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Ultrasonic and Ionic Study of Aqueous KCL through Walden Plot

Manoj Kumar Praharaj[1], Sarmistha Mishra[2]

[1,2]Department of Physics, ABIT, BPUT, CDA-1, Cuttack, Odisha-753014, India.

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Abstract - Ultrasonic velocity, density, viscosity, and electrical conductivity have been measured for an aqueous solution of KCl at different concentrations and different temperatures, the frequency is maintained at a constant value. Using the above experimental data, parameters such as Rao's constant, Wada's constant, solvation number, and surface tension were calculated. Using Walden's plot, the ionicity of the solution was studied.

Key Words: Arrhenius plot, Walden plot; solvation number; surface tension; ultrasonic velocity.

1. INTRODUCTION

The ultrasonic technique has been effectively employed to study the nature of molecular interaction in pure liquids [1], liquid mixtures [2] and ionic liquids and ionic interactions in electrolytic solutions [3,4]. Since ionic liquids are attracting growing interest as an alternative to molecular liquids, it is important to study the various properties of ionic liquids through ultrasonic studies. Ionic liquids have unusual properties including non-volatility, non-flammability, high ionic density, conductivity, chemical, and electrochemical stability. Room-temperature ionic liquids have been currently applied as a novel solvent in organic synthesis [5–7], catalysis [8-10], electrochemistry [11] and chemical separation [12]. The present work investigates electrical and thermodynamical parameters of an aqueous solution of KCl at different temperatures, different molality, and frequency 6 MHz.

2. EXPERIMENTAL METHODS

Fresh distilled water has been used as a solvent for preparing potassium chloride (KCl) solutions of different concentrations. Potassium chloride used as a solute for the solution is of analytical reagent (AR) grade. The density, viscosity, and ultrasonic velocity were measured as a function of the concentration of KCl at 288 K, 298 K and 318K. An ultrasonic interferometer (Model M-84) is used to measure ultrasonic velocity. A digital constant temperature bath (Model SSI-03 Spl.), has been used to circulate water through the outer jacket of the double-walled measuring cell containing the experimental liquid. The densities of the mixture are measured using a 10-ml specific gravity bottle by relative measurement method. An Oswald viscometer (10 ml) is used for the viscosity measurement.

3. THEORY

Rao's constant (R): Rao's constant is also known as molar sound velocity and it is an additive property and can be evaluated by an equation given by Bagchi et al.

$$R = \left(\frac{M_{eff}}{\rho}\right).U^{\frac{1}{3}} = V_m.U^{\frac{1}{3}} \qquad (1)$$

Wada's constant: Wada's constant also known as Molar compressibility is dependent on adiabatic compressibility and density is given by

$$W = \left(\frac{M_{eff}}{\rho}\right).\beta^{\frac{-1}{7}} \qquad (2)$$

Surface tension: Surface tension can be calculated by using the relation

$$S = 6.3 \text{ X } 10^{-4}.\rho.U^{\frac{3}{2}} \qquad (3)$$

Solvation number: Solvation number is determined by using the formula

$$S_n = \frac{M}{M_o}\left(1 - \frac{\beta}{\beta_o}\right)\left(\frac{100-x}{x}\right) \qquad (4)$$

Where M and Mo are molecular weight of Solvent and Solution respectively, β and β_o are adiabatic compressibility's of Solvent and Solution respectively and 'x' is the number of grams of salt in 100g of the solution.

4. RESULT AND DISCUSSION

Experimental values of density, viscosity, ultrasonic velocity and electrical conductivity are presented in table-1. Calculated values of molar electrical conductivity and Rao's constant are shown in table-2. Calculated values of Wada's constant and surface tension are shown in table-3. Calculated values of solvation number and Gibb's free energy are shown in table-4. Acoustic impedance and free volume are presented in table-5.

Table -1(a): Experimental values of density (ρ) and viscosity (η).

