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MOLECULAR INTERACTION STUDY IN BINARY LIQUID SOLUTION USING ULTRASONIC TECHNIQUE

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ABSTRACT

The ultrasonic velocity, density and viscosity have been measured for binary liquid solution of zinc chloride ($ZnCl_2$) and cadmium chloride ($CdCl_2$) with distilled water at 300K. The acoustic parameters such as adiabatic compressibility, free length, free volume, internal pressure, relaxation time, acoustic impedance and Gibb's free energy values have been calculated from the experimental data. Above parameters are used to study the molecular interaction in the solution.

Key words: Molecular interaction, Binary liquid solution, Ultrasonic technique.

INTRODUCTION

The ultrasonic technique is extensively used in scientific research. In this, direct interaction of the wave with the material takes place[2]. This plays a vital role in the study of molecular interactions, material characterization etc. which plays an important role in the development of molecular sciences[2,3]. The ultrasonic studies are used to estimate the thermodynamic properties and predict intermolecular interactions of binary solution[4]. Using the measured values of sound velocity, density and viscosity, the thermodynamic parameters such as compressibility, free length, free volume etc, can be calculated[4,5].

The spectroscopic methods play a major role in the molecular interaction studies. Now the non-spectral studies such as magnetic, ultrasonic velocity and viscosity measurements have been widely used to study the molecular complexes formed between interacting molecules[7].

Here we have evaluated the acoustic parameters namely the Adiabatic compressibility (β), Intermolecular free length(Lf), free volume (V_f) internal pressure (π_i), Relaxation time (τ), Acoustic impedance (Z) and Gibb's free energy (ΔG*) for binary solution of zinc chloride ($ZnCl_2$) and cadmium chloride ($CdCl_2$) with distilled water[8,9].

Theory –

Adiabatic compressibility –

Adiabatic compressibility is the fractional decrease of volumes per unit increase of pressure when no

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heat flows in or out. It can also be calculated from the speed of sound (U) and the density of the medium (ρ) using the equation of Newton Laplace as -

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

Intermolecular free length (L_f)

Intermolecular free length is the distance between the surface of the neighboring molecules(11,12) and is given by

$$L_f = K_T \beta^{1/2}$$

Where, K_T is the temperature dependant constant having value 201.1209 x 10^{-8}

Free volume (V_f)

The molecules of a liquid are not quite closely packed and there are some free space between the molecules for movement and the volume V_f is called the free volume. Free volume in terms of ultrasonic velocity (U) and the viscosity of the liquid (η) as [13]

$$V_f = \left[\frac{UM_{eff}}{K\eta}\right]^{\frac{3}{2}}$$

Where M_{eff} is the effective molecular weight.

$M_{eff} = \sum m_i X_i$, m_i and X_i are the molecular weight and the mole fraction of the individual constituents resp.

K is temperature independent constant which is 4.28 x 10^9 for all liquids.

Internal pressure (π_i)

The internal pressure is the cohesive force which is resultant of force of attraction and force of repulsion between the molecules[14].

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

Where, b stands for cubic packing which is assumed to be 2 for liquids.

R is gas constant

T is absolute temperature

K is Boltzmann constant.

Relaxation time (τ): Relaxation time is the time taken for the excitation energy to appear as translational energy and it depends on temperature and on impurities.

$$\tau = \frac{4}{3}\beta\eta$$

Acoustic Impedence (Z)

The specific acoustic impedance

$Z = U\rho$

Gibb's free energy (ΔG^*) –

The relaxation time for a given transition is related to the activation free energy.

$$\Delta G^* = - KT \log \left(\frac{h}{KT\tau}\right)$$

Where, K is Boltzmann constant

h is plank's constant

T is absolute temperature

RESULTS AND DISCUSSION

The experimental values of density, viscosity and ultrasonic velocity for the binary solution of zinc chloride and cadmium chloride are given in Table 1.

Table 1.

Molar solution	Adiabatic compressibility (Ξ) x 10^{-10} m^2 /N	Free Length (L_f)x 10^{-10} m	Free volume V_f x10^{-13} m^3 mol^{-1}
0.01 M	7.8328	0.5629	0.4972
0.02 M	6.8540	0.5265	4.5970
0.03 M	4.7968	0.4405	20.6027
0.04 M	4.3038	0.4172	53.8394
0.05 M	3.6946	0.3866	125.4629

The adiabatic compressibility (β), free length (L_f) and free volume (V_f) are given in Table 2 & the internal pressure (π_i), relaxation time (τ), Acoustic impedance (Z) and Gibb's free energy (ΔG^*) are given in Table 3.

Table 2.

