Conductance Study on Solvation Behaviour of Tetrabutyl Ammonium Bromide in 2- Ethoxy Ethanol+Water Mixtures AT 288.15K - 318.15K

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ABSTRACT

Precise conductance for Tetra butyl ammonium bromide in 2- ethoxy ethanol + water mixtures containing 0 to 1 mole fractions of 2-ethoxyethanol (X_{EE}) have been measured at 288.15K to 318.15K.The densities, viscosities and dielectric constants of the solvent mixtures at desired temperatures were reported. The electrical Conductivity data were analyzed by three major conductivity models such as Debye-Huckel – Onsagar, Kraus-Bray and Shedlovsky. Limiting molar conductance, Stokes radius, Walden product and dissociation constant were evaluated for all solvent compositions. Limiting molar conductance ($\Lambda°_m$) decreases with increase in concentration of 2- ethoxy ethanol. Walden product ($\Lambda°_m \eta_0$) is found to be maximum at X_{EE} = 0.0136 for 2- ethoxy ethanol + water mixtures. Thermodynamic relations related to solvation were computed by using Born equations. The results obtained from the conductometric investigations were used to interpret ion-ion and ion-solvent interactions.

KEY WORDS: Limiting molar conductance, Dielectric constant, Stokes radius, 2-ethoxy ethanol.

1. INTRODUCTION

Knowledge of the behaviour of electrolytes in solution, ion association and solvent – solvent interactions are essential for proper understanding ion- solvation (Evans, 1971; Aijaz Ahmed Ansari, 1988; Ishwara Bhat, 2003; Victor, 2000; Ranjit De, 2006; Franks, 1966; Ahamed Ansari, 1988; Kay, 1976). The extensive studies of the reactions taking place in solution are the important ways for understanding the different phenomena associated with solution chemistry (Murthy, 1993; Kraus, 1930). In this paper an attempt has been made to reveal the nature of various types of interactions prevailing in the solution of Tetra butyl ammonium bromide (TBAB) in 2- ethoxy ethanol + water mixture by conductomeric investigation at 288.15K to 318.15K. Tetra butyl ammonium bromide is water soluble, stable and finds the applications (Shadpour Mallkpour, 2008) as a phase transfer agent, antiseptic agent, emulsifying agent and as a pigment dispersers.

2. EXPERIMENTAL

Purified solvent 2- ethoxy ethanol (Merck, AR grade) and triply distilled water (sp. conductance, $2.3X10^{-6}$ ohm-' cm^{-1}) were used for preparing solution. Mixed solvents of desired mole fractions of 2- ethoxy ethanol were prepared. Tetra butyl ammonium bromide (Merck, AR grade) was dried at 70^0C to 80^0C for two days and stored in a desiccator. TBAB is dissolved in solvent mixture to obtain desired concentrations ranging from 0.001N to 0.01N. Conductance measurements were carried out using digital conductivity meter (Model CM-180, Elico Private Ltd. Hyderabad) with a dip type cell (cell constant $0.999cm^{-1}$). A digital thermostat (Kumar Make, Bombay) was used to maintain the required temperatures with an accuracy of $\pm 0.01^0$C. A pyknometer (10 cc capacity, accuracy of±0.002%) was used to determine density of all solutions. The uncertainty in density is estimated to be ± $1x10^{-4}$ g/cm^3. A dielectric constant meter (BI-870, Brookhaven, USA) was used to measure dielectric constant of 2- ethoxy ethanol + water mixtures at different temperatures. From the above experimental data interactions of solute in solvent mixture have been studied with increasing temperatures.