Conc. of KCl	Density (Kg.m^{-3})			Viscosity (NSm^{-2} x 10^{-3})		
	288 K	298 K	308 K	288 K	298 K	308 K
0.856	1007.6	1004.2	1000.5	1.412	1.074	0.748
1.711	1010.5	1007.1	1003.8	1.443	1.098	0.7722
2.566	1014.9	1011.5	1007.2	1.471	1.117	0.7858

3.422	1018.8	1015.1	1011	1.501	1.142	0.7989
4.278	1022.4	1019.2	1014.1	1.528	1.172	0.8129

Table -1(b): Experimental values of ultrasonic velocity (U) and electrical conductivity

Conc. of KCl	Velocity (m.s^{-1})			Electrical conductivity		
	288 K	298 K	308 K	288K	298K	308K
0.856	1501.2	1506.2	1510.1	57.6	64.4	71.7
1.711	1513.1	1518.4	1523.6	109.7	116.1	123
2.566	1516.5	1521.8	1527.9	149.9	156.3	163.5
3.422	1521.8	1527.4	1532.1	183.3	190.2	198
4.278	1525.4	1530.4	1535.4	213.5	220.4	227.6

Temperature remaining constant, velocity increases as concentration increases. With the increase in the concentration of KCl the H-bonded structure of water is disrupted. Electrolytes occupy the interstitial space and tend to break the original ordered structure of water. Interaction between solute and solvent molecules results in a decrease in free length and increase in density, viscosity, and velocity.

Concentration remaining constant as temperature increases, the intermolecular distance increases. This results in a decrease in density and viscosity. KCl in solution breaks into K+ and Cl-ions which are hydrated by water molecules. The hydrated moles are strongly held by electrostatic forces and are thus highly incompressible. This results in a decrease in the compressibility of the solution and an increase in ultrasonic velocity through it.

It is observed that the ultrasonic velocity in an aqueous solution containing sodium ions [3] is larger than the solution containing potassium ions. This suggests that there is a higher-order in the aqueous solution of NaCl than the KCl solution.

Table -3: The Calculated value of molar electrical conductivity and Rao's constant.

Conc. Of KCl	Molar electrical conductivity			Rao's constant		
	288 K	298 K	308 K	288 K	298 K	308 K
0.856	85.84	95.98	106.86	0.21239	0.21335	0.21432
1.711	81.87	86.64	91.79	0.21984	0.22084	0.22181
2.566	74.47	77.65	81.22	0.22633	0.22736	0.22863
3.422	68.29	70.86	73.77	0.23283	0.23396	0.23515
4.278	63.64	65.69	67.84	0.23911	0.24012	0.24159

Table -4: The Calculated values of Wada's constant and Surface tension

Conc. of KCl	Wada's constant			Surface tension		
	288 K	298 K	308 K	288 K	298 K	308 K
0.856	0.01501	0.01507	0.01513	36922.1	36981.5	36988.5
1.711	0.01554	0.01560	0.01566	37469.5	37539.8	37609.2
2.566	0.01600	0.01606	0.01614	37759.6	37830.6	37896.5
3.422	0.01647	0.01654	0.01661	38103.6	38175.0	38196.4
4.278	0.01692	0.01698	0.01707	38374.0	38442.1	38437.4

Vander Waal's and hydrogen bonding interactions are believed to govern the room temperature ionic liquids (RTIL). The change in viscosity with temperature can be shown through an Arrhenius dependence.

$$Ln(\eta) = Ln(\eta_0) + \left(\frac{E_n}{K_B.T}\right)$$

Where η is viscosity at any temperature T and η0 is a constant defined as the maximum viscosity which would be the viscosity at infinite temperature, K_B is the Boltzmann's constant and E_n is the activation energy for the viscous flow.

Analogous to the viscosity data, the electrical conductivity data of ionic liquids at various temperatures were fitted to Arrhenius equation,

$$Ln(\Lambda) = Ln(\Lambda_0) + \left(\frac{E_k}{K_B.T}\right)$$

Where Λ is the conductivity at any temperature, Λ_0 is maximum conductivity at infinite temperature, E_k is the activation energy for electrical conduction.

