



**DENSITIES AND SPEEDS OF SOUND OF CaCl₂, MgCl₂, BaCl₂ IN AQUEOUS
2-METHOXY ETHANOL AT 303K**

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ABSTRACT: Densities(ρ), Viscosities(η) and ultrasonic speeds(U) of the electrolytes Calcium chloride(CaCl_2), Magnesium Chloride(MgCl_2) and Barium Chloride(BaCl_2) in 5,15,25% of aqueous 2-Methoxy ethanol at 303K were measured over the entire composition range. From the experimental data, the internal pressure (π_i), molar free volume (V_f), solvation number (S_n) and Viscosity B coefficients were calculated. The properties of the electrolytes are correlated with concentration of 2-Methoxy ethanol using the above parameters, which in turn are employed to predict the properties of electrolytes with good accuracy and are used to investigate the ion-ion and ion-solvent interactions present in the system.

Keywords: Ternary system, Internal pressure, Free volume, Solvation number, Jones-Dole Viscosity B coefficient, Molecular interactions.

INTRODUCTION

Ultrasonic study (Kiyohara O et al 1978; Johnson I et al 2001) is a useful technique for understanding the physico-chemical properties of liquids. Ultrasonic measurements are extensively used to study the molecular interactions in pure liquids, liquid mixtures and ionic interactions in single and mixed salt solutions (Ranga Nayakulu, et al 2005) and they provide significant information on the arrangement of matter in electrolytic solutions. It is desirable that any discussion and interpretation of thermodynamic properties of electrolytes is related to a single ion as ions are the species actually present in an electrolyte solution. The solvent properties like the viscosity have also been taken into account in determining the extent of ionic association and the solute-solvent interactions, which enabled to interpret the unique structure of the solvent. Ion-ion or ion-solvent interactions or the behaviour of electrolytes in solution can be informative depending on the transport properties of the electrolytes in solutions. Studies on the apparent and partial molar volumes of electrolytes and the dependence of viscosity on concentration of solutes have been employed as function of studying ion-ion and ion-solvent interactions. It has been found that the addition of electrolyte could either break or make the structure of a liquid. Because a liquid's viscosity depends on the intermolecular forces, the structural aspects of the liquid can be inferred from the viscosity of solutions at different concentrations and temperatures. The viscosity of electrolyte solutions is another important parameter to study their solution behaviour. The temperature and concentration dependence of viscosity of aqueous electrolyte solutions help to understand ion-solvent (solvation) and long-range ion-ion electrostatic interactions. The Jones-Dole viscosity B coefficient is important in the description and understanding of ionic processes, for example, solvation effects of cations and anions (Abdul Wahab et al 2006).

Experimental

Analytical grade Calcium Chloride, Magnesium Chloride and Barium Chloride were obtained from SD Fine Chemicals Ltd., India. These salts were used without any further purification, but they were dried in a vacuum desiccator before use. The velocity of sound waves was found using an ultrasonic interferometer (Mittal Enterprises, New Delhi) at a fixed frequency of 3MHz with an accuracy of $\pm 2\text{ms}^{-1}$.

The density was measured using pycnometer of capacity 5ml and gave an estimated reproducibility of 0.0001gcm⁻³. Viscosity measurements were carried out with an Oswald's viscometer having time of efflux 0.01s and the accuracy was found to be $\pm 3 \times 10^{-6}$ Nm⁻²s. Uncertainty in the measured viscosities was ± 0.005 cp. Flow time measurements were performed using an automatic viscosity (time) measurement unit with a resolution of ± 0.1 second. The temperature around the viscometer was maintained within 0.1K in an electronically controlled thermostatic water bath.

