

Solvation Behaviour of Sodium Thiocyanate in 2-Propanol + Water Mixtures at 298.15, 303.15, 308.15 and 313.15 K

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ABSTRACT

Electrical conductivity of sodium thiocyanate has been measured in 2-propanol + water mixtures at four different temperatures. The data obtained was analysed using Kraus-Bray model of electrical conductivity to obtain limiting molar conductance and dissociation constant. Walden product, Stoke's radius and Stokes corrected radius were also computed. The limiting molar conductance and Walden product values were found to decrease with increase in x_{2pr} (mole fraction of 2-propanol). Weak structure breaking behavior is found for sodium thiocyanate in the solvent media explored. The results obtained from the study were used to explain ion-ion and ion-solvent interactions.

Keywords: Limiting molar conductance, Walden product, 2-Propanol, Sodium Thiocyanate, Ion Solvation

1. INTRODUCTION

Conductivity studies on various electrolytic solutions have gained much attention in the recent years [1-7] due to the valuable information it provides, and also due to its simplicity and accuracy [8]. The present work on sodium thiocyanate, a vital precursor for the synthesis of pharmaceuticals, insecticides and other specialty chemicals [9], is a continuation to our systematic investigations on different electrolytes in 2-propanol + water mixtures. Since the second half of the last century, various properties of sodium thiocyanate in aqueous, organic and aquo-organic solvent media became a subject of intense scrutiny [10-13]. Sodium thiocyanate is an effective hydrotrope as evident from the maximum enhancement factor and relatively high Setschenow constant values reported by Nagendra Gandhi et al [14]. M. N. Roy et al [15] measured the electrical conductance of sodium thiocyanate in water + tetrahydrofuran mixtures at 298.15 K, and analysed the data using Fuoss conductance equation and reported slight ionic association for the electrolyte in the solvent mixtures. Nikos et al [16,17] used Raman spectroscopy to explore the ion-solvent and solvent-solvent interactions in water + N, N-Dimethylformamide mixtures, and reported the

presence of ion pairs and stronger sodium ion solvation by the aprotic solvent molecules in the co-solvent rich region [18].

Exploring the solvation behavior of sodium thiocyanate will be appealing as its molecular size and properties differ slightly with that of potassium thiocyanate and ammonium thiocyanate. The cationic radius of sodium ion as reported by Goldschmidt is 0.98 Å [19] and it is a structure maker since cations having radius is lower than 1.06 Å are considered as structure makers. Nevertheless, Marcus [6] treated Na⁺ as a case of borderline behavior as far as structure making/breaking property is concerned. The aforementioned fact should be mulled over with the information that SCN⁻ is a strong structure breaker [6] in aqueous medium. Though sodium thiocyanate is having versatile applications, its solvation behavior in 2-propanol + water mixtures is not explored to date.

2. METHODOLOGY

Sodium thiocyanate (Merck, AR Grade) was dried at 100-120°C, triply distilled water (specific conductance 1×10⁻⁶ mho cm⁻¹) and 2-propanol purified by standard procedure [20] were used for preparing 1M sodium thiocyanate stock solutions in different 2-propanol + water mixtures. These solutions were further diluted to obtain solutions of desired concentrations. Conductance measurements were made using a digital microprocessor based conductivity meter (Model-308, Systronics India Limited). All the measurements were made in a thermostat maintained at the desired temperature with an accuracy of ±0.1°C

3. RESULTS AND DISCUSSION

3.1 Limiting molar conductance (Λ_m°):

The specific conductance (k) values of electrolyte solutions (0.01-0.1M) were directly read from the instrument. Solvent corrected [21] specific conductance was used for determining molar conductance (Λ_m) of electrolyte solutions at an assortment of compositions of 2-propanol + water mixtures at different temperatures. Molar conductance was calculated on the basis of the following relation

$$\Lambda_m = \frac{1000k}{M} \quad (1)$$

where M is the molarity of the solution. The computed molar conductance values of NaSCN in different compositions of 2-propanol + water were analysed by Kraus-Bray [22] model of conductivity (Equation 2) to evaluate molar conductance at infinite dilution Λ_m° and dissociation constant K_c .

$$\frac{1}{\Lambda_m} = \frac{1}{\Lambda_m^\circ} + \frac{\Lambda_m C}{\Lambda_m^\circ K_c} \quad (2)$$

Kraus-Bray plots were drawn for sodium thiocyanate in different 2-propanol + water mixtures by taking $\Lambda_m C$ along the X-axis and $1/\Lambda_m$ along the Y-axis, and the plots were found to be linear (Fig. 1). The linearity of the plot is an indication for the presence of ion pairs of the electrolyte in equilibrium with the ions [5].

