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Ultrasonic studies on molecular interaction of a fragrant moiety with aprotic polar solvent in their binary mixtures

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Ultrasonic study is an enabling technique for understanding the nature of molecular interactions in binary mixtures. Ultrasonic velocity (u), density (ρ), and viscosity (η) for binary mixtures of dihydromyrcenol (DHMOH: a commercial fragrant entity) with acetone, bearing different molar concentrations were measured at the temperatures 298.15K, 303.15K, and 308.15K. The acoustic derived parameters such as adiabatic compressibility (κ), acoustic impedance (*Z*), intermolecular free length (L_f), and molar volume (V_m) were also determined. The effect of molar concentration and temperature variations on various parameters was taken into consideration. The measured values of ultrasonic velocity, density and viscosity were found to increase with the increase in concentration of the solute and decrease with increase in temperature. The chosen acoustic parameters revealed a strong relationship with both concentration and temperature of binary mixtures.

Keywords: Ultrasonic velocity, Viscosity, Density, Acetone, Intermolecular interactions.

INTRODUCTION

The experimental determination of density, viscosity and ultrasonic velocity provides a better tool to understand the nature of molecular interactions in a binary mixture. The properties of the binary mixture depend upon its composition and find many applications in different chemical, industrial and biological processes [1, 2]. Therefore, the study of intermolecular interactions in the binary liquid mixtures is of considerable importance. Hence, to study the thermodynamic properties and nature of molecular interactions in the binary mixtures of dihydromyrcenol (DHMOH, 2,6-dimethyl-7-octen-2-ol) with acetone, the ultrasonic velocity, density and viscosity were measured in different compositions at 298.15, 303.15, and 308.15 K. Dihydromyrcenol is widely used as a fragrance ingredient in many useful products [3]. The molecular structure of dihydromyrcenol is shown in Figure 1. The molecules of acetone have a carbonyl functional (C=O) group. It is the simplest and smallest ketone having polar aprotic nature. Acetone is a colourless liquid solvent miscible with water. Thus, the growing demand of acetone and dihydromyrcenol in various products emphasizes the need to study the thermodynamic properties of liquids and their binary mixtures at different temperatures. Hence, in the present work, the density, viscosity, and ultrasonic velocity were measured at three temperatures, 298.15, 303.15, and 308.15 K. By using the experimental values, parameters such as adiabatic compressibility (κ), acoustic impedance (*Z*), molecular free length (L_f), and molar volume (V_m) were calculated by using the standard relation [1, 2, 4-7] and discussed in the next section. These parameters were helpful in understanding the nature of molecular interaction between solute and solvent. The variations in the derived parameters with temperature and molar concentration were further discussed in terms of molecular interaction between the components of the binary mixtures. Thus, the present study gives a better understanding of the intermolecular interactions in the binary system.

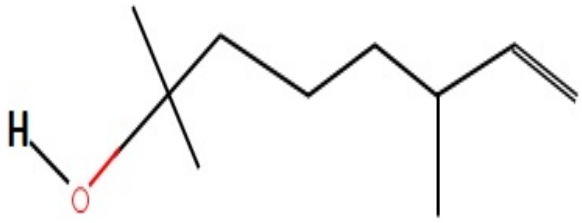

Figure 1. Structure of dihydromyrcenol (2,6-dimethyl-7-octen-2-ol) in 2D.

EXPERIMENTAL

The chemical liquid used as a solvent was purchased from S. D. Fine Chemicals, India and dihydromyrcenol (DHMOH) from Hina Chemicals,

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Gujarat (India). Binary mixtures were prepared by weighing the liquids in specially designed ground glass stoppered weighing bottles. After that, a stock solution was prepared which was diluted to different desired molar concentrations. An electronic balance of sensitivity OF 0.0001 g was used for weighing appropriate mass of the solute. The densities and viscosities of the liquids were measured at three temperatures with a specific gravity bottle and Cannon Fenske viscometer. The time taken for the flow of liquids in Cannon Fenske viscometer was measured by an electronic digital stop watch with an accuracy of ±0.01 sec. An electrically operated constant temperature-circulating water bath (Mittal Enterprises, New Delhi) was used to keep the temperature constant during the experimental observations. The ultrasonic velocities were determined by using a single frequency ultrasonic interferometer of frequency 2 MHz (Model: F-05 Mittal Enterprises, New Delhi). Before starting the experimental measurements with the ultrasonic interferometer, its measuring cell of capacity 10 mL was properly cleaned and dried to eliminate any factor which may create experimental error in the measured values. For accurate calibration of instruments some pure solvents such as 1-propanol, 2-propanol, 1-butanol, 2-butanol and acetone were used to determine the density (ρ), viscosity (η) and ultrasonic velocity (u) at 303.15 K, related to the standard data described in the available literature and depicted in Table 1.

