"INVESTIGATION OF PHYSIOCHEMICAL BEHAVIOR OF ION-SOLVENT INTERACTIONS USING ULTRASONIC TECHNIQUE IN DMSO DRUG AT DIFFERENT TEMPERATURES"

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Summary

Ultrasonic velocities, densities and viscosities have been measured in very weak concentration at 303.15, 308.15, 313.15 and 318.15K temperatures for $ZnSO_4$ + DMSO system. From these data acoustical parameters such as adiabatic compressibility's, specific acoustic impedances, intermolecular free lengths and solvation numbers have been estimated using standard relations to investigate ion-solvent interactions in the given solutions. It is observed that ion-solvent interactions are increases in increasing the concentration of Zn^{++} ions in DMSO solvent showing the structure promoting tendency and ion-solvent interactions decreases with temperature showing the structure breaking tendency of Zn^{++} ions.

Keywords: DMSO, ultrasonic velocity, ion-solvent, acoustic impedance, physiochemical,

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Introduction

Ultrasonic energy is used in medicine, engineering, agriculture, defence and industry. In chemical industries ultrasonic energy is found useful in studying the chemical processes and in synthesis of chemical substances. A survey of literature[8-28] indicates that acoustical parameters are useful in understanding the nature and strength of molecular interactions in the mixtures. Recently an ultrasonic wave has been extensively used to determine the ion-solvent interactions in aqueous solutions containing electrolytes. A number of researchers have studied acoustical properties of solution containing transition metal ions. 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 parameters may be affected[14]. Literature survey[8-28] shows that attempt has not been made by any of researchers to study the ion-solvent interactions in non aqueous solutions at varying temperatures.

In this paper an attempt has been made to determine ultrasonic velocity (U), density (ρ), and viscosity (η), and hence the acoustical parameters such as acoustical impedance (Z), adiabatic compressibility (β), Intermolecular free length (Lf) and solvation number (Sn) in ZnSO4 + Dimethylsulfoxide (DMSO) system for very weak concentration and varying temperature to investigate physiochemical behavior of ion-solvent interactions.

Dimethylsulfoxide (DMSO) is the chemical compound with the formula $(CH_3)_2SO$. It was first synthesized in 1866 by the Russian scientist Alexander Saytzeff, who reported his findings in a German chemistry journal in 1867[1]. It is highly polar self associated liquid and has ability to participate in hydrogen bonding[2]. Dimethylsulfoxide dissolves a variety of organic substances, including carbohydrates, polymers, peptides, as well as many inorganic salts and gases. Loading levels of 50-60 wt. % are often observed verses 10-20 wt. % with typical solvents. For this reason, DMSO plays a role in sample management and high-throughput screening operations in drug design[3].

In 1964 Jacob, Bischel, and Herschler[4] first described the remarkable medicinal properties of DMSO. When applied to intact human skin, the drug penetrates rapidly and produces a wide range of pharmacologic actions, including anti inflammation, local analgesia, bacteriostasis, diereses, cholinesterase inhibition, and enhancement of the action of concomitantly administered drugs, influence on collagen, non specific enhancement of immunity, vasodilatation, and lessening of adhesiveness of blood platelets[5]**.** As a result the drug has been used widely as treatment for various conditions, including arthritis, bursitis, acute musculoskeletal trauma, scleroderma, troublesome urogenital disorders, and various postoperative pain syndromes. To date little, if any, local or systemic toxicity has been noted in the human after the administration of DMSO[6].

Materials and Methods

Ultrasonic velocity for the solutions was measured using a single crystal ultrasonic interferometer of 2 MHz frequency(Model F-81) supplied by Mittal enterprises, New Delhi that has a reproducibility of 0.4m/sec at 25° C. The temperature was kept constant by constant temperature water bath with an accuracy of ± 0.1K. The temperature of the circulating water near the cell was measured by using PT-100 sensor and was found to be accurate to 0.23^{0}C. The densities of various concentrations have been measured using 25ml capacity specific gravity bottle and digital balance (Shinko, model HTR-220E, made in Japan) with an accuracy of 0.0001gm. The viscosities have been determined by using Ostwald viscometer.

The Merck made hydrated salt $ZnSO_4.7H_2O$ of Anal-R grade having 99.5% assay was used without further purification for the present investigation and solvent DMSO was distilled as per the standard procedure before use[7].

Theory

Various physical parameters was calculated from the measured values of ultrasonic velocity (U), density (ρ) and viscosity (η) using the following standard expressions[8].

