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THERMO PHYSICAL PROPERTIES OF SOME THIOCYANATES IN BINARY AQUEOUS MIXTURES OF ACETONITRILE AT FIVE EQUIDISTANT WORKING TEMPERATURES

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Abstract

In the present study density data has been used for determining the thermo physical parameters viz; partial molar volumes and expansibilities of solutions of some thiocyanates in different binary aqueous mixtures of acetonitrile (ACN) at a temperature range (298.15, 303.15, 308.15, 313.15, 318.15) K. The Masson's equation has been referred to analyse the obtained parameters and results are interpreted in terms of solute- solute and solute - solvent interactions. In the present work thiocyanate salts were found structure breaker in binary aqueous solutions of ACN.
Keywords: Density; Partial molar volume; Partial molar expansibility; Structure maker/breaker.

Introduction

Recently a lot of work is done in the field of solution chemistry and recently focus has been diverted for the interpretation of various types of molecular interactions present in electrolytic and non-electrolytic solutions. Partial molar volume (PMV) is very useful parameter in analysing different types of interactions occurring in the solutions (Thakur *et al*., 2014; Juglan *et al*., 2018; Juglan *et al*., 2018; Juglan *et al*., 2017; Juglan *et al*., 2017, Kundu *et al*., 2003; Parmar *et al*., 2006; Saini *et al*., 2015; Sharma *et al*., 2016; Sharma *et al*., 2017; Sarkar *et al*., 2008). In the present study thiocyanate salts viz; sodium thiocyanate, potassium thiocyanate and ammonium thiocyanate were taken and are analysed for the thermodynamic properties. Thiocyanate salts have many applications in oil field, paint, pharma and ink industries. On the other hand, ACN is one of the main starting materials for synthesis of vitamins B_1 and A, cortisone, some amino acids and carbonate drugs and has many more applications in the Pharma industry. It is also used as a solvent system for the production of insulin and antibiotics and is also used as a mobile phase in high-performance liquid chromatography (HPLC). A lot of work has been done to study the thermodynamic properties of various systems but studies of thiocyanate salts in ACN as solvent medium are yet to be explored. Present study is focussed to analyse various interactions exiting between these thiocyanate salts in binary aqueous mixtures of ACN.

Experimental

All salts were taken of AR grade and procured from S.D Fine-Chem Limited. Specifications of all the chemicals used in the present study are mentioned in Table. 1.

Table 1 : Specification of chemicals

Chemical name	Molar Mass	Mass Fraction purity
Sodium thiocyanate (NaSCN)	81.07	>0.99
Potassium thiocyanate (KSCN)	97.18	>0.99
Ammonium thiocyanate (NH_4SCN)	76.12	>0.98
Acetonitrile (C_2H_3N)	41.05	>0.99

The different concentrations of the thiocyanate solutions were prepared by weight in triple distilled deionised water having 7 pH .The molality (m) of different salts solution was converted into molarity (c) by using the following relation.

$$C = \frac{md1000}{1000 + mM_2} \qquad ...(1)$$

where c is the molarity, d is density of salt solution, m is molality and M_2 is molecular weight of salt.

For measuring partial molar volumes, density values were calculated using "Ward and Millero" (Ward *et al.*, 1974) method and also used by (Thakur *et al*., 2016) in their experimental work as shown in Figure.1.

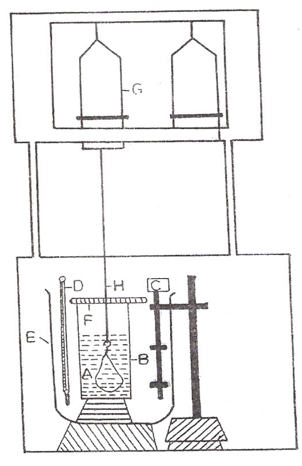

Fig. 1. APPARATUS FOR MEASUREMENT OF DENSITY

A 28.895 g float of volume 26.528 ± 0.003 cm^3 at 308.15K was used in the present study and dioxane was used for calibration. Density of the dioxane by using our method was found to be 1.02250 gcm^{-3} at 308.15 K and was found in good agreement with literature value of density equal to 1.02230 gm^{-3} (Timmermans, 1950).The density data was used to determine the apparent molar volumes (ϕ_v) using following expression (Millero *et al.*,1971).

$$\phi_v = \frac{1000(d_0 - d)}{m d d_0} + \frac{M_2}{d_0} \qquad ...(2)$$

where ρ_0 is the density of solvent used and ρ is the density of solution, m is the molal concentration of thiocyanate salts and M is the molar mass of thiocyanate salts.

Results and Discussion

Density values of solutions of thiocyanate salts in binary aqueous solutions of ACN at 303.15 K, were used to calculate the apparent molar volumes (ϕ_v) and it has been found that the (ϕ_v) values vary linearly with molality according to following Masson's equation (Masson, 1929).

$$\phi_v = \phi_v^0 + S_v^* m \qquad ...(3)$$

Plot for sodium thiocyanate in different compositions of ACN + water at 303.15 K is shown in Fig. 2. which confirms the linear variation.