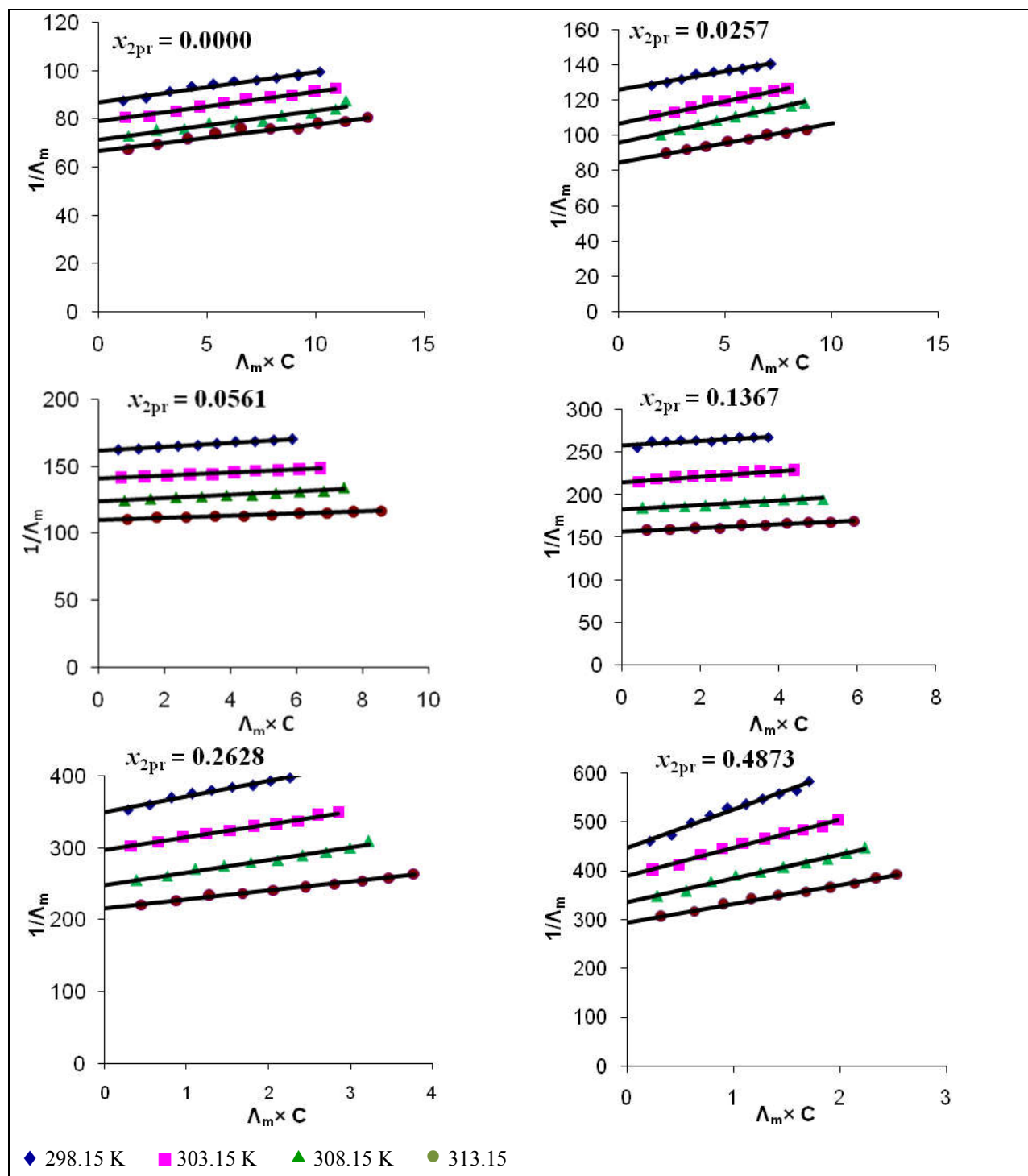


Fig. 1: Plot of $1/\Lambda_m$ (ohm $\text{cm}^2 \text{mol}$) Vs $\Lambda_m C$ (mho cm^{-1}) for NaSCN in 2-propanol + water mixtures at different temperatures

