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Ultrasonic study of ternary electrolytic mixtures at 303, 308 and 313K

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Ultrasonic velocity (U), viscosity (η) and density (ρ) of pottassium chloride (KCl), magnesium sulphate ($MgSO_4$) and mercury chloride ($HgCl_2$) mixtures have been measured at different molalities at 303, 308 and 313K. The derived acoustical parameters namely adiabatic compressibility (β), apparent molal compressibility (φ_K) apparent molal volume (φ_V), limiting apparent molal compressibility (φ_K^0), limiting apparent molal volume (φ_V^0), and their constants (S_K, S_V), viscosity B-coefficient and molal hydration number (H_n) have been computed from the experimental data. The variation in these parameters with respect to the molality of $HgCl_2$ has been explained on the basis of ion-solvent and structure making/breaking tendency of the electrolytes.

Keywords: Ultrasonic velocity, Adiabatic compressibility, Viscosity B-coefficient, Molal hydration number

1 Introduction

Ultrasonic technique has become a powerful tool in providing the molecular behaviour of liquids. An ultrasonic wave propagation study in a medium plays an important role for evaluating the physical properties of the medium. The ultrasonic techniques are used frequently because of their ability of characterising the physico-chemical behaviour of the liquid system. The measurement of ultrasonic velocity in liquid mixtures reveals the degree of deviation from ideality whenever there are interactions among the component molecules.

In recent years, the studies of acoustical properties of aqueous mixed electrolytic solutions have been found to be useful in understanding the specific ion-ion and ion-solvent interaction in solutions. The accurate measurement of density, viscosity, sound velocity and hence the derived parameters such as adiabatic compressibility, apparent molal compressibility and apparent molal volume will give significant information regarding the state of affairs in a solution. Such studies on binary electrolytes have been made by many researchers[1-4]. However, ultrasonic velocity studies on ternary electrolytes have not received much attention as that of binary electrolytes[5-6]. Since molecular interaction determines solubility, the solvation approach is also used to interpret ion-solvent interaction[7-9]. The study of structural changes in solvent due to solute is termed as solvation. In the present study, acoustical parameters have been determined for KCl + $MgSO_4$ + $HgCl_2$ mixtures from ultrasonic velocity measurements at different molalities and temperatures.

2 Materials and Methods

Fresh conductivity water has been used for preparing KCl + $MgSO_4$ + $HgCl_2$ mixture at different molalities with an accuracy of 0.1mg. All the chemicals used in the present study were Analytical (AR) reagent grade and Spectroscopic (SR) reagent grade of minimum assay of 99.9% obtained from E-Merck and Sdfines. The purity of the samples is checked by measuring their refractive indices. The density, viscosity and velocity at different molality of KCl + $MgSO_4$ + $HgCl_2$ mixtures were measured at 303, 308 and 313K. The density was determined using a specific gravity bottle by relative measurement method. The weight of the sample was measured using electronic digital balance with an accuracy of ± 0.1 mg (Model: SHIMADZU AX 200). An Ostwald's viscometer (10ml capacity) is used for the viscosity measurement and Efflux time was determined using a digital chronometer within ± 0.01S. An ultrasonic interferometer having the frequency 2MHz with an overall accuracy of ± 2 ms^{-1} has been used for velocity measurement. An electronically digital operated constant temperature bath (RAAGA Industries) has been used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at the desired temperature. The accuracy in the temperature measurement is ± 0.1 K.

3 Theory

Using the measured data, some acoustical parameters have been calculated using the standard relations.

Adiabatic compressibility $\beta = \frac{1}{U^2\rho}$ … (1)

The apparent molal compressibility has been calculated from relation:

$$\phi_K = \frac{1000}{m\rho_0}(\rho_0\beta - \rho\beta_0) + \left(\frac{\beta_0 M}{\rho_0}\right) \quad \ldots (2)$$

where β, ρ and β_0, ρ_0 are the adiabatic compressibility and density of solution and solvent respectively, m is the molal concentration of the solute, and M the molecular mass of the solute. ϕ_K is the function of m as obtained by Gucker[9] from Debye Huckel theory[10] and is given by:

$$\phi_K = \phi_K^0 + S_K m^{1/2} \quad \ldots (3)$$

where ϕ_K^0 is the limiting apparent molal compressibility at infinite dilution and S_K is a constant. ϕ_K^0 and S_K were obtained by least square method.

The apparent molal volume ϕ_V has been calculated using the relation:

$$\phi_V = \frac{1000}{m\rho_0}(\rho_0 - \rho) + \left(\frac{M}{\rho_0}\right) \quad \ldots (4)$$

The apparent molal volume ϕ_V has been found to differ with concentration according to Mason[11] empirical relation as:

$$\phi_V = \phi_V^0 + S_V m^{1/2} \quad \ldots (5)$$

where ϕ_V^0 is the limiting apparent molal volume at infinite dilution and S_V is a constant. These values were determined by least square method.

