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EFFECT OF TEMPERATURE ON THE VOLUMETRIC STUDIES OF SOME THIOCYANATES IN WATER

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ABSTRACT
Apparent molar volumes, partial molar volumes and partial molar expansibilities of some thiocyanates salts viz: sodium thiocyanate, potassium thiocyanate and ammonium thiocyanate have been determined in aqueous medium with the help of density measurements. The densities were measured by using Ward and Millero method and results have been analysed by Masson's equation and interpreted in terms of ion-ion or ion – solvent interactions. Structure making or breaking capacities of thiocyanate salts have also been inferred from the sign of $\left(\frac{\partial^2 \phi_v^0}{\partial T^2}\right)_p$ i.e second derivative of partial molar volume with respect to temperature at constant pressure.
Key words: Partial molar volumes, partial molar expansibilities, structure breaker.

INTRODUCTION

The study of electrolytic and non electrolytic solutions is an area of interest in physical chemistry and it has expanded in several directions during the last two decades. Partial molar volume is one of the important thermodynamic properties which have been proved a very useful tool in determining the various types of interactions like solute-solute, solute - solvent and solvent - solvent interactions occurring in aqueous as well as non-aqueous solutions[1-10]. The study of these interactions is very helpful in determining the structural properties of the solutions. In the present study sodium thiocyanate, potassium thiocyanate and ammonium thiocyanate are taken as the aqueous data of these salts is required in many industries as analytical reagents in the oil field industry, as an anti-fouling agent in ship paints, in the textile industry and in the production of ink for ink-jet printers, in the synthesis of certain medicines and dye. Ammonium thiocyanate is used in chemical analysis, in photography and sometimes also used as a fertilizer. An appreciable work has been done on thermodynamic properties of various electrolytes in different binary aqueous mixtures but studies on thiocyanate salts in aqueous medium is yet to be estimated. Hence, the present study seeks an attempt to understand the different types of interactions present in the aqueous mixtures of sodium thiocyanate, potassium thiocyanate and ammonium thiocyanate and also to see the effect of temperature on these interactions.

EXPERIMENTAL

Reagents sodium thiocyanate (NaSCN - 81.07 g), potassium thiocyanate (KSCN - 97.18 g), ammonium thiocyanate (NH_4SCN - 76.12 g) were taken of AR grade. All these reagents were used after drying over calcium oxide desiccators and are kept in dry atmosphere. Fresh triple distilled water was used as standard solvent for preparing the solutions. The different concentrations of the thiocyanates salts were prepared by weight.

Densities of above mentioned salts were measured with the help of an apparatus shown in Fig.1, similar to the one described by "Ward and Millero."[11]

In this apparatus a glass float A is suspended from a balance pan G with the help of a nylon thread H into a cylindrical sample container B of 250 ml capacity. The glass cell has a Bakelite top F with a hole in the centre of nylon thread to pass through. The cell was placed in water-bath having a stirrer E and thermometer D. The whole assembly of sample container and water-bath was placed in thermo-stat whose

temperature was controlled with the help of an electronic relay. The fluctuation in the temperature was always within ± 0.01^0C.
The sample container and glass float was thoroughly cleaned by washing them with chromic acid first and then with acetone. The float was completely dried with the help of hot air blower.

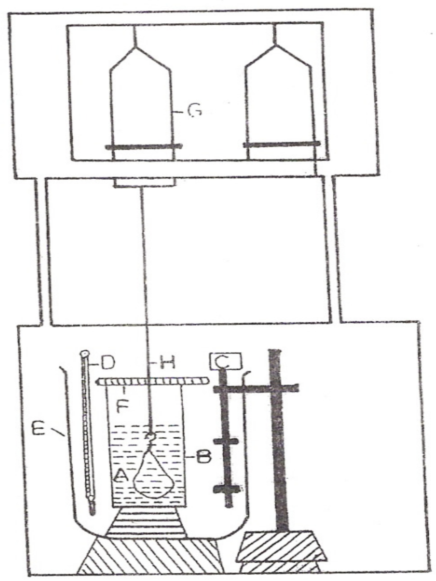

Fig.-1: Ward and Millero apparatus to measure the density.

