

## **Thermo-acoustical properties of ternary mixtures containing strong electrolytes (metal chlorides) at various temperatures and 2MHz frequency -An Ultrasonic study**

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### **Abstract**

Ultrasonic technique has been employed extensively to assess the nature and strength of molecular interactions of strong electrolytes in water + ethanol co-solvent systems along with effect of temperatures and concentrations at 2MHz frequency. Measurements of ultrasonic velocity (U) and density (d) of strong electrolytes like zinc chloride and magnesium chloride in 5, 10 and 15 wt% of aqueous ethanol have been carried out in different concentrations over the temperature range 298.15K to 313.15K at 5K interval to evaluate various thermo-acoustical parameters, viz. acoustic impedance (Z), isentropic compressibility ( $K_s$ ), apparent molar isentropic compressibility ( $K_{s,\phi}$ ), intermolecular free length ( $L_f$ ), solvation number ( $S_n$ ), relative association ( $R_A$ ). These parameters are used to explain the solute-solute, solute-solvent and solvent-solvent interactions through solvation and hydrogen bonding. The qualitative intermolecular elastic forces between the solute and solvent molecules are explained in terms of compressibility. The structural arrangement of molecules in electrolyte solutions has been discussed on the basis of electrostatic field of ion.

**Keywords:** Strong electrolytes, Aqueous ethanol, Relative association, Isentropic compressibility, Solvation number.

## INTRODUCTION

Ultrasonic method is a versatile non-destructive technique, which behaves like a powerful probe to assess the acoustic properties and predict the intermolecular interactions in binary and ternary mixtures [1, 2], because these mixtures find practical applications in several pharmaceutical, medicinal, industrial and technological processes. Ultrasonic velocity, density and related acoustic parameters of electrolytes in mixed solvent systems assist in characterizing the structure and physical properties of solutions. The investigation of ultrasonic velocity and thermo-acoustic properties of electrolytes in aqueous and mixed solvent systems has been the area of interest of many researchers [3, 4].

In continuation of our earlier work in aqueous medium [5], the present investigation deals with the study of molecular interactions of strong electrolytes (zinc chloride and magnesium chloride) in 5, 10 and 15 wt% aqueous ethanol solvent systems in different concentrations over the temperature range 298.15K to 313.15K at 5K interval and 2MHz frequency. Various thermo-acoustical parameters, such as acoustic impedance ( $Z$ ), isentropic compressibility ( $K_s$ ), apparent molar isentropic compressibility ( $K_{s,\phi}$ ), intermolecular free length ( $L_f$ ), solvation number ( $S_n$ ), relative association ( $R_A$ ) have been computed from ultrasonic velocity ( $U$ ) and density ( $d$ ) data which provide qualitative information regarding nature and strength of the molecular interactions in the electrolytic solutions. The chemicals used in the work have wide applications in pharmacology, immunology, medicine and industry. Zinc is a trace element, which is essential for proper stabilization and catalytic activity of many metalloenzymes in living organisms [6]. Various zinc containing enzymes in the body are responsible for proper absorption of  $CO_2$  by red blood cells and for maintaining proper pH in the muscles and tissues. Magnesium is an essential mineral which plays important roles in physiological function of the body organ. It may exist as protein bound, complexed or in free form and critically stabilizes enzymes including many ATP generating reactions [7]. It is used as an important factor in both cellular and humoral immune reactions [8]. Ethanol is a primary alcohol with dielectric constant ( $\epsilon=25.08$  at 298.15K) and dipole moment ( $\mu=1.69$ ). It is a versatile solvent well miscible with water and the polar nature of the hydroxyl group causes ethanol to dissolve many ionic compounds. It is widely used as a solvent in many substances intended for human consumption, including medicine, flavouring, coloring and personal care product like perfumes and deodorant. Ethanol is psychoactive and recreational drugs. It is metabolized by the human body as an energy providing nutrient. It is both an essential solvent and a feedstock used for the synthesis of products in chemical industry.

## EXPERIMENTAL DETAILS

### Materials and Methods

Zinc chloride and magnesium chloride used were of GR or AR grades obtained from Merck and dried over anhydrous  $CaCl_2$  in desiccator before use. Ethanol from Merck

with purity  $\geq 99.9\%$  was dehydrated by 4A molecular sieve and used. Conductivity water (Sp. cond.  $\sim 10^{-6}$  S.cm<sup>-1</sup>) was used for preparing water + ethanol (5, 10 and 15 wt %) mixtures. The ethanol content in the mixed solvents was accurate within  $\pm 0.01\%$ . The solutions were prepared on the molal basis and conversion of molality to molarity was done by using standard expression [9] using the density data at the corresponding temperature. The solute content of the solutions varied over a concentration range of  $6.0 \times 10^{-3}$  M to  $8.0 \times 10^{-2}$  M for all measurements.