The importance of viscometric study of electrolyte solution in mixed solvent systems is well established[12-13]. The entire viscosity data have been analysed in the light of Jones-Dole semi empirical equation[14]:

$$\frac{\eta}{\eta_0} = 1 + Am^{1/2} + Bm \quad \ldots (6)$$

where η and η_0 are the viscosities of the solution and solvent, respectively and m is the molal concentration of the solute-solvent system. A and B are constants which are definite for a solute-solvent system. A is known as the Falkenhagen coefficient which characterises the ionic interaction and B is the Jone-Dole or viscosity B-coefficient which depends on the size of the solute and the nature of solute-solvent interactions.

Molal hydration number has been computed using the relation:

$$H_n = \left(\frac{n_1}{n_2}\right)\left(1 - \frac{\beta}{\beta_0}\right) \quad \ldots (7)$$

where β and β_0 are adiabatic compressibilities of solution and solvent respectively, n_1 and n_2 are mole fractions of solute and mixture respectively.

4 Results and Discussion

The experimental values of density, viscosity and ultrasonic velocity for different molal composition of KCl + $MgSO_4$ + $HgCl_2$ mixtures at 303, 308 and 313K are presented in Table 1. The values of density increase with increase in molal concentration of $HgCl_2$, but it decrease with rising of temperatures. The gradual increase in density with the increase in molal concentration of $HgCl_2$ may be due to association between solute and solvent molecules.

From the values of viscosity, it is observed that the viscosity increases with increase in solute concentration and decreases with rising of temperature. This increasing trend indicates the existence of molecular interaction occurring in the mixture. The ultrasonic velocity increases with increase in concentration of $HgCl_2$ as well as increasing of temperature. The variation of ultrasound velocity throws light on the structural changes associated with the present system. Molecular association is thus responsible for the observed increase in ultrasonic velocity in these mixtures. The increase in ultrasonic velocity in these solutions may be attributed to the cohesion brought about by the ionic hydration. The decrease in density and increase in velocity with temperature indicates decrease in intermolecular forces due to increase in the thermal energy of the system.

The values of adiabatic compressibility, apparent molal compressibility, apparent molal volume and molal hydration number are given in Table 2. It is

Table 1—Values of density (ρ),viscosity (η) and ultrasonic velocity (U) of KCl + $MgSO_4$ + Hg Cl_2 mixtures at 303, 308 and 313K.

Molality m/(mol. Kg^{-1})			Density ρ/(kg/m^3)			Viscosity η/($\times10^{-3}$ NSm^{-2})			Ultrasonic Velocity U/(ms^{-1})		
X_1	X_2	X_3	303 K	308 K	313 K	303 K	308 K	313 K	303 K	308 K	313 K
0.225	0.225	0.050	926.43	924.20	921.65	0.7501	0.6878	0.6161	1387.84	1455.50	1491.00
0.200	0.200	0.100	971.00	969.23	967.92	0.7859	0.7166	0.6557	1451.20	1490.20	1522.40
0.175	0.175	0.150	974.48	973.01	971.69	0.7980	0.7291	0.6570	1501.50	1516.20	1540.40
0.150	0.150	0.200	974.82	973.43	972.38	0.8190	0.7319	0.6618	1513.04	1531.80	1567.44
0.000	0.000	0.250	991.44	990.26	989.71	0.7880	0.7269	0.6573	1524.00	1557.60	1576.80

Table 2—Values of adiabatic compressibility (β), apparent molal compressibility (φ_K), apparent molal volume (φ_V) and hydration number (H_n) of KCl + $MgSO_4$ + Hg Cl_2 mixtures at 303, 308 and 313K.

Molality m/(mol. Kg^{-1})			Adiabatic compressibility β/($\times10^{-10}$ m^2 N^{-1})			Apparent molal compressibility $-\varphi_K$ /($10^{-7}m^2$ N^{-1})			Apparent molal volume φ_V /(m^3 mol^{-1})			Hydration number (H_n)		
X_1	X_2	X_3	303 K	308 K	313 K	303 K	308 K	313 K	303 K	308 K	313 K	303 K	308 K	313 K
0.225	0.225	0.050	5.6041	5.1075	4.8807	1.8510	4.4382	4.6537	464.2108	475.6218	465.3202	-0.0276	-0.0184	-0.0141
0.200	0.200	0.100	4.8902	4.6461	4.4576	1.8083	0.9429	0.9124	-237.685	-237.6975	-257.5572	-0.0273	-0.0155	-0.0084
0.175	0.175	0.150	4.5517	4.4692	4.3341	0.9602	0.7628	0.7072	-182.8233	-187.9458	-203.1197	-0.0110	-0.0109	-0.0039
0.150	0.150	0.200	4.4810	4.4300	4.1888	0.7566	0.6153	0.5707	-139.0960	-141.1459	-152.5268	-0.0082	-0.0109	-0.0083
0.000	0.000	0.250	4.3427	4.1624	4.0639	0.7013	0.6019	0.4550	-181.1079	-183.7629	-195.2200	-0.1003	-0.0461	-0.0499

found that the adiabatic compressibility decreases with increasing the concentration of the solutes as well as temperature. The increase in velocity and decrease in compressibility were attributed to the formation of hydrogen bonds between solute and solvent molecules. The values of φ_K are all negative and decrease over the entire range of molality and increase in temperature. The negative values of φ_K indicate electrostriction, hydrophilic and hydrophobic interaction occurring in these systems.