Theory:

Internal pressure (π_i):

Internal pressure (Geetha D et al 2007) is calculated using the relation

$$\pi_i = bRT \left[\frac{K\eta}{U} \right]^{1/2} \left[\frac{\rho^{2/3}}{M^{7/6}} \right] \quad (1)$$

Where T- absolute temperature

η - shear velocity

U- Ultrasonic velocity

M- Effective molecular weight

b- cubic packing factor, b = 2 for liquids

R- Gas constant

ρ - density

Free volume (V_f):

This is the free space between the molecules for movement, denoted as V_f and is given by (Hemalatha B et al 2009).

$$V_f = \left[\frac{M_{eff} U}{K\eta} \right]^{3/2} \quad (2)$$

Where M_{eff} - Effective molecular weight

K-dimensionless constant = 4.28×10^9 which is independent of the nature of liquids and temperature.

Solvation number (S_n):

The solvation number has been calculated using the following equation (Raju K et al 2002)

$$S_n = \frac{M_2}{M_1} \left[1 - \frac{\beta}{\beta_0} \right] \left[\frac{100 - x}{x} \right] \quad (3)$$

Where M_1 and M_2 are the molecular weights of the solvent and the solution respectively. β_0 and β are the adiabatic compressibilities of the solvent and solution respectively and x is the number of grams of salt in 100 gram of the solution.

A, B Coefficients:

The viscosity data have been analyzed by using the Jones-Dole equation .

$$\frac{\eta}{\eta_0} = 1 + Am^{1/2} + Bm \quad (4)$$

Where η and η_0 are the viscosities of the solute and solvent respectively. A is a known as Falkenhagen coefficient and B is Jones-Dole coefficient. Coefficient A accounts for the solute-solute interactions and B is a measure of structural modifications induced by the solute-solvent interactions (Bai TC et al., 2003; Feakins D et al 1974).

Relative association (R_a):

The relative association is calculated using the relation (Azhagiri S et al 1999):

$$R_a = \frac{\rho_0 U_0}{\rho U} \quad (5)$$


Where,

ρ & ρ_0 are the densities of the solution and solvent

U and U_0 are the ultrasonic velocities of the solution and solvent respectively.

RESULTS AND DISCUSSION

The experimental values of the density, viscosity and ultrasonic velocity for CaCl_2 , MgCl_2 and BaCl_2 in 2-Methoxy ethanol-water mixtures at 303K are given in Table 1. The calculated values of free volume, internal pressure and solvation number for the three ternary systems at different molalities at 303K are listed in Table 2. The values of viscosity coefficient are given in Table 3. Table 1 reveals that the density and viscosity increases with increase in molality as well as with increase in concentration of 2-Methoxy ethanol for all the systems. For these electrolytic solutions, the ultrasonic velocity increases with increasing molality and increase in concentration of 2-Methoxy ethanol.

Table 1: Values of Density (ρ), Viscosity (η) and Velocity (U) for Calcium chloride, Magnesium Chloride and Barium Chloride at 303K

