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Review

Study of Molecular Interactions among Esters, Toluene and Aniline using Ultrasonic Technique

R. Ezhil Pavai[1*], S. Renuka[1], L. Balu[2] and P. Vasantharani[1]

[1]Department of Physics, Annamalai University, Annamalainagar – 608 002, Tamil Nadu, India; [2]Faculty of Engineering and Technology, Annamalai University, Annamalainagar – 608 002, Tamil Nadu, India

Abstract

The interactions of esters (ethyl acrylate and ethyl benzoate) with common binary of toluene + aniline were studied using ultrasonic velocity, density and viscosity measurements at 303, 308 and 313K. From the experimental data, the acoustical parameters such as adiabatic compressibility (β), free length (Lf), free volume (Vf), internal pressure (πi), acoustic impedance (Z) and their excess values were estimated using standard relation. The results of these parameters are attributed to weak hydrogen bond between solute and solvent molecules.

Keywords: Ultrasonic study; ternary mixtures; acoustical parameters; molecular interaction

Introduction

As a part of our ongoing research program concerning the physico-chemical properties of ternary liquid mixtures, we present here the results of ternary mixtures of esters (ethyl acrylate and ethyl benzoate) in the common binary of toluene + aniline at 303, 308 and 313K. Ester is one of the best candidates that exist as dipolar associates in their pure liquid state and find wide industrial applications [1]. It is used as solvents, essences and perfumes and they play an important role as flavoring agents in many chemical formulations. Aniline molecule is highly polar (μ = 1.51 D at 298.15K) [2], and self associated through hydrogen bonding of their amino group [3]. It is used in the manufacturing of synthetic dyes, drugs etc. and toluene is aprotic and polar in nature due to the presence of electron releasing methyl group. Therefore, interesting results may be obtained regarding molecular interactions between unlike molecules in the ternary mixtures. A survey of literature indicates that there has been practically no study of the ternary mixtures of these systems from the point of view of their ultrasonic behavior. The measurement of ultrasonic speed enables the accurate determination of some useful parameters and their excess functions, which are highly sensitive to molecular interactions and can be used to provide qualitative information about the physical nature and strength of molecular interaction in the liquid mixtures. Ultrasonic velocity studies in conjunction with density and viscosity studies also play a vital role in the investigation of intermolecular interaction in mixed liquid systems.

The present note deals with the study of ultrasonic velocity (U), density (ρ), viscosity (η), adiabatic compressibility (β), free length (L_f), free volume (V_f), internal pressure (π_i), acoustic impedance (Z) and their excess values for two ternary systems. The results were analyzed in terms of intermolecular interactions between the constituent components of the mixture.

Experimental details

Ethyl acrylate, ethyl benzoate, aniline and toluene (AR grade) were purified by the standard method [4]. Liquid mixtures of different compositions were prepared by mixing measured amounts of the pure liquids in cleaned and dried flasks. In both the systems, the second component, toluene was kept constant (X_2=0.3) while the concentrations of the remaining two (X_1 and X_3) were varied from 0.0 to 0.7, so as to have the mixtures of different compositions. Ultrasonic velocity measurements were made using ultrasonic interferometer [Model F81. Mittal enterprises, New Delhi] at 3 MHz. Density and viscosity was determined using a specific gravity bottle and Ostwald's viscometer respectively. All the measurements were made at 303, 308 and 313K with the help of thermostat with an accuracy of ±0.01K.

Theory

The following parameters have been determined from the experimentally measured ultrasonic velocity (U), density (ρ) and viscosity (η) values,

Adiabatic compressibility

$$\beta = 1/\rho U^2 \quad \ldots (1)$$

Intermolecular free length

$$L_f = K_T \beta^{1/2} \quad \ldots (2)$$

Free volume

$$V_f = \left[M_{eff} U / K\eta\right]^{3/2} \quad \ldots (3)$$

Internal pressure

$$\pi_i = bRT\left[K\eta/U\right]^{1/2}\left[\rho^{2/3}/M_{eff}{}^{7/6}\right] \quad \ldots (4)$$

Acoustic impedance

$$Z = U\rho \quad \ldots (5)$$

where K_T, M_{eff}, K, b, R and T are the temperature dependent constant (K_T=199.53×10^{-8} at 303 K, 201.12×10^{-8} at 308 K and 203.18×10^{-8} at 313 K) molecular effective weight, absolute temperature, space packing factor (b=2), gas constant, and temperature independent constant having a value of 4.28×10^9 respectively.

The excess parameters are determined by

$$A^E = A_{exp} - A_{id} \quad \ldots (6)$$

Where A represents any parameter, A^E is the excess parameter, A_{exp}, experimental value and A_{id} is the theoretical value (ideal value).

