Viscosity B-Coefficients of Some Thiocyanates In Aqueous Medium

R.C.Thakur*, Vishali Gill and Ravi Sharma

Department of Chemistry, School of Chemical Engineering and Physical Sciences, Lovely Professional University, Punjab

Email: drthakurchem@gmail.com

Abstract: Viscosities of some thiocyanates were determined in water at five equidistant different temperatures using suspended level viscometer. Viscosity data has been analyzed by using Jones – Dole equation in terms of molecular interactions. The obtained B-Coefficient parameters were expressed in terms of different interactions and in the present study all the thiocyanates were found structure breakers in the aqueous medium.

Keywords: Thiocyanates, Viscosities and Jones Dole equation.

INTRODUCTION

In solution chemistry, it is very interesting to anaylse the behavior of electrolytes in different solvent systems. As we know that when any electrolyte is added in to the solvent, it brings about changes in the structure of the solvent and also leads to various types of interactions [1-4]. Recently a lot of work has been done [5-14] in this direction and it was inferred that electrolyte either breaks or promotes the structure of the solvent in the solution and this can also be considered as a measure of ion-solvent interactions. In our study different thiocyanates were taken as these play an important role in oil field industry, paint industry, textile industry, pharma industry and ink jet industries. Thermodynamic properties of these thiocyanates have been studied by Thakur and others [15] but study on transport properties are explored in the present study. Hence here an attempt has been made to analyse the transport properties and different types of interactions occurring in the aqueous solutions of these thiocyanates.

Experimental:

All the chemicals viz; sodium thiocyanate (NaSCN), potassium thiocyanate (KSCN) and ammonium thiocyanate (NH_4SCN) were taken of analytical grade and specifications are given in Table 1.

Table 1

Specifications of chemicals:

Chemical name	Molecular weight (gm)	Provenance	Mass Fraction purity
Sodium thiocyanate	81.07	S D Fine Chemical Limited	>0.99
Potassium thiocyanate	97.18	S D Fine Chemical Limited	>0.99
Ammonium thiocyanate	76.12	S D Fine Chemical Limited	>0.98

Densities of thiocyanate salts were determined by "Ward and Millero" method and are mentioned in our earlier studies [15].Viscosity measurements are made with the help of suspended level type viscometer having flow time of 100 seconds for water at 303.15K. Runs are repeated until three successive readings are obtained within $\pm$0.1 second.

The viscometer was cleaned by filling it with chromic acid, followed by washing with water and finally with acetone. It was then dried by applying vacuum. Viscosities of solutions were determined at different temperatures in water thermost at controlled temperature upto ±0.01^{0}C by means of an electronic relay and contact thermometer. The relative viscosities of solutions are than obtained by using following equation:

$$\eta_r = \eta/\eta_o = d.t / d_o .t_o \qquad (1)$$

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where η and η_o are the viscosities of solution and solvent respectively, η_r is the relative viscosity, d and d_o are the densities of solution and solvent respectively, t and t_o are their respective flow times. The calibration of the viscometer was done with the help of conductivity water used as a standard liquid. The viscosities of the thiocyanates salts were determined with the above mentioned viscometer at 303.15K.The relative viscosities of the solutions were determined by usual procedure [16-18]. In order to analyze the effect of temperature on density and viscosity all the measurements were made in air and water thermostat (± 0.01K) respectively.

RESULTS AND DISCUSSION

All the measurements of densities and viscosities were made at 298.15, 303.15, 308.15, 313.15 and 318.15K and are recorded in Table 2 for all the aqueous solutions of sodium thiocyanate, potassium thiocyanate, ammonium thiocyanate.

TABLE -2. Densities, viscosities and relative viscosities of sodium thiocyanate, potassium thiocyanate and ammonium thiocyanate in water at different temperatures.

Concentration $C\times10^2$ (mol lt^{-1})	Density d (gcm^{-3})	Viscosity η (cP)	Relative Viscosity η/η_0
SODIUM THIOCYANATE			
298.15 K			
0.005	0.99712	0.89957	1.00657
0.007	0.99720	0.90200	1.00928
0.01	0.99731	0.90523	1.02191
0.03	0.99824	0.92476	1.03475
0.05	1.00010	0.94661	1.05921
0.07	1.00251	0.97175	1.08734
303.15 K			
0.005	0.99571	0.80575	1.00631
0.007	0.99580	0.80797	1.00908
0.01	0.99588	0.81047	1.01220
0.03	0.99676	0.82822	1.03437