From the intercept and slope of the linear plots, the limiting molar conductance and dissociation constant were obtained and are shown in TABLE 1 and 2 respectively. Limiting molar conductance values for NaSCN in 2-

propanol + water mixtures are not available in the literature for comparison. However, Λ_m° value of sodium thiocyanate in water is in agreement with literature value [23]. The limiting molar conductance (Λ_m°) increased with increase in temperature for all the compositions studied due to increase in thermal energy, and in turn the ionic mobility. Analogous observation was found for potassium thiocyanate [24]. The decrease in Λ_m° with increasing x_{2pr} is a consequence of various factors such as decrease in dielectric constant, increased viscosity of solvent mixture, destruction of tetrahedral-like structure of water [25], increased solvated ion size and hydrophobic interactions due to isopropyl groups. It is also known that the mixed-solvent basicity increases with gradual addition of alcohol to water, and the solvation of the cation (Na^+) becomes more intensive accordingly [26] causing a decrease in conductivity. Solvent-solvent interactions increase as the concentration of 2-propanol increases and thereby decreasing the mobility of the ions which in turn diminish the conductance [27]. Conductance data was not taken beyond 0.4873 mole fraction of 2-propanol due to poor solubility of NaSCN. The conductance of sodium thiocyanate solutions are noticeably less when compared with that of potassium thiocyanate solutions. Therefore more intense solvation is expected in the case of sodium thiocyanate. This is in tune with the thermodynamic quantities of ion solvation for Na^+ , and K^+ reported by Marcus [6]. The incremental increase in limiting conductance of sodium thiocyanate and potassium thiocyanate with the increase in temperature is almost the same.

Table 1: Experimental molar conductance at infinite dilution (Λ_m° : mho $\text{cm}^2 \text{mol}^{-1}$) for sodium thiocyanate in 2-propanol + water mixtures at different temperatures obtained from Kraus-Bray model

T (K)	x_{2pr}					
	0.0000	0.0257	0.0561	0.1367	0.2638	0.4873
298.15	115	79	62	39	29	22
303.15	127	93	71	46	34	26
308.15	140	104	81	55	40	30
313.15	150	118	91	64	46	34

3.2 Dissociation Constant (K_c):

Dissociation constants (K_c) were calculated from the linear plots of Kraus-Bray (Fig. 1) at different temperatures and compositions of 2-propanol + water and are provided in TABLE 2. Exothermic nature of dissociation is indicated by the lowering of K_c values with increasing temperature for all compositions examined. As reported in the case of potassium thiocyanate [24], the influence of hydrated 2-propanol aggregates [28] in dissociating sodium thiocyanate is evident from the maxima observed for K_c at $x_{2pr} = 0.1367$. It is also noteworthy that at $x_{2pr} = 0.1367$, relatively larger K_c values are found for sodium thiocyanate when compared with that of potassium thiocyanate. In other compositions also, the K_c values are larger for sodium thiocyanate in comparison with potassium thiocyanate.

This may be an outcome of the relatively advanced solvation of the Na⁺ in the medium when compared with that of K⁺. On increasing x_{2pr} beyond 0.1367, the hydrophobic interactions due to isopropyl groups become stronger especially in the primary solvation shell and it causes disruption of a well formed solvent cage around the ions lowering the stability of the ions. Thus the K_c values decrease after $x_{2pr} = 0.1367$.

