Conductometric Studies of Potassium Thiocyanate in 2-Propanol + Water Mixtures

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Conductometric behaviour of the solutions of potassium thiocyanate in water and 2-propanol + water solvent mixtures have been investigated at varying conditions. Conductivity data were analyzed by Debye-Huckel-Onsager, Kraus-Bray and Shedlovsky models and used to evaluate limiting molar conductance, association constant, dissociation constant and Walden product for different compositions. The limiting molar conductance $\lambda_m°$ sharply decreased with the increase in 2-propanol. Walden product ($\lambda_m°\eta$) is found maximum at x_{2pr} (mole fraction of 2-propanol) = 0.0257 for 2-propanol + water solvent mixtures. Born relations were used to compute thermodynamics of solvation. Conductometric investigations revealed the structure breaking property of K^+ ion. The results obtained from the study were used to interpret ion-ion and ion-solvent interactions.

Key Words: Ion solvation, Molar conductance, Walden product, 2-Propanol, Potassium thiocyanate.

INTRODUCTION

Investigations on transport property of an electrolyte and the effect of ion solvation on it in various aqueous, partial aqueous and nonaqueous media have received much attention in recent years, since it gives valuable information regarding ion-ion and ion-solvent interactions[1-5]. Potassium thiocyanate is used in electroplating, dyeing industries, as an analytical reagent namely cryogen, pharmaceutical and agrochemical industries[6-8]. 2-Propanol is used in the manufacture of acetone, glycerol, isopropyl acetate, shellacs, quick drying inks and creosote. It is a solvent for essential and other oils, alkaloids, gums, resins, coatings and cellulose and a deicing agent for liquid fuels, lacquers and extraction processes. Potassium thiocyanate has been used for conductance studies in pure solvents and in mixed solvents[9]. Conductometric and ultrasonic investigations on potassium thiocyanate in methanol + water and ethanol + water mixtures in the temperature range T = (288.15-313.15) K detected ultrasonic velocity maxima at 0.12 mol fraction of methanol and 0.086 mol fraction of ethanol and this phenomenon was explained on the basis of complex formation[10]. Large-angle X-ray scattering investigation of the structure of 2-propanol + water mixtures suggested that both 2-propanol and water aggregates co exist in the solvent mixture when the mole fraction range of 2-propanol is 0.1-0.7[11]. It has been shown

that microphase structures occur in mixtures of water and alcohol and "clathrate-like" structures is believed to be the cause of unusual properties in the case of alcohols with 3- or 4-carbon atoms[12]. The above findings prompted us to probe ion-ion, ion-solvent and solvent-solvent interactions in 2-propanol + water mixtures containing potassium thiocyanate as solute.

EXPERIMENTAL

Potassium thiocyanate (Merck, AR Grade) was dried at 100-120 °C for 3 h and stored in a vacuum desiccator. Triply distilled water (specific conductance 1×10^{-6} mho cm^{-1}) and purified 2-propanol were used[13]. Potassium thiocyanate solution (1 mol L^{-1}) was prepared in water and known mole fractions of 2-propanol + water mixtures and diluted further to obtain the solutions of desired concentrations.

Conductance measurements were made with a digital direct reading conductivity meter (model CM 180, Elico make) and a calibrated dip type conductivity cell. All the measurements were made in a thermostat maintained at the desired temperature with an accuracy of ± 0.01 °C. The instrument was standardized with usual procedure. The uncertainty in conductance measurements is ± 0.02 %. Densities of all the solutions were determined by using a pyknometer of 10 cc capacity. The uncertainty in density was estimated to be $\pm 1 \times 10^{-4}$ g cm^{-3}.

RESULTS AND DISCUSSION

Limiting molar conductance: Molar conductance of potassium thiocyanate solution in water and various compositions of 2-propanol + water solvent mixtures were calculated from specific conductance obtained from a direct reading digital conductivity meter at (298.15, 303.15, 308.15 and 313.15) K. The data generated were analyzed by Debye Huckel Onsager (eqn. 1), Kraus-Bray model (eqn. 2) and Shedlovsky model (eqn. 3).

