ULTRASONIC STUDIES ON SOME ELECTROLYTES IN N,N, DIMETHYLFORMAMIDE +WATER MIXTURES AT 303K

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ABSTRACT

The study of interaction between solute-solute and solute-solvent interaction of sodium acetate (CH_3COONa), sodium propionate (C_2H_5COONa) and sodium salicylate ($C_7H_5O_3Na$) in 10, 20, 30, and 40% of N,N, Dimethylformamaide-water solvents by measuring ultrasonic velocity(U), density(ρ) and viscosity(η) in different concentration of solute in 10% to 40% of solvents has done at 303K. In the present investigation, different acoustical parameters such as free volume (V_f), internal pressure (π_i), relative association (R_a) Falkenhagen coefficient A, Jone-Dole coefficient B have been analyzed. The molecular association such as ion-ion, ion-solvent, solute-solvent, solute-solute etc., are identified and critically discussed in terms of the structure-making and structure-breaking behavior of electrolyte in the solvent mixture.

Keywords: free volume, internal pressure, Jone-Dole co-efficient, molecular interaction, solute-solvent interaction.

INTRODUCTION

Knowledge on thermo acoustic properties of liquid mixture and solutions are more essential for their application in chemical, textile, leather and nuclear industries. Different methods like infra red, raman effect, di-electric, magnetic resonance are used to know molecular interaction and solution properties like other methods, measurement of ultrasonic velocity in liquid mixture and solutions is very useful and convenient tool to recognize the physico-chemical behavior and molecular interactions [1]. Ultrasonic energy is used in medicine, engineering, agriculture, defence and industry. In chemical industries ultrasonic energy is found useful in studying the chemical process and in synthesis of chemical substances. In solution of ionic solute the attraction between the solute and solvent is of ion-dipole type. When electrolyte is dissolved in solvent it causes volume contraction due to interactions between ions and solvent molecules and therefore other acoustical parameter may be affected. Many researchers have used ultrasound to investigate the ion-solvent interactions in aqueous solution containing electrolytes [2]. In the modern technology, the application of the salt is well understood by studying the ionic solvation or ion association. Ionic association of electrolytes in solution depends on the mode of solvation of its ions, which in turn depends on the nature of the solvent/solvent mixture [3] Aqueous mixed electrolytic solutions are implicated in many industrial and environmental processes, such as desalination, chemical separation, marine chemistry, geology and environment [4]. Electrolytes dissolving in water have been classified as structure makers or strucker breakers, depending on the charge density [5].   The measurements of ultrasonic waves are useful in study of molecular interactions in liquids, which provides valuable information regarding internal structure, complex formation, internal pressure and molecular association [6]. The study of free volume and other related properties of aqueous salt solutions have proven to be very useful in obtaining information regarding interactions which involve accurate measurements of ultrasonic velocity and density [7]. Solute–solvent interaction is of great importance in biological chemistry, physical chemistry, surface chemistry, environmental chemistry and geochemistry. To understand the processes occurring in living cells the nature of ion hydration is prerequisite information. Sodium acetate is widely used in molecular biology applications [8]. Salicylic acid derivatives are widely used in

the medicinal field [9]. The present work provides useful information in medical and pharmaceutical chemistry for the prediction of solute-solvent interaction. Ultrasound velocity, density and viscosity of ternary liquid mixtures of sodium acetate, sodium propionate and sodium salicylate with aqueous N,N, DMF have been determined at 303K. The data obtained during the study is used for determining the most significant acoustic parameters like free volume (V_f), internal pressure (π_i), Falkenhagen coefficient A, Jone-Dole coefficient B and relative association (R_a). These parameters explore solute-solvent interactions in aqueous N,N, DMF mixtures.

MATERIALS AND METHODS

The densities were measured with pre-calibrated bicapillary pyknometer. The estimated accuracy in density measurement was ±0.01kgm^{-3}. The ultrasonic speeds in solvents and in solutions were measured using a single crystal variable path multi frequency ultrasonic interferometer (M-81 Mittal India) operated at 3MH$_Z$ with an accuracy of ±2ms^{-1} . An average of 5 readings was taken as a final value of speed of sound. Water from thermostat water bath circulated through the brass jacket was well insulated and the temperatures of the solutions under study were maintained to an accuracy of 0.01K in an electrically controlled thermostatic water bath. Thermostated water was maintained at a desired temperature for about 30 minutes prior to recording of readings at 303K studied so as to minimize thermal fluctuations. The viscosity measurements have been carried out using an Ostwald's viscometer. The overall accuracy of the measurement of viscosity is ±0.001 N·s·m^{-2}.