A 21.902 g float of volume 10.784± 0.004 cm^3 at 308.15K was used. The volume of float was determined with the help of following equation [12]:

$$V_f = \left[\frac{W_{air} - W_{water}}{d_0}\right]_T \quad (1)$$

Where, W_{air} is the weight of float in air and W_{water} is weight of float in water. The quantity $W_{air} - W_{water}$ is loss of weight of float in water and d_0 is the density of water at a particular temperature T. The densities of solutions were calculated using the following relation:

$$d - d_0 = \frac{W_0 - W}{V_f} \quad (2)$$

Where. d is the density of solution under study and d_0 is the density of pure water at a particular temperature, W_0 is the weight of float in pure water, W is the weight of float in solution under study, V_f is the volume of float. The density of dioxane was calculated using the above mentioned setup and it was found 1.02250 gcm^{-3} at 303.15 K which is in good agreement with literature value of density of dioxane[13] (d = 1.02230 gm^{-3}).
The solutions of six different concentrations of above mentioned thiocyanate salts were prepared by weight .The density was measured with the help of an apparatus similar to the one reported by Ward and Millero. The accuracy in the density measurements was 1 x 10^{-4} gcm^{-3}.
The apparent molar volumes (ϕ_v) were calculated from the density data using the following expression:

$$\phi_v = \frac{1000(d_0 - d)}{mdd_0} + \frac{M}{d^0} \quad (3)$$

Where d_0 is the density of water as solvent and d is the density of solution; m is the molal concentration of thiocyanate salts and M is the molecular weight of respective thiocyanate salts. The density measurements were taken in a well stirred water bath with a temperature control of ± 0.01 K.

RESULTS AND DISCUSSION

The densities and apparent molar volumes, for all the above salts in water at five equidistant temperatures (298.15, 303.15, 308.15, 313.15 and 318.15K) are determined and recorded in table – 1**.** It has been observed that the apparent molar volumes (ϕ_v) of above mentioned thiocyanates vary linearly with the molal concentration of all the thiocyanate salts in water in conformity with Masson's equation[14].

$$\phi_v = \phi_v^0 + S_v^* m \quad (4)$$

The plots of apparent molar volumes (ϕ_v) verses molal concentration (m) were found to be linear with negative slopes in water. Plot of apparent molar volumes (ϕ_v) verses molal concentration (m) for sodium thiocyanate, potassium thiocyanate and ammonium thiocyanate in water at 303.15K is shown in fig.2. Also the linear plots of ϕ_v vs m have been obtained for all the salts in water at different temperatures. A sample plot for Sodium thiocyanate is shown in fig. 3.The values of limiting apparent molar volume (ϕ_V^0) and experimental slopes (S_V^*) have been obtained by using least – squares treatment to the Masson equation and are also reported in Table - 1.

Table-1: Molalities (m), densities (d), apparent molar volumes(ϕ_V), partial molar volumes (ϕ_v^0) and experimental slopes (S_v^*) for sodium thiocyante, potassium thiocyanate and ammonium thiocyanate in water at different temperatures

m (mol Kg^{-1})	d (gm cm^{-3})	ϕ_V (cm^3 mol^{-1})	ϕ_v^0 (cm^3 mol^{-1})	S_v^* ($cm^3 lit^{1/2} mol^{-3/2}$)
Sodium Thiocyanate; 298.15 K				
0.005	0.99712	64.52	66.13	-903.6
0.007	0.99720	58.66		
0.010	0.99731	54.27		
0.030	0.99824	41.25		
0.050	1.00010	19.93		
0.070	1.00251	3.19		
303.15 K				
0.005	0.99571	68.33	69.22	-904.7
0.007	0.99580	60.04		
0.010	0.99588	58.04		
0.030	0.99676	44.05		
0.050	0.99852	23.60		
0.070	1.00094	5.65		
308.15 K				
0.005	0.99408	72.17	72.88	-912.9
0.007	0.99415	64.13		
0.010	0.99422	61.85		
0.030	0.99508	46.24		
0.050	0.99677	26.34		
0.070	0.99904	9.52		
313.15 K				
0.005	0.99226	72.29	73.60	-914.4
0.007	0.99232	65.56		
0.010	0.99240	61.93		
0.030	0.99322	47.52		
0.050	0.99491	27.03		
0.070	0.99720	9.67		
318.15 K				
0.005	0.99024	76.20		