Molality of the Salt	$\rho/(\text{Kg m}^{-3})$	$\eta/(x 10^{-3} \text{ NSm}^{-2})$	$U/(\text{ms}^{-1})$	Molality of the Salt	$\rho/(\text{Kg m}^{-3})$	$\eta/(x 10^{-3} \text{ NSm}^{-2})$	$U/(\text{ms}^{-1})$	Molality of the Salt	$\rho/(\text{Kg m}^{-3})$	$\eta/(x 10^{-3} \text{ NSm}^{-2})$	$U/(\text{ms}^{-1})$
Calcium Chloride				Magnesium Chloride				Barium Chloride			
2-Methoxy ethanol-water (5:95%)				2-Methoxy ethanol-water (5:95%)				2-Methoxy ethanol-water (5:95%)			
0.0000	919.89	0.7944	1543.0	0.0000	919.89	0.7944	1543.0	0.0000	919.89	0.7944	1543.0
0.0499	944.91	0.8106	1549.4	0.0493	945.26	0.8448	1550.2	0.0500	952.74	0.8476	1552.8
0.1002	954.19	0.8332	1554.4	0.1003	958.60	0.8616	1555.6	0.1003	973.85	0.8843	1563.2
0.1508	963.85	0.8702	1562.1	0.1502	964.30	0.8810	1555.6	0.1500	978.78	0.9196	1571.8
0.2011	968.12	0.8812	1567.1	0.2013	968.36	0.9052	1574.0	0.1999	985.01	0.9385	1576.3
0.2499	973.74	0.8915	1573.8	0.2505	976.93	0.9180	1579.9	0.2498	992.11	0.9854	1580.4
2-Methoxy ethanol-water (15:85%)				2-Methoxy ethanol-water (15:85%)				2-Methoxy ethanol-water (15:85%)			
0.0000	952.70	1.0572	1591.3	0.0000	952.70	1.0572	1591.3	0.0000	952.70	1.0572	1591.3
0.0496	960.11	1.0770	1597.8	0.0500	962.90	1.0977	1603.8	0.0500	975.42	1.0986	1611.9
0.0997	964.79	1.1027	1602.3	0.1007	966.90	1.1253	161.04	0.0999	978.23	0.1395	1618.5
0.1499	967.97	1.1310	1609.8	0.1502	968.31	1.1549	1616.1	0.1502	981.68	1.1706	1622.2
0.2002	971.91	1.1587	1616.0	0.1999	972.85	1.1824	1620.2	0.1999	989.10	1.2077	1627.2
0.2501	976.23	1.1774	1620.4	0.2503	976.97	1.2062	1626.0	0.2498	993.29	1.2462	1634.5
2-Methoxy ethanol-water (25:75%)				2-Methoxy ethanol-water (25:75%)				2-Methoxy ethanol-water (25:75%)			
0.0000	959.50	1.3930	1634.1	0.0000	959.50	1.3930	1634.1	0.0000	959.50	1.3930	1634.1
0.0497	966.35	1.4246	1636.6	0.0498	968.15	1.4628	1635.8	0.0498	978.86	1.4767	1639.5
0.0998	970.14	1.4851	1638.8	0.0998	973.00	1.5056	1640.2	0.1005	981.15	1.5232	1649.2
0.1501	974.39	1.5197	1639.1	0.1501	975.93	1.5554	1640.2	0.1501	984.77	1.5682	1654.3
0.1999	978.54	1.5555	1641.0	0.2008	979.57	0.6041	1650.7	0.2001	991.22	1.6464	1660.3
0.2495	982.43	1.5857	1643.7	0.2502	982.90	1.6604	1657.0	0.2499	996.16	1.6861	1666.9

Table 2: Values of free volume(V_f), Internal pressure (π_i) Solvation number(S_n) and Relative association (R_a) for Calcium chloride ,Magnesium Chloride and Barium Chloride at 303K

