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Study of molecular interactions in binary liquid containing cord liver oil+ aniline of various concentrations at different temperatures

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ABSTRACT
The ultrasonic velocity, density and viscosity have been measured for the binary liquid mixture of Cord liver oil + aniline as a function of different composition (0.2%,0.4%,0.6%,0.8% and 1%) and different temperatures such as 303,308,313,318and 323K. The experimental data has been used to calculate some excess parameters namely, adiabatic compressibility (κ), intermolecular free length (Lf), free volume (V_f), internal pressure (πi), relaxation time (τ), absorption coefficient (α/f^2) and relative association (RA). The results are discussed and interpreted about structural and specific interactions that predominated by hydrogen bonding.

Introduction

Ultrasonic velocities[1], densities, viscosity and derived thermodynamic and acoustical parameters are of considerable interest in understanding the inter-molecular interactions in cord liver oil and aniline mixtures.

When a non polar liquid is mixed with a non-polar liquid there can be three types of interactions, namely di-pole-di-pole[2-5], di-pole-induced di-pole [6-8] and induced di-pole-induced di-pole interactions. The strength of these attractive forces is in the order of di-pole-di-pole interactions>di-pole-induced di-pole>induced di-pole-induced di-pole interactions.

Experimental details

The chemicals used were of analytical grade. The ultrasonic velocities (U) of the liquids mixtures were measured using multi-frequency ultrasonic interferometer at a frequency of 2 MHz (Mittal Enterprises-Model F-05). The accuracy in the measurement of ultrasonic velocity was within ±0.01 ms-1. The densities (ρ) of these solutions were measured using 10 ml specific gravity bottles in an electronic balance precisely within ±0.1 mg accuracy. Ostwald's viscometer was used to measure the viscosities (η) of the solutions. The temperature was maintained constant at 298 K using proportional temperature controller (accuracy ±0.1°C), during the measurement of ultrasonic velocity, density and viscosity values. Acoustical parameters such as adiabatic compressibility (β), free volume (Vf) [9], internal pressure (πi), intermolecular free length (Lf), absorption coefficient (α/f2), relaxation time (τ), Rao constant (R), cohesive energy (CE) and the molecular interaction parameters about velocities (χ) were calculated using standard equations [10-11]

The acoustical parameters are calculated from U, ρ, and η using following relation.

1. Ultrasonic Velocity **(U)**

The relation used to determine the ultrasonic velocity is given by,

$$\mathbf{U = f\lambda \ ms^{-1}}$$

Where, f - Frequency of ultrasonic waves λ - Wave length

2. Adiabatic compressibility **(κ)**

Adiabatic compressibility is defined as[12]

$$\mathbf{\kappa = (1/U^2\,\rho)\quad kg^{-1}\ ms^2}$$

Where, U – Ultrasonic velocity ρ – Density of the solution.

3. Free Volume **(Vf)**

Free volume in terms of the ultrasonic velocity (U) and the viscosity of the liquid (η) as $\mathbf{Vf = (MeffU/k\eta)^{3/2}\quad m^3}$

Where, Meff is the effective molecular weight (Meff =Σ mi xi, in that mi and xi are the molecular weight and the mole fraction of the individual constituents respectively and 'k' is a temperature independent constant equal to 4.28×10^9 for all liquids.

4. Acoustic impedance **(Z)**

The acoustic impedance[13] is computed by the formula

$$\mathbf{Z = U\rho\ kgm^{-2}s^{-1}}$$

Where U –Ultrasonic velocity ρ –Density of the solution

5. Free Length **(Lf)**

Jacobson[14] introduced the concept of the free length in liquids. He suggested the following relation to calculate the intermolecular free length.

$$\mathbf{Lf = (K/U\,\rho^{1/2})\ m}$$

Where U - Ultrasonic velocity of liquid ρ - Density of liquid

K - Jacobson temperature dependent constant defined as

$$\mathbf{K = (93.875 + 0.345T) \times 10^{-8}}$$

6. Absorption Coefficient **(α/f^2)**

The absorption coefficient (α/f^2), also sometimes called attenuation coefficient. It is defined as

$$\mathbf{\alpha/f^2 = 8\pi^2\eta/3\rho U^3}$$

7. Available Volume **(Va)**

The available volume (Va) is a direct measure of compactness and the strength of bonding among the molecules of a liquid or liquid mixture. It may be calculated from following relation

$$\mathbf{Va = Vm(1- U/Ua)\ m^3}$$

Where Vm is the molar volume and Ua=1600ms^{-1}

8. Relative Association **(RA)**

$$\mathbf{RA = (\rho/\rho 0)}$$

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9. Viscous Relaxation time (τ)