0.007	0.99031	67.01	75.67	-919.3
0.010	0.99040	62.01		
0.030	0.99117	49.43		
0.050	0.99272	30.74		
0.070	0.99513	10.49		
Potassium Thiocyanate; 298.15 K				
0.005	0.99723	60.16	61.55	-514.9
0.007	0.99732	57.50		
0.010	0.99745	56.44		
0.030	0.99862	44.69		
0.050	1.00010	36.09		
0.070	1.00205	25.87		
303.15 K				
0.005	0.99583	62.06	64.30	-517.7
0.007	0.99590	61.53		
0.010	0.99604	58.33		
0.030	0.99712	48.41		
0.050	0.99863	37.73		
0.070	1.00045	28.71		
308.15 K				
0.005	0.99419	65.86	68.44	-520.9
0.007	0.99426	64.25		
0.010	0.99439	61.17		
0.030	0.99526	56.21		
0.050	0.99672	43.48		
0.070	0.99873	30.11		
313.15 K				
0.005	0.99236	67.80	70.30	-522.6
0.007	0.99243	65.65		
0.010	0.99255	63.10		
0.030	0.99336	59.05		
0.050	0.99487	44.02		
0.070	0.99675	32.31		
0.005				
0.005	0.99035	69.77	71.74	-526.7
0.007	0.99042	67.07		
0.010	0.99054	64.10		
0.030	0.99133	60.04		
0.050	0.99281	45.32		
0.070	0.99466	33.58		
Ammonium Thiocyanate; 298.15 K				
0.005	0.99710	63.28		
0.007	0.99715	60.35		

0.010	0.99723	56.76	66.79	-918.1
0.030	0.99818	38.14		
0.050	0.99974	22.20		
0.070	1.00223	2.11		
		303.15 K		
0.005	0.99569	68.97	69.55	-945.4
0.007	0.99575	61.75		
0.010	0.99584	57.75		
0.030	0.99676	39.08		
0.050	0.99826	23.83		
0.070	1.00075	3.33		
		308.15 K		
0.005	0.99406	70.94	71.39	-947.4
0.007	0.99412	63.17		
0.010	0.99420	59.69		
0.030	0.99509	40.95		
0.050	0.99654	25.84		
0.070	0.99902	4.81		
		313.15 K		
0.005	0.99223	72.95	73.79	-950.7
0.007	0.99228	65.95		
0.010	0.99236	61.65		
0.030	0.99319	43.47		
0.050	0.99457	28.79		
0.070	0.99708	6.42		
		318.15 K		
0.005	0.99022	74.98	76.38	-952.1
0.007	0.99027	68.76		
0.010	0.99034	63.63		
0.030	0.99106	47.89		
0.050	0.99249	30.45		
0.070	0.99490	8.83		

It is evident from the table - 1 that the values of(S_V^*) are negative for all the thiocyanates in the entire temperature range studied here, thereby showing the existence of weak ion-ion interactions. It is also clear from the table - 2 that values of(S_V^*) further decrease with the increase in temperature thereby showing that these interactions are further weakened with the increase in temperature for all the electrolytes. Also it is clear from table - 1 that the values of ϕ_v^0 are positive indicating the strong ion solvent interactions which are further increasing with increase in temperature for all the thiocyanate salts in water, thereby showing that ion – solvent interactions are strengthened with increase in temperature. The increase in ϕ_v^0 values may be due to increase in solvation of thiocyanate salts with rise in temperature.

The temperature dependence of ϕ_v^0 water for selected thiocyanate salts can be expressed by the following relations:

$\phi_v^0 = - 340.44 + 2.10\ T - 0.0025\ T^2$ for sodium thiocyanate (5)

$\phi_v^0 = - 1671.24 + 5.90\ T – 0.0089\ T^2$ for potassium thiocyanate (6)

$\phi_V^0 = -423.17 + 2.71\,T - 0.0036\,T^2$ for ammonium thiocyanate (7)

It may also be concluded from the ϕ_V^0 values that ion – solvent interactions follow the following order for sodium thiocyanate, potassium thiocyanate and ammonium thiocyanate in water-

Ammonium thiocyanate > Sodium thiocyanate> Potassium thiocyanate.

Since thiocynate ion (SCN^-) is a common ion in all the salts studied here in water, so it may be inferred that the solvation order for the cations of above mentioned salts in water follow the following order:

$NH_4^+ > Na^+ > K^+$

Where, the temperature T is expressed in Kelvin (K).