### **Velocity measurement**

Ultrasonic velocity measurements in the solutions were made by using a multi frequency ultrasonic interferometer (Model No-M84, Mittal enterprises, New Delhi, India) operating at a frequency of 2MHz at different temperatures ranging from 298.15K to 313.15K at 5K intervals. The temperature was controlled by a thermostat accurate to within  $\pm 0.05$ K. The precision of the ultrasonic velocity measurements was within  $\pm 0.5$  ms<sup>-1</sup>.

### **Density measurement**

The densities of solutions were measured by relative measurement method using a specific gravity bottle (25mL capacity) as described earlier [10]. At least five observations were taken and the differences in any two readings did not exceed  $\pm 0.02\%$ .

### **Theoretical Aspects**

The ultrasonic velocities (U) of the solutions at different molar concentrations (c) were fitted to an equation of the form [11-13],

$$U = U_0 + A'c + B'c^{3/2} + C'c^2 \quad (1)$$

where  $U_0$  is the ultrasonic velocity in pure solvent and  $A'$ ,  $B'$  and  $C'$  are the empirical constants.

The ultrasonic velocity through a liquid medium depends on the density (d) and degree of compactness, i.e., isentropic compressibility ( $K_s$ ) of the medium by the relation [11-13],

$$U = (K_s d)^{-1/2} \quad (2)$$

The values of  $K_s$  obtained from equation (2) were fitted to an equation of the form,

$$K_s = K_s^0 + A''c + B''c^{3/2} + C''c^2 \quad (3)$$

where  $A''$ ,  $B''$  and  $C''$  are the empirical constants and  $K_s^0$  is the isentropic molar compressibility at infinite dilution. The apparent molar isentropic compressibility,  $K_{s,\phi}$  has been computed from the relation [11-13],

$$K_{s,\phi} = 1000 K_s c^{-1} - K_s^0 d_0^{-1} (1000 c^{-1} d - M) \quad (4)$$

where M is the molecular mass of the solute,  $d_0$  and  $d$  are the densities of pure solvent and solution, respectively.

The  $K_{s,\phi}$  data obtained were fitted to Eqn. (5)

$$K_{s,\phi} = K_{s,\phi}^0 + A'' c^{1/2} + B'' c \quad (5)$$

to obtain  $K_{s,\phi}^0$ , the limiting apparent molar isentropic compressibility, where  $A''$  and  $B''$  are the empirical constants.

From the experimental values of ultrasonic velocity (U) and density (d) the following thermo-acoustical parameters have been calculated by the standard relations [14-16]

$$\text{Acoustic impedance (Z):} \quad Z = Ud \quad (6)$$

$$\text{Intermolecular free length (L}_f\text{):} \quad L_f = K_T \sqrt{K_s} \quad (7)$$

$$\text{Solvation number (S}_n\text{):} \quad S_n = n_1 n_2^{-1} (1 - K_s / K_s^0) \quad (8)$$

$$\text{Relative association (R}_A\text{):} \quad R_A = (d/d_0)(U_0/U)^{1/3} \quad (9)$$

Where  $K_T = \{(93.875 + 0.375T) \times 10^{-8}\}$  is the temperature dependent Jacobson's constant.  $n_1$  and  $n_2$  are the number of moles of solvent and solute, respectively.

## RESULTS AND DISCUSSION

The values of ultrasonic velocity (U) and density (d) of zinc chloride and magnesium chloride in various solvent systems (5, 10, and 15 wt% of ethanol + water) are given in Table 1-2.

**Table 1:** Values of density (d) for electrolytes in aqueous ethanol systems at different temperatures.

Conc. $\times 10^{-3}$ (mol.m <sup>-3</sup> )	d (Kg.m <sup>-3</sup> )							
	Zinc chloride				Magnesium chloride			
	298.15K	303.15K	308.15K	313.15K	298.15K	303.15K	308.15K	313.15K
5wt% ethanol								
0.000	987.91	986.24	984.25	981.91	987.91	986.24	984.25	981.91
0.006	988.12	986.45	984.36	982.02	990.23	988.60	986.88	985.01
0.008	988.54	986.87	984.78	982.44	990.65	989.02	987.30	985.43
0.009	988.76	987.08	984.99	982.57	990.82	989.19	987.47	985.60
0.010	988.97	987.29	985.20	982.87	990.99	989.36	987.64	985.77
0.030	990.86	988.98	986.88	984.55	992.54	991.08	989.41	987.49
0.050	993.17	991.50	989.41	987.07	994.02	992.55	990.88	988.97
0.080	996.96	995.29	993.20	990.86	996.54	995.08	993.41	991.49