Molality of the Salt	$V_f / (x10^7 m^3 mol^{-1})$	$\pi_i / (x10^6 Nm^{-2})$	S_n	R_a	Molality of the Salt	$V_f / (x10^7 m^3 mol^{-1})$	$\pi_i / (x10^6 Nm^{-2})$	S_n	R_a	Molality of the Salt	$V_f / (x10^7 m^3 mol^{-1})$	$\pi_i / (x10^6 Nm^{-2})$	S_n	R_a
Calcium Chloride					Magnesium Chloride					Barium Chloride				
2-Methoxy ethanol-water (5:95%)					2-Methoxy ethanol-water (5:95%)					2-Methoxy ethanol-water (5:95%)				
0.0000	2.48	2317.56	-	-	0.0000	2.48	2317.56	-	-	0.0000	2.48	2317.56	-	-
0.0499	2.44	2360.75	28.76	1.0257	0.0493	2.31	2402.17	29.80	1.0259	0.0500	2.31	2411.11	38.68	1.0335
0.1002	2.38	2387.48	20.69	1.0347	0.1003	2.28	2418.71	22.97	1.0392	0.1003	2.22	2459.01	32.62	1.0540
0.1508	2.27	2432.39	18.83	1.0429	0.1502	2.26	2420.33	20.65	1.0426	0.1500	2.15	2477.13	25.42	1.0574
0.2011	2.26	2433.19	16.08	1.0478	0.2013	2.22	2430.14	17.54	1.0457	0.1999	2.13	2478.11	20.99	1.0631
0.2499	2.25	2434.05	14.87	1.0515	0.2505	2.21	2432.02	16.23	1.0536	0.2498	2.02	2516.70	18.31	1.0699
2-Methoxy ethanol-water (15:85%)					2-Methoxy ethanol-water (15:85%)					2-Methoxy ethanol-water (15:85%)				
0.0000	1.91	2447.10	-	-	0.0000	1.91	2447.10	-	-	0.0000	1.91	2447.10	-	-
0.0496	1.89	2459.48	10.57	1.0065	0.0500	1.86	2475.09	17.34	1.0081	0.0500	1.87	2485.37	32.08	1.0194
0.0997	1.85	2475.09	8.66	1.0104	0.1007	1.82	2481.60	12.54	0.0109	0.0999	1.84	2488.78	19.28	1.0210
0.1499	1.81	2488.22	8.42	1.0121	0.1502	1.79	2486.08	10.05	1.0112	0.1502	1.78	2503.73	14.33	1.0238
0.2002	1.77	2502.46	8.11	1.0149	0.1999	1.75	2494.42	8.96	1.0150	0.1999	1.73	2520.30	12.65	1.0305
0.2501	1.75	2508.68	7.65	1.0185	0.2503	1.73	2496.28	8.50	0.0181	0.2498	1.69	2530.27	11.52	1.0333
2-Methoxy ethanol-water (25:75%)					2-Methoxy ethanol-water (25:75%)					2-Methoxy ethanol-water (25:75%)				
0.0000	1.51	2507.11	0.00	-	-	1.51	2507.11	-	-	0.0000	1.51	2507.11	-	-
0.0497	1.47	2527.12	5.67	1.0062	0.0498	1.42	2555.99	6.06	1.0086	0.0498	1.41	2578.26	14.63	1.0190
0.0998	1.40	2566.71	4.62	1.0101	0.0998	1.39	2571.69	5.86	1.0128	0.1005	1.38	2581.89	10.98	1.0194
0.1501	1.37	2585.29	3.91	1.0145	0.1501	1.35	2587.00	5.87	1.0145	0.1501	1.35	2589.65	8.94	1.0221
0.1999	1.33	2603.01	3.79	1.0184	0.2008	1.31	2604.17	5.43	1.0175	0.2001	1.28	2627.31	8.36	1.0275
0.2495	1.31	2614.56	3.71	0.0219	0.2502	1.26	2623.93	4.52	1.0217	0.2499	1.26	2630.02	7.88	1.0313

Free volume and Internal pressure

It is seen from the Table II that the free volume decreases with increasing molality of salt and also with increasing concentration of 2-Methoxy ethanol whereas, a reverse trend is observed in the case of internal pressure where it increases with increasing molal concentration. With increase in salt concentration, a large number of solute molecules go into the bulk solution and the ionic nature of the solute molecules puts them into closer and closer packing as their number increases, resulting in a decrease in free volume, which suggests that there is a significant interaction between the ions and the solvent molecules. Thus, the increase in internal pressure and decrease in free volume suggest the existence of ion- solvent interactions due to which structural arrangement is considerably affected. The decrease in the value of L_f with increase in ultrasonic velocity indicates that there is significant interaction between the molecules of the two liquids (Thiyagarajan R et al 2007). The variations in π_i may be attributed to two reasons:

- Enormous number of component molecules is formed due to splitting of a major component or
- The enlargement of existing molecules due to the added component.

The contribution due to first reason will make the net inward chaos to be more and hence the π_i increases. Also the enlargement of the molecules reduces the available volume between the components and it weakens the surface layer that is reflected as the increase of π_i (Thiyagarajan R et al 2007).