Relaxation time (τ) and absorption coefficient are directly correlated[15]. The absorption of a sound wave is the result of the time lag between the passing of the ultrasonic wave and the return of the molecules to their equilibrium position. It is calculated using the relation.[16]

$$\tau = 4\eta / 3\rho U^2$$

Where η - viscosity of the solution ρ - density of solution U - Ultrasonic velocity of the solution.

10. Internal pressure (π_i)

On the basis of statistical thermodynamics, Suryanarayana derived an expression for the determination of internal pressure through use of concept of free volume[17]

$$\pi_i = \mathrm{bRT}\,(k\eta/U)\ 1/2\ (\rho^{2/3}/\mathrm{Meff}^{7/6})$$

Where T – Absolute temperature, **ρ** - Density, and R is the gas constant, Meff – effective molecular weight.

Result And Discussion

The measured ultrasonic velocities(U), densities (ρ), viscosity's (η) and other acoustical parameters such as adiabatic compressibility (κ), free volume (Vf), free length (Lf), acoustic impedance (Z), absorption coefficient(α/f^2), viscous relaxation time (τ),relative association and internal pressure values at 303, 308, 313, 318 and 323K is given in the tables 1,2 and 3.

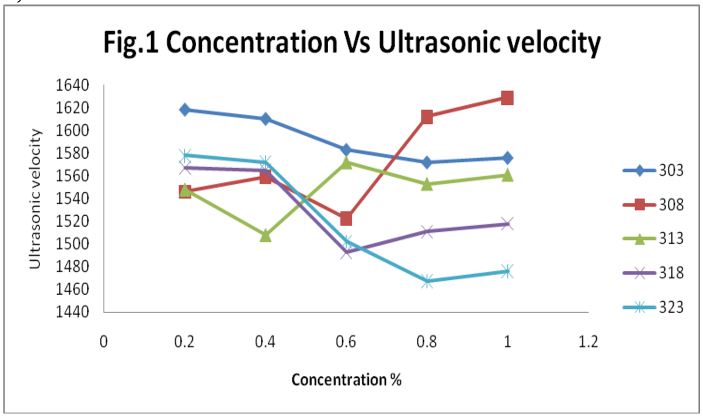

Figure 1 From the graph it is observed that the ultrasonic velocities are decreasing with the increasing value of temperature. But it is decreasing with increasing solute concentration at particular temperature. Plot has been drawn for various velocities, that are various with different concentration and temperature. The increase in ultrasonic velocity at higher temperature because of solvent-solute interaction and decrease in velocity with increase in concentration because the weakening of intermolecular forces among the molecules.

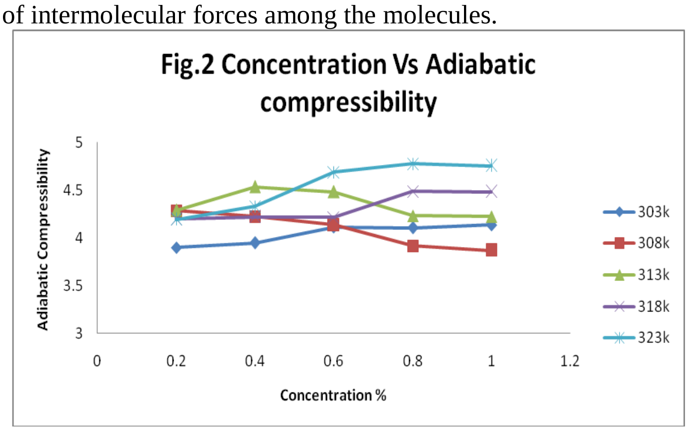

Figure 2 Describe the variation of adiabatic compressibility with different values of temperature as well as concentration. The adiabatic compressibility was calculated from ultrasonic velocity and density. Compressibility values "increases up to maximum value as concentration increases". The minimum the compressibility indicates the poor bond strength and the maximum compressibility indicates the enhancement of bond strength.