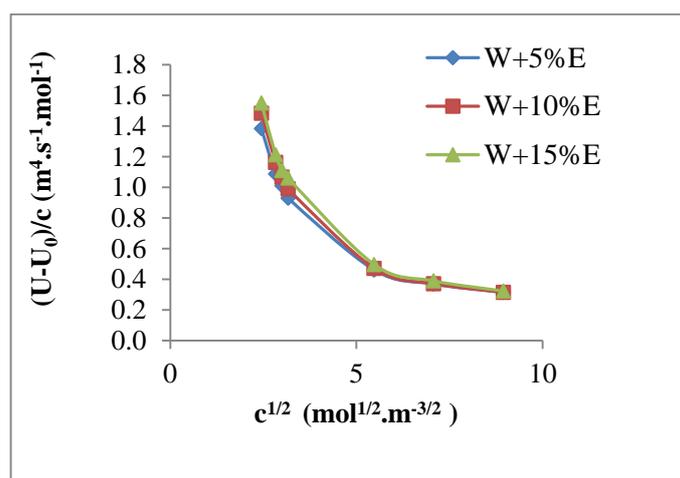
10wt% ethanol								
0.000	980.55	978.78	976.72	974.32	980.55	978.78	976.72	974.32
0.006	980.76	978.88	976.78	974.45	982.23	980.52	978.72	976.76
0.008	980.97	979.09	976.99	974.66	982.44	980.73	978.93	976.97
0.009	981.10	979.17	977.08	974.79	982.57	980.85	979.06	977.10
0.010	981.39	979.30	977.20	975.00	982.65	980.94	979.14	977.18
0.030	983.49	981.40	979.31	976.97	984.34	982.62	980.82	978.87
0.050	986.02	983.93	981.83	979.50	985.60	983.88	982.09	980.13
0.080	989.39	987.29	985.20	982.87	988.12	986.41	984.61	982.65
15wt% ethanol								
0.000	972.68	970.59	968.28	965.74	972.68	970.59	968.28	965.74
0.006	972.76	970.67	968.37	965.82	974.66	972.94	971.14	969.19
0.008	973.39	971.30	969.21	966.66	975.08	973.36	971.56	969.61
0.009	973.61	971.51	969.42	966.87	975.29	973.57	971.78	969.82
0.010	973.82	971.72	969.63	967.08	975.50	973.78	971.99	970.03
0.030	976.55	974.25	972.15	969.82	977.18	975.47	973.67	971.71
0.050	978.44	976.35	974.26	971.92	978.87	977.15	975.35	973.40
0.080	982.02	979.72	977.62	975.29	981.39	979.68	977.88	975.92

**Table 2:** Values of ultrasonic velocity (U) for electrolytes in aqueous ethanol systems at different temperatures.

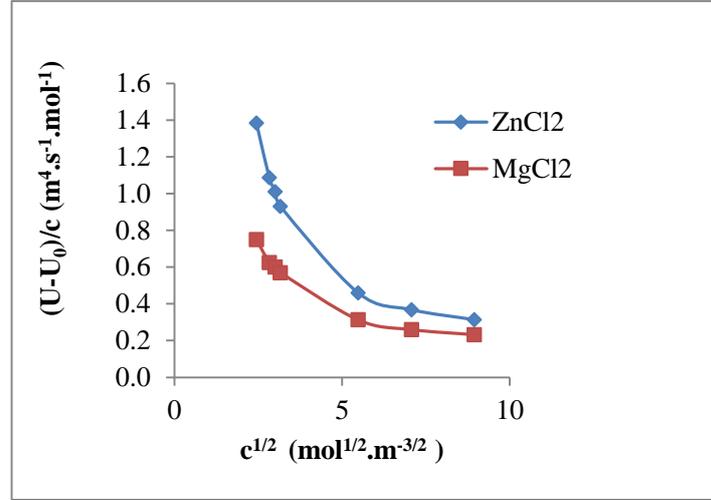
Conc. $\times 10^{-3}$ (mol.m <sup>-3</sup> )	U (m.s <sup>-1</sup> )							
	Zinc chloride				Magnesium chloride			
	298.15K	303.15K	308.15K	313.15K	298.15K	303.15K	308.15K	313.15K
5wt% ethanol								
0.000	1525.0	1534.5	1543.0	1550.3	1525.0	1534.5	1543.0	1550.3
0.006	1533.3	1543.2	1552.3	1560.4	1529.5	1538.9	1547.4	1554.7
0.008	1533.7	1543.6	1552.6	1560.9	1530.0	1539.3	1547.9	1555.3
0.009	1534.1	1543.9	1553.1	1561.3	1530.4	1539.8	1548.2	1555.6
0.010	1534.3	1544.3	1553.4	1561.6	1530.7	1540.1	1548.6	1555.9
0.030	1538.8	1548.7	1557.7	1565.9	1534.4	1543.8	1552.4	1559.7
0.050	1543.4	1553.2	1562.4	1570.6	1538.0	1547.5	1556.1	1563.3
0.080	1550.1	1560.0	1569.1	1577.2	1543.6	1553.0	1561.5	1568.9
10wt% ethanol								
0.000	1552.5	1559.0	1564.8	1569.8	1552.5	1559.0	1564.8	1569.8
0.006	1561.4	1568.8	1575.3	1580.8	1557.0	1563.6	1569.3	1574.4
0.008	1561.8	1569.1	1575.7	1581.2	1557.4	1563.8	1569.7	1574.7
0.009	1562.1	1569.5	1576.0	1581.5	1557.6	1564.1	1570.0	1574.9
0.010	1562.4	1569.8	1576.3	1581.7	1557.8	1564.2	1570.2	1575.2
0.030	1566.6	1574.0	1580.5	1586.1	1561.9	1568.4	1574.3	1579.2
0.050	1571.0	1578.3	1584.7	1590.2	1565.7	1572.4	1578.1	1583.1
0.080	1577.6	1585.0	1591.5	1596.9	1571.5	1578.0	1583.8	1588.7

