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ACOUSTICAL AND MOLECULAR BEHAVIOR OF AQUEOUS NACL , KCL , BACL$_2$,NA$_2$SO$_4$ AND MGSO$_4$ SOLUTIONS AT 298.15K

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ABSTRACT

Densities and Ultrasonic velocities of aqueous NaCl, KCl , BaCl$_2$, Na$_2$SO$_4$ and Na$_2$SO$_4$ have been determined experimentally at different molalities at 298.15 K. From these experimental results the adiabatic compressibility K_s, acoustic impedance Z, apparent molar volume ϕ_v, adiabatic compressibility, ϕK_s, and partial molal volume $\phi^0{}_v$ and partial molal adiabatic compressibility, $\phi^0 K_s$ at infinite dilution. The results are interpreted in terms of solute-solute and solute-solvent interactions in these systems. It has been observed that there exist strong solute-solvent interaction and dehydration effect in these binary systems. The properties of these electrolytes in water systems are discussed in terms of charge, size and hydrogen bonding effect.

KEYWORDS: Aqueous electrolytes, adiabatic compressibility, acoustic impedance, apparent molal volume and apparent molal adiabatic compressibility.

INTRODUCTION

Ultrasonic investigation in aqueous solutions of electrolytes and non-electrolytes provides useful information in understanding the behavior of liquid systems. Also, Ultrasonic technique has been found to be more accurate and comprehensive in understanding solute-solvent interactions. There are various types of interactions are that exist between ions in solution of electrolytes; solute-solvent interactions are most important. Ultrasonic velocity and density data have been used to study the solute-solvent interactions. Ultrasonic velocities in aqueous solutions of ZnBr$_2$, CaBr$_2$ and NaBr have been measured in ionic strength range of 0-8 at 25^{0}C by Grzybkowski and Atkinson [1]. They reported that the relative ultrasonic velocities in dilute solutions were positive but very small and become, even negative and large in magnitude. The negative values of these properties relative sound velocities have been observed in the case of only few systems such as NaI and KI which display rather strong structure breaking properties. There has been number of physicochemical studies of amino acids in aqueous carbohydrates solutions [2-6]. Amino acids have zwitter-ion and are the constituents of the most important class of biopolymers, i.e. Proteins. Disarrangement water and electrolyte balance in living systems cause a wide variety of health problems. In physiological media such as blood, membranes, cellulose fluids etc., the dipolar character of amino acids (in presence of ions such as Na$^+$, K$^+$, Mg^{+2}and Cl$^-$ etc., dissolved in body water) has an important bearing on their biological functions.

Recently, we have made systematic effort to investigate the volumetric properties of amino acids in concentrated electrolytic solution [7-10]. It was found that NaCl and MgCl$_2$ increase the apparent molar volume of glycine. This increase could be attributed to the interactions of the ions of the NaCl , MgCl$_2$ L-Proline and L- Glutamine electrolytes and zwitter-ion head group of amino acids, causing the transfer of hydrated water molecule to the bulk state.

In the present paper, we report densities, ρ and ultrasonic velocities, u of binary systems of *a*queous NaCl, KCl , BaCl$_2$ Na$_2$SO$_4$ and Na$_2$SO$_4$ *have been determined experimentally at 298.15K. From these experimental* data a number of thermodynamic parameters namely, *the adiabatic compressibility* K_s, *acoustic impedance, apparent molal volume* ϕ_v, *adiabatic compressibility,* ϕK_s, *and partial molal volume* $\phi^0{}_v$ *and partial molal adiabatic compressibility,* at infinite dilution respectively have been calculated. These parameters were utilized to study various interactions taking place in the solutions of these ternary systems were measured at 298.15K.

EXPERIMENTAL

Chemicals and preparation

NaCl, KCl, $BaCl_2$, $MgSO_4$ and $NaSO_4$ (99.5% purity) were procured from ARS grade. The ultrasonic velocities and densities of the aqueous electrolytes solutions at various concentrations as well as in double distilled de-ionized water were measured experimentally. The double distilled water was used to make aqueous solutions of NaCl, KCl, $BaCl_2$, $MgSO_4$ and $NaSO_4$ and to prepare 0.1, 0.15, 0.20, 0.25, 0.30, 0.35, 0.40, 0.45 and 0.50m by weight dilution method. All the solutions were prepared by mass in dry box and were stored in special air-tight bottles and kept in dark to avoid photo chemical degradation. The weighing was done on an Afcoset ER-120A electronic balance with an accuracy ± 0.1 mg.

