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Ultrasonic Velocity and Compressibility Variation in Inorganic Sulphates with Aqueous Polymer Solutions

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Abstract: *Ultrasonic velocity measurements have been carried out in the mixtures of Zinc sulphate, and manganese sulphate with PVP (Polyvinylpyrrolidone) to study the molecular interactions. The basic acoustical parameters like ultrasonic velocity (U), density (ρ) and viscosity (η) have been measured for the mixtures of aqueous PVP (polyvinylpyrrolidone) with aqueous sulphates for temperatures 303K, 308K, and 313K.The measured parameters are used to calculate acoustical parameters such as acoustic impedance, intermolecular free length, adiabatic compressibility, and relaxation time. The acoustical velocity, adiabatic compressibility and impedance vary with concentration of the mixtures and temperatures. It is the evidence for the presence of strong molecular interactions occurred in the liquid mixtures.*

Keywords: ultrasonic velocity, acoustic impedance, adiabatic compressibility.

Introduction

The study of molecular interaction in the liquid mixtures with the help of ultrasonic investigation is very much useful in assessing the nature and the structural properties of the molecules. Ultrasonic velocity and acoustical parameters provide much information on molecular interactions of polymer solutions.The energy of ultrasonics is applied in various fields as diagnostic tool[1-5]. The structural arrangement and the shape of the molecules are influenced by intermolecular interactions. [6-8]. Water soluble polymers and sulphates have wide range of applications in cosmetic and medical industries. The present work is an attempt to study the ultrasonic and thermo dynamical properties of aqueous mixtures of zinc sulphate and manganese sulphate with polyvinyl pyrrolidone (PVP) at 303K, 308K and 313 K.

Material and Methods

The sulphates used are AR (analytical grade reagent). grade were obtained from Merck. The aqueous solutions of the salts were made by dissolving them in distilled water. Standard procedure was followed for measuring density by using specific gravity bottle of 10ml. Ostwald's viscometer is used for the viscosity measurements of liquid mixtures. PVP (HiMedia) used is AR grade with a molecular weight of 40,000.It was dissolved in distilled water and the solutions were prepared at different concentrations. Liquid mixtures at various concentrations are prepared. The aqueous sulphate solutions were mixed with aqueous PVP at various concentrations. Ultrasonic velocities in the two binary liquid mixtures have been measured using the ultrasonic liquid interferometer of frequency 2 MHz manufactured from Mittal enterprises at temperatures 303K, 308K, 313K with an accuracy of ultrasonic velocity of ±.02%. From the measured parameters like Ultrasonic Velocity (u), Density (ρ), c viscosity (η) the following acoustical parameters have been calculated for the mixtures of various concentrations at different temperatures [9].

Calculations

Adiabatic Compressibility [10] is calculated using the relation

$$\beta = \frac{1}{U^2 \rho} \qquad (1)$$

Intermolecular free length [10] is determined from the relation

$$L_f = KT\sqrt{\beta} \qquad (2)$$

Where, K is a temperature dependent constant.

The relaxation time [11] is calculated from the relation

$$\tau = \frac{4}{3}\eta\beta \qquad (3)$$

The acoustic impedance [12] can be calculated using the formula

$$Z = U\rho \qquad (4)$$

Results and Discussion

Ultrasonic velocity, density, viscosity and the acoustical parameters like adiabatic compressibility (β), intermolecular free length (L_f), relaxation time (**τ**), acoustic impedance (Z) of the mixture of aqueous Manganese Sulphate and aqueous zinc sulphate with aqueous PVP are listed in Table 1 and 2.They are computed using the equations (1-4) .Ultrasonic velocity variation in the any solution reflects the presence of molecular association in the solution

It is clear from Table 1 that density values increase regularly with increase in concentration of manganese sulphate in PVP. Also, the viscosities increase with increase in concentration of manganese sulphate in PVP. Ultrasonic velocity (U) values tend to increase with the increase of concentration of manganese sulphate in PVP at various temperatures. This suggests that disruption of water structure is enhanced further with the addition of Manganese sulphate.The fig.1, 2, 3, 4 shows the variations in the Ultrasonic Velocity, adiabatic compressibility variation with the mole fraction of the sulphates of liquid mixtures at 303,308 and 313K.

The increase in Ultrasonic Velocity in solute concentration is due to the association between solute and solvent molecules. At lower concentrations, the interaction is between the polymer and the solvent molecules. As the concentration of polymer increases, one macromolecule may influence another indirectly by way of mutual .Variation in the free length is the evidence for strong polymer solvent interaction. According to Eyring and Kincaid, for sound propagation, ultrasonic velocity increases on decrease of free length.

