International Journal of Applied Engineering Research
ISSN 0973-4562 Volume 10, Number 9 (2015) pp. 24165-24172

http://www.ripublication.com

Molecular Interaction Studies of Acetonitrile With Chlorobenzene and Bromobenzene In A Non Polar Solvent At 303, 308 and 313K

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Abstract

Densities, viscosities and ultrasonic speeds of ternary mixtures of Acetonitrile with chlorobenzene and bromobenzene in benzene have been measured at (303K, 308K, and 313K) over the entire composition range. From the measured values, Density, Viscosity, Ultrasonic Velocity, Adiabatic Compressibility(β), Free Length(L_f), Free Volume(V_F), Internal Pressure(π_i), Relaxation time(τ), Acoustic impedance(Z), Gibb's free energy(ΔG), Classical absorption coefficient($\frac{d}{f^2}$) and cohesive energy(H) have been calculated. The properties have been used to discuss the presence of significant interactions between the component molecules in the ternary mixtures.

Keywords: Viscosity, Ultrasonic Velocity, Adiabatic compressibility.

Introduction

In recent years the measurement of ultrasonic velocity has got great importance in understanding the nature of molecular interactions in pure liquid and liquid mixtures. Ultrasonic velocity of a liquid is fundamentally related to the binding forces between the atoms or the molecules and has been adequately employed in understanding the nature of molecular interaction in pure liquids [1].Ultrasonic velocity measurement provides an important tool to study the liquid state. The variation of ultrasonic velocity and related parameters throw much light upon the structural changes associated with the liquid mixtures having weakly interacting components as well as strongly interacting components [2,3]. The increase or decrease in ultrasonic velocities has been employed in understanding the nature of molecular interaction in pure liquids binary mixtures [4, 5] and ternary mixtures [6].

Chlorobenzene is neither acidic nor basic colorless liquid with a pleasant smell. Chlorobenzene is insoluble in water and soluble in alcohol, benzene and ether. The rate of reaction with chlorobenzene is faster because it is more reactive. Bromobenzene is less reactive because of its double bond character between carbon and bromine atom [1]. Thus the molecular interactions are likely to be more affected with respect to the ultrasonic related parameters.

The present paper deals with the measurement of density, viscosity, ultrasonic velocity and their excess values of ternary liquid mixtures of acetonitrile with chlorobenzene and bromobenzene in benzene at 303, 308, and 313K.

Materials and Methods

The chemicals used in the present work Acetonitrile, Chlorobenzene, Bromobenzene and Benzene were analytic Reagent grade obtained from E-Merck, India. The mixtures of various concentrations in mole fraction were prepared by taking analytical reagents. In all the mixtures, the mole fraction of Benzene (X_2= 0.4) was kept fixed while the mole fractions of remaining Acetonitrile with Chlorobenzene and Bromobenzene were varied from 0.0 to 0.6 so as to have mixture of different concentration.

The density was determined using a specific gravity bottle (25ml) by relative measurement method. The weight of the sample was measured using a electronic digital balance. An Ostwald's viscometer (10 ml) was used for the viscosity measurement. An Ultrasonic Interferometer having a frequency of 2MHz (Mittal Enterprises, New Delhi, Model: F-81) has been used for velocity measurement. An electronically digital operated constant temperature water bath has been used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at the desired temperature.

Theory and Calculations

Using the measured data of density (ρ), velocity (U) and viscosity (η), the acoustical parameters such as adiabatic compressibility (β), free length (L_f), free volume (V_f), internal pressure (π_i) and Gibb's free energy (ΔG) have been calculated by the following standard expressions [7,8].