THEORY

The experimental values of density and viscosity for all the ternary mixtures at 303 K were fitted to equations of the following type

Free volume and internal pressure is calculated by using the relation [7]

$$V_f = \left[\frac{M_{eff} U}{K\eta} \right]^{3/2} \tag{1}$$

$$\pi_i = bRT \left[\frac{K\eta}{U} \right]^{1/2} \left[\frac{\rho^{2/3}}{M_{eff}^{7/6}} \right] \tag{2}$$

where $M_{eff} = M_1 X_1 + M_2 X_2 + M_3 X_3$ is the effective molecular weight, U is the ultrasonic velocity, K is a constant (4.28×10^9), η is the viscosity, ρ is the density, b is the packing factor, R is the gas constant and T is the temperature.

A, B Coefficients- The viscosity data have been analyzed by using the Jones-Dole equation [8]

$$\frac{\eta}{\eta_0} = 1 + Am^{1/2} + Bm \tag{3}$$

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 [10]. Coefficient A accounts for the solute-solute interactions and B is a measure of structural modifications induced by the solute-solvent interactions.

Relative association (R_a):

The relative association is calculated using the relation [11]

$$R_a = \left[\frac{\rho}{\rho 0} \right] \left[\frac{Uo}{U} \right]^{1/3} \tag{4}$$

Where,

ρ & ρ_o is the densities of the solution and solvent

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

RESULTS AND DISCUSSION

The experimental values of density (ρ), viscosity (η), and ultrasonic velocity (U) for CH_3COONa, C_2H_5COONa and $C_7H_5O_3Na$ in 10, 20, 30, and 40% of N,N, Dimethylformamaide - water mixtures at different molalities at 303K are reported in [Table 1]. Then plots of molality

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versus free volume (V_f) and internal pressure (π_i) at 303K for the three salts in the four solvent containing in 10, 20, 30 and 40% in   N, N Dimethylformamide and water mixtures are shown in Figs. [1-6].The variation of relative associations (R_a) and viscosity B co-efficient are presented in Tables [2, 3] respectively.

The values of density (ρ), viscosity (η) and ultrasonic velocity (U) [Table 1] increases with increase in molal concentration of salts. The increase in density and viscosity is due to the association between solute and solvent interactions. This increasing trend indicates the existence of molecular interaction occurring in the mixtures. The variation of ultrasonic velocity throws light on the structural changes associated with the present system. Molecular association is thus responsible for the observed increase in ultrasonic velocity, which may be attributed to the cohesion brought about by the ionic hydration [12] .

Free volume and internal pressure- It is observed from the Figs. [1-3], the free volume decreases with increasing molality of salt as well as with increasing DMF content, a large number of solute molecules go into the bulk solutions and ionic nature of the solute molecules puts them into closer and closer packing as their number increases, resulting in a decrease in free volume (V_f), which suggests that there is a significant interaction between the ions and solvent molecules. DMF has a strongly electronegative attraction (hydrogen bond) with a hydrogen atom of a water molecule. As the DMF content is increased, more and more hydrogen –bonded DMF-water molecules formed [13], which results in a further reduction of the free volume in the mixtures.

It is seen from the Figs[4-6], the internal pressure (π_i) increases with increasing concentration of solutes in 10, 20, 30 and 40% DMF-water mixtures. The primary effect of dissolving an electrolyte is to lower the compressibility of the solvent molecules. This lowering of compressibility results in an increase of the ultrasonic velocity and hence π_i increase with concentration. As the molality of the electrolyte increase, ion-solvent interaction increases resulting in an overall increase in π_i. The value of π_i is a measure of interaction. Further, with increasing DMF content, the internal pressure (π_i) was found to decrease, as complex formation was enhanced to strong ion-solvent interaction [7].

Viscosity *B*-coefficient and Relative Association -Viscosity is one of the most important factors affecting the mobility of ions and ion clusters. Numerous studies [11,12] have shown that viscosity measurements are very useful in providing information regarding ion-solvent interaction, particularly as regards the modification induced by the solute on the solvent structure. For this reason, viscosity changes are of particular interest in the course of mixed-solvent investigations over a wide range of salt concentration. It can be seen that [Table 1], the viscosity of the electrolyte solutions increases with increasing concentration of sodium acetate sodium propionate and sodium salicylate, and increases with increasing content of DMF.