$$\Lambda_m = \Lambda^\circ_{m-} (A + B\Lambda^\circ_m) \sqrt{C} \tag{1}$$

$$1/\Lambda_m = 1/\Lambda^\circ_m + \Lambda_m C/K_c (\Lambda^\circ_m)^2 \tag{2}$$

$$1/S\Lambda_m = 1/\Lambda^\circ_m + (C\Lambda_m Sf_\pm^2 K_a)/(\Lambda^\circ_m)^2 \tag{3}$$

where Λ_m and Λ°_m are equivalent conductance's at a given concentration C and at infinite dilution, respectively. A and B are constants dependent only on the nature of the solvent and the temperature. K_a and K_c are the association constant and dissociation constant, respectively. It was found that the theoretical Onsager slope and experimentally calculated Onsager slope are not well comparable indicating that the systems do not fully comply with Onsager model. Linearity of Kraus-Bray plot point to the formation of ion pair of the electrolyte[14]. The plot of $1/S\Lambda_m$ *versus* $C\Lambda_m Sf_\pm^2$ is given in Fig. 1. Λ°_m values obtained from the three models are presented in Table-1. The limiting molar conductance Λ°_m increases with increase in temperature due to increased thermal energy and breaking of weak bonds. Limiting molar conductance decreased as x_{2pr} is increased up to 0.4873. The decrease in dielectric constant, increased viscosity of solvent mixture, destruction of tetrahedral-

like structure of water, increased solvated ion size and hydrophobic interactions due to methyl groups must be responsible for the above observation. The magnitude of solvent-solvent interactions has greater significance as x_{2pr} is increased. 2-Propanol + water mixture has maximum viscosity at $x_{2pr} = 0.2628$ as shown in Table-2.
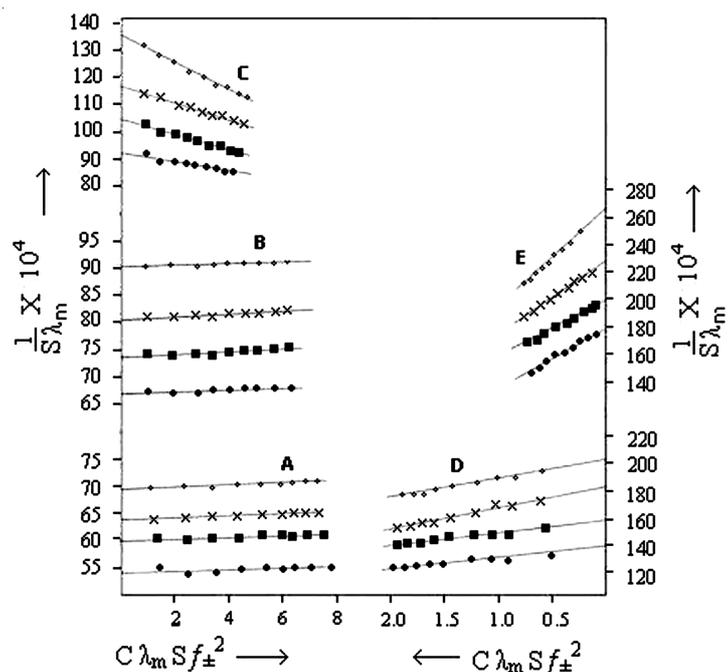
Fig. 1. Plot of $1/S\Lambda_m$ (ohm cm^{-2} mol) *versus* $C\Lambda_mSf_{\pm}^2$ for KSCN in A: $x_{2pr} = 0.0000$, B: $x_{2pr} = 0.0257$, C: $x_{2pr} = 0.0561$, D: $x_{2pr} = 0.1367$, E: $x_{2pr} = 0.2628$, • 298 K; ■ 303 K; × 308 K; ◇ 313 K

TABLE-1
EXPERIMENTAL MOLAR CONDUCTANCE AT INFINITE DILUTION Λ°_m (S cm^2 mol^{-1}) FOR KSCN FROM DIFFERENT MODELS IN VARIOUS COMPOSITIONS (v/v) OF 2-PROPANOL + WATER MIXTURES AT DIFFERENT TEMPERATURES

T (K)	x_{2pr}																
	0.0000			0.0257			0.0561			0.1367			0.2628			0.4873	
	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2
298	140	137	143	108	108	110	72	71	74	48	45	49	37	35	37	24	23
303	152	148	155	122	122	124	84	83	86	53	51	54	42	40	43	27	26
308	161	157	165	133	130	135	95	92	96	60	59	62	48	46	49	32	30
313	176	174	183	145	143	148	106	103	107	67	67	70	54	52	55	37	35

1: DHO model 2: Kraus-Bray model 3: Shedlovsky model.