Measurement of density and ultrasonic velocity

The densities were measured with a single capillary pycnometer (made of Borosil glass) of bulb capacity of $8x10^{-6}m^3$. The marks of the stems were calibrated using double distilled water at 298.15 K. The pycnometer was kept for about 30 minutes in a thermostatic water bath so that the thermal fluctuation in density was minimized. The ultrasonic velocities in solutions were measured using a single crystal variable path interferometer at 3MHz.The temperature of the test solutions was maintained at 298.15 ± 0.02%K in an electronically controlled thermostatic water bath. The velocity and density data were found to be accurate with in ± 0.10%and ± 0.01% respectively.

RESULTS AND DISCUSSION

The densities and ultrasonic velocities of the aqueous electrolytes NaCl, KCl, $BaCl_2$, $MgSO_4$ and $NaSO_4$ solutions were determined at 298.15 K are recorded in Table 1.The values of u and ρ increase with increase in molalities (0.1 – 0.5)m of the binary systems under investigation, which appear to be due to hydrophobic properties of solutes i.e. H-bond forming. The change in structure of solution as a result of H- bond formation leads to decrease in intermolecular free length [12] which indicates ion-solvent interactions are strong. The variation of ultrasonic velocity of electrolytes solution with the molalities in water can also be expressed in terms of derivations of (du/dc) can be shown to depend upon the molalities derivations of the density and adiabatic compressibility of the system investigated.

Thus in the relation:

$$du/dm = -u/2 \, [\, 1/\rho \, (d\rho/dm) + (1/K_s)(\, d\, K_s/dm)\,] \qquad (1)$$

The quantity $(1/\rho)(d\rho/dm)$ is negative while $(1/K_s)(\, dK_s/dm)$ is positive in the present case and the net value is negative. The H-bonded structure of water is either disrupted by the addition of solutes. which is in good agreement with the results reported for adenosine mono,-di-and tri-phosphates + dixane + H_2O [13]. Consequently, the values of relative ultrasonic velocities Δu increase with increase in molalities of aqueous solutions of electrolytes NaCl, KCl, $BaCl_2$, $MgSO_4$ and $NaSO_4$ which indicates structure making properties. The values of relative ultrasonic velocities Δu were calculated by equation:

$$\Delta u = u - u_0 \qquad (2)$$

Where u and u_0 are ultrasonic velocity of solution and solvent . Millero et al [14] have measured the relative ultrasonic velocities (Δu) of aqueous NaCl, $MgCl_2$, $MgSO_4$ and $NaSO_4$ solution at $0\text{-}45^0C$. The relative ultrasonic velocities values are increase with increase in molalities of electrolytes solution are given in Table 1. All the halide solutions of Na^+, K^+ and Ba^{+2} is slightly lower in the presence of sulphate solutions. This result reveals that relative ultrasonic velocities decrease with increase the size of ions . The Cl^- and SO_4^{-2} ions are therefore structure makers.
Acoustic Impedance

The values of acoustic impedance, Z of these binary systems (water + electrolytes) were calculated by the following relation and are reported in Table 1.

$$Z = u \, . \, \rho \qquad (3)$$

$$Z^0 = u^0 \, . \, \rho^0 \qquad (4)$$

The values of ΔZ were calculated by this relation

$$\Delta Z = Z - Z_0 \tag{5}$$

The values of Z and ΔZ increase with increase in molalities of electrolytes which indicates solute-solvent interaction are strong and they behave as structure makers are shown in Table 1.The specific acoustic impedance of the medium for the particular type of wave being propagated and through it. The transmission of acoustic wave from one medium to another is important for transmission phenomenon in fluids. It may also correlated with ionic size Na^+, K^+, Mg^{+2} and Ba^{+2} of ions. A definite correlation the specific acoustic impedance and dielectric constant of the solvent medium. The behavior of acoustic impedance can be explained on the basis of lyophobic interaction between solute (NaCl, KCl , $BaCl_2$ and $MgSO_4$ and $NaSO_4$ and solvent (aqueous) molecules, which maximum ion- solvent interaction and become responsible for the propagation of ultrasonic wave.