Intermolecular free length

$$Lf = K_T \beta^{1/2} m$$

Where K_T is temperature dependent constant called as Jacobson constant and β is the adiabatic compressibility that can be calculated from the velocity of sound and the density of the medium.

$$N^{-1}m^{2.} \quad \beta = \frac{1}{\rho U^2}$$

The relation for free volume in terms of ultrasonic velocity and viscosity of the liquid

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

The expression for the internal pressure by the use of free volume as

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

Gibb's free energy (ΔG*)

$\Delta G^* = 2.303KT \log \frac{h}{KT\tau}$

Viscous Relaxation time (τ)

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

Acoustic impedance (Z)

$Z = U\rho$

Classical Absorption coefficient

$$\frac{d}{f^2} = \frac{8\eta\pi^2}{3U^2\rho}$$

Cohesive energy

$H = \Pi_I\left(\frac{M_{eff}}{\rho}\right)$

Results and Discussion

The experimentally determined values of density, viscosity and ultrasonic velocity for the three systems at different temperatures and hence from these observed values various acoustical parameters like density, viscosity and velocity from fig. 1, adiabatic compressibility, free length and free volume from Table 1, internal pressure, Gibb's free energy, and relaxation time from Table 2 and acoustic impedance, absorption coefficient and cohesive energy are depicted in Table 3.

Table 1: Adiabatic compressibility, free length and free volume of liquid mixtures at 303, 308,313K.

X_1	X_3	**Adiabatic compressibility**			**Free length**			**Free volume**		
		$x10^{-10}$ $N^{-1}m^2$			**$x10^{-10}$ m**			**$x10^{-7}m^3mol^{-1}$**		
		303K	**308K**	**313K**	**303K**	**308K**	**313K**	**303K**	**308K**	**313K**
Acetonitrile+benzene+chlorobenzene										
0.6000	0	7.186	7.458	8.013	0.5348	0.5492	0.5746	2.503	2.732	2.876
0.5000	0.1000	7.128	7.527	8.219	0.5327	0.5518	0.5820	2.431	2.696	2.767
0.4000	0.2000	7.180	7.291	7.797	0.5346	0.5430	0.5668	2.440	2.676	2.822
0.3000	0.2999	7.033	7.300	7.636	0.5291	0.5434	0.5610	2.386	2.637	2.833
0.1999	0.4000	7.077	7.143	7.567	0.5308	0.5375	0.5584	2.430	2.756	2.857
0.1000	0.4999	7.018	7.289	7.789	0.5285	0.5430	0.5665	2.514	2.741	2.852
0	0.6000	7.256	7.816	7.974	0.5374	0.5622	0.5732	2.414	2.607	2.845
Acetonitrile+benzene+bromobenzene										
0.6000	0	6.761	6.8984	7.003	0.5200	0.5282	0.5372	2.381	2.693	2.770
0.5000	0.1000	6.304	6.4090	6.543	0.5009	0.5091	0.5193	2.729	3.031	3.180
0.4000	0.2000	6.205	6.4867	6.533	0.4970	0.5122	0.5193	2.915	3.139	3.360
0.3000	0.2999	5.984	6.1486	6.639	0.4881	0.4987	0.5231	3.012	3.356	3.270
0.1999	0.4000	5.983	6.1653	6.597	0.4880	0.4993	0.5214	3.204	3.295	3.400
0.1000	0.4999	5.839	5.8785	6.411	0.4821	0.4876	0.5140	3.438	3.572	3.490
0	0.6000	5.729	6.1256	6.222	0.4775	0.4977	0.5064	3.386	3.247	3.290

The ultrasonic velocity, density, viscosity decreases in all the cases as temperature increases. The same result was obtained by A.N. Kannappan et al [2]. From the Tables (2,3) it was observed that with rise in temperature increase in free volume and decrease in internal pressure are noticed. The relaxation time increases with increase in mole fraction of chlorobenzene and bromobenzene. With rise in temperature, increase in free volume and decrease in internal pressure noticed. This suggest that the closed packing of molecules inside the shield. Similar results in some liquid mixtures were also reported by others [10].

Table 2: Internal Pressure, Gibb's free energy and Relaxation time of Liquid mixtures at 303, 308,313K.