0.05	0.99858	0.84760	1.05858
0.07	1.00094	0.86949	1.08592
308.15 K			
0.005	0.99408	0.72661	1.00568
0.007	0.99415	0.72889	1.00884
0.01	0.99422	0.73105	1.01183
0.03	0.99508	0.74667	1.03345
0.05	0.99676	0.76453	1.05871
0.07	0.99904	0.78304	1.08379
313.15 K			
0.005	0.99226	0.65698	1.00561
0.007	0.99232	0.66142	1.00826
0.01	0.9924	0.66354	1.01149
0.03	0.99322	0.67734	1.03253
0.05	0.99491	0.69384	1.05769
0.07	0.9972	0.71021	1.08264
318.15 K			
0.005	0.99024	0.60176	1.00494
0.007	0.99031	0.60338	1.00765
0.01	0.9904	0.60524	1.01076
0.03	0.99117	0.61748	1.03119
0.05	0.99272	0.63203	1.05549
0.07	0.99513	0.64731	1.08100
POTASSIUM THIOCYANATE			
298.15 K			
0.005	0.99723	0.90466	1.01226
0.007	0.99732	0.90704	1.01493
0.01	0.99745	0.91011	1.01836
0.03	0.99862	0.92837	1.03879
0.05	1.00010	0.94374	1.05600
0.07	1.00210	0.96007	1.07426
303.15 K			
0.005	0.99583	0.80970	1.01124
0.007	0.99590	0.83126	1.01431

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0.01	0.96040	0.81511	1.01799
0.03	0.99712	0.83127	1.03817
0.05	0.99863	0.8446	1.05473
0.07	1.00045	0.85875	1.07250
308.15 K			
0.005	0.99405	0.72999	1.01124
0.007	0.99415	0.73171	1.01275
0.01	0.99419	0.73429	1.01631
0.03	0.99463	0.74819	1.03556
0.05	0.99545	0.75993	1.05181
0.07	0.99728	0.77201	1.06853
313.15 K			
0.005	0.99221	0.6625	1.00992
0.007	0.99223	0.66422	1.01253
0.01	0.99231	0.66636	1.01579
0.03	0.99255	0.6792	1.03536
0.05	0.99351	0.68993	1.05172
0.07	0.99481	0.70174	1.06973
318.15 K			
0.005	0.99021	0.60446	1.00945
0.007	0.99023	0.60606	1.01212
0.01	0.99027	0.60827	1.01582
0.03	0.99055	0.61964	1.03480
0.05	0.99142	0.62955	1.05136
0.07	0.99271	0.63978	1.06844
AMMONIUM THIOCYANATE			
298.15 K			
0.005	0.99704	0.89755	1.00431
0.007	0.99706	0.89896	1.00588
0.01	0.99714	0.90119	1.00838
0.03	0.99763	0.91242	1.02095
0.05	0.99855	0.9236	1.03346
0.07	1.00011	0.93741	1.04891
303.15 K			

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0.005	0.99565	0.80407	1.00421
0.007	0.99567	0.80535	1.00581
0.01	0.99576	0.80683	1.00766
0.03	0.99618	0.81715	1.02054
0.05	0.99733	0.82752	1.03350
0.07	0.99872	0.83896	1.04778
308.15 K			
0.005	0.99403	0.72521	1.00375
0.007	0.99404	0.72638	1.00537
0.01	0.99413	0.72786	1.00742
0.03	0.99454	0.73707	1.02017
0.05	0.99555	0.74661	1.03336
0.07	0.99715	0.75674	1.04738
313.15 K			
0.005	0.99221	0.65839	1.00364
0.007	0.99222	0.65923	1.00492
0.01	0.99231	0.66048	1.00683
0.03	0.99269	0.66849	1.01904
0.05	0.99389	0.67718	1.03229
0.07	0.99521	0.68658	1.04661
318.15 K			
0.005	0.99021	0.60091	1.00352
0.007	0.99022	0.60147	1.00446
0.01	0.99031	0.60241	1.00603
0.03	0.99069	0.60985	1.01846
0.05	0.9918	0.61742	1.03110
0.07	0.99337	0.62641	1.04611

From the observations recorded in Table 2 it is obvious that relative viscosity values for the solutions of above mentioned thiocyanates increase with increase in concentration of an individual thiocyanate. Further, variation of relative viscosities of the solution of the above mentioned electrolytes in water at different temperatures can be represented by Jones – Dole Equation. According to this equation a straight line plot should be obtained if $(\eta_r - 1)/C^{1/2}$ is plotted against the square root of molar concentration ($C^{1/2}$) and same has to be found to be true in present investigation for all the above mentioned salts in water. A sample plot of $(\eta_r - 1)/C^{1/2}$ versus $C^{1/2}$ for sodium thiocyanate at different temperatures is shown in figure - 2.