3. RESULTS AND DISCUSSIONS

Limiting molar conductance (Λ^0_m): The specific conductance of the TBAB solutions were measured at 288.15, 298.15, 308.15 and 318.15K using digital conductivity meter and the value used to calculate molar conductance (Λ_m).The data have been analyzed conveniently by Kraus Bray (Eq.1), Debye Huckel (Eq.2) and Shedlvosky models (Eq.3),which enables one to evaluate the molar conductance at infinite dilution (Λ^0_m), and dissociation constant (K_c).

$$1/ \lambda_m = 1/ \lambda^0_m + \lambda_m C/ \lambda^0_m{}^2 K_c \quad (1)$$

$$\lambda_m = \lambda^0_m - [82.4/ (\varepsilon T)^{1/2}\eta + 8.2 X 10^5/ (\varepsilon T)^{1/2}. \lambda^0_m] \sqrt{c} \quad (2)$$

$$1/S \lambda_m = {}_1/ \lambda^0_m + C \lambda_m Sf_{\pm}^2 K_a / \lambda^0_m{}^2 \quad (3)$$

Where λ_m and λ^0_m are molar conductance at a given concentration and at infinite dilutions respectively. ε and η are dielectric constant and viscosity of the medium and T is the temperature in absolute scale . K_c is the dissociation constant obtained from the intercept and slope of the linear plot of Λ_mC Vs 1/ Λ_m.The linearity of the Kraus Bray gives the information about ion pair of the electrolyte (Ishwara Bhat, 2003). Λ^0_m and K_a values are obtained from the intercept and slope of the linear plot of 1/S λ_m Vs C λ_m $Sf_{\pm}^2$ (Fig.2) and presented in the table.1. Shows that for TBAB in all the compositions of 2- ethoxyethanol + water molar conductance (λ^0_m) increase as the temperature increases. Increase in the temperature enhances the mobility of ions. But there is sharp decline in λ^0_m values of TBAB with the increase in concentration of co-solvent in the solvent mixture. Similar behaviour was reported in literature (Ranjith, 2007). This variation is may be due to decrease in the dielectric constant and increase in viscosity values as shown in the table.2 and table.3. The measured λ^0_m of TBAB in water at 25^0C is well agreed with literature value. When 2-ethoxy ethanol is added to water viscosity of the solvent mixture increases. Added organic solvent causes the destruction of tetrahedral structure of water molecule leading to solvent-solvent interaction resulting in gradual decrease in λ^0_m. At the same time ion-solvent interaction also increases causing continuous decrease in conductivity of TBAB till X_{2EE}=1.0000 for 2- ethoxy ethanol (Shivakumar, 2010).