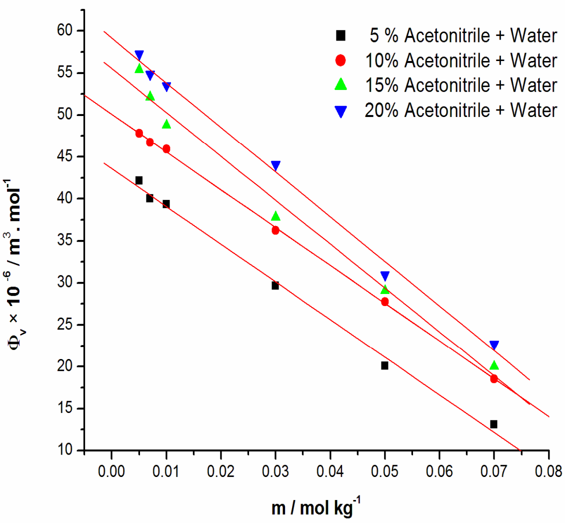

Fig. 2: Variation of apparent molar volumes with molality for sodium thiocyanate in different compositions of ACN + H_2O at 303.15K.

The partial molar volume $(\phi_v^0 = \overline{V}_2^0)$, has been calculated by using the least square fit to the linear plots of the experimental values of ϕv vs m, using Masson's equation. The values of Partial molar volumes (ϕ_V^0) and experimental slopes (S_V^*) obtained for above mentioned salts in water at 303.15K are recorded in Table. 2.

It is clearly observed that S_V^* values are negative for all the thiocyanate salts at 303.15 K highlighting the poor ion-ion interactions and do not follow a regular trend with increase in composition of ACN in water. On the other hand, positive values of PMV (ϕ_V^0) indicate the strong ion- solvent interactions and further increase with the increase of ACN content in water. These interactions were found maximum in ammonium thiocyanate as compared to other thiocyanates.

Effect of temperature

In order the analyse the effect of temperature lowest composition of ACN in water has been taken as trend was also found similar in the other compositions. Density values were used to calculate apparent molar volumes (AMV) at different temperatures and a sample plot of ϕ_v vs molality for NaSCN in 5% (w/w) ACN + water at different temperatures is shown in Fig.3.

Table 2: PMV and experimental slopes for thiocyanates in ACN + H_2O mixtures at 303.15K temperature.

Composition of ACN + Water (wt.%)	ϕ_V^0 (m^3 mol^{-1})	S_V^* (m^3 $lt^{1/2}$ $mol^{-3/2}$)
Sodium Thiocyanate		
5	43.58	-449.2
10	63.99	-725.7
15	69.10	-695.3
20	72.70	-705.0
Potassium thiocyanate		
5	54.45	-870.2
10	59.37	-645.2
15	60.56	-715.7
20	69.48	-720.7
Ammonium thiocyanate		
5	77.73	-766.4
10	77.90	-762.3
15	77.99	-764.0
20	78.55	-463.1

The values of partial molar volumes (ϕ_V^0) and experimental slopes (S_V^*) were obtained by using least – squares treatment to the plots of apparent molar volumes vs molality of the solutions and as per Masson equation and were recorded in Table. 3.

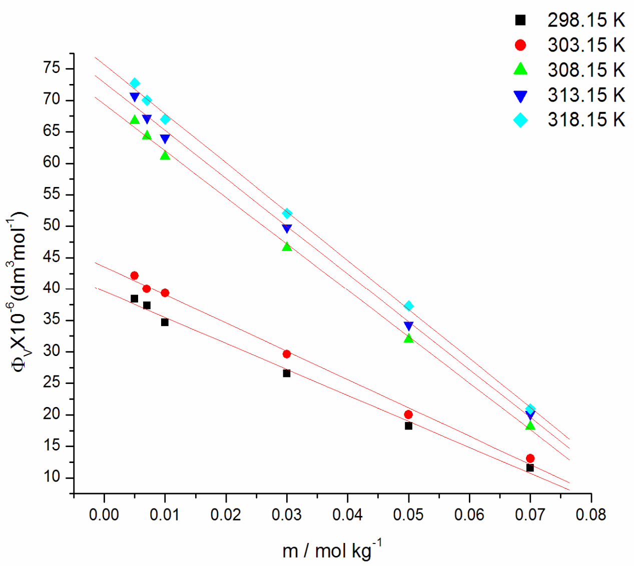

Fig. 3: Variation of AMV with molality for sodium thiocyanate in 5% (w/w) ACN+ H_2O at different temperatures.