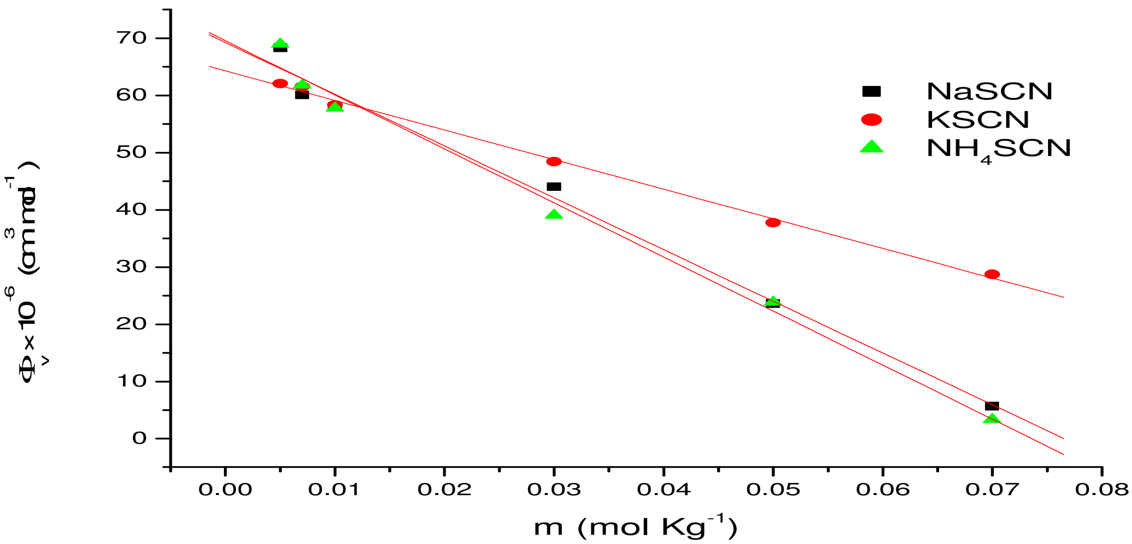

Fig.-2: Plot of apparent molar volumes (ϕ_v) verses molal concentration (m) for sodium thiocyanate, potassium thiocyanate and ammonium thiocyanate in water at 303.15K.

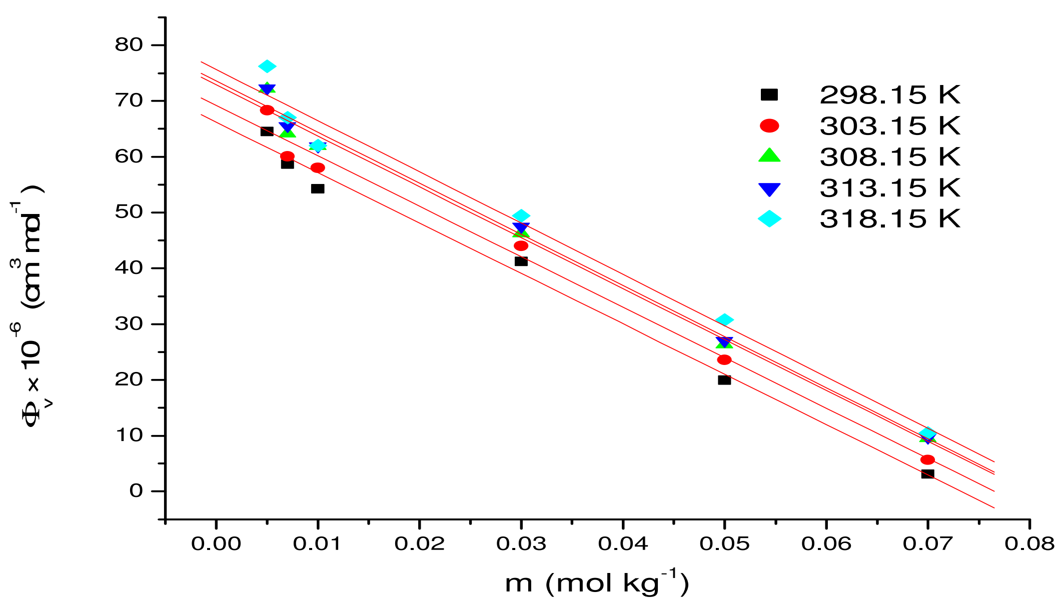

Fig.-3: Plot of ϕ_v vs molal concentration for sodium thiocyanate in water at different temperatures.

Partial molar volume expansibilities also known as limiting apparent molar expansibilities $\phi_E^0 = \left[\frac{\partial \phi_v^0}{\partial T}\right]_P$, which is temperature dependence function of ϕ_v^0, were calculated for the above mentioned thiocyanate salts by using relations (5),(6) and (7) are given in table 2. From table 2, it is clear that ϕ_E^0 values for thiocyanate salts at different temperatures are positive and decrease with rise in temperature showing that these thiocyanate salts are not behaving like symmetrical tetra alkyl ammonium salts[15] and but like common salts[16,17]as in the case of common electrolytes the molar volume expansibilities should decrease with the rise in temperature. The decrease in the magnitude of ϕ_E^0 values indicates the absence of "packing effect"[15,16.] The plot of ϕ_E^0 verses temperature is found to be linear for all thiocyanate salts in water and is shown in fig.4.