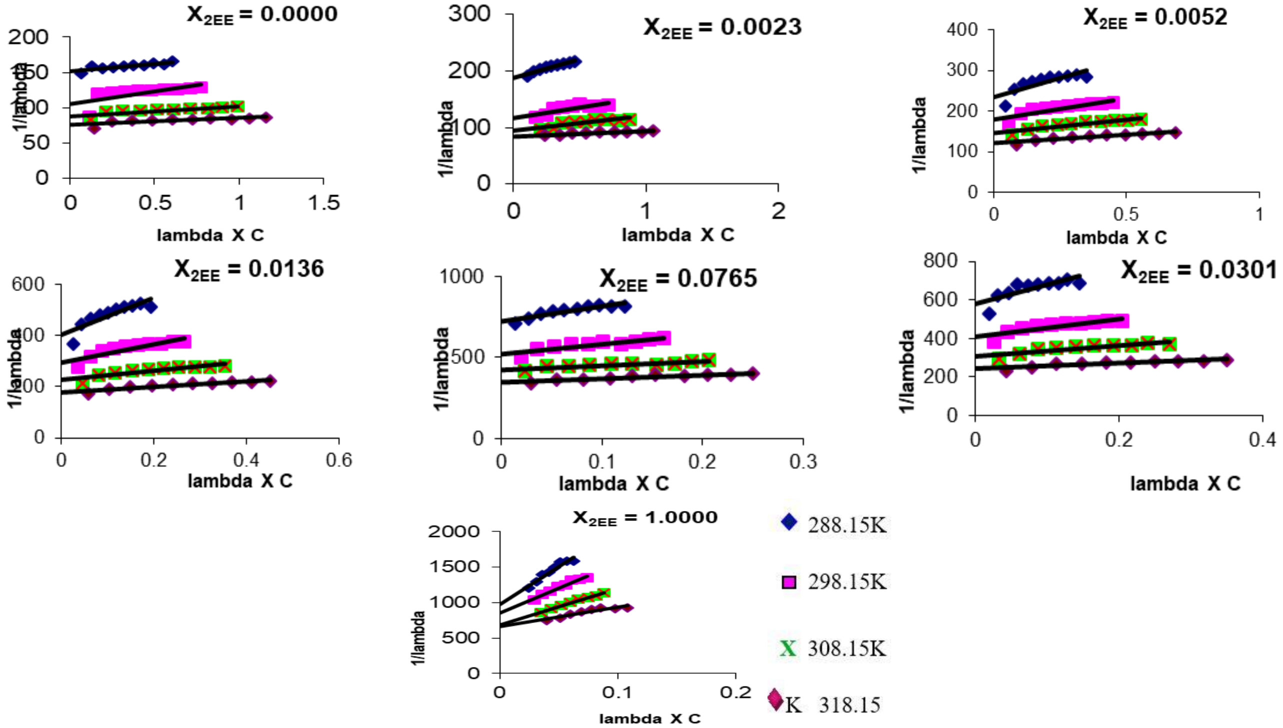

Figure.1. Plot of $1/\Lambda_m$ (mho cm^{-2} mol) Vs Λ_m C (mho cm^{-1}) for TBAB in 2-ethoxyethanol+water mixtures at different temperatures