Results

The experimental values of density, viscosity and ultrasonic velocity for both the systems at 303, 308 and 313K are presented in Table 1. The values of adiabatic compressibility, free length and free volume for the mixtures at three different temperatures are given in Table 2. Table 3 shows the internal pressure and acoustic impedance for the both systems. The respective excess values of these parameters have been evaluated and presented in Figs. 1-10.

Discussion

The density, viscosity and ultrasonic velocity decrease with increase in concentration of ethyl acrylate (aliphatic ester). But in second system, the density increases, viscosity and velocity decrease with increase in concentration of ethyl benzoate (aromatic ester). This behavior is different from the ideal mixture behavior and this can be attributed to the intermolecular interaction in the systems [5-7]. However, the density, viscosity and velocity decrease with increase in temperature indicates the decrease in intermolecular force due to increase in thermal energy of the system which causes a volume expansion and hence an increase in free length. When compared with aliphatic ester, the aromatic ester has higher values of velocity.

** Corresponding Author, Email: ezhilpavaibalu@yahoo.com*

The mixing of toluene with aniline, dipole - induced dipole interaction arises between the lone pair of electron on nitrogen of aniline and hydrogen atom of toluene. When ester is added with toluene, the dipole – induced dipole or charge transfer interaction exists between the ester and toluene molecules. The interaction between the molecules of toluene with esters is found to be weaker then the interaction with aniline. As stated earlier, the molecules of aniline are self associated through hydrogen bonding of their amino group (N-H) and ester molecules are polar group C=O, thus the mixing of aniline molecules with ester molecules forming new H-bond (N–H.....O=C) between hydrogen atom of aniline and oxygen atom of ester. This contributes to an increase in free length and hence compressibility. The regular increase in free length is due to the loose packing of the molecules inside the shield, which may be brought by weakening of molecular interaction.

Table 1: Values of Density (ρ), viscosity (η) and velocity (U) of the System 1 and 2

		ρ kgm^{-3}			η x 10^3 Nsm^{-2}			U ms^{-1}		
Mole fraction		**TEMPERATURE (K)**								
X_1	X_3	303	308	313	303	308	313	303	308	313
System 1: Ethyl acrylate + toluene + aniline										
0.0000	0.7000	958.99	956.37	954.00	1.5309	1.3915	1.2487	1484.0	1478.0	1434.5
0.0999	0.6000	947.17	945.03	943.05	1.3026	1.2014	1.0618	1465.5	1446.1	1432.9
0.1999	0.5000	938.92	936.37	933.69	1.0758	0.9988	0.8995	1422.5	1412.5	1388.5
0.2999	0.4000	931.47	928.42	925.34	0.9290	0.8522	0.7704	1380.3	1364.3	1341.2
0.4000	0.3000	917.17	915.88	912.59	0.8073	0.7196	0.6504	1339.6	1310.5	1295.0
0.4999	0.2000	908.52	905.35	903.05	0.7128	0.6538	0.5638	1281.1	1257.7	1222.4
0.6000	0.0999	898.79	896.59	894.59	0.6137	0.5655	0.5241	1243.5	1234.2	1219.5
0.7000	0.0000	887.76	884.26	881.95	0.5443	0.5045	0.4596	1238.5	1221.5	1196.1
System 2: Ethyl benzoate + toluene + aniline										
0.0999	0.6000	966.54	963.92	958.08	1.4857	1.3576	1.2153	1466.0	1456.0	1418.0
0.2000	0.4999	968.82	965.51	961.62	1.4130	1.2958	1.1702	1438.0	1434.0	1401.5
0.3000	0.4000	976.48	970.90	966.34	1.3261	1.2025	1.1170	1417.5	1405.5	1366.5
0.4000	0.2999	979.87	975.86	972.50	1.2490	1.1513	1.0327	1385.0	1374.0	1341.0
0.5000	0.1999	983.93	981.73	977.79	1.1900	1.1031	1.0146	1368.0	1351.0	1333.0
0.5999	0.1000	988.50	985.51	981.27	1.1103	1.0163	0.9842	1335.5	1324.0	1317.0
0.6999	0.0000	991.48	989.88	984.46	1.0271	0.9597	0.8890	1317.5	1290.0	1273.0

Table 2 : Values of adiabatic compressibility (β), free length(L_f) and free volume(V_f) of the System 1 and 2