Adiabatic Compressibility

The adiabatic compressibility of the aqueous electrolytes NaCl, KCl, $BaCl_2$, $MgSO_4$ and $NaSO_4$ solutions were determined at 298.15 K are recorded in Table-2 from the density and velocity data. The adiabatic compressibility was calculated by this relation

$$K_s = 1/u^2\rho \tag{6}$$
$$\Delta K_s = K_s - K_s^0 \tag{7}$$

Where, K_s and K_s^0 are the adiabatic compressibility of solution and solvent respectively. These variation have been found to be linearly convergent in the case of electrolytes solution which shows strong interactions in electrolytic solutions. The observed values of the adiabatic compressibility ,K_s Table 2 is found to decrease with the concentration of aqueous electrolytes in all the binary systems. This decrease in compressibility is expected due to structure making effect of NaCl, KCl, $BaCl_2$, $MgSO_4$ and $NaSO_4$. An increase is expected due to structure breaking effect of NaI and KI. This clearly suggested that the strength of interaction in the binary systems decreases with increasing concentration of electrolyte in the solutions .The compressibility behavior of aqueous electrolytes molecules in the present systems can be explained by considering the strong electrostatic compression of the solvent dipolar molecules [15]. Consequently, these polar end groups would be able to cause more electrostrictive contraction of neighboring water molecules. Lowering in the compressibility ΔK_s of the electrolytic solution have been studied and found to increase with increasing molalities of aqueous electrolytes solution. The negative values shown in Table -2

Apparent molal volume

The apparent molal volume, ϕ_v were calculated from measured density data by using the following equation:

$$\phi_v = [1000\,(\rho^0 - \rho) / m\rho\,\rho^0] + M/\rho \tag{8}$$

Where M is the molecular mass of the solute, ρ^0 and ρ are densities of solvent and solution. The calculated values of ϕ_v of these binary systems are given in Table 1 & 2. In these cases where molarity dependence of ϕ_v , having definite trend points and increase with increase the temperature which indicates ion-solvent interactions are strong with rise the temperature The ϕ_v values increase due to reduction in the electrostriction effect at terminals in the binary systems whereas it decreases due to disruption of side group hydration by that of the charged end.

The partial molal volume at infinite dilution ϕ^o_v was calculated by taking an average data points. The linear variation is obtained by least square fitting to the following equation.

$$\Phi_v = \phi^0_v + S_v\, C^{1/2} \tag{9}$$

The intercept which is the partial molal volume at infinite dilution ϕ^0_v is the experimental slope, S_v which is considered to be volumetric pair wise coefficient. The derived values ϕ^0_v of along with S_v are summarized in Table 3. The values of ϕ^0_v are positive of these binary systems which indicate ion-solvent interactions are strong. The values of ϕ^0_v are less in presence of NaCl, KCl, $BaCl_2$ than $MgSO_4$ and $NaSO_4$. Table 3 shows the values of ϕ^0_v are larger in case of $MgSO_4$ and $NaSO_4$ has an intense force field and hence a strong hydration co sphere around it. Therefore hydration of $MgSO_4$ and $NaSO_4$ (ion-solvent) will be much more than that of NaCl, KCl, $BaCl_2$. The SO_4^{-2} ion results in intense electric field and thus, the possibility of interactions with is larger in case of $MgSO_4$ and $NaSO_4$. The S_v values of NaCl, KCl, $BaCl_2$ are negative and positive $MgSO_4$ and $NaSO_4$ which indicates solute-solute interactions are weak in case NaCl, KCl, $BaCl_2$ than $MgSO_4$ and $NaSO_4$ The studies suggest that ion- solvent interactions are stronger and solute -solute interaction are weak .The extent of interactions and structure making ability is greater in case of $MgSO_4$ and $NaSO_4$.