RESULTS

The experimental values of density, viscosity and ultrasonic velocity of the binary mixtures of DHMOH and acetone as a function of molar concentration at three temperatures are listed in Table 2. Experimental values of these fundamental parameters were further used to compute parameters, such as adiabatic compressibility (κ), acoustic impedance (Z), molecular free length (L_f) and molar volume (V_m). The expressions used for the calculation of the derived parameters, which are available in literature [1, 4-7] are as follows:

Adiabatic compressibility $\kappa = \frac{1}{\rho u^2}$ (1)

Acoustic impedance $Z = \rho u$ (2)

Molecular free length $L_f = \frac{K_T}{u\rho^{1/2}}$ (3)

where K_T is Jacobson constant that depends on temperature and is given by:

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

Molar volume of the liquid mixture is:

$$V_m = \frac{\bar{M}}{\rho} \quad (4)$$

where $\bar{M}$ is mean molecular weight of the mixture.

Table 1. Comparison of density (ρ), viscosity (η) and ultrasonic velocity (u) with available literature data.

Liquids	Density (ρ) kg/m^3		Viscosity (η)mPa.s		u (ms^{-1})	
	Expt.	Lit.	Expt.	Lit.	Expt.	Lit.
1-propanol	795.42	798.00 [12] 795.71 [14]	1.590	1.610 [12]	1191.2	1189.2 [12] 1189.8 [14]
2-propanol	777.75	776.80 [10,11] 776.50[14]	1.812	1.800 [10,11]	1127.6	1126.3 [14]
1-butanol	802.80	802.60 [8] 804.40 [9] 804.00 [12]	2.104	2.222 [8] 2.151 [9] 2.054 [12]	1228.8	1228.1 [8] 1229.1 [9] 1228.4 [12]
2-butanol	796.42	798.12[15] 798.80 [16]	2.352	2.553 [16]	1193.6	1194.0 [15]
Acetone	780.23	779.00 [13] 780.33 [15]	0.313	0.292 [13] 0.295 [15]	1142.2	1141.2 [13]

Table 2. Measured values of density (ρ), viscosity (η) and ultrasonic velocity (u) of binary mixtures in terms of molar concentration at different temperatures.

Conc. (Moles/lt)	Density, (ρ×10^{3}kg/m^3), at different temperatures (K)		
(M)	298.15K	303.15K	308.15K
0.00	0.7851	0.7802	0.7761
0.01	0.7857	0.7808	0.7770
0.02	0.7864	0.7814	0.7775
0.03	0.7870	0.7821	0.7781

0.04	0.7877	0.7827	0.7786
0.05	0.7885	0.7835	0.7794
0.06	0.7891	0.7842	0.7801
0.07	0.7899	0.7850	0.7806
0.08	0.7906	0.7857	0.7812
0.09	0.7914	0.7866	0.7819
0.10	0.7922	0.7874	0.7825
	Viscosity, η (mPa.s), at different temperatures (K)		
0.00	0.3157	0.3132	0.2990
0.01	0.3191	0.3164	0.3024
0.02	0.3225	0.3198	0.3058
0.03	0.3260	0.3235	0.3095
0.04	0.3301	0.3274	0.3134
0.05	0.3332	0.3305	0.3165
0.06	0.3363	0.3336	0.3196
0.07	0.3391	0.3364	0.3224
0.08	0.3419	0.3392	0.3252
0.09	0.3451	0.3424	0.3284
0.10	0.3479	0.3452	0.3312
	Ultrasonic velocity, u (ms^{-1}), at different temperatures (K)		
0.00	1153.21	1142.20	1122.00
0.01	1156.30	1145.31	1128.06
0.02	1161.31	1150.11	1135.70
0.03	1166.40	1155.20	1139.12
0.04	1172.81	1160.28	1143.88
0.05	1176.50	1165.12	1149.08
0.06	1182.73	1171.66	1155.28
0.07	1186.40	1176.68	1160.12
0.08	1193.74	1180.44	1164.02
0.09	1199.30	1186.04	1169.56
0.10	1203.11	1193.27	1174.92

Table 3. Calculated values of adiabatic compressibility (κ_s), acoustic impedance (Z), molecular free length (L_f) and molar volume (V_m) at different concentrations and temperatures.