Mole fraction		β X 10^{10} Pa^{-1}			L_f X 10^{11} m			V_f X 10^{7} m^3mol^{-1}		
		TEMPERATURE (K)								
X_1	X_3	303	308	313	303	308	313	303	308	313
System 1: Ethyl acrylate + toluene + aniline										
0.0000	0.7000	4.7350	4.7866	5.0939	4.3418	4.4002	4.5858	0.9639	1.1056	1.2436
0.0999	0.6000	4.9159	5.0601	5.1646	4.4239	4.5241	4.6174	1.2191	1.3324	1.6015
0.1999	0.5000	5.2634	5.3527	5.5553	4.5776	4.6531	4.7889	1.5706	1.7372	1.9811
0.2999	0.4000	5.6349	5.7029	6.0077	4.7364	4.8029	4.9801	1.8916	2.1390	2.3992
0.4000	0.3000	6.0757	6.3575	6.5341	4.9182	5.0711	5.1937	2.2572	2.5953	2.9669
0.4999	0.2000	6.7066	6.9828	7.4107	5.1672	5.3146	5.5312	2.5723	2.8484	3.4082
0.6000	0.0999	7.1953	7.3221	7.5164	5.3522	5.4422	5.5705	3.1126	3.4795	3.8304
0.7000	0.0000	7.3437	7.5794	7.9254	5.4071	5.5370	5.7200	3.7441	4.1096	4.5797
System 2: Ethyl benzoate + toluene + aniline										
0.0999	0.6000	4.8141	4.8937	5.1909	4.3779	4.4491	4.6292	1.0828	1.2269	1.3923
0.2000	0.4999	4.9916	5.0367	5.3556	4.4579	4.5137	4.7021	1.2340	1.3993	1.5167
0.3000	0.4000	5.0967	5.2301	5.5418	4.5046	4.5995	4.7831	1.4389	1.6453	1.7618
0.4000	0.2999	5.3311	5.4280	5.7064	4.6070	4.6857	4.8536	1.6402	1.8313	2.0785
0.5000	0.1999	5.4308	5.5808	5.7556	4.6499	4.7512	4.8745	1.8610	2.0464	2.2737
0.5999	0.1000	5.6720	5.7885	5.8754	4.7520	4.8388	4.9250	2.1339	2.4053	2.5039
0.6999	0.0000	5.8105	6.0707	6.2682	4.8097	4.9554	5.0870	2.5100	2.6925	2.9605

From Table 2, it is noticed that as the concentration of esters increases, free volume increases whereas the internal pressure decreases. This suggests that the strength of interaction decreases gradually with increase in solute concentration and this represents the existence of weak interaction between the solute and solvent molecules. When the temperature is increased, there is a tendency for the solute molecules to move away from each other, reducing the possibility for interaction, which may further reduce the cohesive force and ultimately leads to an increase in free volume [8& 9].

Table 3 : Values of internal pressure (n_i) and acoustic impedance (Z) of the System 1& 2

Mole fraction		n_i X 10^{-6} Pa TEMPERATURE (K)			Z X 10^{-6}kgm^{2}s^{-1}		
X_1	X_3	303	308	313	303	308	313
System 1: Ethyl acrylate + toluene + aniline							
0.0000	0.7000	522.59	506.56	494.17	1.4231	1.4135	1.3685
0.0999	0.6000	476.85	469.86	448.46	1.3881	1.3666	1.3513
0.1999	0.5000	433.53	425.35	412.94	1.3356	1.3226	1.2964
0.2999	0.4000	403.32	392.66	383.21	1.2857	1.2759	1.2411
0.4000	0.3000	374.52	363.05	352.01	1.2286	1.2003	1.1818
0.4999	0.2000	354.58	347.57	332.14	1.1639	1.1387	1.1039
0.6000	0.0999	328.78	321.49	315.94	1.1176	1.1066	1.0910
0.7000	0.0000	305.15	299.91	293.46	1.0995	1.0801	1.0549
System 2: Ethyl benzoate + toluene + aniline							
0.0999	0.6000	485.62	472.64	458.63	1.4601	1.4489	1.4038
0.2000	0.4999	448.49	436.18	427.07	1.4534	1.4366	1.3959
0.3000	0.4000	413.39	399.50	396.40	1.4339	1.4200	1.3864
0.4000	0.2999	382.97	374.73	364.74	1.4179	1.3979	1.3584
0.5000	0.1999	357.05	351.10	343.57	1.3937	1.3751	1.3383
0.5999	0.1000	331.86	323.48	322.23	1.3818	1.3580	1.3380
0.6999	0.0000	305.91	303.44	297.68	1.3542	1.3539	1.3253

Further, in both liquid systems, the value of acoustic impedance (Z) is found to be decreased, which are listed in Table 3. When an acoustic wave travels in a medium, there is a variation of pressure from particle to particle. The ratio of the instantaneous pressure excess at any particle of the medium to the instantaneous velocity of that particle is known as 'specific acoustic impedance' of the medium. This factor is governed by the inertial and elastic properties of the medium. It is important to examine specific acoustic impedance in relation to concentration and temperature. The decrease in specific acoustic impedance indicates significant interaction between the component molecules. This is in agreement with the results of Anwar Ali [10].