		Internal Pressure			**Gibb's free energy**			**Relaxation time**		
		$x10^6$ Pa			**$x10^{-20}$ KJmol^{-1}**			**$x10^{-12}$ sec**		
X_1	X_3	**303K**	**308K**	**313K**	**303K**	**308K**	**313K**	**303K**	**308K**	**313K**
Acetonitrile+benzene+chlorobenzene										
0.6000	0	480.5	472.4	469.4	0.3967	0.3945	0.4105	0.4092	0.3944	0.3968
0.5000	0.100	462.4	452.1	452.7	0.4433	0.4413	0.4690	0.4575	0.4403	0.4543
0.4000	0.200	441.7	434.6	431.7	0.4803	0.4729	0.4885	0.4998	0.4742	0.4753
0.3000	0.299	428.5	420.0	415.3	0.5144	0.5104	0.5158	0.5422	0.5180	0.5063
0.1999	0.400	409.5	397.6	398.2	0.5435	0.5249	0.5433	0.5813	0.5360	0.5396
0.1000	0.499	390.0	384.1	384.1	0.5900	0.5596	0.5794	0.6032	0.5815	0.5867
0	0.600	381.2	376.5	370.2	0.6044	0.6163	0.6136	0.6724	0.6645	0.6350
Acetonitrile+benzene+bromobenzene										
0.6000	0	503.3	489.7	491.5	0.3897	0.3725	0.3812	0.4023	0.3744	0.3707
0.5000	0.1000	449.1	439.8	438.4	0.3978	0.3850	0.3902	0.4102	0.3856	0.3785
0.4000	0.2000	415.5	411.3	408.2	0.4266	0.4291	0.4254	0.4395	0.4277	0.4107
0.3000	0.2999	393.9	385.4	395.1	0.4519	0.4414	0.4800	0.4669	0.4404	0.4660
0.1999	0.4000	361.6	363.3	364.9	0.4802	0.4935	0.5140	0.4996	0.4978	0.5042
0.1000	0.4999	343.9	344.2	352.6	0.4864	0.4920	0.5323	0.5071	0.4959	0.5259
0	0.6000	333.4	345.6	351.7	0.5157	0.5573	0.5708	0.5438	0.5783	0.5751

Table 3: Acoustic impedance, classical absorption coefficient, and cohesive energy of liquid mixtures at 303, 308,313K.

		Acoustic impedance			**Absorption coefficient**			**Cohesive energy**		
		$x10^6$Kgm^2/sec			**$x10^{-12}$Npm^{-1}s^{-2}**			**$x10^{-5}$KJmol^{-1}**		
X_1	X_3	**303K**	**308K**	**313K**	**303K**	**308K**	**313K**	**303K**	**308K**	**313K**
Acetonitrile+benzene+chlorobenzene										
0.6000	0	1.0703	1.0474	1.0063	8.0786	7.7874	7.8328	21.308	21.439	21.616
0.5000	0.1000	1.1010	1.0678	1.0172	9.0322	8.6935	8.9692	22.897	23.053	23.267
0.4000	0.2000	1.1194	1.1095	1.0687	9.8669	9.3613	9.3825	24.485	24.545	24.740
0.3000	0.2999	1.1541	1.1302	1.1023	10.704	10.225	9.9943	25.915	26.032	26.163
0.1999	0.4000	1.1736	1.1588	1.1236	11.362	10.581	10.654	27.481	27.649	27.760
0.1000	0.4999	1.1873	1.1625	1.1222	11.908	11.480	11.582	29.074	29.199	29.325
0	0.6000	1.1798	1.1341	1.1195	13.275	13.118	12.359	30.705	30.847	31.028
Acetonitrile+benzene+bromobenzene										
0.6000	0	1.1310	1.1150	1.1044	7.9007	7.3838	7.3116	20.380	20.467	20.549
0.5000	0.1000	1.2222	1.2079	1.1923	8.0618	7.6048	7.4651	22.586	22.665	22.783
0.4000	0.2000	1.2783	1.2467	1.2413	8.6427	8.4354	8.0994	24.5604	24.630	24.668
0.3000	0.2999	1.3502	1.3278	1.2776	9.1783	8.6844	9.1896	26.178	26.262	26.267
0.1999	0.4000	1.3666	1.3413	1.2958	9.8161	9.8168	9.9426	28.847	28.954	28.990
0.1000	0.4999	1.4307	1.4201	1.3601	9.9588	9.7806	10.3719	30.033	30.157	30.145
0	0.6000	1.4668	1.4303	1.4256	10.8141	11.4045	11.3408	31.699	31.437	31.156