Conc. (Moles/lt) (M)	Adiabatic compressibility K× 10^{-10} (m^2/N) 298.15K	303.15K	308.15K
0.00	9.578	9.825	10.235
0.01	9.519	9.764	10.113
0.02	9.429	9.675	9.972
0.03	9.340	9.581	9.904
0.04	9.230	9.490	9.816
0.05	9.163	9.401	9.717
0.06	9.059	9.289	9.605

0.07	8.994	9.201	9.518
0.08	8.876	9.134	9.448
0.09	8.785	9.037	9.349
0.10	8.720	8.919	9.258
		Acoustic impedance $Z\times 10^5$ (Kg m^{-2} s^{-1})	
0.00	9.054	8.911	8.708
0.01	9.085	8.943	8.765
0.02	9.133	8.987	8.830
0.03	9.180	9.035	8.863
0.04	9.238	9.082	8.906
0.05	9.277	9.129	8.956
0.06	9.333	9.188	9.012
0.07	9.371	9.237	9.056
0.08	9.438	9.275	9.093
0.09	9.491	9.329	9.145
0.10	9.531	9.396	9.194
		Intermolecular free length $L_f\times 10^{-11}$ m	
0.00	6.3653	6.5056	6.7002
0.01	6.3459	6.4854	6.6603
0.02	6.3157	6.4559	6.6134
0.03	6.2857	6.4246	6.5910
0.04	6.2486	6.3940	6.5615
0.05	6.2259	6.3642	6.5284
0.06	6.1907	6.3258	6.4905
0.07	6.1684	6.2956	6.4613
0.08	6.1278	6.2728	6.4372
0.09	6.0963	6.2396	6.4038
0.10	6.0739	6.1986	6.3722
		Molar volume, $V_m\times 10^{-4}$ (m^3/mol)	
0.00	0.7398	0.7444	0.7484
0.01	0.7517	0.7564	0.7601
0.02	0.7635	0.7684	0.7723
0.03	0.7754	0.7803	0.7843
0.04	0.7872	0.7922	0.7964
0.05	0.7989	0.8040	0.8082
0.06	0.8107	0.8158	0.8200
0.07	0.8223	0.8274	0.8321
0.08	0.8340	0.8392	0.8440
0.09	0.8456	0.8507	0.8558
0.10	0.8571	0.8623	0.8677

ANALYSIS OF THE RESULTS

The experimental values of density, viscosity and ultrasonic velocity at temperatures 298.15K, 303.15K, and 308.15 Kare listed in Table 2. The values of adiabatic compressibility (κ), acoustic impedance (Z), molecular free length (L_f), and molar volume (V_m) at three different temperatures are given in Table 3. The experimental values of ultrasonic velocity, density, and viscosity are plotted as a function of molar concentration as shown in Figs. 1, 2 (a) & 2(b). From these figures, it can be observed that the experimental values of fundamental parameters increased with the increase in molecular concentration of DHMOH. However, the experimental values of said parameters decreased with the increase in temperature. This shows that the intermolecular forces decrease due to increase in thermal energy causing agitation in molecules of the system [2, 9]. From Table 2, it can be easily inferred that the measured values linearly increase with the increase in solute concentration. There may be an intermolecular interaction in the binary system which contributes to this behaviour [2, 6]. Further, the values of derived parameters, i.e., κ, Z, L_f and V_m, given in Table 3, are plotted in terms of molar concentration (M) as shown in Figs. 3(a,b,c &d).The results show that the adiabatic compressibility and intermolecular free length values show inverse relationship with ultrasonic velocity which is on expected lines as it is clear from the derived equations. These said parameters decreased with molecular concentration. The decreasing behaviour of 'κ' and L_f indicates that there is strong interaction between the molecules which causes the molecules to become closer together, thus resulting in a less compressible nature [6]. This may be due to the formation of a strong envelope around the solute molecules by the solvent leading to a decrease in compressibility. This fact is also supported by the increase in acoustic impedance. Eyring and Kincaid model [17] proposed that ultrasonic velocity increases with the decrease in intermolecular free length and *vice versa* when mixing two components. Similar trends were observed in the present study for intermolecular free length and ultrasonic velocity.