Specific acoustic impedance (Z) = ρU ($Kgm^{-2}S^{-1}$)

Adiabatic compressibility (β) = $1/U^2\rho$ ($Kg^{-1}ms^{-2}$)

Intermolecular free length (Lf) = $k\sqrt{\beta}$ *(m)*

Where k is temperature dependent constant called as Jacobson constant it is 2.075×10^{-6}, 2.095×10^{-6}, 2.115×10^{-6} and 2.135×10^{-6} for 303.15, 308.15, 313.15 and 318.15K respectively (9)

Solvation number[10, 11] (S_n) = $\frac{n_s}{n_i}\left(1-\frac{\beta}{\beta_0}\right)$

n_s = number of moles of solvent (mol/kg)

n_i = number of moles of solute (mol/kg)

β = Adiabatic compressibility of solution at a particular temperature ($N^{-1}m^2$)

β_0 = Adiabatic compressibility of solvent at a particular temperature ($N^{-1}m^2$)

Result and discussion

The experimental values of velocities, densities and viscosities and the calculated values of acoustic impedance, adiabatic compressibility's, Intermolecular free lengths and solvation numbers for $ZnSO_4$ + DMSO system are given in table 1.

Figure 1 shows the graph of U against the concentration for $ZnSO_4$ + DMSO system. It is observed from table 1 that U, ρ and η increases with increase in concentration of Zn^{++} ions for all temperatures showing the increase in the ion-solvent interactions. At 0.00605M concentration for all temperatures, there is slight decrease in U, ρ and η. Which suggest the structure breaking tendency of Zn^{++} ions. However there is regular decrease in ultrasonic velocity with the increase in temperature. This shows that Zn^{++} ions behave as a structure breaker for the clusters of DMSO molecules suggesting the decrease in ion-solvent interactions between Zn^{++} ions and DMSO molecules[12, 16].

As the temperature is increased, thermal energy facilitates the breaking of bonds between the associated molecules of DMSO. This weakens the molecular forces between solute and solvent molecules and hence decreases the ultrasonic velocity[8].Every solvent has a limiting compressibility. The compressibility of a solvent is higher than that of solution and it decreases with the increase in concentration of the solution. With increase in ionic concentration, their electrostrictive forces cause the structure to break and the solute surrounded DMSO molecules are more compactly packed. This effect in turn reduces the compressibility with increase in the Zn^{++} ions concentrations[12, 13, 21, 26].

Table 1 shows that adiabatic compressibility (β) decreases with increase in concentrations of Zn^{++} ions in DMSO; this confirms the increase in ion-solvent interactions through ion-dipole interactions between Zn^{++} ions and surrounding DMSO molecules. However, as the temperature increases β values increases suggesting the corresponding decrease in Zn^{++} ion-DMSO solvent interactions. At 0.00605M concentration for all temperatures compressibility was found to be increased showing weak ion-solvent interactions due to the structure breaking nature of Zn^{++} ions in DMSO solvent[12]. When acoustic wave travel through a medium there is a variation of pressure from particle to particle. The ratio of instantaneous pressure excess at any particle of the medium to the instantaneous velocity of that particle is known as "specific acoustic impedance (Z)" of the medium. This factor is governed by the inertial and elastic properties of the medium[13, 14]

From table 1 and figure 3, it is observed that Z values gradually increases with increasing concentration of Zn^{++} ion in DMSO solvent for all temperatures, confirms the increase in ion-solvent interaction due to the structure promoting nature of Zn^{++} ions. As the temperature increases specific acoustic impedance decreases, which suggest the structure breaking tendencies of solute molecules showing the decrease in ion-solvent interaction[8,12] Intermolecular free length shows a similar behavior as reflected by the compressibility values. The decreased compressibility brings the molecules to a closer packing resulting in a decrease of intermolecular free length. The variation of ultrasonic velocity in a solution depends upon the increase or decrease of intermolecular free lengths after mixing the component[12, 14].

The Ultrasonic velocity should increase if the intermolecular free length decreases as a result of mixing the components. If the free length decreases on increasing the concentration of solute then it indicates significant interactions between the ions - solvent molecules suggesting a structure promoting tendency of the added solute.

The solvation number of solute molecules is explained on the basis of solute-solvent interactions[12, 14] which picture three different solvent structure regions in the neighborhood of solute. Just outside the molecule, there is a layer of immobilized and compressed solvent molecules as a result of electrostrictive and other attractive forces exerted by the solute. This is known as primary sheath of solvation. This layer is surrounded by slightly less compressed or "structure–broken" region of solvent molecules distantly affected by these forces. This layer is called as secondary sheath of solvation.

The outermost layer is bulk solvent which is not affected by any of the above forces**.**

Table 1. Ultrasonic velocities (U), densities (ρ), viscosities (η), specific acoustic impedances(Z), adiabatic compressibility's(β), intermolecular free lengths(L_f), solvation numbers(S_n) at 303.15K and 308.15K,313.15K and 318.15K.