The values of apparent molal volume φ_V are all negative (except at 0.05 molality of $HgCl_2$) over the entire range of molality and increasing of temperature. The values of φ_V decrease with the increase of $HgCl_2$ and increase with the elevation of temperatures. These observations clearly suggest that the negative values of φ_V in mixture indicate the presence of ion-solvent interaction. The decrease in φ_V is due to strong ion-ion interaction and vice-versa. The negative values of φ_V indicate electrostrictive solvation of ion[15].

The interaction between the solute and the water molecules in the solvent is termed as hydration. It is observed that the values of H_n are negative and decrease over the entire range of molality of $HgCl_2$ as well as temperatures. The negative values of H_n indicate an appreciable solvation of solutes[16]. This is an added support for the structure promoting nature of the solutes as well as the presence of appreciable ion-solvent interaction between solute and water molecules. The values of H_n decrease with increase in concentration of $HgCl_2$ is due to weakening of ion-solvent interactions in the mixtures. The effect of rise of temperature also shows decrease in hydration number. The values of limiting apparent molal compressibility φ_K^0, limiting apparent molal volume φ_V^0 and their constants S_K and S_V and viscosity A and B parameters of Jones-Dole equation are presented in Table 3.

The limiting apparent molal compressibility[11] due to φ_K^0 and the related constant S_K have been computed using least square method. φ_K^0 provides information regarding solute-solvent interactions and S_K, that of solute-solute/ion-ion interaction in the solution. φ_K^0 values are negative and decrease with rising of temperature. Appreciable negative values of φ_K^0 reinforce the existence of ion-solvent interaction in the present system. The positive value of S_K indicates the existence of ion-ion interaction with increase of temperature and suggests structure making/breaking effect of the $HgCl_2$.

Table 3—Values of limiting apparent molal compressibility (φ_K^0) and limiting apparent molal volume (φ_V^0), their constants S_K and S_V and Viscosity Coefficients of KCl + $MgSO_4$ + Hg Cl_2 mixtures at 303, 308 and 313K.

Temperature K	Limiting apparent molal compressibility $-\varphi_K^0$ ($\times 10^{-7}$ m^2 N^{-1})	Constant $S_K/(\times 10^{-7}$ N^{-1} m^{-1} $mol^{-1})$	Limiting apparent molal volume $-\varphi_V^0$ ($\times m^3$ mol^{-1})	Constant S_V m^8 $lt^{-/2}$ $mol^{-3/2}$	Viscosity coefficients	
					A/$dm^{3/2}$ $mol^{-1/2}$	B/dm^3 mol^{-1}
303	19.17	4.64	633.39	– 1798.10	– 0.43	1.08
308	9.78	2.00	630.55	– 1798.05	– 0.36	0.86
313	7.80	1.58	614.02	– 1779.98	– 0.09	0.46

The values of φ_V^0 in mixtures are positive and decrease with increase of temperature. This observation suggests that the existence of ion-solvent interactions and the decrease in φ_V^0 value is due to the enhancement of electrostriction in the mixture. It is evident from the Table 3 that negative values of S_V, suggest the presence of weak ion-ion interaction in the mixtures.

From the values of viscosity *A* and *B* parameters, it is observed that the values of *A* are negative and *B*-coefficient are positive and these values decrease with rise of temperature. Since *A* is a measure of ionic interaction[17] it is evident that there is a weak ion-ion interaction in the mixtures studied, which is indicated by the smaller magnitude of *A* values. *B*-coefficient is also known as measure of ion-solvent interaction in the mixtures. The behaviour of *B*-coefficient in the mixtures suggests the absence of significant ion-solvent interaction.

5 Conclusions

The existence of intermolecular interaction of electrostriction, hydrophilic and hydrophobic nature exists in the mixture studied. The existence of ion-solvent interactions resulting in attractive forces promote the structure making tendency while ion-ion interaction resulting in dipole-dipole, dipole-induced dipole and electrostrictive forces enhance the structure breaking properties of the mixtures. An appreciable existence of ion-solvent interaction is present with increase in concentration of $HgCl_2$. But ion-solvent and ion-ion interaction gets weakened with rising of temperature. Similar ion-solvent interactions have been discussed earlier[18] which supports our present ultrasonic study.

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