Molar solution	Density (ρ) in Kgm^{-3}	Viscosity (η) in Nsm^{-2}	Ultrasonic velocity (U) in $msec^{-1}$
0.01 M	948.775	0.6755 x 10^{-3}	1160
0.02 M	948.875	0.6557 x 10^{-3}	1240
0.03 M	951.750	0.6477 x 10^{-3}	1480
0.04 M	954.775	0.6398 x 10^{-3}	1560
0.05 M	959.0	0.6125 x 10^{-3}	1680

Table 3.

Molar solution	Relaxation time (τ) x 10^{-12} sec	Acoustic impedance (Z) x 10^6 k gm^2/sec	Gibb's free energy (ΔG^*) x 10^{-20} KJ/mol	Internal pressure (π_i) x 10^6 Pa
0.01M	0.7055	1.1006	0.2666	1044.5652
0.02 M	0.5992	1.1766	0.2372	197.5302
0.03 M	0.4143	1.4086	0.1709	69.9186
0.04 M	0.3671	1.4895	0.1492	34.6614
0.05 M	0.3017	1.6111	0.1139	19.4651

From Table 1 it is noted that density and ultrasonic velocity increases with increase in molar solution, and viscosity decreases. The increase in velocity is due to the decrease in free length and adiabatic compressibility of the liquid solution. The adiabatic compressibility and free length are the deciding factors of the ultrasonic velocity in the liquid solution. The interdependence of L_f and U has been evolved from model by Erying & Kincaid[15]. The internal pressure decreases and free volume increases with increasing molar solution. The internal pressure may give information regarding the nature and strength of force existing between the molecules. The increase in free volume shows that the strength of interaction decreases gradually with the increase in solute concentration. It represents that there is weak interaction between molecules of the solution.

The relaxation time decreases with increase in molar solution. The dispersion of ultrasonic velocity is the system should contain information about characteristic time τ of the relaxation process that causes dispersion. The relaxation time which is in the order of 10^{-12} sec is due to the structural relaxation process[16] and in such situation it is suggested that the molecules get arranged due to co-operative process[17].

The Gibb's free energy decreases with increasing molar solution. This may be due to the intermediate compound formation between binary liquids. It is observed generally free energy decrease favors the formation of product from reaction.