Temp	Conc./M	(U) ms^{-1}	(ρ) Kgm^{-3}	(η) $/10^{-3}$ Nsm^{-2}	(Z) $/10^{6}$ $Kgm^{-2}S^{-1}$	(β) $/10^{-10}$ Kg^{-1} ms^{-2}	(L) $/10^{-11}m$	S_n
303.15K	0.00000	1469.3	1095.1	1.695	1.6090	4.2300	4.2676	-----
	0.00105	1475.8	1095.6	1.755	1.6168	4.1910	4.2479	107.59
	0.00205	1478.1	1095.8	1.764	1.6197	4.1770	4.2408	73.10
	0.00405	1479.9	1096.3	1.771	1.6224	4.1650	4.2347	44.83
	0.00605	1475.1	1096.1	1.767	1.6168	4.1930	4.2489	17.01
	0.00805	1480.4	1097.3	1.783	1.6245	4.1580	4.2312	25.17
308.15K	0.00000	1451.6	1091.1	1.534	1.5838	4.3495	4.3666	-----
	0.00105	1456.9	1091.5	1.574	1.5903	4.3160	4.3498	90.20
	0.00205	1460.2	1091.8	1.575	1.5942	4.2960	4.3397	72.03
	0.00405	1462.6	1092.5	1.584	1.5979	4.2790	4.3311	47.46
	0.00605	1457.2	1092.1	1.564	1.5914	4.3120	4.3478	16.83
	0.00805	1462.1	1093.5	1.583	1.5988	4.2780	4.3306	24.07
313.15K	0.00000	1436.5	1085.9	1.395	1.5598	4.4630	4.4628	-----
	0.00105	1441.4	1086.2	1.436	1.5657	4.4310	4.4468	84.4
	0.00205	1442.1	1087.4	1.452	1.5681	4.4220	4.4423	54.05
	0.00405	1445.0	1087.7	1.455	1.5717	4.4030	4.4327	39.6
	0.00605	1439.9	1087.2	1.443	1.5655	4.4360	4.4493	11.9
	0.00805	1448.6	1089.3	1.465	1.5779	4.3750	4.4186	29.0
318.15K	0.00000	1416.3	1081.4	1.318	1.5316	4.6100	4.5760	----
	0.00105	1420.6	1082.2	1.343	1.5373	4.5790	4.5606	79.46
	0.00205	1421.1	1084.0	1.355	1.5405	4.5680	4.5551	53.83
	0.00405	1421.8	1085.5	1.367	1.5434	4.5570	4.5496	33.96
	0.00605	1416.9	1085.0	1.345	1.5373	4.5910	4.5666	8.12
	0.00805	1424.6	1086.6	1.376	1.5479	4.5350	4.5386	24.03

Figure 1. Concentration and temperature dependence of Ultrasonic velocity (U) for $ZnSO_4$ + DMSO System.

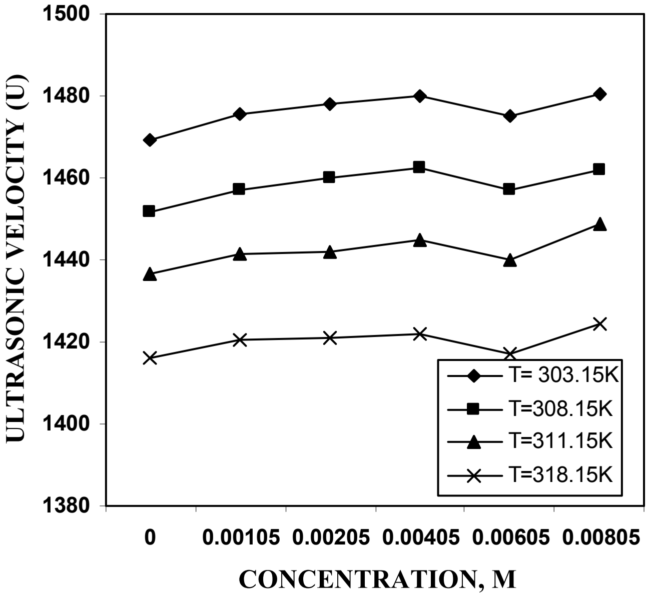
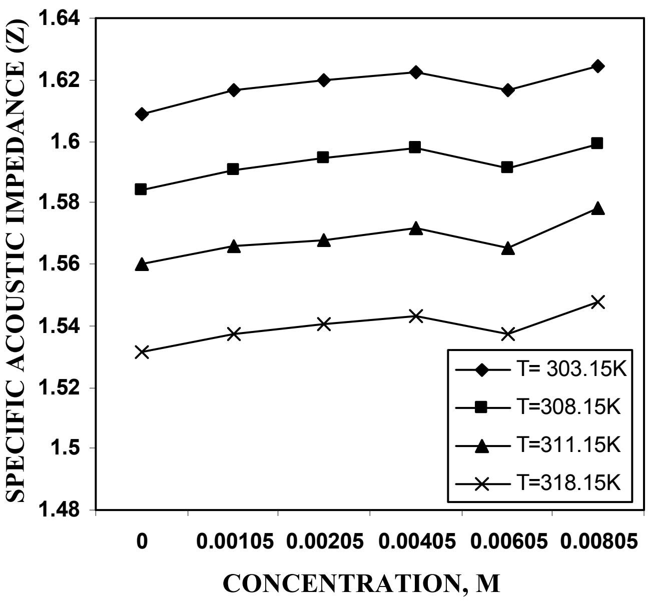


Figure 2. Concentration and temperature dependence of Specific acoustic impedance (Z) for $ZnSO_4$ + DMSO System.