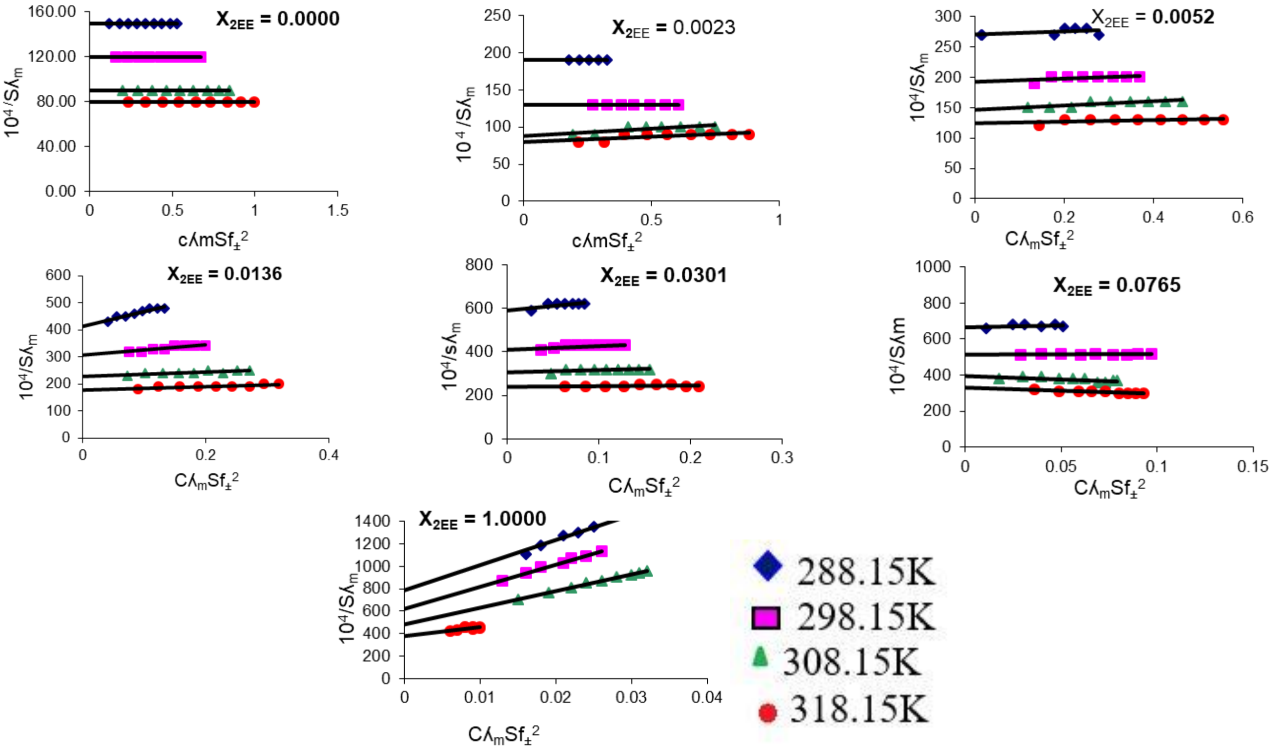

Figure.2. Plot of $10^4/S\Lambda_m$ (mho cm^{-2} mol $^{-1}$) Vs $C\Lambda_m Sf_{\pm}^2$ for TBAB in 2-ethoxyethanol+water mixtures at different temperatures

Table.1. Experimental molar conductance at infinite dilution (Λ°_m/mho.cm^2.mol^{-1}) for *TBAB* from different models in various compositions of 2-ethoxy ethanol + water mixtures at different temperatures

T/ K	X2EE: 0.0000			0.0023			0.0052			0.0136			0.0301			0.0765			1.0000		
	1	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**
288.15	66	66	67	55	56	55	42	43	43	24	25	26	17	17	18	14	14	15	09	11	12
298.15	96	96	97	90	91	94	55	56	57	33	34	36	24	24	26	19	19	20	10	12	14
308.15	113	113	116	112	113	117	67	68	71	44	44	46	32	32	35	23	24	25	13	14	13
318.15	132	133	135	129	129	133	82	83	86	56	56	59	41	41	44	29	29	31	16	18	20

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

Table.2. Experimental values of viscosity (*η*/poise) of various mole fractions of 2 Ethoxy ethanol + water mixtures at different temperatures

T/ K	X2EE						
	0.0000	0.0023	0.0052	0.0136	0.0301	0.0765	1.0000
288.15	0.01114	0.01343	0.02179	0.03676	0.04690	0.04343	0.02194
298.15	0.00890	0.01191	0.01599	0.02574	0.03349	0.03158	0.01736
308.15	0.00719	0.00947	0.01220	0.01808	0.02405	0.02370	0.01430
318.15	0.00546	0.00680	0.00847	0.01250	0.01670	0.01590	0.01045

Table.3. Experimental values of dielectric constant (ε) of various mole fractions of 2 Ethoxy ethanol + water mixtures at different temperatures.

T/ K	X2EE						
	0.0000	0.0023	0.0052	0.0136	0.0301	0.0765	1.0000
288.15	81.5	75.5	68.8	56.0	43.3	30.5	17.8
298.15	78.3	72.0	65.7	53.2	40.6	28.1	15.5
308.15	74.5	68.5	62.1	50.6	38.6	26.7	14.7
318.15	71.5	65.7	59.9	44.2	35.7	24.9	13.2

Walden product $\lambda^0_m\eta_0$: Walden product the product of Limiting molar conductance of an electrolyte and viscosity of the solvent. It is given by Walden (1920) as $\Lambda^0_m\ \eta_0$,. Where λ^0_m and η_0 are molar conductance at infinite dilutions and viscosity of the specified solutions respectively. Walden product was calculated for TBAB in 2- ethoxy ethanol + water mixture at different temperatures and the values are shown in the table.4. It is found to increase marginally with addition of organic solvent till X_{2EE}=0.0136 of 2-ethoxyethanol and later it decreases till X_{2EE} =1.0000 at all temperatures. The negative temperature coefficient of Walden product shows the structure breaking property of Bu_4N^+ of TBAB. This may be due to thermal expansion of solvated ions (Shivakumar, 2010).

Corrected Stoke's radius is calculated for all the solutions using the formula,

$$r_i = 0.82Z/\ \Lambda^0_m\ \eta_0 + 0.0103\varepsilon + r_y \qquad (4)$$

Where r_y = 0.85A^0 for dipolar unassociated solvents and 1.13A^0 for protic and other associated solvents and the values are shown on table.5. The initial decrease in radius with 2- ethoxyethanol is a consequence of increased solvent–solvent interaction reducing the magnitude of solvation. However increased radius was observed after X_{2EE}=0.0301 due to relatively large sized 2- ethoxyethanol molecules occupying the primary solvation shell.