Table-2: Partial molar volumes expansibilities (ϕ_E^0) for sodium thiocyante, potassium thiocyanate and ammonium thiocyanate in water at different temperatures.

Temperature	Sodium Thiocyante	Potassium Thiocyanate	Ammonium Thiocyanate
(K)	ϕ_E^0 ($cm^3\ mol^{-1}\ K^{-1}$)		
298.15	0.609	0.593	0.563
303.15	0.584	0.504	0.527
308.15	0.559	0.415	0.491
313.15	0.534	0.326	0.455
318.15	0.509	0.237	0.419

In last few years, it has been observed by the number of workers that S_v^* is not the only criterion for determining the structure making or breaking nature of any solute.Hepler[19] has given a method of finding the sign of $\left(\frac{\partial^2 \phi_v^0}{\partial T^2}\right) p$ for different types of solutes in forms of long range structure making or structure breaking capacities of the solutes in aqueous solutions using the general thermodynamic relation:

$$(\partial Cp)/\partial P)_T = -T\left(\frac{\partial^2 \phi_v^0}{\partial T^2}\right)_p \qquad (8)$$

On the basis of equation (8), It has been found that the positive values of $\left(\frac{\partial^2 \phi_v^0}{\partial T^2}\right)_p$ indicate the structure making nature of solutes and negative values of $\left(\frac{\partial^2 \phi_v^0}{\partial T^2}\right)_p$ indicate the structure breaking nature of solutes. In our present study, it is found from equations (5) to (7) , $\left(\frac{\partial^2 \phi_v^0}{\partial T^2}\right)_p$ values are negative for these thiocyanate salts in water suggesting that the all these thiocyanate salts taken in present study act as structure breakers in water. This indicates that the addition of thiocyanate salts break the structure of water.

CONCLUSION

It is evident from the study that the values of partial molar volume ϕ_v^0 and partial molar volume expansibilities ϕ_E^0 indicates the presence of strong solute- solvent interactions with the entire range of temperature (298.15 - 318.15) K .Also the negative values of $\left(\frac{\partial^2 \phi_v^0}{\partial T^2}\right)_p$ indicates that all the thiocynates salts viz; sodium thiocyante, potassium thiocyanate and ammonium thiocyanate act structure breaker in water.

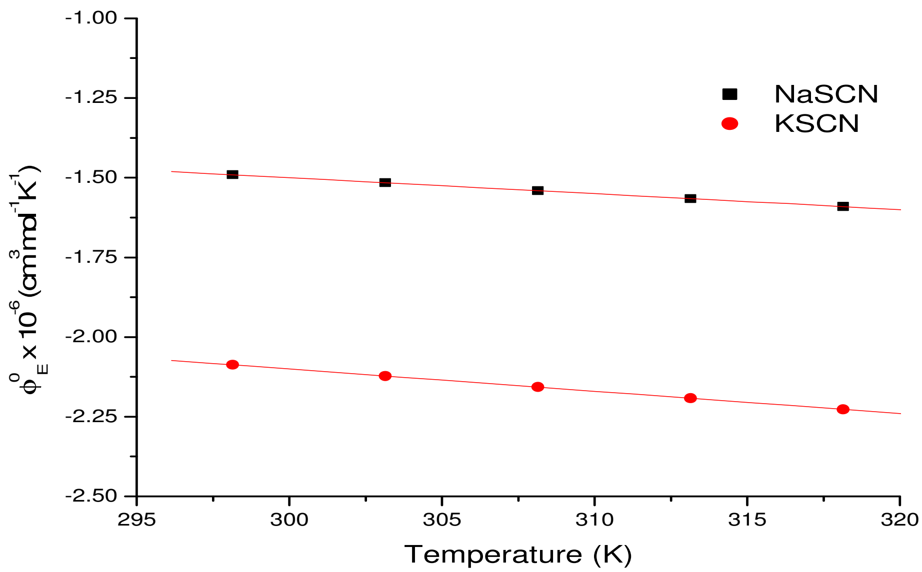

Fig.-4: Plot of ϕ_E^0 verse temperature for Sodium Thiocyante, Potassium Thiocyanate, Ammonium Thiocyanate in water at different temperatures.

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