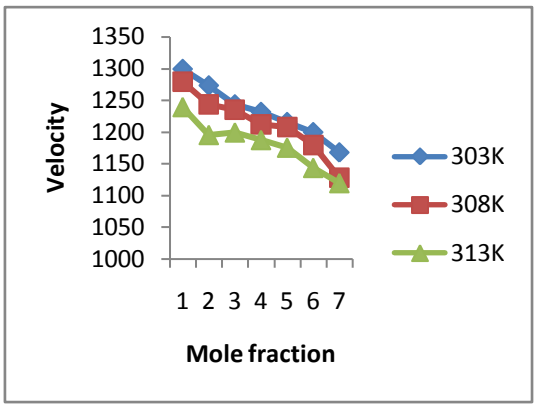


Figure 1:

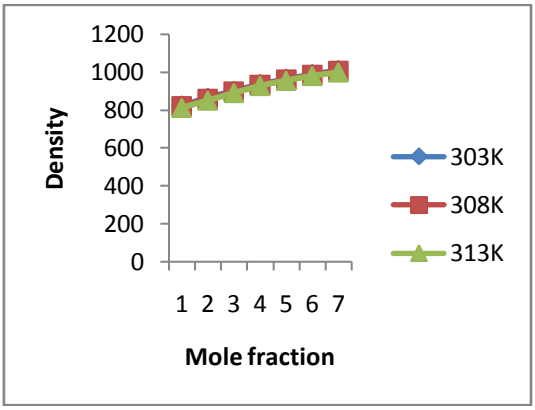
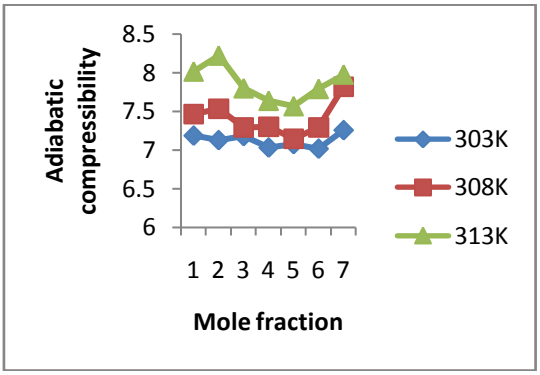


Figure 2:



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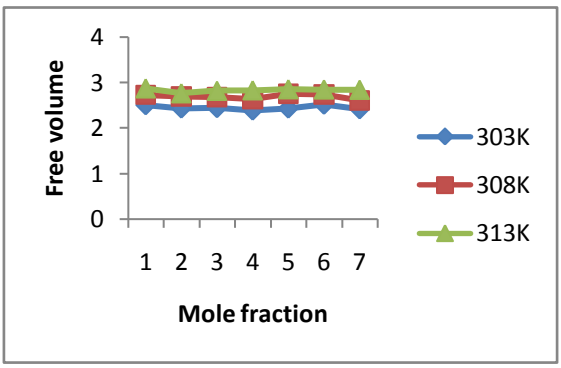