Apparent molal adiabatic compressibility
The density and adiabatic compressibility values were employed for calculating apparent molal adiabatic compressibility, ϕK_s of solutes in aqueous electrolytes solutions at different concentration using the equation

$$\phi K_s = [1000 (\rho^0 K_s - \rho K_s^0) / m\rho \rho^0] + MK_s/\rho \qquad (10)$$

Table 3 shows that the positive values of ϕK_s which indicates strong solute-solvent interactions. The partial molal adiabatic compressibility, $\phi^o K_s$ at infinite dilution are obtained from the plot of ϕK_s versus $C^{1/2}$ by least square method. The molarity dependence of this parameter has been expressed in terms of the following equation

$$\Phi_{Ks} = \phi^0_{Ks} + S_{Ks}\, m^{½} \qquad (5)$$

where ϕ^0_{Ks} is the partial molal adiabatic compressibility at infinite dilution. It provides information regarding solute-solvent interaction. S_{Ks} is the experimental slope. The values of ϕ^0_{Ks} and S_{Ks} are also included in Table 3 . The values of S_{Ks} of NaCl, KCl, $BaCl_2$ + water indicating the presence of weak ion-pair interactions than $MgSO_4$ and $NaSO_4$. Appreciable more negative values of ϕ_{Ks} for both the binary systems, which indicate ion- solvent interaction, are strong. The apparent molal volume and compressibility of aqueous solutions of some transition metal (Mn^{+2}, CO^{+2}, Ni^{+2} Zn^{+2}) chlorides have been determined by Surdo et al [16]. At the infinite dilution partial molal volumes and compressibility of ions , it is possible to examine how ion-water interactions depends upon the size and charge of the ions. Since values of ϕ^0_{Ks}, are more sensitive to structural changes associated with ion- water interactions.

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Table 1
Densities (ρ) and ultrasonic velocity (u) , and related thermodynamic properties of aqueous Potassium chloride, sodium chloride, Barium chloride, Magnesium sulphate and sodium sulphate at 298.15K

m (mol^{-1})	$\rho\times10^{-3}$ (kg m^{-3})	u (ms^{-1})	Δu (ms^{-1})	$Z\times10^{-3}$ (kg m^{-2}s^{-1})	$\Delta Z\times10^{-3}$ (kg m^{-2}s^{-1-})
Potassium chloride					
0.10	1.001	1504	9.00	1506	12.00
0.15	1.002	1509	14.00	1512	20.00
0.20	1.004	1511	16.00	1017	25.00
0.25	1.005	1512	24.00	1019	27.00
0.30	1.009	1528	33.00	1541	49.00
0.35	1.012	1554	59.08	1572	80.00
0.40	1.014	1562	67.00	1582	90.00
0.45	1.019	1568	73.00	1597	105.0
0.50	1.020	1572	77.00	1603	110.0
sodium chloride					
0.10	1.001	1502	7.00	1504	12.00
0.15	1.002	1505	10.00	1508	20.00
0.20	1.004	1515	28.00	1523	31.00
0.25	1.008	1531	36.00	1543	51.00
0.30	1.009	1533	38.00	1547	55.00
0.35	1.010	1548	48.00	1563	71.00
0.40	1.014	1549	54.00	1566	74.00
0.45	1.019	1554	59.00	1579	87.0
0.50	1.020	1578	83.00	1621	129.0
Barium chloride					
0.10	1.013	1503	8.00	1523	31.00
0.15	1.020	1504	9.00	1534	42.00
0.20	1.028	1505	10.00	1046	54.00
0.25	1.040	1506	11.00	1066	74.00
0.30	1.049	1528	33.00	1589	97.00
0.35	1.050	1537	42.08	1613	130.00
0.40	1.060	1559	64.00	1652	164.00
0.45	1.077	1569	74.00	1690	200.0
0.50	1.086	1577	82.00	1713	221.0

			Magnesium sulphate		
0.10	1.011	1503	8.00	1519	27.00
0.15	1.015	1508	13.00	1530	38.00
0.20	1.016	1513	18.00	1037	45.00
0.25	1.017	1520	25.00	1045	53.00
0.30	1.019	1523	28.00	1552	60.00
0.35	1.021	1530	35.00	1562	70.00
0.40	1.026	1535	40.00	1570	78.00
0.45	1.028	1540	45.00	1580	88.60
0.50	1.020	1542	47.00	1585	93.00
			sodium sulphate		
0.10	1.001	1504	9.00	1506	12.00
0.15	1.002	1509	14.00	1512	20.00
0.20	1.004	1511	16.00	1017	25.00
0.25	1.005	1512	24.00	1019	27.00
0.30	1.009	1528	33.00	1541	49.00
0.35	1.012	1554	59.08	1572	80.00
0.40	1.014	1562	67.00	1582	90.00
0.45	1.019	1568	73.00	1597	105.0
0.50	1.020	1572	77.00	1603	110.0