Table-4: The Calculated values of solvation number and Gibb's free energy

Conc. of KCl	Solvation number			**Gibb's free energy**		
	288 K	298 K	308 K	288 K	298 K	308 K
0.856	-60.53	-57.3	-55.5	0.638	0.560	0.439
1.711	-25.45	-23.85	-22.81	0.639	0.562	0.443
2.566	-17.38	-15.45	-13.72	0.643	0.565	0.446
3.422	-12.48	-12.27	-11.51	0.647	0.570	0.449
4.278	-10.52	-8.74	-7.52	0.651	0.577	0.454

Table-5: The Calculated values of acoustic impedance and free volume

Conc. of KCl	Acoustic impedance			Free volume		
	288 K	298 K	308 K	288 K	298 K	308 K
0.856	1.52261	1.51953	1.51666	0.100	0.152	0.262
1.711	1.53279	1.53018	1.52789	0.103	0.156	0.266
2.566	1.54598	1.54131	1.53891	0.106	0.161	0.274
3.422	1.55341	1.55046	1.54895	0.108	0.164	0.281
4.278	1.56057	1.55908	1.55725	0.110	0.165	0.287

Electrical conductivity increases both as to temperature increases for a particular concentration and as concentration increases at a particular temperature. The increase in conductivity depends on the solvent added and also the extent to which the ions are dissociated. As temperature or concentration increases more K+ ions are available in KCL solution. As K+ ions are less hydrated, their mobility is more. This leads to an increase in the conductivity of the KCl solution.

Rao's and Wada's constant remain almost constant when the temperature increases. This may be due to the increase in conductivity of the KCl solution, with an increase in temperature. Because of this, there is no accumulation of solute molecules in a given region. However, the above two constants increase, when concentration increases.

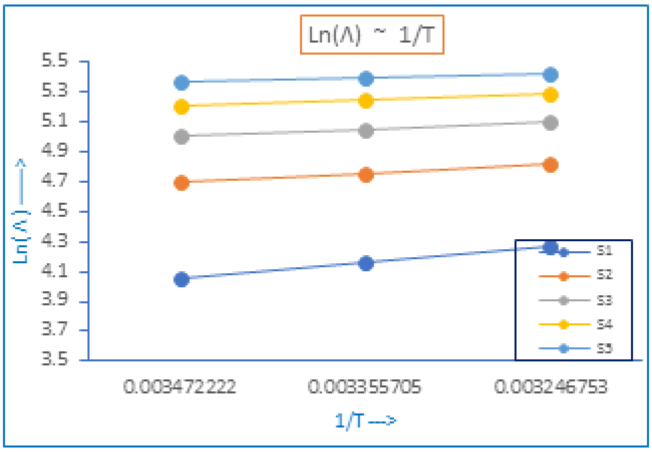

Figure-1: Variation of Ln(η) with the inverse of temperature

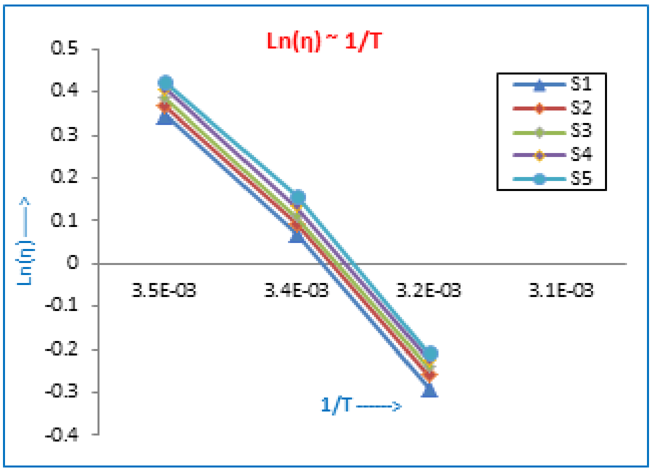

Figure-2: Variation of Ln(Λ) with inverse of temperature.

Surface tension increases rapidly with the increase of concentration of KCl (when the temperature remains constant). At higher concentrations, there is a strong molecular association between adjacent molecules causing strong surface film. However, when concentration remains constant, the surface tension changes slowly even when the temperature increases. This is because the weak electrostatic interaction of the ions does not affect the surface tension appreciably.

ΔG decreases rapidly as temperature increases (concentration remaining constant), but increase slowly as concentration increases (temperature remaining constant). Since potassium ions are less hydrated, they move faster as temperature increases and thus the distance between them increases decreasing the value of ΔG rapidly.