Walden product ($\Lambda^{\circ}_m \eta_0$): Walden product was computed for different compositions at four different temperatures for KSCN in 2-propanol + water mixture.

Walden product decreased with increase in temperature (Table-3). Walden product is found to be maximum at $x_{2pr} = 0.0257$ and this may be explained on the basis of hydrophobic hydration of cation due to the presence of co-solvent in water rich region. Deviation of Walden product from unity at $x_{2pr} = 0.4873$ can be attributed to selective solvation of ions by the solvent. The temperature coefficient of Walden product is negative in the case of solvent mixtures, hinting the structure breaking property of K^+ of KSCN. This negative temperature coefficient may be due to the thermal expansion of solvated ions. In these cases the decrease in conductivity is not compensated by increase in viscosity as expected. Selective solvation of the ions depends upon the viscosity of the medium, the exchange of ions with neighbouring solvent molecules and movement of ions through the holes in the hydrogen bonded solvent mixtures.

TABLE-2
EXPERIMENTAL VALUES OF VISCOSITY (MILLIPOISE)
OF VARIOUS COMPOSITIONS (v/v) OF 2-PROPANOL+WATER
MIXTURES AT DIFFERENT TEMPERATURES

Temperature (K)	x_{2pr}					
	0.0000	0.0257	0.0561	0.1367	0.2628	0.4873
298	8.937	12.387	17.232	21.144	23.966	21.753
303	8.007	10.874	14.590	17.371	19.886	18.436
308	7.200	9.493	12.390	14.499	16.520	15.533
313	6.500	8.488	10.919	12.381	13.994	13.130

TABLE-3
ESTIMATED WALDEN PRODUCT (S mol^{-1} poise) OF KSCN IN 2-PROPANOL +
WATER MIXTURES AS A FUNCTION OF TEMPERATURE

Temperature (K)	x_{2pr}					
	0.0000	0.0257	0.0561	0.1367	0.2628	0.4873
298	1.25	1.34	1.24	1.01	0.86	0.53
303	1.22	1.33	1.23	0.93	0.84	0.51
308	1.16	1.27	1.18	0.88	0.80	0.50
313	1.15	1.23	1.16	0.83	0.76	0.49

Dissociation/association constant: The dissociation constant (K_c) and association constant (K_a) were determined, respectively from the slopes of Kraus-Bray and Shedlovsky plots and are presented in Table-4. Maxima for dissociation constants is found at $x_{2pr} = 0.1367$. It is known that hydrated 2-propanol aggregates are formed when mole fraction of 2-propanol exceeds 0.1315. Hence it may be concluded that hydrated 2-propanol aggregates can play a pivotal role in dissociation of potassium thiocyanate in 2-propanol + water mixtures. On increasing the x_{2pr} beyond 0.1367 hydrophobic interactions among the methyl groups causes disruption of a well formed solvent cage around the ions leading to decrease in K_c values. The steady decrease in K_c values with respect to increase in temperature about $x_{2pr} = 0.0561$ indicates destabilization of solvent cage due to thermal energy.

TABLE-4
EXPERIMENTAL VALUES OF K_c AND K_a FOR KSCN IN
VARIOUS MOLE FRACTIONS OF 2-PROPANOL + WATER
MIXTURES AT DIFFERENT TEMPERATURES

T (K)	x_{2pr}											
	0.0000		0.0257		0.0561		0.1367		0.2628		0.4873	
	K_c	K_a	K_c	K_a	K_c	K_a	K_c	K_a	K_c	K_a	K_c	K_a
298	0.39	3.6	0.37	5.7	0.93	-0.4	1.94	-0.3	0.38	-0.1	0.33	–
303	0.46	4.3	0.35	4.8	0.72	-0.5	1.80	-0.2	0.38	-0.1	0.28	–
308	0.48	5.3	0.43	2.1	0.80	-0.4	1.24	-0.3	0.33	-0.1	0.24	–
313	0.44	6.6	0.39	2.0	0.71	-0.5	0.95	-0.2	0.34	-0.1	0.20	–

Association is found to decrease with increase in percentage of 2-propanol although there is a decrease in dielectric constant. The above trend may be a consequence of increased ion-solvent interaction[16]. Association constant is lowest at x_{2pr} = 0.1367 for solutions complimenting the observed trend in K_c values. Shedlovsky plot loses linearity as x_{2pr} reached 0.4873. Hence K_a is not reported for this composition.