The solvation number in the primary sheath corresponds to coordination number and it is concentration independent, while the solvation number in the secondary sheath is concentration dependent[15]. From table 1 and figure 4 it is observed that S_n values decreases with increase in temperature and concentration of Zn^{++} ion in DMSO medium shows weakening of solute-solvent interactions[12, 14, 16].

Figure 3. Concentration and temperature dependence of Intermolecular free length (L_f) for $ZnSO_4$ + DMSO System.

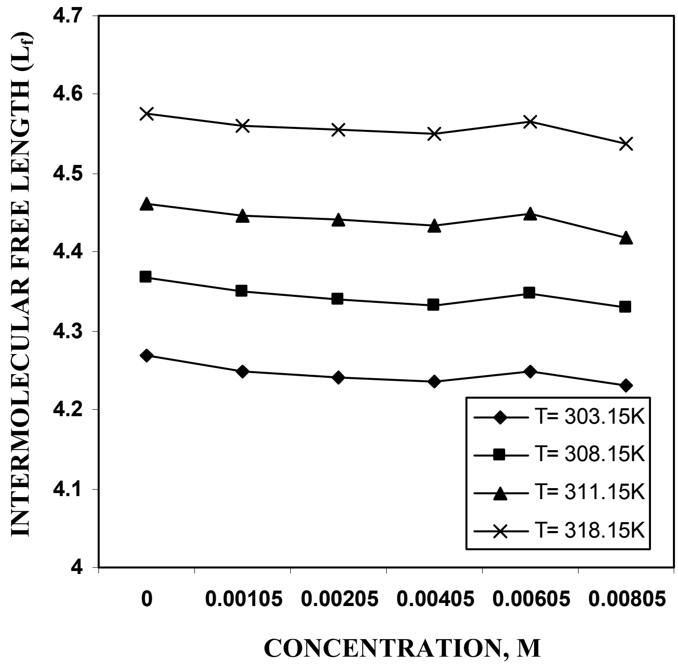
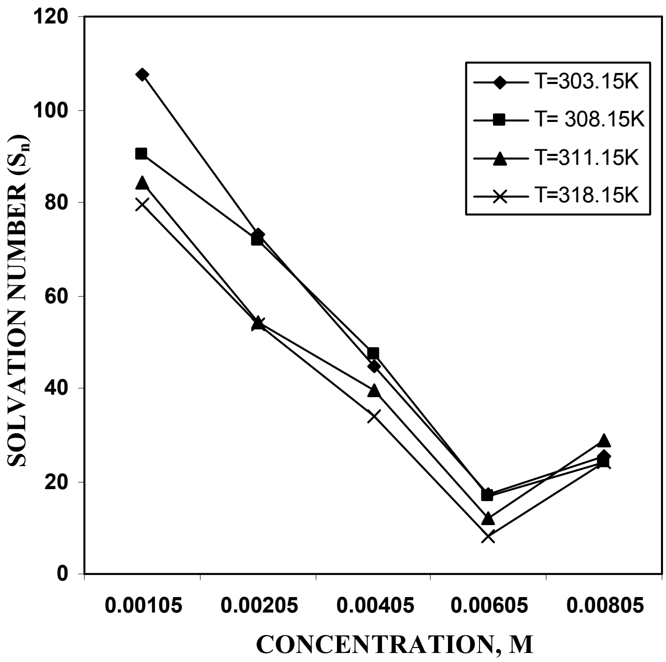


Figure 4. Concentration and temperature dependence of Solvation number (S_n) for $ZnSO_4$ + DMSO System.



Conclusion

Investigation of physiochemical behavior of Zn^{++} ion in DMSO has been carried out in very dilute concentration at different temperatures. The experimental parameters such as ultrasonic velocity, density, viscosity and the other acoustical properties contain valuable information regarding ion-solvent interactions in non aqueous solutions. There is uniform decrease in density and increase in intermolecular free length with increase in temperature indicating the loosening of intermolecular forces due to thermal agitation of the molecules in non aqueous solutions of $ZnSO_4$ at high temperatures. The ultrasonic studies provide comprehensive investigations between Zn^{++} ion + DMSO molecules arising due to hydrogen bonding.

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