The decrease in acoustic impedance (Z) indicates weak interaction and vice versa. For the KCl solution, as concentration increases (temperature remaining constant) Z increases. However, when temperature increases (concentration remaining constant) Z decreases.

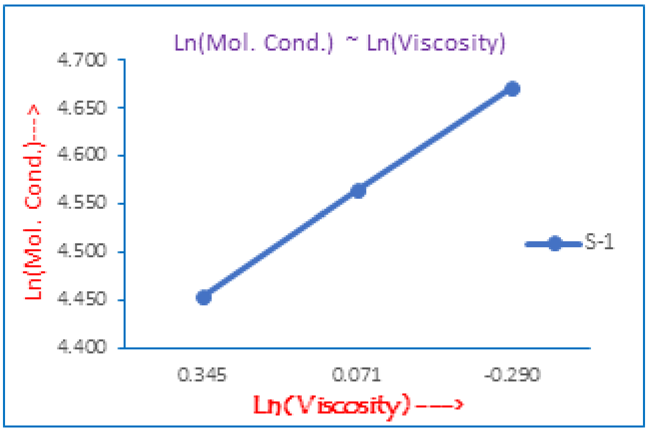

Figure-3: Variation of Ln(Λ_m) with L(η) for sol.-3

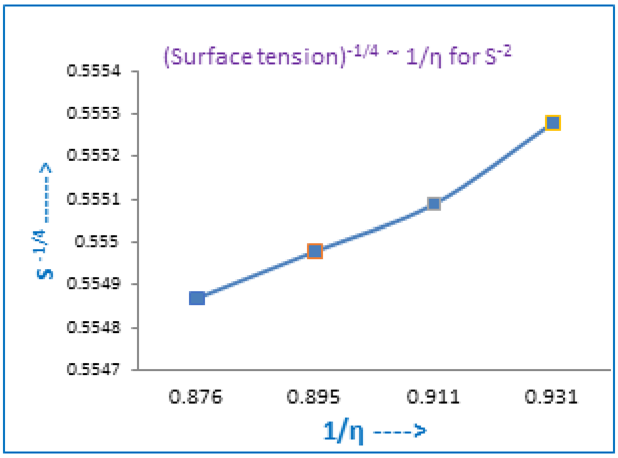

Figure-4: Variation of $S^{-1/4}$ with reciprocal of viscosity.

Free volume is the average volume in which the center of a molecule can move freely amongst surrounding molecules. Effective free volume some time changes due to transmission of collision effect through molecules. This is the reason, why free volume increases sharply as temperature increases, whereas it increases slowly (practically remains constant) when concentration increases.

Figures-5 indicates the change in Rao's constant, Wada's constant and surface tension for various concentrations and temperatures. It is obvious that electrical conductivity changes in the same way as Rao's constant, Wada's constant and surface tension of the ionic liquids.

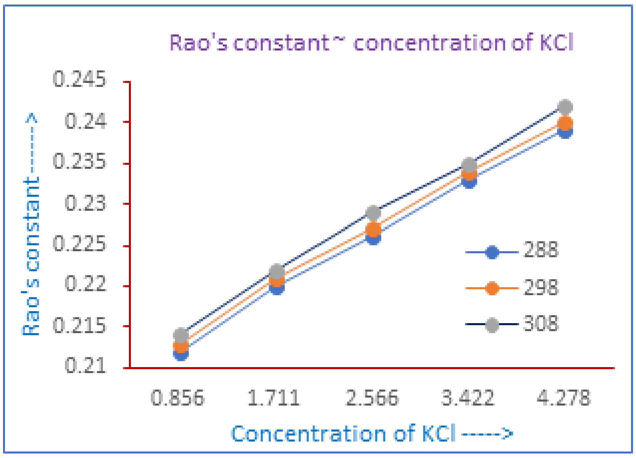

Figure-5: Variation of Rao's constant with the concentration of KCl.