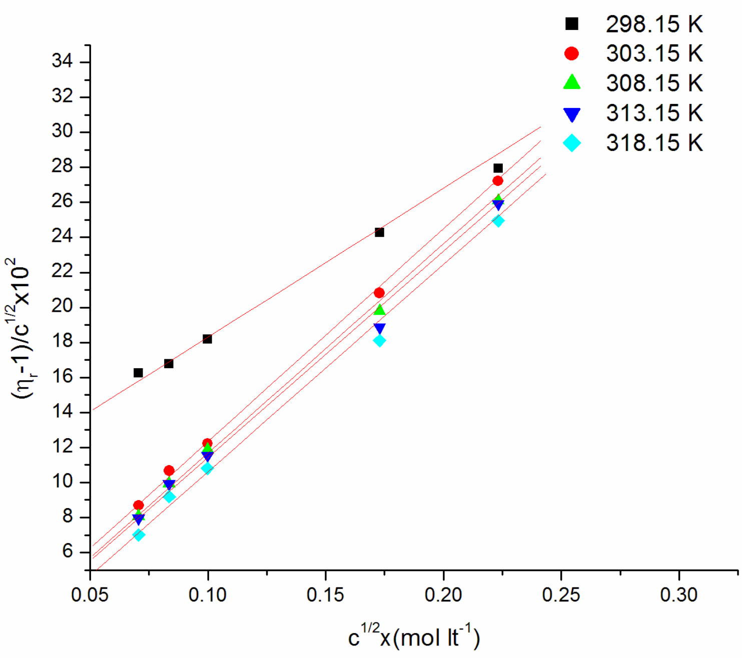

FIG. 2 .Vaiation of $(\eta_r - 1)/C^{1/2}$ verses $C^{1/2}$ for Sodium Thiocyanate in water at five equidistant temperatures.

The obtained viscosity data has been analyzed using the Jones Dole equation [19].

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

where A, B are two constants parameters and η ,η_0 are the viscosities of solution and solvent respectively. A coefficient depicts the presence of solute- solute interactions and B coefficient depicts the presence of solute- solvent interactions. Both A and B parameters have been calculated by plotting a graph between $(\eta_r - 1)/C^{1/2}$ versus $C^{1/2}$ for all the thiocyanate salts in water at five equidistant temperatures. The obtained values of A and B are reported in table 3.

TABLE 3. Values of Jones – Dole equation parameters (A and B) for thiocyanates in water at five equidistant temperatures.

Temperatures (K)	A ($lt^{1/2}mol^{-1/2}$)	B ($lt\ mol^{-1}$)
SODIUM THIOCYANATE		
298.15	1.211	1.050
303.15	1.162	2.178
308.15	1.156	2.681
313.15	1.147	3.343
318.15	1.124	4.079
POTASSIUM THIOCYANATE		
298.15	0.526	13.85
303.15	0.506	14.63
308.15	0.493	15.38
313.15	0.457	16.53
318.15	0.454	16.95
AMMONIUM THIOCYANATE		
298.15	0.610	1.903
303.15	0.598	2.617
308.15	0.591	3.196
313.15	0.583	3.698
318.15	0.581	4.020

From the above table (Table 3), it can be inferred that values of A coefficient of Jones- Dole equation are very small as compared to the B-Coefficient values indicating very small magnitude of ion-ion concentrations with respect to ion-solvent interactions. With the rise in temperature values of A Coefficient are further reduced indicating that ion –ion interactions are weakened further with the rise in temperature.

On the other hand values of B Coefficient are large indicating the large ion-solvent interactions which are further strengthened with the rise in temperature. With the increase in temperature solvation of all thiocyanates is enhanced

The positive temperature coefficient of B (dB/dT), suggests that these salts act as structure breakers in water. These conclusions from viscous flow for all the thiocyanate salts solution in water are excellent in agreement with our earlier findings from the studies of partial molar volumes [15].

CONCLUSION

In the present study the values of B-coefficients are positive for all thiocyanate in water and these values increase with increase in temperature. This indicates the structure breaking nature of thiocyanates in water.

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