From the [Table 3], it is observed that the A & B values are found to be positive for all the systems (except A values in 10, 20% of sodium Acetate). Where A is constant, independent of concentration and B is a Jones-Dole co-efficient and is related to the effect of the ions on the structure of water [8]. The positive values of A indicate the presence of strong ion-ion interaction whereas, the negative values of A are indicate of weak ion-ion interaction in the electrolytic solutions [14]. The viscosity B co-efficient provides information about the solvation of the solutes and their effects on the structure of the solvent in the near environment of the solute molecules. It originally introduced as an empirical term has been found to depend upon solute-solvent interactions and on the relative size of the solute and solvent molecules. The positive values of B further confirm the strong solute-solvent interactions in addition to the structure making ability of the solute [15].

The relative association R_A, measures the ability of molecules to build associates or **supra molecular** structure by intermolecular interactions**.** The relative association (R_a) in present investigation increases with increase in concentration of electrolytes [Table 3].The R_a is influenced by two factors:-

    i.   Breaking of the solvent molecules an addition of solute and

    ii.   Solvation of ions that are simultaneously present

The association between solute and solvent molecule is further confirmed by relative association (R_a) values because of the continuous increase in the values of R_a with concentration for all the compounds [16].

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CONCLUSION

The density, ultrasonic velocity and viscosity of solutions of electrolytes in water and in aqueous N,N-DMF solvents (10,20,30 and 40%) were measured at 303K. From the experimental data, various parameters viz., V_f, π_i, R_A, Falkenhagen coefficient A and Jones-Dole coefficient B were calculated. The results indicate that there exist strong solute-solvent (Hydrophilic-ionic group and hydrophilic-hydrophilic group) interactions in these systems, which increase with increase in DMF concentration. It is also observed that electrolyte acts as structure-maker in these aqueous DMF solvent. In comparing the relative association values for the studied salts in the same experimental condition, we can note the following order: $CH_3COONa>C_2H_5COONa.>Ph(OH)COONa$. The order of the studied salts may be related to the competition between ability of each system to form intramolecular and intermolecular hydrogen bonds. The formation of intrahydgrogen bonds as in the case of salicylate leads to the decrease in the association process between Na^+ and anions.

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Table 1. Values of Density (ρ) Viscosity (η) and Velocity (U) of Soduim acetate, sodium propionate and sodium salicylate in aqueous solution of N,N,Dimethylformamide at 303K

Molality of salt (m) (mol.kg^{-1})	ρ/(kgm^{-3}) $^{DMF+water}$				η/(x 10^{-3} Nsm^{-2}) $^{DMF+Water}$				U/(ms^{-1}) $^{DMF+Water}$			
	10%	20%	30%	40%	10%	20%	30%	40%	10%	20%	30%	40%
Sodium acetate in DMF+water mixtures												
0.0	990.117	989.706	987.799	986.716	0.9225	1.1303	1.3461	1.5915	1566.15	1604.55	1644.84	1661.40
0.2	997.170	995.076	994.404	991.313	0.9890	1.2062	1.4445	1.6982	1588.00	1623.75	1660.20	1667.55
0.4	1006.190	1003.773	1002.826	1001.730	1.0584	1.2872	1.5271	1.8164	1599.25	1639.00	1666.35	1674.96
0.6	1016.171	1015.423	1013.006	1010.414	1.1300	1.3733	1.6136	1.9334	1605.60	1642.30	1678.32	1688.80
0.8	1024.158	1022.401	1021.616	1017.791	1.2004	1.4647	1.7399	1.9985	1634.20	1665.60	1687.80	1694.80
1.0	1029.901	1028.992	1027.721	1024.805	1.2794	1.5257	1.8121	2.1458	1646.55	1685.90	1699.05	1708.92
Sodium propionate in DMF+water mixtures												
0.0	990.117	989.706	987.799	986.716	0.9225	1.1303	1.3461	1.5915	1566.15	1604.55	1644.84	1661.40
0.2	998.440	997.294	995.650	992.410	1.0202	1.2489	1.4862	1.7399	1598.70	1625.10	1663.80	1675.35
0.4	1008.346	1005.792	1003.499	1003.250	1.0910	1.3502	1.5985	1.8293	1614.45	1652.28	1669.92	1685.00
0.6	1019.298	1017.703	1015.585	1012.470	1.1743	1.4172	1.7093	1.9881	1621.95	1661.25	1679.88	1694.80
0.8	1025.802	1025.302	1024.432	1023.476	1.2528	1.5324	1.8679	2.1225	1640.25	1677.40	1696.65	1698.60
1.0	1032.630	1031.048	1030.039	1026.051	1.3449	1.6320	1.9406	2.2101	1655.15	1696.05	1700.70	1710.36