15wt% ethanol								
0.000	1576.5	1579.5	1582.1	1584.2	1576.5	1579.5	1582.1	1584.2
0.006	1585.8	1590.1	1593.8	1596.8	1581.1	1584.0	1586.7	1588.8
0.008	1586.2	1590.5	1594.1	1597.2	1581.5	1584.5	1587.2	1589.2
0.009	1586.5	1590.9	1594.5	1597.5	1581.6	1584.6	1587.4	1589.5
0.010	1587.1	1591.4	1595.1	1598.0	1581.8	1584.9	1587.6	1589.7
0.030	1591.4	1595.8	1599.4	1602.4	1585.7	1588.6	1591.3	1593.5
0.050	1596.0	1600.3	1604.0	1607.1	1589.3	1592.3	1594.9	1596.9
0.080	1602.4	1606.8	1610.6	1613.5	1595.0	1598.1	1600.7	1602.8

It is observed that density values of all electrolytes in aqueous ethanol solution increase with the increase in concentration of solution as expected and decrease with rise of temperature due to thermal energy of the system which diminishes the intermolecular forces [17]. The ultrasonic velocity increases with increase in concentration of electrolytes as well as ethanol content in water. With rise in temperature, there occurs a structural rearrangement as a result of hydration [18] leading to a comparatively more order state and hence velocity increases with rise in temperature in all the systems. It also suggests that disruption of water structure is enhanced with the addition of ethanol and electrolyte. This is well agreeing with the earlier studies in various mixed solvent systems [16, 19]. In the present study, the values of ultrasonic velocity in aqueous ethanol solutions of the electrolytes are in the order:  $ZnCl_2 > MgCl_2$  at all temperatures. Hence, ultrasonic velocity of electrolytes tends to increase due to increase in their molecular mass. The values of  $U$  were fitted to Eq. (1) and the empirical constants  $A'$ ,  $B'$  and  $C'$  are given in Table 3. Typical plots of  $(U-U_0)/c$  vs  $c^{1/2}$  are shown in Fig. 1(a)-(b) over the concentration range at 298.15K.



**Fig. 1(a).**Plot of  $U-U_0/c$  versus  $c^{1/2}$  for  $ZnCl_2$  in different aqueous ethanol solutions at 298.15K



**Fig. 1(b).**Plot of  $U-U_0/c$  versus  $c^{1/2}$  for different electrolytes in 5wt% ethanol + water at 298.15K

It is observed that, the acoustic impedance ( $Z$ ), which determines the elastic property (i.e., the bulk modulus of elasticity) of the medium increases with increase in ethanol content in water and concentration of electrolytes in all the solvent systems [16]. This is well agreeing with the theoretical requirement as density and ultrasonic velocity increase with increase in the concentration of electrolytes. The increase in  $Z$  values with concentration of electrolytes at all temperatures may be attributed to the effective solute-solvent interactions. The  $Z$  values also increase with increase in temperature due to structural rearrangement as a result of solvation leading to a comparatively more ordered state [20]. Since  $Z$  is a function of elastic property of the medium and depends on the structural changes of the solution, the higher  $Z$  values in aqueous ethanol solution as compared to that in water [5] suggest the solution medium in each case starts gaining its elastic behaviour.  $Z$  increases with increase in the concentration of solution, the ethanol content in water and temperature, as ultrasonic velocity increases.