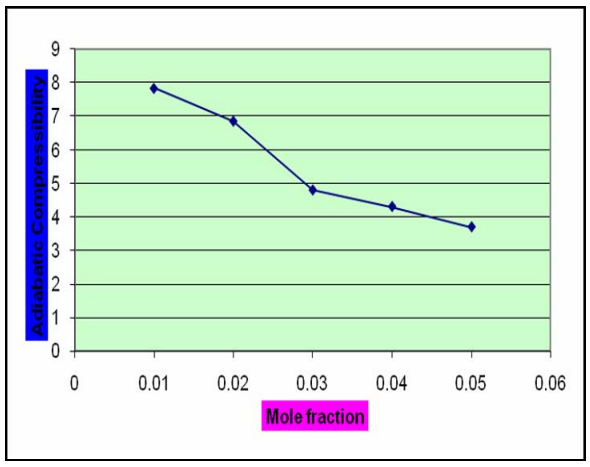

Fig. 1: Adiabatic compressibility Vs mole fraction

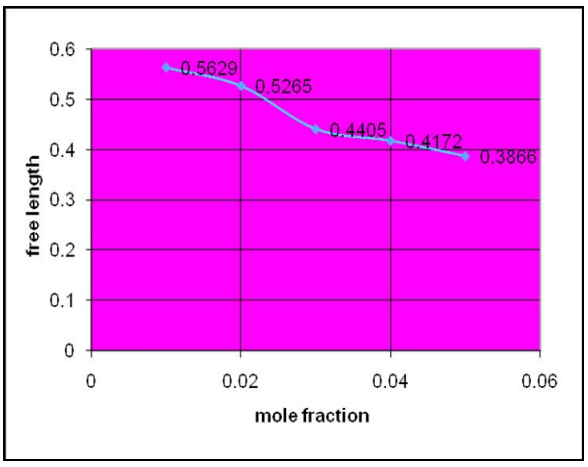

Fig. 2: Free length Vs mole fraction

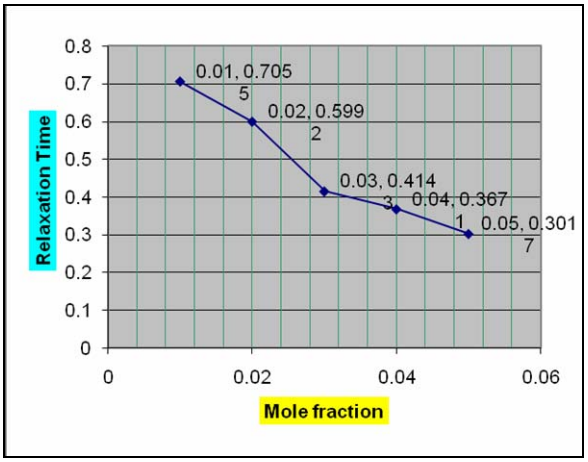

Fig. 3: Relaxation time Vs mole fraction

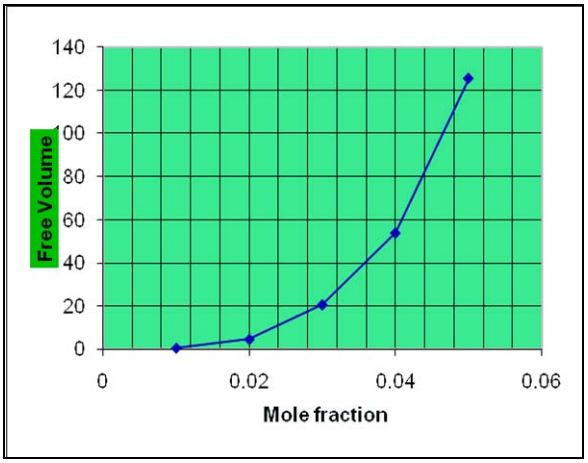

Fig. 4: Free volume Vs mole fraction

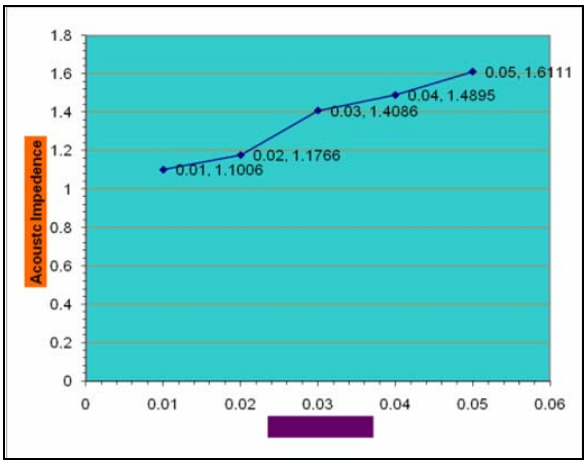

Fig. 5: Acoustic impedence Vs mole fraction

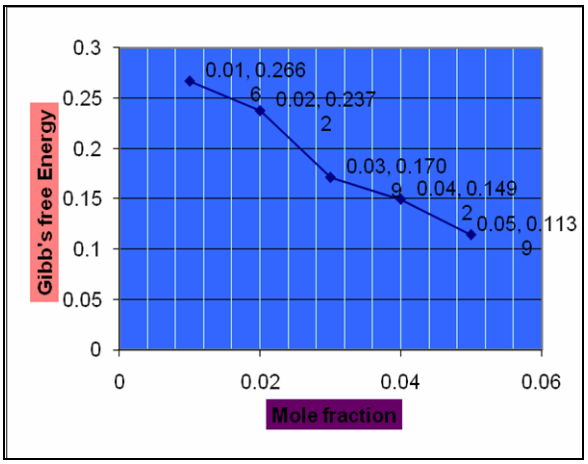

Fig. 6: Gibb's free energy Vs mole fraction

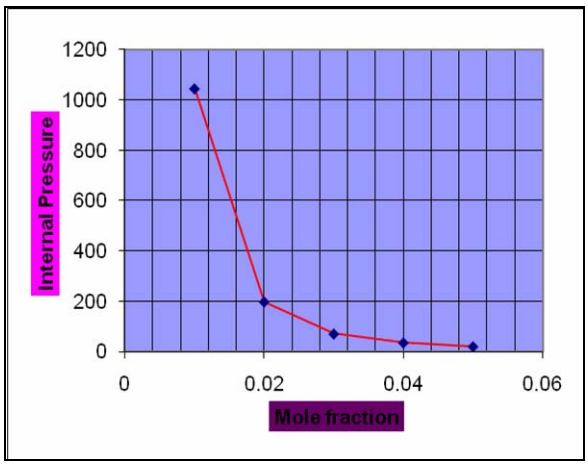

Fig. 7: Internal pressure Vs mole fraction

CONCLUSION

From the data of ultrasonic velocity, density and viscosity, computed acoustical parameters and their values point to the presence of specific molecular interaction in the binary liquid solution. The increase in free volume shows that strength of interaction decreases gradually hence it is concluded that there exists weak interaction between molecules of binary solution of zinc chloride and cadmium chloride with distilled water at 300K. the decrease in Gibb's free energy favors the formation of product from reaction due to intermediate compound formation between binary liquids. Molecules in the binary solution gets arranged due to co-operative process as relaxation time is in the order of 10^{-12} sec.

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