The S_V^* values for all the thiocyanate salts were again found negative and the values rises with increase in temperature indicating the occurrence of poor ion-ion interactions leading to the increase of the solvation of thiocyanate salts with increase in temperature. On the other hand, values of ϕ_V^0 were found increasing with rise in temperature showing the strengthening of the ion – solvent interactions and increase in solvation of thiocyanates with increase in temperature. Partial molar volume expansibilities (ϕ_E^0) is one of other component that help in elucidating the behaviour of the electrolyte in terms of structure making/breaking capacity of the solute in a solvent system.Temperature equations, for the above-mentioned salts can be represented as follows:

ϕ_V^0 = -667.73+ 3.922T -0.0052 T^2 for sodium thiocyanate (4)

ϕ_V^0 = -868.42 +6.020 T -0.0096 T^2 for potassium thiocyanate (5)

ϕ_V^0 =-2603.76+17.119T-0.0273 T^2 for ammonium thiocyanate (6)

Table 3: Values of PMV and experimental slopes for thiocyanates in 5% (w/w) ACN +H_2O at varied temperatures.

Temp (K)	ϕ_V^0 (m^3 mol^{-1})	S_V^* (m^3 $lt^{1/2}$ $mol^{-3/2}$)
Sodium Thiocyanate		
298.15	39.60	-412.6
303.15	43.58	-449.2
308.15	69.37	-739.0
313.15	72.83	-760.6
318.15	75.67	-778.5
Potassium Thiocyanate		
298.15	73.21	-866.0
303.15	74.45	-870.2
308.15	76.86	-876.9
313.15	79.14	-893.2
318.15	81.08	-908.1
Ammonium Thiocyanate		
298.15	74.21	-733.8
303.15	77.73	-766.4
308.15	78.60	-770.7
313.15	78.88	-787.6
318.15	79.02	-841.7

Partial molar volume expansibilities (PMVE) have been determined for the above-mentioned salts by taking single derivative of equations 4, 5 and 6 with respect to temperature and are reported in Table. 4.

From the above table it is clear that values of partial molar expansibilities are decreasing with the increase in temperature and hence these thiocyanate salts are not behaving like symmetrical tetra alkyl ammonium salts (Millero, 1971) but behave like common salts (Millero *et al.*, 1968, Millero *et al.*, 1971) and confirms the absence of "packing effect" salts (F.J. Millero.,1971). Variation of partial molar expansibilities with temperature is shown in the following graph for sodium and potassium thiocyanates in 5% ACN + water mixture as shown in Fig. 4.

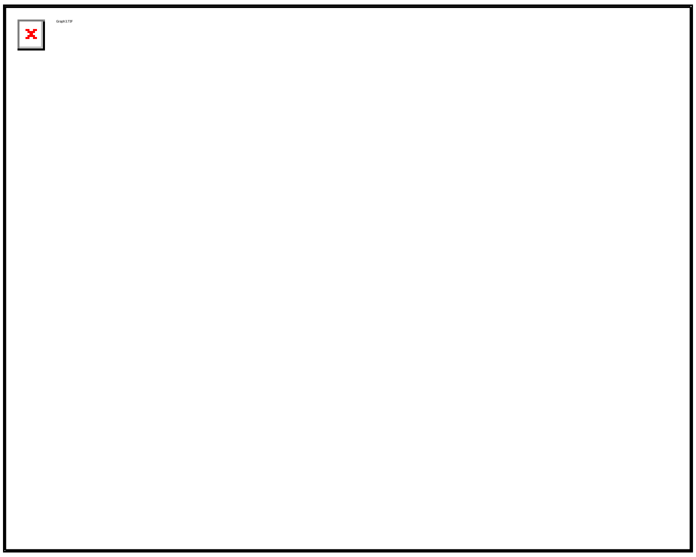

Fig. 4: Variation of partial molar expansibilities with temperature for sodium thiocyanate and potassium thiocyanate in 5% ACN + H_2O.

Structure making or breaking capacity has been analysed by using Hepler's Criterion (Hepler *et al.*, 1969) using the following general thermodynamic relation:

$$(\partial Cp/\partial P) = -\left(\frac{\partial^2\phi_V^0}{\partial T^2}\right)P \qquad ...(7)$$

Positive values $\left(\frac{\partial^2\phi_V^0}{\partial T^2}\right)P$ indicates the structure making nature of solutes where as negative values indicate the structure breaking nature and in the present study, it is found that the values for $\left(\frac{\partial^2\phi_V^0}{\partial T^2}\right)P$, are negative (using equations 4-6) for all the electrolytes indicating that all thiocyanate salts act as structure breakers in binary aqueous mixture of ACN in water.

Table 4 : PMVE for thiocyanates in 5% (w/w) ACN + H_2O at different temperatures

TEMP (K)	ϕ_E^0 (m^3 mol^{-1} K^{-1})		
	Sodium thiocyanate	**Potassium thiocyanate**	**Ammonium thiocyanate**
298.15	0.821	0.296	0.840
303.15	0.769	0.200	0.567
308.15	0.717	0.104	0.294
313.15	0.665	0.008	0.021
318.15	0.613	-0.088	-0.252

Conclusion

In the present work the analysis has been done with respect to structure making/breaking behaviour of thiocyanates by using various thermodynamic parameters like partial molar volumes, partial molar expansibilities in binary aqueous compositions of ACN in water. On the basis of Hepler criterion it was found that that these salts behave as structure breakers in binary aqueous mixtures of ACN.

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