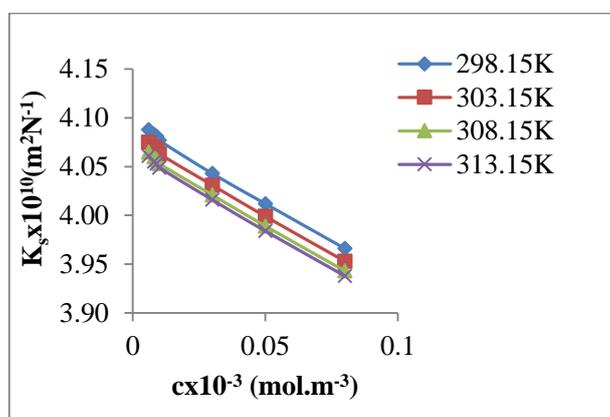
**Table 3:** Values of empirical constants  $A'$ ,  $B'$ ,  $C'$  of equation(1),  $A''$ ,  $B''$ ,  $C''$  of equation(3),  $A'''$ ,  $B'''$  and  $K_{s,\phi}^0$  (m<sup>3</sup>mol<sup>-1</sup>Pa<sup>-1</sup>) of equation(5) for electrolytes in aqueous ethanol systems at different temperatures.

Constants	Zinc chloride				Magnesium chloride			
	298.15K	303.15K	308.15K	313.15K	298.15K	303.15K	308.15K	313.15K
5wt% ethanol								
$10A'$	23.7±2.4	24.9±2.5	26.8±2.7	29.4±2.8	12.4±0.8	12.0±0.8	12.0±0.8	12.2±0.7
$-10^2B'$	54.2±10.2	57.4±10.8	62.1±11.7	68.6±12.2	26.0±3.4	24.8±3.5	24.6±3.5	25.1±3.1
$10^3C'$	35.3±9.2	37.4±9.6	40.5±10.4	44.6±10.9	16.5±3.0	15.8±3.2	15.6±3.1	15.9±2.8
$-10^{13}A''$	13.5±1.1	14.0±1.1	14.7±1.2	15.9±1.3	10.0±0.5	9.7±0.5	9.9±0.6	10.5±0.6

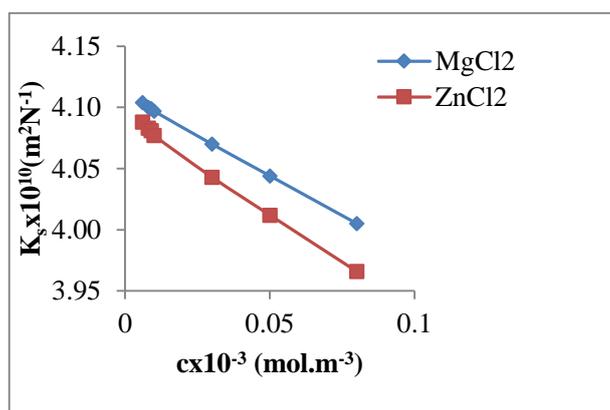
$10^{14}B''$	29.5±4.7	30.9±4.9	32.7±5.3	35.8±5.6	21.1±2.3	20.1±2.4	20.6±2.5	22.3±2.6
$-10^{15}C''$	19.1±4.2	20.1±4.4	21.3±4.7	23.2±5.0	13.3±2.0	12.6±2.1	12.9±2.2	14.1±2.3
$-10^{10}K_{s,\phi}^0$	13.5±0.8	14.1±0.9	14.6±1.0	15.8±1.1	13.0±0.6	12.6±0.6	13.2±0.7	14.4±0.8
$10^{11}A'''$	28.2±3.6	29.9±3.9	31.4±4.3	34.4±4.6	27.4±2.7	26.3±2.7	27.6±3.1	30.9±3.5
$-10^{12}B'''$	18.2±3.3	19.4±3.5	20.4±3.8	22.3±4.1	17.3±2.4	16.5±2.5	17.3±2.8	19.5±3.1
10wt% ethanol								
$10A'$	25.7±2.6	28.4±2.9	30.7±3.1	32.2±3.4	12.1±1.2	12.2±1.4	12.1±1.1	12.3±1.3
$-10^2B'$	59.7±11.2	66.6±12.7	72.5±13.6	76.1±14.6	25.6±5.0	25.9±6.2	25.3±4.6	26.2±5.5
$10^3C'$	39.0±10.0	43.5±11.3	47.3±12.1	49.7±13.1	16.6±4.5	16.9±5.5	16.3±4.1	17.0±5.0
$-10^{13}A''$	13.8±1.3	14.9±1.5	15.9±1.6	16.7±1.7	8.5±0.8	8.6±0.9	8.8±0.7	9.5±0.9
$10^{14}B''$	30.6±5.6	33.9±6.5	36.5±6.9	38.3±7.2	17.9±3.3	18.1±3.9	18.5±3.2	20.3±4.0
$-10^{15}C''$	19.9±5.0	22.1±5.8	23.8±6.1	25.0±6.5	11.5±2.9	11.7±3.5	11.9±2.9	13.1±3.5
$-10^{10}K_{s,\phi}^0$	13.6±1.2	14.7±1.4	15.6±1.5	16.5±1.6	10.5±0.9	10.6±1.0	11.2±0.9	12.4±1.2
$10^{11}A'''$	29.0±5.2	32.1±6.2	34.5±6.6	36.7±6.8	21.9±3.8	22.3±4.5	23.6±4.0	26.8±5.0
$-10^{12}B'''$	18.8±4.7	21.0±5.6	22.6±5.9	23.9±6.1	14.1±3.4	14.4±4.0	15.1±3.5	17.3±4.5
15wt% ethanol								
$10A'$	26.7±2.6	30.8±3.0	34.1±3.5	36.9±3.8	12.6±1.3	12.4±1.1	12.8±1.0	12.7±1.1
$-10^2B'$	61.5±11.4	71.6±13.1	80.2±15.1	87.4±16.6	27.1±5.5	26.7±4.6	27.6±4.5	27.2±4.6
$10^3C'$	39.8±10.2	46.4±11.7	52.1±13.5	56.8±14.9	17.7±5.0	17.4±4.1	17.9±4.0	17.6±4.1
$-10^{13}A''$	13.7±1.0	15.7±1.2	17.5±1.3	18.8±1.5	8.9±0.7	9.3±0.6	10.2±0.7	10.9±0.8
$10^{14}B''$	29.5±4.4	34.7±5.3	39.1±5.8	42.4±6.6	18.9±2.9	19.8±2.7	21.9±2.9	23.7±3.4
$-10^{15}C''$	18.7±3.9	22.1±4.7	25.0±5.2	27.1±5.9	12.1±2.6	12.7±2.4	14.0±2.6	15.2±3.0
$-10^{10}K_{s,\phi}^0$	13.4±0.7	15.5±0.9	17.3±0.9	18.6±1.1	11.3±0.7	12.2±0.7	13.7±0.8	15.2±1.0
$10^{11}A'''$	26.8±2.8	32.2±3.7	36.7±3.9	39.7±4.6	23.6±3.0	25.7±3.0	29.6±3.6	33.3±4.4
$-10^{12}B'''$	16.7±2.5	20.2±3.3	23.0±3.4	24.9±4.1	14.9±2.7	16.3±2.7	18.8±3.2	21.3±3.9