Table 2: Experimental values of K_c for sodium thiocyanate acid in 2-propanol + water mixtures at different temperatures

T (K)	x_{2pr}					
	0.0000	0.0257	0.0561	0.1367	0.2638	0.4873
298.15	0.59	0.76	1.72	2.35	0.56	0.26
303.15	0.50	0.45	1.70	1.45	0.50	0.26
308.15	0.42	0.35	1.17	1.29	0.35	0.23
313.15	0.40	0.33	1.52	1.08	0.38	0.23

3.3 Walden Product and Stoke's Radius:

The Walden product was calculated for sodium thiocyanate in various compositions of 2-propanol + water mixtures at four different temperatures

$$\Lambda_m^\circ \eta_\circ = \frac{Ze_\circ F}{6\pi r} \quad (3)$$

where e_\circ is the electronic charge, F is Faraday constant, Z is the charge on the ion and ' r ' is the effective Stoke's molecular radius; and is shown in Table 4.3. The Walden product values are found to be smaller in magnitude when compared with that of potassium thiocyanate solutions. This can be ascribed to the relatively lower conductance of sodium ions in solution. The plot of Walden product versus temperature is given in Fig. 2. The linear plot is found to have negative slope indicating structure breaking behavior of NaSCN in aqueous as well as in solvent mixture media. However, the structure making character of Na⁺ is evident from the extremely small magnitude of the slope in comparison with that of potassium thiocyanate solutions [24]. On increasing the temperature, the solvent shell around the ions expands due to the activation of solvent molecules and hence the Walden product decreases [29]. Walden product maxima is detected at $x_{2pr}=0.0561$, thereafter it decreases monotonically with increasing mole fraction of 2-propanol. Similar reports of Walden product maxima for electrolytes in alcohol + water mixtures in the water rich region are available in the literature [30-33]. The presence of maxima is an indication of varying degree of solvation of the cations with increasing amount of 2-propanol in the mixture [34]. The increase in Walden product up to the maxima may be due to the more feasible ionization of the added solute, where the solute-solvent interaction appear to be weak [35] in comparison with the strong solvent-solvent interaction prevailing in water rich region of the solvent mixture. The fall in Walden product values after the maxima can be explained on the basis of

increased solute-solvent interaction and ion-solvent relaxation effect [36]. The Walden product maxima for sodium thiocyanate is significantly lower than that of potassium thiocyanate since the structure breaking characteristics of sodium thiocyanate is relatively poor [37]. According to Walden rule the product of limiting conductance and viscosity should remain constant for a given electrolyte in different solvents. But as in the case of potassium thiocyanate, here also a deviation from the Walden rule is noticed which may be ascribed to the change of ion solvation and of the solvent structure [38].

Table 3: Estimated values of Walden Product ($\Lambda_m^\circ \eta_0$: S cm² mol⁻¹ Poise) for NaSCN in 2-propanol + water mixtures at different temperatures

T (K)	x_{2pr}					
	0.0000	0.0257	0.0561	0.1367	0.2628	0.4873
298.15	1.03	1.00	1.09	0.82	0.70	0.51
303.15	1.02	1.03	1.06	0.81	0.68	0.50
308.15	1.02	1.00	1.02	0.81	0.68	0.49
313.15	0.98	1.02	1.01	0.81	0.67	0.46

