ρ_0 and ρdefine the densities (in kg m^{-3}), of solvent and working solution respectively[13].

Table 1 depicts the apparent volumes (ϕ_v)and densities of aluminium chloride.

Table 1.Apparent volumes (ϕ_v)and densitiesof aluminum chloride atvaried concentrations of acetonitrile and water at temperature value of 303.15 K

$C^{1/2} \times 10^2$ ($mol^{1/2}.L^{-1/2}$)	$\rho \times 10^{-3}$ ($kg.m^{-3}$)	$\phi_v \times 10^6$ ($m^3.mol^{-1}$)
5 % acetonitrile + water		
4.81	0.77372	55.77
6.21	0.77403	54.64
7.35	0.77435	51.75
8.79	0.77484	47.90
15.22	0.77809	42.72
19.64	0.78152	35.58
10 % acetonitrile + water		
4.82	0.77522	67.27
6.22	0.77552	65.02
7.36	0.77583	61.67
8.80	0.77631	56.64
15.23	0.77958	44.81

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19.66	0.78298	38.03
15 % acetonitrile + water		
4.82	0.77664	84.19
6.22	0.77693	78.63
7.36	0.77723	73.86
8.80	0.77768	70.27
15.25	0.78084	55.69
19.68	0.78428	43.39
20 % acetonitrile + water		
4.83	0.77911	90.137
6.23	0.77939	85.71
7.38	0.77969	79.09
8.82	0.78014	74.10
15.27	0.78321	62.33
19.71	0.78668	46.71

It is observed that the densities for aluminium chloride are increasing in higher concentration of acetonitrile in aqueous solution respectively at 303.15 K. Further, it seems that the apparent molar volumes that have been obtained using equation 2 are increasing with increase in concentration of acetonitrile in solution signifying the increased solute – solvent interactions. Graphical representation for apparent molar volumes versus square root values of molar concentration for aluminium chloride at different concentration of acetonitrile in water at 303.15K is shown in Figure 1.

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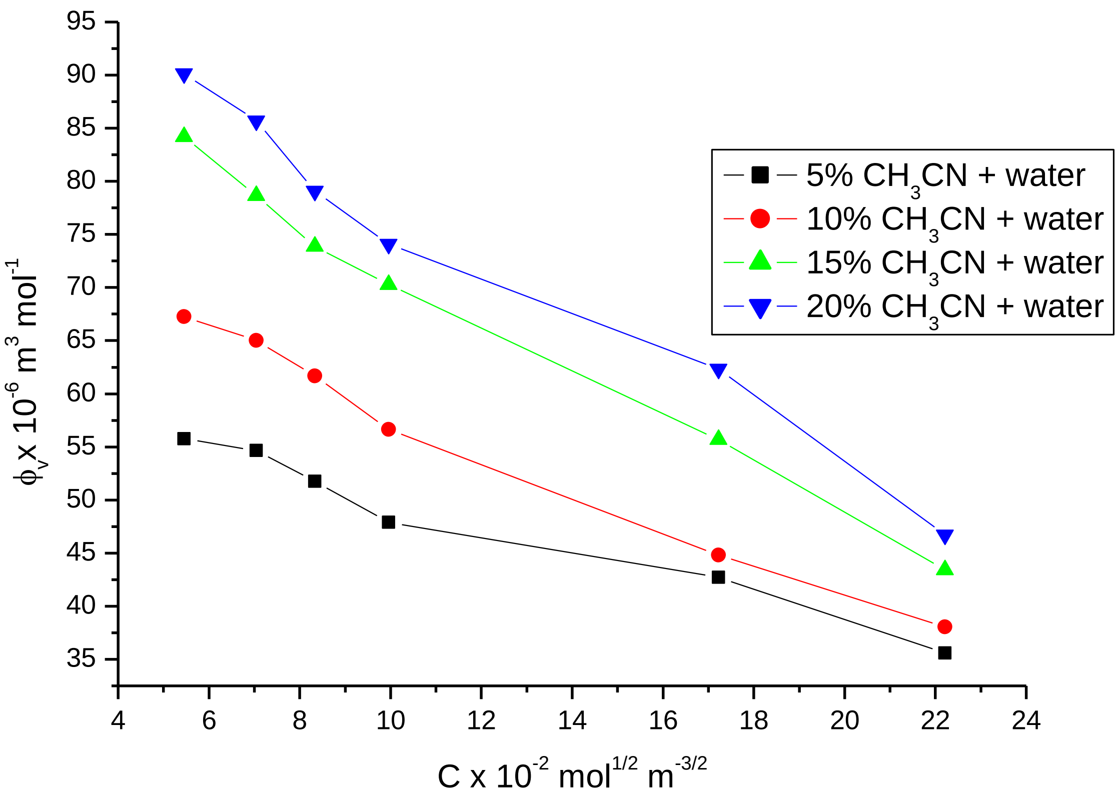