The values of isentropic compressibility,  $K_s$  as calculated by Eq. (2) were fitted to Eq. (3) and the empirical constants  $A''$ ,  $B''$  and  $C''$  are given in Table 3. From Fig. 2(a)-(b), it is observed that the isentropic compressibility ( $K_s$ ) decreases as the concentration of electrolytes increases and also with increase in ethanol content in water at all temperatures. The decrease in  $K_s$  with concentration is due to the occupation of interstitial spaces in water by the solute molecules making the medium less compressible, i.e., providing greater electrostriction. This is possible due to electrostatic field of ion causing compactness of the medium due to ion-solvent interaction. Further, the decrease in  $K_s$  with increase in ethanol content in water may be due to filling of the interstitial spaces in water by organic co-solvent molecules thereby making a tight structure. Hence, isentropic compressibility ( $K_s$ ) describes the molecular arrangement in the solution medium. The decrease in the value of  $K_s$  with increase in temperature in all the solvent systems may be due to fact that the compression of the medium becomes more prominent resulting in decrease in the  $K_s$ .

values [16]. The  $K_s$  values of electrolytes in all solvent systems are in the order:  $ZnCl_2 < MgCl_2$ . Typical plots of  $K_s$  versus  $c$  are shown in Fig. 2(a)-(b).



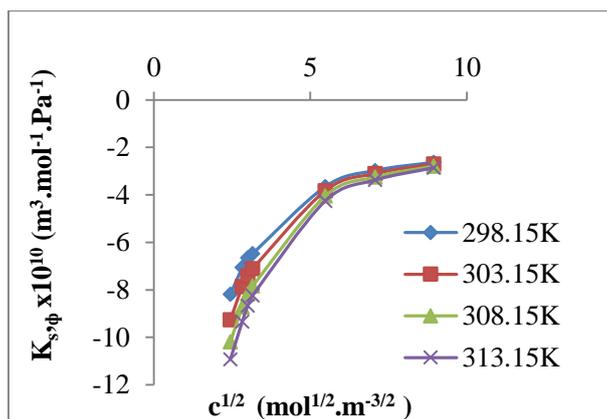
**Fig. 2(a).**Plot of  $K_s$  versus  $c$  for  $ZnCl_2$  in 15wt% ethanol + water at different temperatures



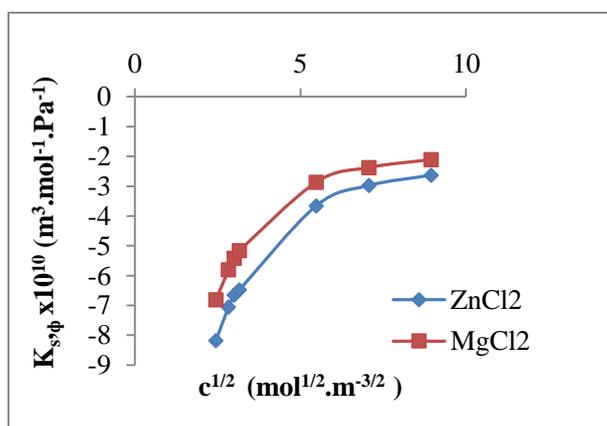
**Fig. 2(b).**Plot of  $K_s$  versus  $c$  for different electrolytes in 15wt% ethanol + water at 298.15K