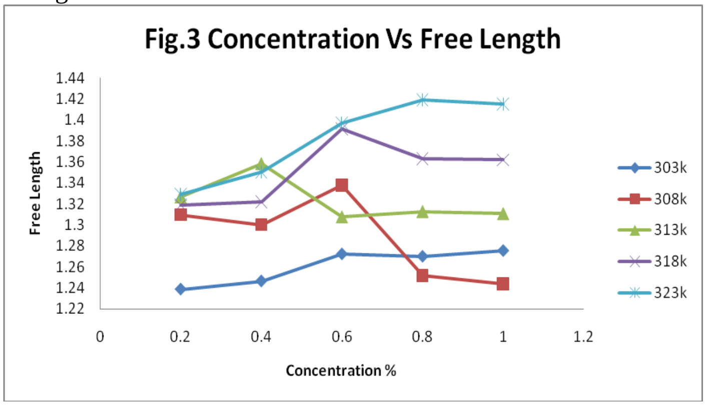

Figure 3 Shows the variation of adiabatic compressibility with different values of temperature as well as concentration. The intermolecular free length depends on the adiabatic compressibility and independent of the velocity. The behavior of intermolecular frees length is an inverse behavior of sound propagation. Here by increasing the concentration of Cord Liver oil and aniline, free length increases. The increase in free-length values with decreasing ultrasonic velocity seems to be because of solute-solute interaction.

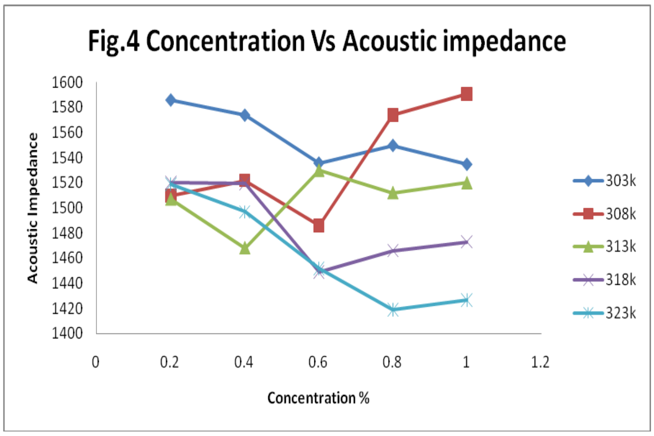

Figure 4 represent the plots among acoustical impedance and temperature. The trend in the variation of impedance with temperature is reversing to that of ultrasonic velocity. Acoustical impedance values also suggest strong molecular interaction among the components at increasing solute concentration. But it is decreases with increasing temperature at all concentrations. It suggested the solute-solvent interaction is fewer at higher temperatures owing to thermal agitation.

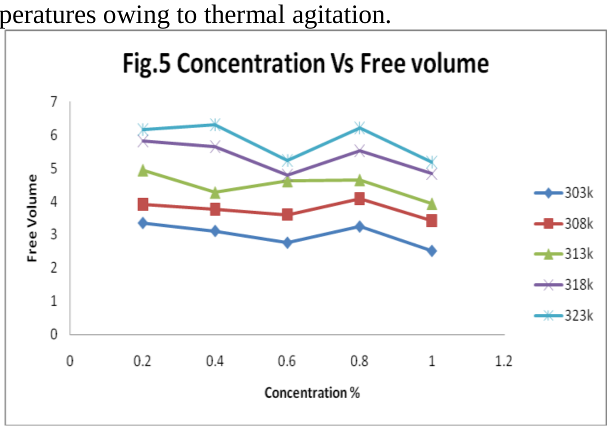

Figure-5 shows that free volume increases with increasing concentrations and frequencies but decreases with increasing temperatures.

Table 1: Ultrasonic velocity, Density, Viscosity and Adiabatic compressibility values for cord liver oil aniline of various concentrations at different temperature