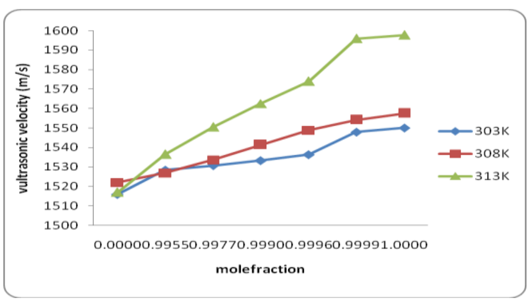
Intermolecular free length is very much essential in the determination velocity variations of the liquid mixture. This is also reflected in the research work of Singh and Singh. The reason for the increase in ultrasonic velocity may be due to Polymer-solvent interactions. The polar forces in a strong localized electric field and the solvating molecules form an incompressible region around polymer chains there by reducing the hydrodynamic volume. [13-15]It must the reason for the decrease of adiabatic compressibility of the mixture of aqueous polymer- salt solutions. Adiabatic compressibility variation in polymer solutions is an indicative of an increase in intermolecular forces forming aggregates of solvent molecules around the solute due to which structural arrangement is affected.

Table 1 : Ultrasonic velocity and acoustical parameters in mixture of aqueous solutions of Manganese Sulphate with aqueous PVP at 303K, 308K, and 313K

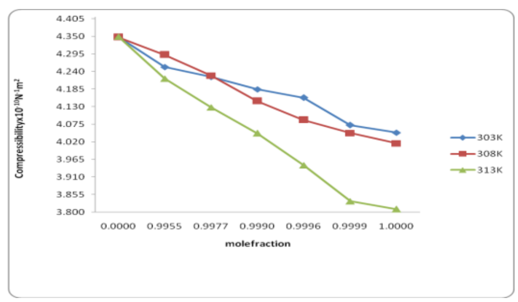
Mole Fraction	U(m/s)	ρ (kg/m^3)	η(Nsm^{-2}) X 10^{-3}	β(N^{-1}m^2) x10^{-10}	L_f(A^0)	τx10^{-12} (s)	Z x10^6 (kgm^{-2}s^{-1})
303K							
0.0000	1516	1001	1.057	4.3478	0.433	0.613	1.517
0.9955	1528	1006	1.068	4.2538	0.428	0.605	1.538
0.9977	1531	1011	1.087	4.2231	0.426	0.612	1.547
0.9990	1533	1017	1.108	4.1842	0.424	0.618	1.559
0.9996	1536	1019	1.115	4.1579	0.423	0.618	1.565
0.9999	1548	1025	1.132	4.0721	0.419	0.614	1.587
1.0000	1550	1028	1.145	4.0485	0.418	0.618	1.593
308K							
0.0000	1522	993	0.901	4.3471	0.440	0.522	1.511
0.9955.	1527	999	0.931	4.2921	0.438	0.533	1.526
0.9977	1534	1006	0.937	4.2270	0.434	0.528	1.543
0.9990	1541	1015	0.945	4.1467	0.430	0.523	1.565
0.9996	1549	1020	0.959	4.0884	0.427	0.523	1.579
0.9999	1554	1023	0.967	4.0473	0.451	0.522	1.590
1.0000	1558	1027	0.971	4.0152	0423	0.520	1.599
313K							
0.0000	1517	999	0.988	4.3489	0.437	0.573	1.516
0.9955	1537	1004	0.998	4.2181	0.430	0.561	1.543
0.9977	1551	1008	1.006	4.1276	0.425	0.554	1.562
0.9990	1563	1012	1.015	4.0466	0.421	0.548	1.581
0.9996	1574	1023	1.031	3.9465	0.416	0.542	1.610
0.9999	1596	1024	1.042	3.8344	0.410	0.533	1.634
1.0000	1598	1028	1.051	3.8095	0.409	0.534	1.643

Table 2: Ultrasonic velocity and acoustical parameters in mixture of aqueous solutions of Zinc Sulphate with aqueous PVP