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Sodium Salicylate in DMF+water mixtures											
0.0	990.117	989.706	987.799	986.716	0.9225	1.1303	1.3461	1.5915	1566.15	1604.55	1644.84	1661.40
0.2	1004.281	1003.350	1002.328	1000.434	1.0363	1.2564	1.5164	1.7941	1674.40	1689.45	1724.00	1783.50
0.4	1015.884	1014.813	1012.184	1011.025	1.1195	1.3618	1.6427	1.9139	1694.25	1722.30	1753.95	1792.20
0.6	1027.185	1024.693	1023.522	1021.902	1.2040	1.4435	1.7379	2.0271	1715.40	1733.80	1755.90	1801.50
0.8	1037.789	1036.346	1034.312	1033.353	1.3100	1.5262	1.8666	2.2879	1718.85	1744.30	1770.96	1809.30
1.0	1049.077	1047.831	1046.211	1043.894	1.3873	1.6796	1.9810	2.4531	1721.11	1758.00	1780.20	1842.75

Table 2 Values of Relative association (R_a) of Sodium Acetate, Sodium Propionate and Sodium Salicylate in N,N

Dimethylformamide – water mixtures   at 303K

Molality of salt (m)	Sodium Acetate	Molality of salt (m)	Sodium Propionate	Molality of salt (m)	Sodium Salicylate
N,N, Dimethylformamide – water (10:90%)					
0.0000	-	0.0000	-	0.0000	-
0.2004	1.0024	0.2012	1.0015	0.2002	0.9919
0.4011	1.0105	0.4004	1.0081	0.4009	0.9994
0.6007	1.0178	0.5997	1.0175	0.5998	1.0064
0.7999	1.0198	0.8005	1.0201	0.7998	1.0161
0.9998	1.0229	0.9995	1.0238	0.9999	1.0267
N,N, Dimethylformamide – water (20:80%)					
0.0000	-	0.0000	-	0.0000	-
0.2018	1.0014	0.2013	1.0032	0.1996	0.9964
0.4012	1.0070	0.3996	1.0062	0.3996	1.0013
0.6014	1.0170	0.5993	1.0155	0.5999	1.0088

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0.7999	1.0202	0.8005	1.0206	0.8000	1.0182
1.0004	1.0218	1.0000	1.0225	0.9997	1.0268
N,N, Dimethylformamide – water (30:70%)					
0.0000	-	0.0000	-	0.0000	-
0.2006	1.0035	0.2010	1.0041	0.2000	1.0029
0.4009	1.0108	0.4004	1.0148	0.4000	1.0070
0.6000	1.0186	0.5995	1.0250	0.6000	1.0179
0.8001	1.0253	0.7999	1.0305	0.7998	1.0257
1.0041	1.0292	0.9996	1.0353	0.9993	1.0357
N,N, Dimethylformamide – water (40:60%)					
0.0000	-	0.0000	-	0.0000	-
0.2001	1.0034	0.2018	1.0029	0.2001	0.9902
0.4008	1.0214	0.3999	1.0119	0.3991	0.9990
0.6000	1.0184	0.6014	1.0193	0.5991	1.0080
0.8001	1.0246	0.7993	1.0296	0.8001	1.0179
1.0039	1.0288	1.0052	1.0298	1.0001	1.0220

Table 3 Values of A and B parameter of Jones- Dole equation of Sodium Acetate, Sodium Propionate and Sodium Salicylate in N, N, and Dimethylformamaide – water mixtures at 303K