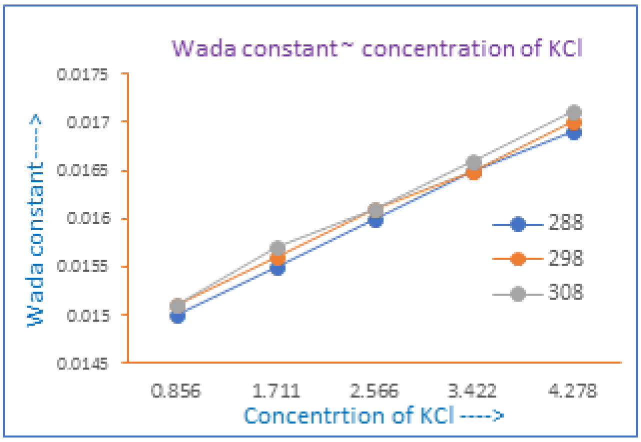

Figure-6: Variation of Wada's constant with the concentration of KCl

A relation between conductivity and viscosity can be studied through Walden plot given as

$$Ln(\Lambda_m) \sim Ln(\eta)$$

Where, Λ_m is the molar conductivity and η is the viscosity.

Walden's plot comes out to be a straight line. These plots indicate the ionicity of the ionic liquids. For 0.01M KCl the straight-line graph should pass through the origin. For other ionic liquids, the linear graph may be above the KCl graph or below it. Those laying above are more ionic and those below are less ionic. For the same concentration (S-1) the ordinate of the Walden plot in KCl solution is larger than that of the NaCl solution, indicating KCl is more ionic than NaCl.

Just as the relation between conductivity and viscosity has been studied through Walden's plot, an equation relating viscosity and surface tension can be obtained by combining the following equations of Batchinski [14] and MacLeod [20] respectively

$$\eta = \frac{C'}{v-w} \quad \text{-------------------- (1)}$$

And $S = C(D-d)^4$ ---------------- (2)

Where 'η' is the viscosity and 'v' is the specific volume, w is the limiting volume, S is the surface tension, D is the density of the liquid, d is the density of the vapor. C and C' are constants for a given liquid. Below the boiling point, the density of vapor may be neglected as compared with the density of the liquid 'D'.

Equating v to 1/D in equation (1) and (2) we get,

$$S^{-\frac{1}{4}} = A\left(\frac{1}{\eta}\right) + B \quad \text{-------------- (3)}$$

Where A and B are constants. In the present paper, the graph between '$S^{-1/4}$' and '1/η' comes out to be a straight line as shown in the figure, confirming the above equation.

The solvation number is an important parameter to study the interaction between the solute and solvent. It can be defined as the number of solvent molecules per ion which remains attached to a given ion long enough to experience its translational motion when the solution is formed [15].

The positive value of the solvation number suggests that the compressibility of the solution under all circumstances will be more than that of the solvent. The zero value of the solvation number indicates that no change occurs in the compressibility of the solvent when the solution is formed. The negative value of the solvation number emphasizes that the compressibility of the solution is less than that of the solvent. In our case, the solvation number is always negative. When an ion is added to water, it attracts some water molecule towards itself and is thus hydrated by a water molecule. The hydrated molecules are held strongly by electrostatic force. These are highly incompressible and the compressibility of the solution is due to the remaining solvents. This indicates the negative value of the solvation number. With increases in the ionic concentration of KCl the additional ions take up water molecules that are not bound strongly to the ion-water complex. This effect, in turn, increases the compressibility. This is evident in our observation where the negative value of the solvation number decreases rapidly with the increase of concentration. For a given concentration as the temperature increases, the hydrated ions become more mobile and hence compressibility of the solution decreases slowly. This is obvious from our observation where the negative solvation number decreases slowly.

If the solvation number of NaCl [3] and KCl are compared for different concentrations and temperatures then it is found that at all stages the solvation number is more negative for KCl solution compared to NaCl solution. This leads us to the conclusion that the compressibility of the NaCl solution is less than that of the KCl solution.

5. CONCLUSION

Ultrasonic and conductometric studies of KCl solution are done to study certain important parameters of the solution for different concentrations and temperatures. It has been seen that KCl has structure forming tendency in the solvent system. The increased cohesion between the molecules in the solution is due to ionic hydration or solvation. Ionicity of KCl is studied through the Walden plot.

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