Figure1. Plot of φ_v vs. $C^{1/2}$ of Aluminum chloride at varied concentrations of acetonitrile and water at temperature 303.15 K.

The apparent molar volumes have further been used to determine the partial molar volumes,ϕ_v^0, by least square fitting of (ϕ_v) with the square root value of molar concentration which is represented by following equation:

$$\phi_v = \phi_v^0 + S_v^* C^{1/2} \quad (3)$$

Here ϕ_v^0, is value of partial molar volume whereas, $S_v^*$is the experimental slopes. These parameters were determined at varied concentrations of acetonitrile in aqueous solution are determined at temperature value of 303.15 K and the respective values are depicted in Table 2.

Table 2.,ϕ_v^0,(Partial molar volumes)and S_v^* (experimental slopes) for aluminium chlorideat varied concentrations of acetonitrile and water at temperature value of 303.15 K.

Composition	**ϕ_v^0x 10^6 ($m^3.mol^{-1}$)**	**S_v^* x 10^4 ($m^3.L^{1/2}.mol^{-3/2}$)**
5%	61.69	-1.164
10%	76.34	-1.775
15%	94.81	-2.323
20%	101.4	-2.433

It can be inferred from the above table, that ϕ_v^0values are positive and increases as the concentration of acetonitrile increases in water thereby suggesting the increased interaction of solute and solvent [14-15].This is further supported by the decrease in S_v^* values on increasing the concentration of acetonitrile in water which corresponds to decrease in interactions resulting in increase in solvation. Further,ϕ_v^0values are found to be in greater magnitudes as compared to S_v^* which indicates the increased solute - solvent interactions as compared to the solute- solute interactions atvaried concentrationof aqueous solutions.

As the behaviour of aluminium chloride has been found to be same in different compositions of acetonitrile. Hence, the effect of temperature on the solutions of aluminium chloride has been studied only in lower composition i.e. 5% (acetonitrile + water).

The values of the densities and apparent molar volumes of aluminium chloride in 5% acetonitrile + water has been represented in below table.

Table 3. Densities and apparent molar volumes of aluminum chloride in 5% acetonitrilein water at varied temperature values

$C^{1/2}$ x10^2 ($mol^{1/2}.L^{-1/2}$)	**ρ x 10^{-3} ($kg.m^{-3}$)**	**ϕ_v x 10^6 ($m^3.mol^{-1}$)**
298.15 K		

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4.82	0.77792	51.33
6.23	0.77824	49.11
7.37	0.77857	45.78
8.81	0.77907	42.45
15.26	0.78248	32.95
19.70	0.78608	24.73
303.15 K		
4.81	0.77372	55.77
6.21	0.77403	54.64
7.35	0.77435	51.75
8.79	0.77484	47.90
15.22	0.77809	42.72
19.64	0.78152	35.58
308.15 K		
4.79	0.76836	71.32
6.19	0.76865	70.16
7.33	0.76895	67.23
8.76	0.76941	63.32
15.16	0.77245	58.58
19.57	0.77575	48.70
313.15 K		
4.78	0.76278	81.52
6.17	0.76306	79.20
7.30	0.76336	73.27
8.72	0.76381	68.82
15.11	0.76682	61.13
19.50	0.77005	51.91

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It is observed that the density and apparent molar volume values for aluminium chloride are of greater value at higher temperature i.e. from 298.15 K to 313.15 K signifying increasedinteractions between solute and solvent. Graphical representation for the values of apparent molar volumes versus square root of the values for the molar concentration for aluminium chloridein 5% acetonitrile+ water at varied temperature valuesis shown in below Figure 2.