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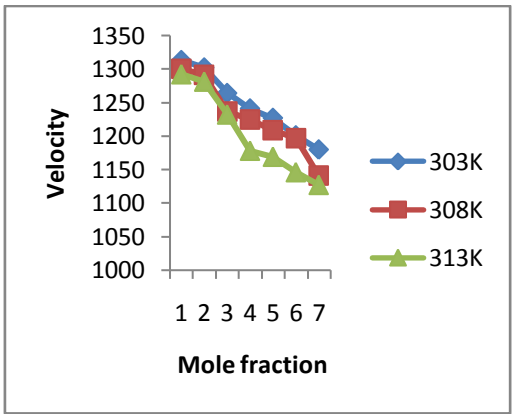

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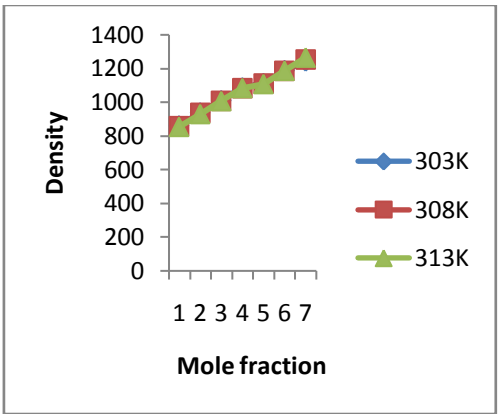

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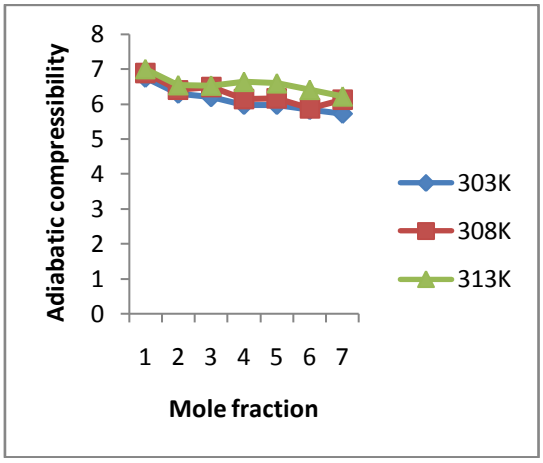

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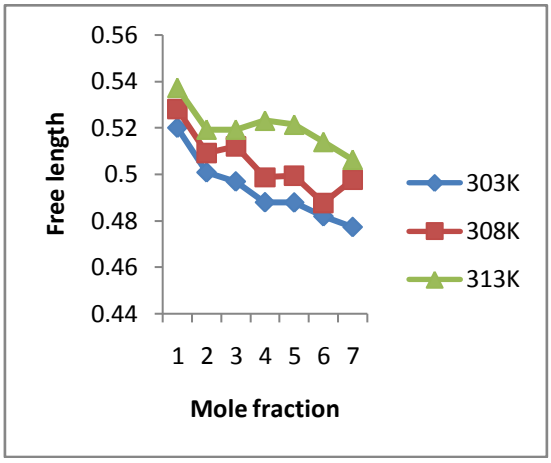

Figure 8:

Absorption coefficient and relaxation time calculated from the ultrasonic velocity, density and viscosity values are given in Table 4 and these values can be used to characterize the intermolecular interactions. It is found that the two parameters do not change significantly at a given temperature. Figure (1 to 4) represents the variation of molefraction with velocity, density, adiabatic compressibility and free length of the concentrations of Acetonitrile with Chlorobenzene and Benzene.. Figure (5 to 8) represents the variation of molefraction with velocity, density, adiabatic compressibility and free length of the concentrations of Acetonitrile with Bromobenzene and Benzene. This suggests that similar interactions exist in the systems. In view of greater force of interaction between the molecules there will be an increase in cohesive energy and the occurrence of structural changes takes place.

Conclusion

The results obtained for the present study indicates that the present study infer that the molecular interaction is present in the liquid mixtures. From Ultrasonic velocity, related acoustic parameters for ternary mixtures of Acetonitrile with Chlorobenzene and Bromobenzene in benzene for various concentration at 303K, 308K, 313K,it has been found that there exist strong molecular interaction between the liquid mixtures.

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