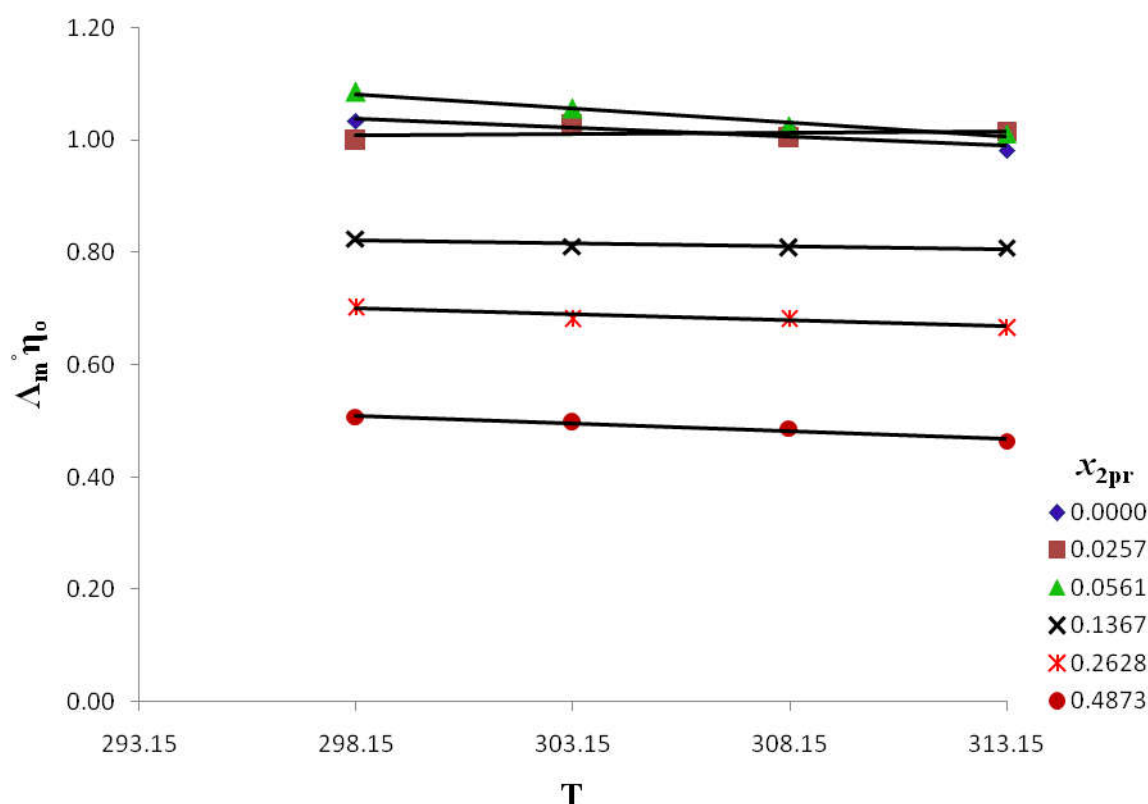


Fig. 2: Plot of Walden Product (S cm² mol⁻¹ Poise) Vs Temperature (K) for NaSCN in 2-propanol + water mixtures

Stoke's molecular radius calculated from conventional primitive model and Stoke's corrected molecular radius are given in Table 4 and they follow the expected trend. As expected from the Walden product values, relatively larger Stoke's radius is observed for sodium thiocyanate indicating stronger solvation [39]. Emulating the trend observed for potassium thiocyanate, in the present case also the Stoke's radius minima is detected at $x_{2pr}=0.0561$ in accordance with the trend observed in the computed Walden product values. Stokes radius is found to increase as the temperature increases because of the thermal expansion of the solvation shell. Increase in thermal energy is also expected to reduce the solvent-solvent interactions which obliquely improves the solute-solvent interactions.

Table 4: (A) Stoke's molecular radius (r_s Å) and (B) Corrected Stoke's molecular radius (r_i Å) for NaSCN in 2-propanol + water mixtures at different temperatures

A							
T (K)	0.0000	0.0257	0.0561	x_{2pr}	0.1367	0.2628	0.4873
298.15	0.793	0.821	0.755		0.994	1.166	1.616
303.15	0.802	0.797	0.777		1.012	1.201	1.647
308.15	0.804	0.817	0.801		1.016	1.201	1.685
313.15	0.835	0.807	0.810		1.014	1.229	1.768

B							
T (K)	0.0000	0.0257	0.0561	x_{2pr}	0.1367	0.2628	0.4873
298.15	2.73	2.69	2.57		2.68	2.70	3.01
303.15	2.72	2.66	2.58		2.68	2.73	3.03
308.15	2.71	2.67	2.59		2.67	2.72	3.06
313.15	2.72	2.64	2.58		2.65	2.74	3.13

4. CONCLUSIONS

Limiting molar conductance values for sodium thiocyanate in 2-propanol + water mixtures has been determined at four different temperatures and the trends in its variation with respect to changes in temperature and composition of the solvent mixture has been appropriately explained with adequate reference to the solvent structure and momentous comparison with previously published works on potassium thiocyanate in the same solvent mixture under identical conditions.

The sharp decline in conductance with respect to increase in 2-propanol content in the solvent mixture is explained on the basis of different factors influencing ionic conductance. The endothermic nature of the system is evident from the K_a values for different systems at different temperatures. The structure breaking character is established from the variation of Walden product with temperature.

5. ACKNOWLEDGEMENTS

The financial support for this investigation given by Visvesvaraya Technological University, Belgaum, India under the grant Ref. No. VTU/Aca/2010-11/A-9/11329 dated 17th December 2010 is gratefully acknowledged.

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