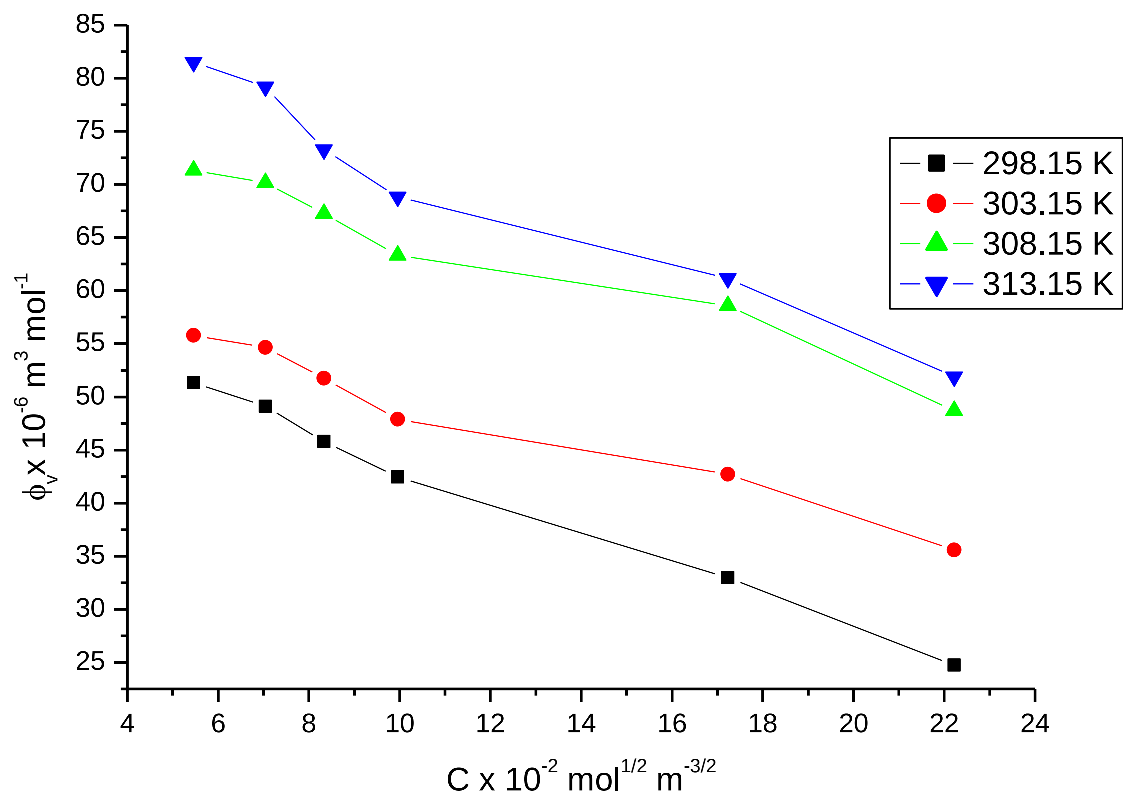

Figure 3.Plot of φ_v vs. $C^{1/2}$ of Aluminum chloride in 5% acetonitrile + water at varied temperatures.

The measurement of the apparent molar volumesvalues have beendone at different temperatures and are reported in Table 4.

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Table 4.Partial molar volumes,ϕ_v^0, and experimental slopes,$S_v^*$for aluminium chloride in 5% acetonitrile in water at varied temperature values

Temp (K)	ϕ_v^0 x 10^6 ($m^3.mol^{-1}$)	S_v^* x 10^4 ($m^3 \cdot L^{1/2}.mol^{-3/2)}$)
298.15 K	59.28	-1.556
303.15 K	61.69	-1.164
308.15 K	78.11	-1.273
313.15 K	88.97	-1.681

It can be depicted from the above table thatϕ_v^0values are positive. Further, these values are found to increase with rise suggesting increase in interactions between solute and solvent. Also the S_v^* values are lesser at high temperature which indicates the decreased interactions. This decrease in the interactions can be attributed to the increased salvation. In addition, ϕ_v^0values are found to be of magnitudes as compared to S_v^*values suggesting the dominancy of solute - solvent interactions as compared to solute- solute interactions at varied concentration of aqueous solution of acetonitrile.