Concentration (%)	Temperature (K)	Ultrasonic Velocity U (ms^{-1})	Density ρ (kg/m^3)	Viscosity $\eta/10^{-4}$, (Nsm^{-2})	Adiabatic compressibility $\kappa/10^{-10}$ ($kg^{-1}ms^2$)
0.2	303	1618	1071.20	3.5915	3.897
	308	1546	1014.19	2.924	4.284
	313	1548	1011.21	2.506	4.284
	318	1567	1008.25	2.273	4.287
	323	1578	1005.31	2.194	4.190
0.4	303	1610	1019.30	3.549	3.947
	308	1559	1016.30	3.027	4.223
	313	1508	1013.32	2.696	4.532
	318	1565	1010.37	2.319	4.219
	323	1572	1007.44	2.132	4.327
0.6	303	1583	1021.10	3.787	4.112
	308	1522	1018.11	3.051	4.132
	313	1572	1015.13	2.672	4.479
	318	1493	1012.18	2.476	4.212
	323	1502	1009.26	2.347	4.686
0.8	303	1572	1023.30	3.383	4.103
	308	1612	1020.31	2.977	3.915
	313	1553	1017.35	2.632	4.232
	318	1511	1014.40	2.279	4.485
	323	1467	1011.48	2.049	4.775
1.0	303	1576	1025.40	4.021	4.134
	308	1629	1022.42	3.392	3.865
	313	1561	1019.46	2.962	4.221
	318	1518	1016.52	2.590	4.478
	323	1476	1013.60	2.331	4.753

Table 2: Free length, Acoustic impedance, Absorption coefficient and Relaxation time values for Cord Liver Oil-Aniline of various concentrations at different temperature

Concentration (%)	Temperature (K)	Free Length Lf / 10^{-9} (m)	Acoustic impedance Z ($kgm^{-2}s^{-1}$)	Absorption coefficient $\alpha/f^2/10^{-8}$ ($Npm^{-1}s^2$)	Relaxation time $\tau/10^{-6}$ (s)
0.2	303	1.2387	1586	2.1481	1.7582
	308	1.3100	1510	2.1305	1.6660
	313	1.3268	1507	1.8240	1.4286
	318	1.3189	1520	1.6006	1.2688
	323	1.3289	1519	1.5388	1.0090
0.4	303	1.2465	1574	2.288	1.8630
	308	1.3005	1522	2.156	1.6999
	313	1.3585	1468	2.129	1.6614
	318	1.3220	1519	1.644	1.3018
	323	1.3505	1497	1.567	1.2268
0.6	303	1.2724	1536	2.587	2.0700
	308	1.3381	1486	2.356	1.8140
	313	1.3079	1530	1.876	1.4919
	318	1.3916	1449	2.036	1.5378
	323	1.3969	1452	1.902	1.4452
0.8	303	1.2701	1550	2.322	1.846
	308	1.2522	1574	1.707	1.5502
	313	1.3130	1512	1.886	1.4815
	318	1.3630	1466	1.779	1.3600
	323	1.4190	1419	1.754	1.3015
1.0	303	1.2756	1535	2.773	2.2110
	308	1.2440	1591	2.115	1.7426
	313	1.3110	1520	2.106	1.6630
	318	1.3620	1473	2.009	1.4280
	323	1.4150	1427	1.973	1.4734

Table 3: Internal pressure, free volume, and Molar volume and Relative Association values for Cord Liver Oil-Aniline of various concentrations at different temperature

Concentration (%)	Temperature (K)	Internal pressure (π_i)	Free volume $Vf/10^{-8}$ (m^3/mol)	Relative Association (RA)
0.2	303	47.141	3.3520	0.9832
	308	45.274	3.9113	0.9839
	313	42.368	4.9398	1.0094
	318	40.546	5.8234	0.9974
	323	40.447	6.1622	0.9888
0.4	303	48.022	3.1150	0.9822
	308	45.602	3.7690	0.9791
	313	43.705	4.2650	1.008
	318	40.715	5.6490	0.9951
	323	39.900	6.3100	0.9910
0.6	303	49.359	2.7620	0.9807
	308	45.595	3.6010	0.9781
	313	42.548	4.6110	0.9943
	318	42.486	4.7850	1.0036
	323	41.920	5.2320	0.9937
0.8	303	47.826	3.2450	0.9989
	308	44.809	4.0820	0.9767
	313	43.410	4.6430	1.0145
	318	41.409	5.5270	1.0160
	323	40.508	6.2030	1.0181
1.0	303	50.975	2.5190	0.9858
	308	46.926	3.4170	0.9660
	313	42.884	3.9280	1.0160
	318	42.675	4.8320	1.0068
	323	42.463	5.17320	1.0082

Free volume is one's of the significant factors in explaining the free space and it is dependent properties have close connection with molecular structure and it can show introduce about interactions between liquid mixtures.

When concentration of solute is increased, because of hydrogen bonding in aniline the molecules of solute may arranged in the solvent in such a way that void space may not be available because of solute becomes less compressible and hence free volume increases. Increase in free volume shows ion-solvent interaction in the solution.