Table 2
Adiabatic compressibility (K_s), apparent molal volume (ϕ_v), apparent molal adiabatic compressibility (ϕ_{Ks}) of aqueous Potassium chloride, sodium chloride, Barium chloride, Magnesium sulphate and sodium sulphate at 298.15K

m ($moll^{-1}$)	$-K_s \times 10^{10}$ ($N^{-1}\ m^{-2}$)	$\Delta K_s \times 10^{10}$ ($N^{-1}\ m^{-2}$)	$(\phi_v) \times 10^6$ ($m^3 mol^{-1}$)	$(\phi_{Ks}) \times 10^{10}$ ($m^5 N^{-1}\ mol^{-1}$)
		Potassium chloride		
0.10	4.416	0.071	35.66	552.3
0.15	4.382	0.105	42.01	575.1
0.20	4.362	0.125	40.17	456.0
0.25	4.352	0.135	43.08	356.4
0.30	4.244	0.243	34.99	668.9
0.35	4.091	0.397	32.08	305.7
0.40	4.046	0.441	32.40	988.8
0.45	3.991	0.496	25.96	1023.1

0.50	3.967	0.520	28.84	950.9
		sodium chloride		
0.10	4.428	0.059	19.49	502.6
0.15	4.406	0.081	25.84	424.0
0.20	4.335	0.152	24.01	662.5
0.25	4.230	0.257	14.88	972.6
0.30	4.213	0.274	18.22	843.9
0.35	4.131	0.355	21.64	941.6
0.40	4.122	0.365	16.23	859.2
0.45	4.075	0.477	19.80	895.8
0.50	3.910	0.577	12.67	1067.7
		Barium chloride		
0.10	4.369	0.118	85.52	825.1
0.15	4.334	0.153	91.87	643.8
0.20	4.298	0.189	90.04	586.7
0.25	4.239	0.248	72.89	727.1
0.30	4.086	0.401	71.48	1111.9
0.35	4.012	0.475	93.40	1036.5
0.40	3.874	0.613	87.28	1292.6
0.45	3.771	0.716	66.91	1465.7
0.50	3.702	0.785	66.71	1462.2
		Magnesium sulphate		
0.10	4.378	0.109	13.24	109.43
0.15	4.332	0.155	22.90	956.21
0.20	4.299	0.188	47.77	754.63
0.25	4.256	0.231	62.70	677.51
0.30	4.231	0.256	69.30	580.43
0.35	4.184	0.303	74.02	577.89
0.40	4.148	0.339	77.56	548.72
0.45	4.109	0.378	78.08	545.55
0.50	4.091	0.396	80.51	488.17

sodium sulphate

0.10	4.447	0.114	139.26	659.41
0.15	4.335	0.152	114.01	419.09
0.20	4.308	0.179	142.48	191.66
0.25	4.281	0.275	147.37	512.06
0.30	4.188	0.299	130.58	485.85
0.35	4.100	0.387	139.24	580.11
0.40	4.043	0.444	138.24	529.90
0.45	3.928	0.559	115.04	275.15
0.50	3.830	0.657	80.51	117.52

Table 3

The partial molal volume (ϕ^0_v), Partial molal adiabatic compressibility (ϕ^0_{Ks}) and its experimental slope, (S_v) and (S_{Ks}), of aqueous Potassium chloride, sodium chloride, Barium chloride, Magnesium sulphate and sodium sulphate at 298.15K

Electrolytes	ϕ^0_v *10^6 (m^3mol^{-1})	S_v *10^6 ($m^3mol^{-3/2}\,l^{-1/2}$)	ϕ^0_{Ks} *10^{10} ($m^5N^{-1}mol^{-1}$)	S_{Ks} *10^{10} ($m^5N^{-1}mol^{-3/2}\,l^{-1/2}$)
Potassium Chloride	20.82	-20.11	-1597.62	-875.5
Sodium Chloride	20.83	-24.89	-1820.90	-811.0
Barium Chloride	39.45	-38.93	-3158.02	-2422.0
Magnesium sulphate	228.53	331.66	-3640.67	-4681.0
Sodium sulphate	379.36	354.44	-6228.10	-8200.0