N,N Dimethylformamide% W/W	A dm$^{3/2}$ mol$^{-1/2}$	B dm^3 mol^{-1}
Sodium Acetate		
10	-0.0229	0.4058
20	-0.0184	0.3779
30	0.0003	0.3472
40	0.0049	0.3358
Sodium Propionate		
10	0.0454	0.4022
20	0.0649	0.3698
30	0.0451	0.4071
40	0.0338	0.3615
Sodium Salicylate		
10	0.0757	0.4273
20	0.0707	0.3884
30	0.1307	0.3355
40	0.0364	0.4823
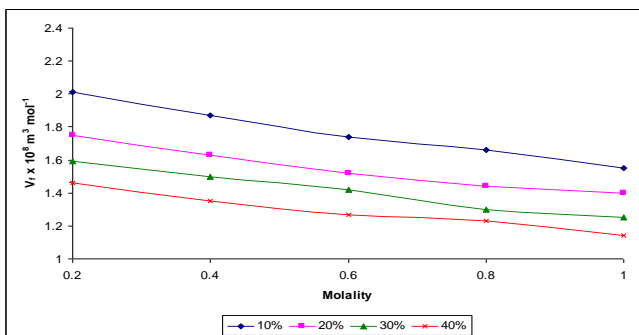
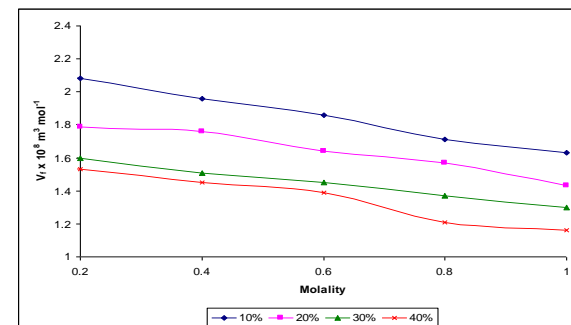Fig 1: Free Volume Vs Molality of sodium acetate   Fig 2: Free Volume Vs Molality of sodium propionate   Fig 3: Free Volume Vs Molality of sodiumsalicylate
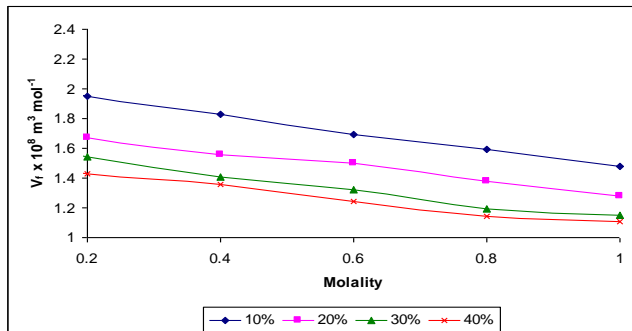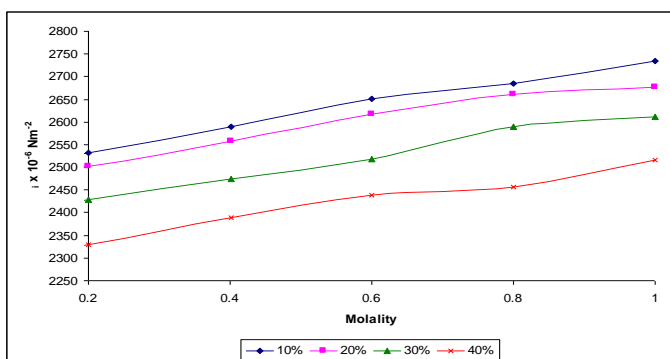

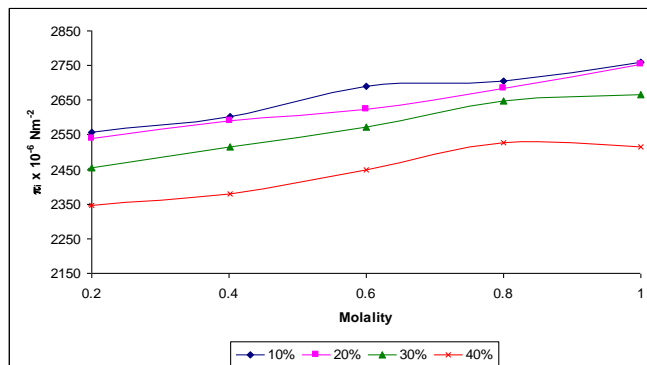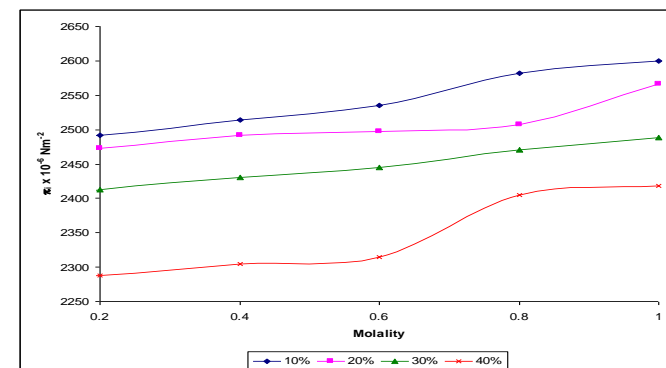Fig4. Internal pressure Vs Molality of sodium acetate   Fig. 5. Internal pressure Vs Molality of sodium propionate   Fig.6. Internal pressure Vs Molality of sodium salicylate