Partial molar expansibility ,ϕ_E^0isan important parameterwhich can help in observing the structure making as well as breaking behaviour of solute in the solvent [16].It is observed that aluminium chloridebehaves in a similar fashion at all the concentrations of acetonitrile. Therefore, the partial molar expansibilities,ϕ_E^0, have been foundonly at the lower concentrations of acetonitrile.

The dependence of ϕ_v^0values at different temperature values in 5% acetonitrile + water for aluminium chloride can be determined by using the following equatinon:

ϕ_v^0= 7515.69 –50.02 T + 0.084 T ^{2} in 5% acetonitrile + water (4)

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Partial molar expansibilities value i.e.$\phi_E^0 = \left[\frac{\partial \phi_v^0}{\partial T}\right]_P$, is determined for aluminium chloride in 5% acetonitrile + water by using above relation are stated in Table 5.

Table 5.Partial molar expansibilities, ϕ_E^0 ,for aluminium chloride in 5% acetonitrile + water at varied temperatures (K).

T (K)	ϕ_E^0 x 10^6 ($m^3\ mol^{-1}\ K^{-1}$)	$(\partial C_p/\partial P)_T$ ($m^3 mol^{-2}\ K^{-1}$)
298.15	-24.98	596.3
303.15	-24.56	606.3
308.15	-24.14	616.3
313.15	-23.72	626.3

From Table 5, partial molar expansibilities valuesare lesser at higher temperature values. This shows that aluminium chloride does not behave like symmetrical tetraalkylammonium salts [17] butis behaving like common salts [18-19] as the molar volume expansibilities values are expected to decrease as the temperature of the common slat increases. The decreasing,ϕ_E^0 values suggests the absence of “packing effect”.

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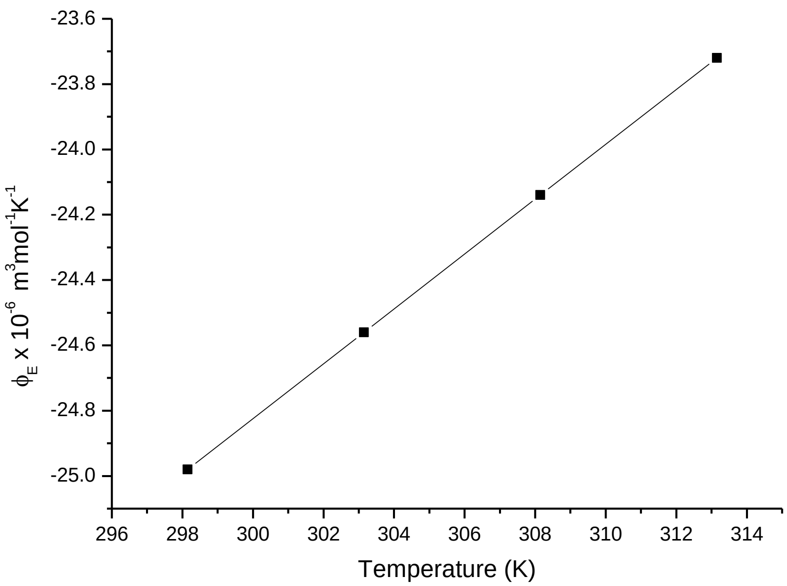

Figure 5.Plot of ϕ_E^0 vs temperature for aluminium chloride in 5%acetonitrile + water mixture.

Partial molar heat capacities values have been foundby the use of following equation at constant pressure.

$$(\partial C_p/\partial P)_T = -T\,(\partial^2\phi_v^0\,/\partial T^2\,)_P(5)$$

Partial molar heat capacities values of aqueous solution of electrolyte are negative most of the timesas per Hepler's theory. The aqueous electrolytes are the solutes which decrease the effective heat capacity of water by breaking up the bulky aggregatesIt has been observed that the values of the heat capacities are positive which shows that aluminium chloride behave as structure maker in mixtures of acetonitrile in water as binary solution.

Conclusion: The study concludes that the aluminium chloride behaves as structure maker in binary aqueous mixtures of acetonitrile**.**

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