Table.4. Estimated Walden product (*$\Lambda^{\circ}_m\ \eta_0$*/S.cm^2.mol^{-1}) of *TBAB* in 2 ethoxy ethanol + water mixtures as a function of temperature.

T/ K	X2EE						
	0.0000	0.0023	0 .0052	0.0136	0.0301	0 .0765	1.0000
288.15	0.74	0.74	0.94	0.95	0.84	0.65	0.26
298.15	0.87	1.05	0.91	0.91	0.80	0.63	0.24
308.15	0.84	1.05	0.83	0.83	0.77	0.59	0.19
318.15	0.74	0.82	0.73	0.74	0.73	0.49	0.17

Table.5. Experimental values of Corrected Stoke's radius (r_iA^0) for TBAB in 2-ethoxy ethanol + water mixtures at different temperatures

T/K	X2EE						
	0.0000	0.0023	0.0052	0.0136	0.0301	0.0765	1.0000
288.15	3.29	3.22	2.89	2.71	2.66	2.78	4.47
298.15	3.01	2.80	2.88	2.72	2.68	2.79	4.70
308.15	3.08	2.80	2.88	2.77	2.69	2.86	5.73
318.15	3.14	2.98	3.03	2.82	2.71	3.12	6.19

Dissociation Constant: Dissociation Constant (K_c) is determined from the slope of the linear plot of Kraus Bray. The values are shown on table.6. Increase in temperature decreases the dissociation process in solvent mixture. The initial increase in K_c may be due to solvent – solvent interaction. Maxima for K_c is found at X_{2EE} = 0.0765, implying the aggregation of hydrated 2- ethoxy ethanol. This plays an important role in dissociation of TBAB in 2- ethoxy ethanol + water mixture. Beyond that K_c value decreases due to hydrophobic interaction of ethyl groups causing disruption of solvent cage around ions.

Table.6. Experimental values of K_c for TBAB in 2-ethoxy ethanol + water mixtures at different temperatures

T/K	X_{2EE}						
	0.0000	0.0023	0.0052	0.0136	0 .0301	0.0765	1.0000
	K_c	K_c	K_c	K_c	K_c	K_c	K_c
288.15	0.057	0.073	0.035	0.030	0.040	0.055	0.016
298.15	0.055	0.035	0.032	0.029	0.034	0.069	0.009
308.15	0.031	0.037	0.031	0.024	0.036	0.045	0.010
318.15	0.021	0.054	0.029	0.022	0.035	0.056	0.009

Thermodynamics of solvation: The activation energy (E_a) of a rate process was calculated using Arrhenius equation (Glasstone, 1987) and the values are shown in the table.7.

$$\lambda^0_m = Ae^{-Ea/RT} \quad (5)$$

Table.7. Experimental E_a and log A values of for TBAB in 2-ethoxy ethanol + water mixtures at different temperatures

	X_{2EE}						
	0.0000	**0.0023**	**0.0052**	**0.0136**	**0.0301**	**0.0765**	**1.0000**
E_a	1.9	2.0	1.9	3.4	2.5	2.0	1.3
logA	2.2	2.2	2.0	1.9	1.8	1.6	1.3

Where, A is the frequency factor and R is the gas constant. From the slope and intercept of the linear plot of log λ^0_m Vs 1/T, the energy of activation E_a and log A were calculated. Increase in E_a values are observed on addition of 2-ethoxyethanol which is the measure of energy required for the movement of species in solvent mixture. The frequency factor Log A is found to decrease with increase in concentration of co- solvent to water.