Thermodynamics of solvation: Solvation is a process where an ion is getting enveloped by the solvent molecules forming a sheath over it. Thermodynamic parameters of solvation such as change in enthalpy (ΔH_{s-s}), change in free energy (ΔG_{s-s}) and change in entropy (ΔS_{s-s}) have been computed using Born relation[17].

$$\Delta G_{s-s} = -(N_a(Z_ie_0)^2/2r_i)\ (1-1/\epsilon) \tag{4}$$

$$r_i = zF^2/6\Pi N_A\Lambda°_m\eta_0 + 0.0103 + r_y \tag{5}$$

$$\Delta S_{s-s} = -(N_a(Z_ie_0)^2/2r_i)(1/\epsilon^2)(\delta e/\delta T) \tag{6}$$

$$\Delta H_{s-s} = \Delta G_{s-s} + T\Delta S_{s-s} \tag{7}$$

All the terms in the above equations have usual meaning and the computed parameters are shown in Table-5. The system is found to obey Born model since the plot of ΔG_{s-s} *versus* $1/r_i$ is linear (Fig. 2). Larger negative ΔG_{s-s} values indicate that the species are stable in the solution. ΔH_{s-s} is found to be negative in all the cases indicating the exothermic nature of solvation.
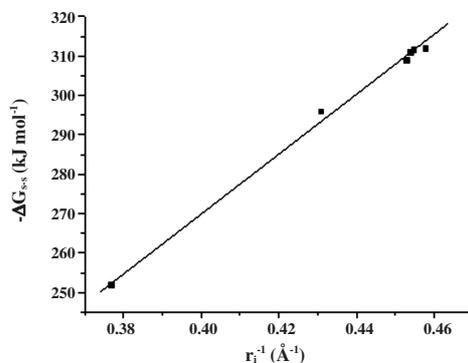
Fig. 2. Plot of $-\Delta G_{s-s}$ (kJ mol⁻¹) *versus* $1/r_i$ (Å⁻¹) for KSCN in water + 2-propanol at 298 K

TABLE-5
COMPUTED THERMODYNAMIC PARAMETERS OF SOLVATION FOR
KSCN IN DIFFERENT COMPOSITIONS OF 2-PROPANOL + WATER
MIXTURES AT DIFFERENT TEMPERATURES

	Thermodynamic parameters	x_{2pr}					
		0.0000	0.0257	0.0561	0.1367	0.2628	0.4873
298 K	$-\Delta G_{s-s}$ in J mol^{-1}	295.73	310.67	311.48	308.76	310.30	251.76
	ΔS_{s-s} in J deg^{-1} mol^{-1}	0.018	0.026	0.031	0.029	0.040	0.071
	$-\Delta H_{s-s}$ in J mol^{-1}	290.37	302.92	302.31	300.18	298.38	230.66
303 K	$-\Delta G_{s-s}$ in J mol^{-1}	295.42	311.36	312.04	300.40	305.22	242.44
	ΔS_{s-s} in J deg^{-1} mol^{-1}	0.019	0.027	0.032	0.030	0.042	0.075
	$-\Delta H_{s-s}$ in J mol^{-1}	289.71	303.23	302.36	291.16	292.64	219.64
308 K	$-\Delta G_{s-s}$ in J mol^{-1}	293.06	307.35	310.85	292.81	399.21	242.35
	ΔS_{s-s} in J deg^{-1} mol^{-1}	0.019	0.027	0.033	0.031	0.043	0.077
	$-\Delta H_{s-s}$ in J mol^{-1}	287.07	298.95	300.68	283.29	285.99	218.68
313 K	$-\Delta G_{s-s}$ in J mol^{-1}	294.97	308.13	311.55	289.71	293.50	237.68
	ΔS_{s-s} in J deg^{-1} mol^{-1}	0.021	0.029	0.035	0.032	0.044	0.086
	$-\Delta H_{s-s}$ in J mol^{-1}	288.50	299.06	300.59	279.59	279.65	210.77

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