The values of apparent molar isentropic compressibility,  $K_{s,\phi}$  computed by means of Eq. (4) were fitted into Eq. (5) to obtain  $K_{s,\phi}^0$ ,  $A'''$  and  $B'''$  and are given in Table 3. The values of  $K_{s,\phi}$  and  $K_{s,\phi}^0$  are negative over the entire range of concentrations and temperatures. The increasing values of  $K_{s,\phi}$  with concentration reveal that there is less strengthening in solute-solvent interactions but are in reverse trend with rise in temperature for all the systems. The negative values may be explained by means of two different phenomena (i) electrostriction and (ii) hydrophobic solvation. The negative values of  $K_{s,\phi}$  indicate the loss of compressibility of the surrounding solvent molecules due to strong electrostatic forces in the vicinity of the solute causing electrostrictive solvation of the ions. So a tight solvation layer is formed around the

ion in the ternary mixtures that are less compressed by the application of pressure. Such negative values of  $K_{s,\phi}^0$  for all the systems reinforce the earlier discussion regarding the existence of solute-solvent interactions. As observed, the values of  $K_{s,\phi}^0$  of electrolytes follow the order  $K_{s,\phi}^0$  (ZnCl<sub>2</sub>) <  $K_{s,\phi}^0$  (MgCl<sub>2</sub>) in all the solvent systems. Typical plots of  $K_{s,\phi}$  versus  $c^{1/2}$  are shown in Fig. 3(a)-(b).



**Fig. 3(a).**Plot of  $K_{s,\phi}$  versus  $c^{1/2}$  for ZnCl<sub>2</sub> in 15wt% ethanol + water at different temperatures

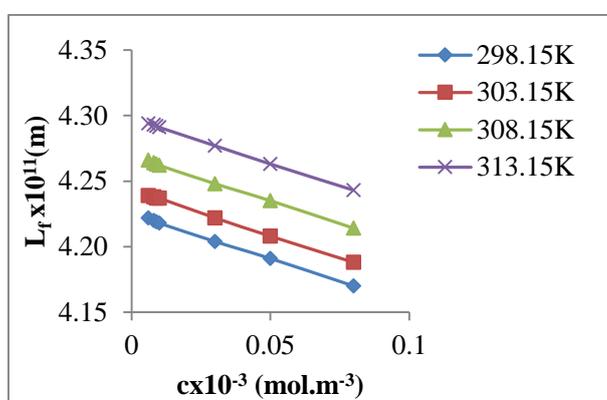


**Fig. 3(b).**Plot of  $K_{s,\phi}$  versus  $c^{1/2}$  for different electrolytes in 15wt% ethanol + water at 298.15K

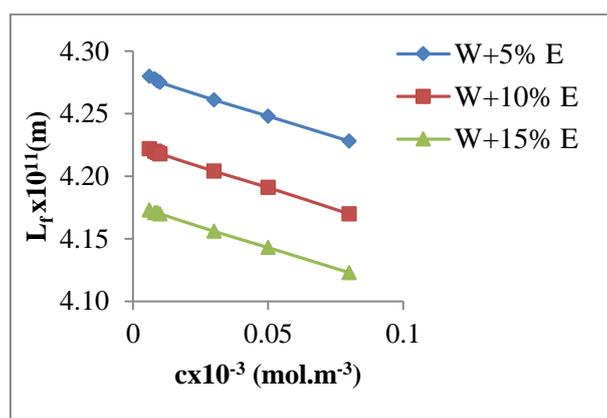
A perusal of Fig. 4(a)-(b) shows that the intermolecular free length ( $L_f$ ) decreases with increase in concentration and increase in ethanol content in water at all temperatures. The decrease of  $L_f$  with increase of concentration indicates that there is a significant interaction between solute and solvent suggesting the structure promoting behaviour on addition of electrolytes [21]. Further, the decrease of  $L_f$  with increase of ethanol

content in water may be due to the effective solvent-solvent interaction in the solution and decrease in isentropic compressibility, i.e.,  $L_f \propto \sqrt{K_s}$ .

The increase of temperature increases the thermal energy of the system and decreases the intermolecular forces thereby causing an expansion in volume and decrease in density, and hence, free length increases. Therefore, intermolecular free length increases with increase in temperature. The intermolecular free length of one electrolyte in aqueous ethanol solution is less than the other is due to the less isentropic compressibility value of former than the latter. Typical plots of  $L_f$  versus  $c$  are shown in Fig. 4(a)-(b).