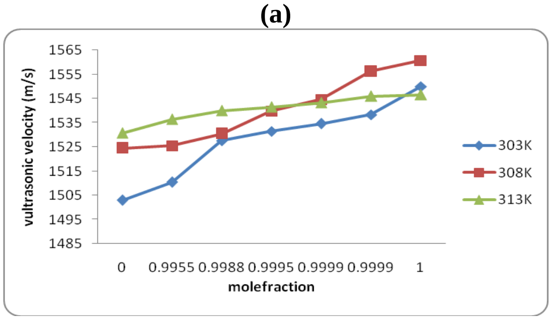
Mole Fraction	U(m/s)	ρ (kg/m^3)	η(Nsm^{-2}) X 10^{-3}	β($N^{-1}m^2$) x10^{-10}	Lf(A^0)	τx10^{-12} (s)	Z x10^6 ($kgm^{-2}s^{-1}$)
303K							
0.0000	1503	1001	1.052	4.4244	0.437	0.621	1.504
0.9955	1510	1001	1.061	4.3805	0.434	0.620	1.511
0.9988	1528	1007	1.083	4.2556	0.428	0.614	1.538
0.9995	1531	1013	1.104	4.2096	0.426	0.619	1.551
0.9999	1535	1016	1.112	4.1776	0.424	0.620	1.560
0.9999	1538	1020	1.126	4.1417	0.422	0.622	1.570
.	1550	1025	1.137	4.0605	0.418	0.615	1.589
308K							
0.0000	1524	995	0.902	4.3268	0.439	0.521	1.516
0.9955	1526	996	0.928	4.3128	0.439	0.533	1.520
0.9988	1530	1003	0.939	4.2556	0.436	0.533	1.535
0.9995	1540	1008	0.948	4.1852	0.432	0.529	1.552
0.9998	1545	1013	0.963	4.1360	0.430	0.531	1.565
0.9999	1556	1017	0.967	4.0590	0.426	0.523	1.583
1.0000	1561	1017	0.971	4.0383	0.425	0.5223	1.587
313K							
0.0000	1531	998	0.992	4.2746	0.433	0.565	1.528
0.9955	1536	999	0.997	4.2411	0.431	0.564	1.535
0.9988	1540	1005	1.004	4.1935	0.429	0.561	1.548
0.9995	1541	1009	1.012	4.1713	0.428	0.563	1.555
0.9999	1543	1013	1.021	4.1435	0.426	0.564	1.564
0.9999	1546	1018	1.031	4.1098	0.425	0.565	1.574
1.0000	1547	1020	1.043	4.0968	0.424	0.570	1.578



(a)



(a)



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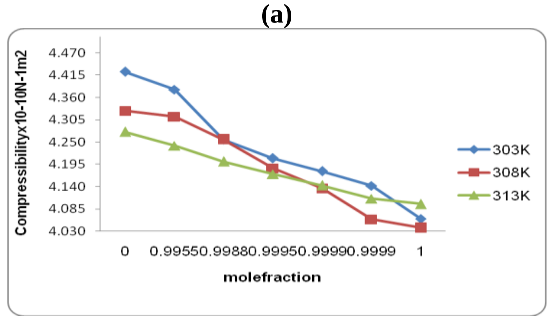

(b)

Figure 1: Ultrasonic velocity versus mole fraction of a) aqueous manganeese sulphate with PVP and b) aqueous zinc sulphate with PVP at 303, 308 and 313 K

Figure 2: Adiabatic compressibility versus mole fraction of a) aqueous manganese sulphate with PVP and b) aqueous zinc sulphate with PVP at 303, 308 and 313 K

The addition of sulphates in PVP tends to break up the molecular clustering, and releasing dipole for interactions. There may be, of the greater attractive force of interaction between sulphates and PVP molecules and will be an increase in cohesive energy, which manifests itself as a decrease incompressibility of the liquid mixtures.

The increase in density of the liquid mixture is because of the increase in concentration of inorganic salts in the polymer and is mainly due to the solutions presence of ions or particles. When the temperatures increase the ultrasonic velocity increases for the both liquid mixtures. It is exhibited in the Figure 1 (a & b).

But at the same time, compressibility decreases with increase in temperature. Polymer chain associations may be the reason for the compressibility decreases. Figures 2 (a & b) shows the compressibility variations in the solutions of PVP + sulphate mixtures with Temperature. Ultrasonic velocity increases with temperature clearly indicate the involvement of attractive forces during the intermolecular interactions between solute solvent molecules. Strong interaction between the molecules of the mixtures may occur.

The variations in the velocity and compressibility of the solutions are not in a linear manner. These nonlinear curves are the indication of presence of phase inversion at some concentrations. The nonlinear trend is because of the hydrogen bonding between liquid mixtures. It leads to the conclusion that strong molecular interactions are present between the molecules of solutions of polymer-sulphate mixtures by overcoming thermal agitation. The variations in the mean free length and relaxation time also prove the occurrence of strong interactions and the segmental motion occur in the polymer chains.

Conclusion

From the experimental data the acoustical and thermo dynamical parameters were determined for the mixtures of aqueous Manganese Sulphate and aqueous zinc sulphate with aqueous PVP at 303K,308K,313K.The experimental observation gives valuable information about the solute-solvent interactions in the mixtures.

It indicates that a strong molecular interaction between sulfate molecules in polymers. It is observed that the interactions are at a greater in the PVP + Zinc sulphate liquid mixtures than the PVP + Manganese sulphate liquid mixtures.

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