Acoustic impedance is the resistance of propagation of ultrasonic waves through the medium. Table 3 and Fig. 3(b), clearly reflect that the values of acoustic impedance decrease with the increase in temperature and increase with the increase in molar concentration. The changes observed in acoustic impedance with temperature and molar concentration further confirm the intermolecular interaction between the molecules [18, 19]. Besides these, the molar volume (V_m) is also found to increase with the increase in concentration of DHMOH.

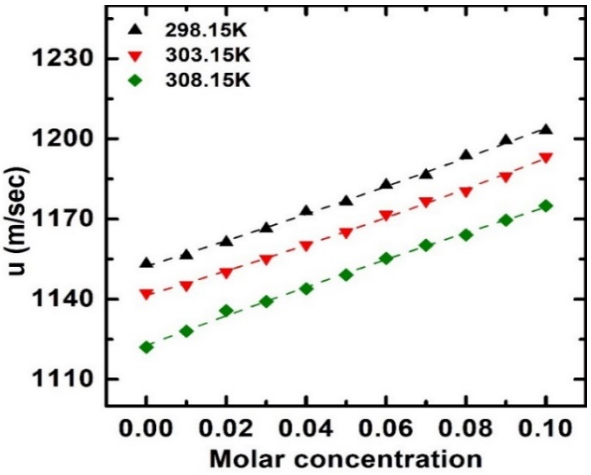

Figure 1. Variation in measured ultrasonic velocity as a function of concentration at different temperatures.

CONCLUSION

The measured values of fundamental parameters were found to increase with concentration of solute in binary mixtures whereas these values decreased with the increase in temperature, thus indicating presence of intermolecular interactions in the experimental binary mixtures. It was also observed that the ultrasonic velocity increased with the concentration of DHMOH whereas the intermolecular free length decreased. On the contrary, ultrasonic velocity showed a reduction in values with the increase in temperature which may be due to the rise in thermal energy of binary system. The decrease in adiabatic compressibility suggests a formation of solvation layer around the solute molecules which indicates a marked molecular interaction in binary mixtures.

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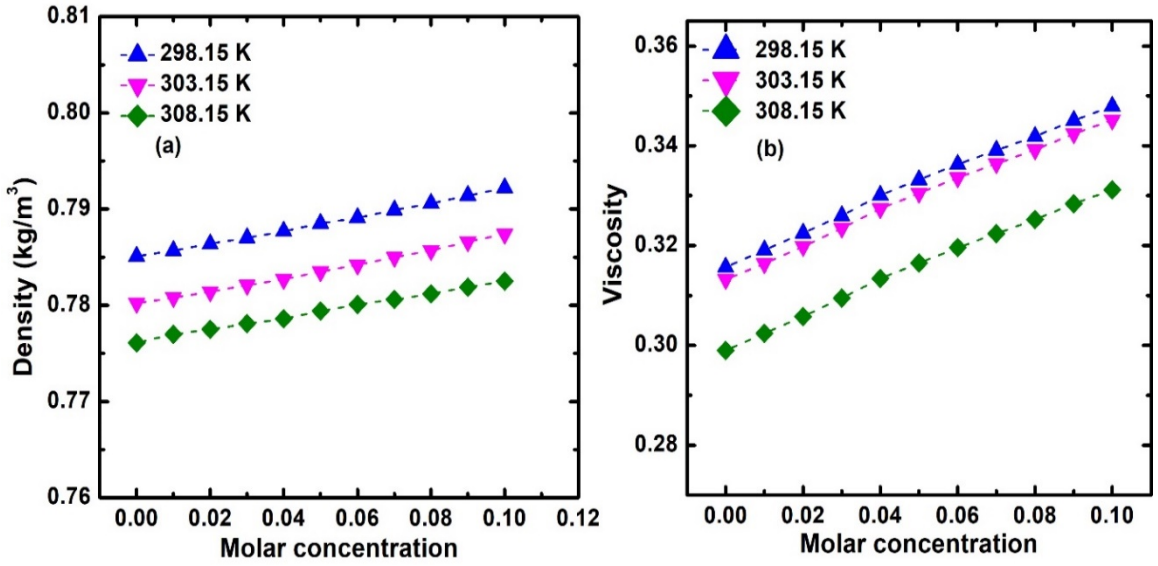

Figure 2. Measured values of density (ρ), viscosity (η) at different molar concentrations and temperatures.