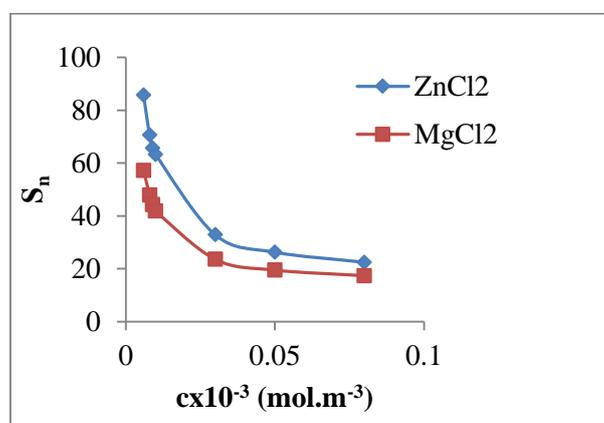
**Fig. 4(a).**Plot of  $L_f$  versus  $c$  for  $\text{MgCl}_2$  in 10wt% ethanol + water at different temperatures



**Fig. 4(b).**Plot of  $L_f$  versus  $c$  for  $\text{MgCl}_2$  in different aqueous ethanol solution at 298.15K

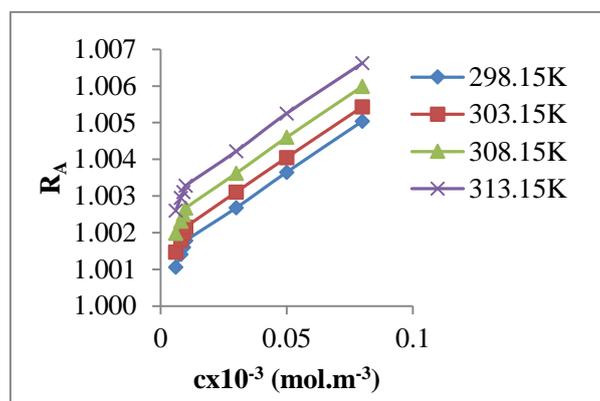
The values of solvation number ( $S_n$ ) are positive for all the electrolytes in all the systems indicating the appreciable solvation of solute. It supports to the structure promoting nature as well as the presence of dipolar interaction between the solute and

water molecules [22]. The values of  $S_n$  are found to decrease with increase in concentration of electrolytes and increase with rise in temperature in all the three systems. The decrease of  $S_n$  with concentration indicates greater solute-solute interactions leading to the reduction in the electrostriction. With rise in temperature, compressibility of the solution decreases as a result of which the solute will gain mobility and there is more probability of containing the solvent molecules which enhance the solute-solvent interaction. Hence,  $S_n$  value increases with temperature. The  $S_n$  values of metal chlorides are comparatively more in aqueous-ethanol system than in water system [5]. So a thick and/or hard solvation layer is formed around the ions. As seen, the values of  $S_n$  are in the order:  $ZnCl_2 > MgCl_2$ . Typical plots of  $S_n$  versus  $c$  are shown in Fig. 5.



**Fig. 5.** Plot of  $S_n$  versus  $c$  for different electrolytes in 15wt% ethanol + water at 298.15K

The relative association ( $R_A$ ) is another important property [23] of the electrolyte solution which is a function of ultrasonic velocity. It is influenced by two factors: (i) breaking up of the associated solvent molecules on addition of the solute and (ii) the solvation of solute molecules. The former leads to a decrease and the latter to an increase in relative association. In the present study,  $R_A$  increases with increase in concentration suggesting the solvation of the metal chlorides predominating over the breaking-up of the solvent structure. As observed from Fig. 6,  $R_A$  values for the electrolytes in aqueous ethanol solvent systems increase linearly with concentration at all experimental temperatures. With rise in temperature,  $R_A$  increases in magnesium chloride but reverse in the case for zinc chloride in all the solvent systems. Typical plots of  $R_A$  versus  $c$  are shown in Fig. 6.



**Fig. 6.** Plot of  $R_A$  versus  $c$  for  $\text{MgCl}_2$  in 15wt% ethanol + water at different temperatures

## CONCLUSION

The results of the present investigation reveal that solute-solute, solute-solvent and solvent-solvent interactions play a vital role for explaining the different thermo-acoustical properties of strong electrolytes in different aqueous ethanol systems at four different temperatures 298.15K, 303.15K, 308.15K and 313.15K. These interactions result in attractive forces which promote the structure forming tendency. The decrease in the value of isentropic compressibility with increase in concentration may be due to the occupation of the interstitial spaces of water by the solute molecules thereby making the medium less compressible. The increase in  $R_A$  values with increase in concentration of solute indicates that, solute-solvent interaction dominates over solute-solute interaction in all the solutions. The variation of  $S_n$  values predicts the degree of hard electrostrictive solvation, i.e., it represents the structural effect of the electrolytes on the solvent in the solution.

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