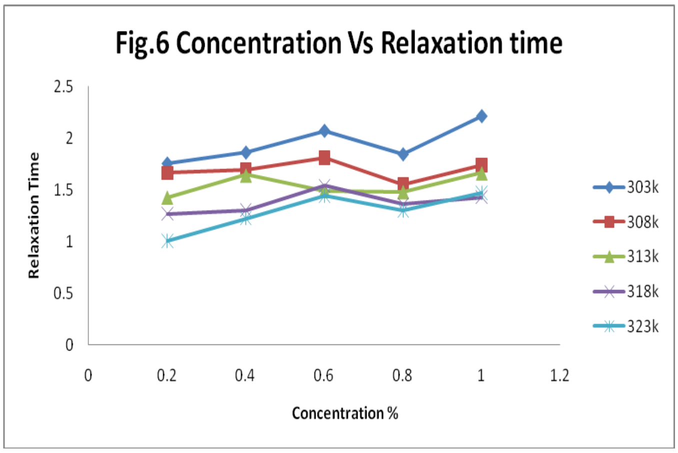

Figure 6 shows variation of relaxation time with concentration and temperature. Acoustic relaxation time increases with increasing concentration. The dispersion of ultrasonic waves are the characteristic time of relaxation processes that causes the dispersion. Increase in relaxation time indicates that degree of cooperation for relaxation of the molecules increases that increases the bulk of cluster when solute is added to solvent.

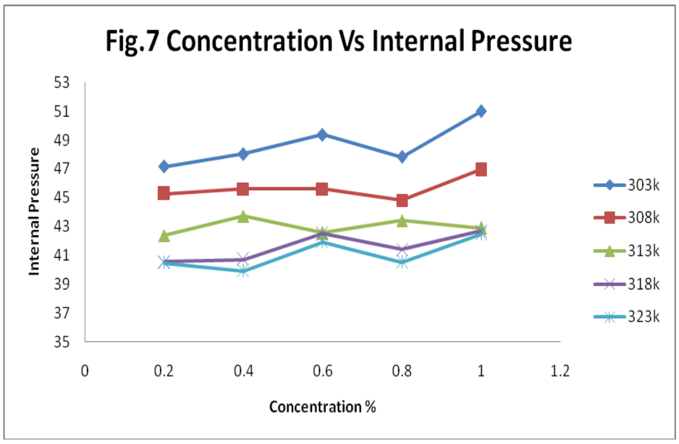

Figure 7 shows variation of internal pressure with concentration and temperature. The internal pressure is a measure of cohesive force among solute and solvent. The internal pressure values are given in a table.3. These values indicate that internal pressure decreases with increasing temperature.

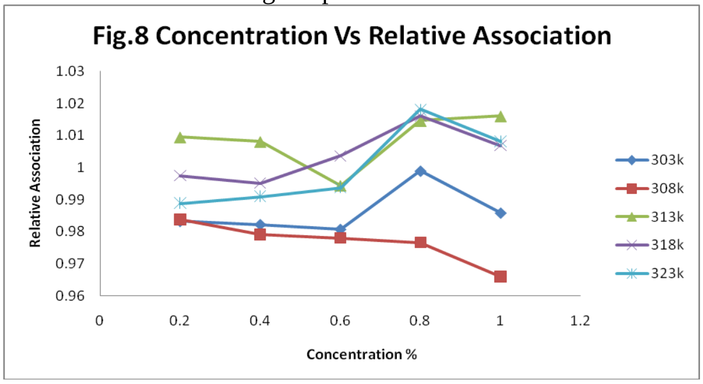

Figure 8 shows variation of Relative Association with concentration and temperature

Relative association is influenced by two factors
1) Breaking's up of associated solvent molecules on addition of solute.
2) The salvation of solute.

When solute is added to solvent salvation of solute takes place and hence relative association increases. This indicates that there can be association of aniline molecules with Cord Liver oil. The increase in relative associations shows strong solute-solvent interaction.[18-20]

Conclusion

The various acoustic parameters as adiabatic compressibility, internal pressure, relaxation time, linear free length, have been evaluated from ultrasonic velocity, viscosity, and density for the binary mixture Cord liver oil at different temperature. Hence it is concluded there is a intermolecular interaction between the cord liver oil and aniline, leading to the possible hydrogen bond formation of the kind of N¨H¨O among unlike molecules.

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