Thermodynamics of solvation like change in free energy (ΔG_{s-s}), change in enthalpy (ΔH_{s-s}) and change in entropy (ΔS_{s-s}) have been computed using following Born relation (Kortya, 1987), Eq.(6)-(8). Calculated values are shown in the table.8.

$$\Delta G_{s-s} = -(N_a(Z_i e_0)^2/2r_i)(1-1/\varepsilon) \quad (6)$$

$$\Delta S_{s-s} = -(N_a(Z_i e_0)^2/2r_i)(1/\varepsilon^2)(\delta e/\delta T) \quad (7)$$

$$\Delta H_{s-s} = \Delta G_{ss} + T\,\Delta S_{s-s} \quad (8)$$

The stability of the species in solution is measured by magnitude of free energy change of a reaction (Arnett, 1967). Observed negative values of ΔG_{s-s} indicates that the species are more stable in solvent media than vacuum. The plot of ΔG_{s-s} Vs $1/r_i$ (Fig.3) was found to be linear suggesting the validity of born relation (Stearn, 1992). The ΔH_{s-s} is found to be negative in all compositions of 2-ethoxy ethanol, indicating that the reaction is exothermic. Decrease in ΔS_{s-s} is observed due to the decreased electrostriction with the increase in the amount of 2-ethoxy ethanol in solvent mixture.

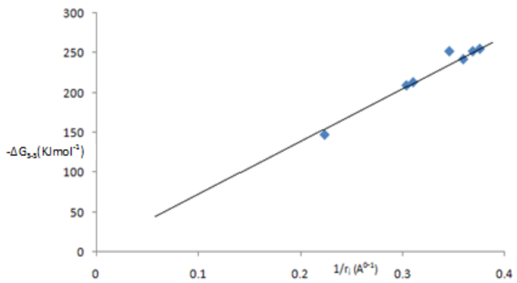

Figure.3. Plot of ΔG_{s-s} (kJ mol^{-1}) Vs $1/r_i$ (A$^{0-1}$) for TBAB in 2-ethoxyethanol+water mixture

Table.9. Computed Thermodynamic Parameters of Solvation for TBAB in different Compositions of 2-Ethoxyethanol + Water mixtures at different temperatures

Thermodynamic parameters		X_{2EE}						
		0.0000	**0.0023**	**0.0052**	**0.0136**	**0.0301**	**0.0765**	**1.0000**
288.15K	$-\Delta G_{s-s}$(J/mol)	208.56	212.87	236.87	251.75	255.11	241.69	146.67
	$-\Delta H_{s-s}$(J/mol)	186.40	186.26	205.29	190.43	187.48	151.62	65.68
	$-\Delta S_{s-s}$(J/deg mol)	0.1093	0.125	0.154	0.311	0.344	0.494	0.716
298.15K	$-\Delta G_{s-s}$(J/mol)	227.83	244.65	237.53	250.58	252.82	240.10	138.26
	$-\Delta H_{s-s}$(J/mol)	202.70	212.31	204.56	196.93	196.57	182.31	113.09
	$-\Delta S_{s-s}$(J/deg mol)	0.130	0.158	0.169	0.344	0.387	0.583	0.898
308.15K	$-\Delta G_{s-s}$(J/mol)	222.52	244.47	237.32	245.82	251.55	233.77	112.98
	$-\Delta H_{s-s}$(J/mol)	191.96	204.26	194.56	155.85	145.08	99.11	28.02
	$-\Delta S_{s-s}$(J/deg mol)	0.140	0.175	0.189	0.373	0.427	0.630	0.819
318.15K	$-\Delta G_{s-s}$(J/mol)	218.13	229.55	225.43	240.75	249.15	213.69	103.72
	$-\Delta H_{s-s}$(J/mol)	218.13	229.55	225.43	240.75	249.15	213.69	103.72
	$-\Delta S_{s-s}$(J/deg mol)	0.150	0.179	0.194	0.481	0.495	0.664	0.940

4. CONCLUSION

The sharp decrease in conductance with respect to increase in 2- ethoxy ethanol in the solvent mixture is explained on different factors influencing ionic conductance .The variation of walden product shows the structure breaking property. The exothermic nature of the system is evident from the negative value of ΔH_{s-s} for different systems at different temperatures.

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