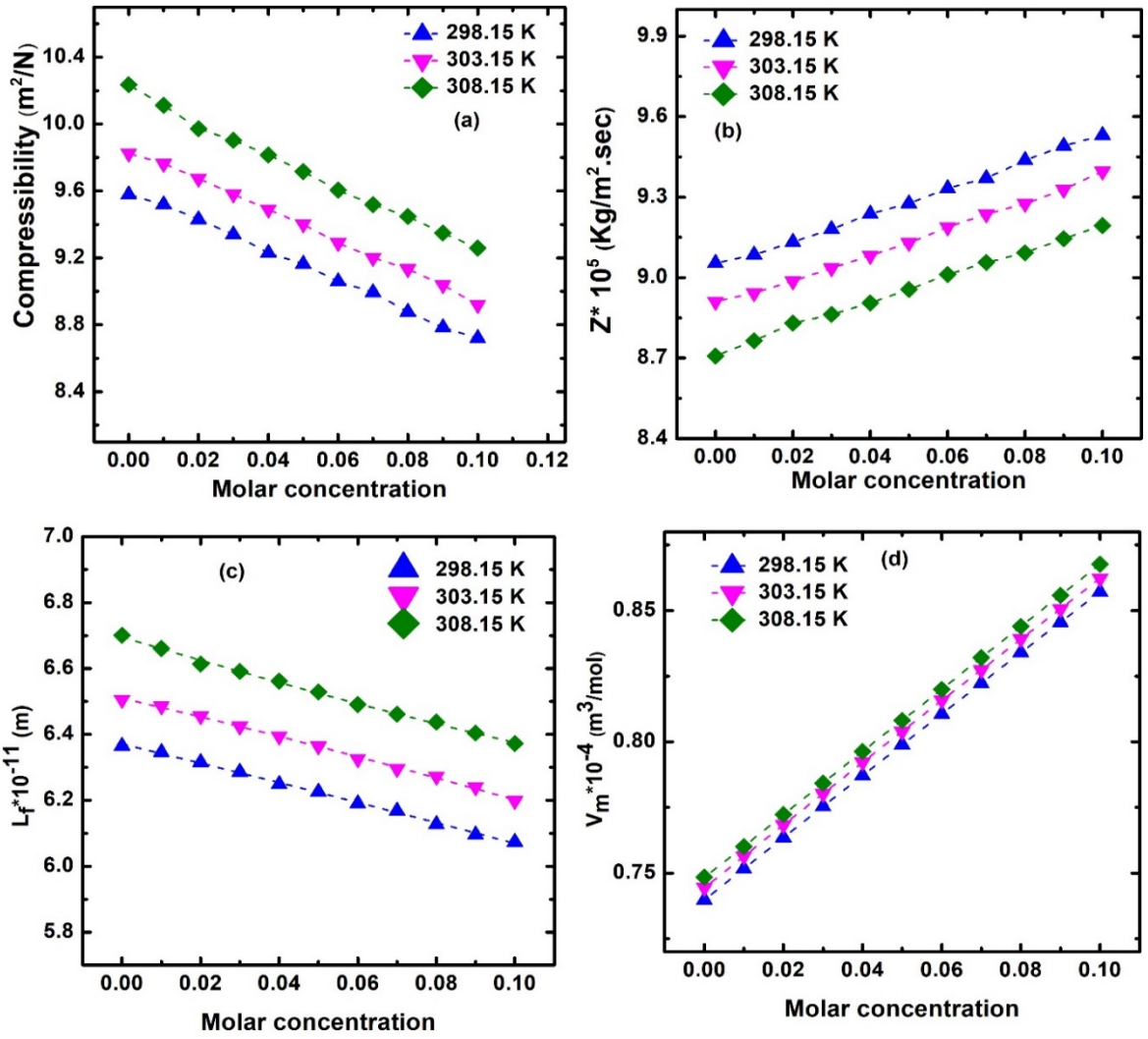

Figure 3. Variation in derived parameters; adiabatic compressibility (κ), acoustic impedance (*Z*), molecular free length (L_f), and molar volume (V_m)sat different molar concentrations at three different temperatures.

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