Table 3: Values of A and B parameter of Jones-Dole equation of the three systems

Temperature 303 K		
2-Methoxy ethanol % w/w	A (dm ^{3/2} mol ⁻¹)	B (dm ³ mol ⁻¹)
Calcium Chloride		
5	-0.0292	0.5998
15	-0.0324	0.5363
25	-0.0108	0.6074
Magnesium Chloride		
5	0.2442	0.1253
15	0.0769	0.4131
25	0.0857	0.5733
Barium Chloride		
5	0.1660	0.5983
15	0.0171	0.6734
25	0.1210	0.5628

The primary effect of dissolving an electrolyte is to lower the compressibility of solvent molecules. This lowering of compressibility results in an increase of the ultrasonic velocity and hence π_i values increases with concentration. As the molality of the electrolyte increases, ion-solvent interaction increases resulting in an overall increase in π_i . The value of π_i is a measure of interaction as observed by Ali A et al 1994.

Viscosity B coefficient and Solvation number:

The viscosity measurements are carried out in order to elucidate the order of molecular interactions. The viscosity measurements depend on molecular interactions as well as size, shape and packing of molecules between unlike molecules for which the molecular interaction decreases. Mahendra Nath Roy et al (2001) reported the viscosity B-coefficients of some electrolytes in TetraHydroFuran (THF)+ water mixture at different temperatures. Combined with concentration dependence of apparent molar volume data, M.A.Motin (2004) obtained a more complete analysis of ion-solvent interactions in the solvent.

In order to get more information about these electrolytes, the role of viscosity B coefficient has also been obtained. B coefficient, which is known for measure of order or disorder introduced by the solute in the solvent. It is also a measure of solute-solvent interaction. Since A is a measure of ionic interaction, it is evident that the negative values of A is the indication of weak ion-ion interaction whereas, the positive values of B indicates the strong solute-solvent interaction (Kannappan A N et al 2004). The B coefficients for Calcium chloride, Magnesium chloride and Barium chloride exhibit positive values and increase with increasing molalities of 2-Methoxy ethanol. This confirms that all these electrolytes behave as structure-makers. Moreover, the magnitude of B values is higher in 15 weight% of Barium chloride, which indicates that Barium chloride is acting as an effective structure-maker over the other two electrolytes and the structure making tendencies are in the order $\text{BaCl}_2 > \text{CaCl}_2 > \text{MgCl}_2$.

The dominance of intermolecular attractions between electrolyte molecules over ion-solvent interactions is due to the insignificant variation in solvation number (Kannappan A N et al 2004). The solvation number computed for all the three electrolytes exhibits positive values at different molalities.

The values of S_n decrease with increase in molality of the salt. It indicates the increased ion-ion interaction (Ali A et al 1999). The viscosity B coefficients provide information about the solvation of the solutes and their effects on the structure of the solvent in the near environment of the solute molecules. The viscosity B coefficient originally introduces as an empirical term has been found to depend upon the solute-solvent interactions and on the relative size of the solute and solvent molecules. They are positive indicating the strong solute-solvent interactions in addition to the structure making ability of the solute.

Relative association

Relative association is influenced by two factors

- Breaking of the solvent molecules on addition of the solute and
- Solvation of ions that is simultaneously present.

The increase in R_a with increasing electrolytic concentration indicates the association between the solute and solvent molecules. In the present investigation, R_a increases with concentration as observed by Jahagirdar DV et al 2000. Hence, the dominance of intermolecular attraction between electrolytic molecules over ion-solvent is due to the insufficient variation in solvation number

CONCLUSION

This study reveals that both ion-solvent and ion-ion interactions are present in the all the systems but in varying degrees. The ion- solvent interactions are much pronounced in lower content of 2-Methoxy ethanol as well as at lower molality of the salt. The ion-ion interactions are very apparent in higher content of 2- Methoxy ethanol and at higher molal concentration of the salt.

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