In order to substantiate the presence of interaction between the molecules, it is essential to study the excess parameters. This gives more qualitative idea regarding strength of molecular interactions in liquid systems by calculating deviation from the ideal behavior. The values of excess adiabatic compressibility [Figs. 1&2] are almost negative over the entire range of mole fraction of esters for both the systems. The observed negative values over whole composition range suggest the formation of hydrogen bond between unlike molecules [11]. Low magnitude values of β^E are indicative of weak interaction between the molecules [12]. Anwar Ali et al. [13] suggested that the negative excess values of compressibility indicate the formation of hydrogen bond. According to Ramamoorthy and Sastri [14], the negative excess free length indicates that the sound wave has to travel a longer distance. This may be attributed to dominant nature of interaction between unlike molecules. All these variation are reflected in the observed excess value of free length [Figs.3&4].

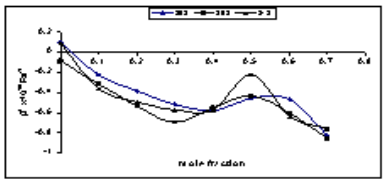

Fig.1 Excess adiabatic compressibility versus mole fraction of ethyl acrylate.

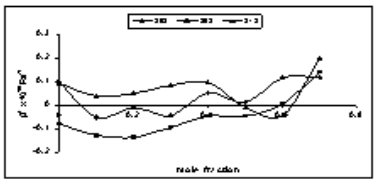

Fig. 2 Excess adiabatic compressibility versus mole fraction of ethyl benzoate.

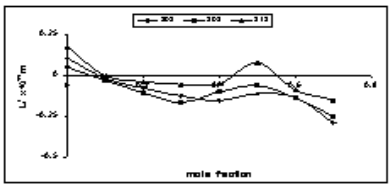

Fig. 3 Excess free length versus mole fraction of ethyl acrylate.

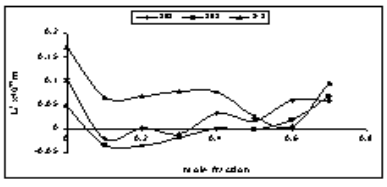

Fig. 4 Excess free length versus mole fraction of ethyl benzoate.

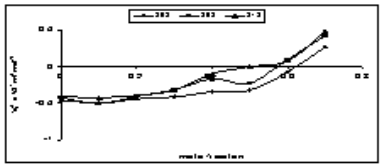

Fig. 5 Excess free volume versus mole fraction of ethyl acrylate.

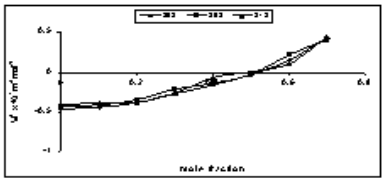

Fig. 6 Excess free volume versus mole fraction of ethyl benzoate.

Figs. 5 & 6 show the variation of the excess free volume as a function of concentration in both the systems. The values of excess free volume are found to be both positive and negative. This indicates the presence of hydrogen bonding. Similar results were reported by Kannappan and Rajendran [15].

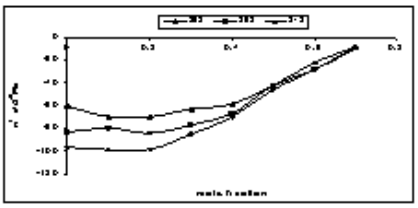

Fig. 7 Excess internal pressure versus mole fraction of ethyl acrylate.

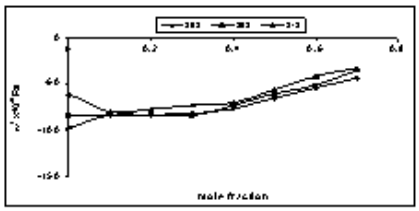

Fig. 8 Excess internal pressure versus mole fraction of ethyl benzoate.

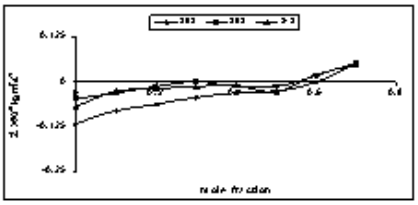

Fig. 9 Excess acoustical impedance versus mole fraction of ethyl acrylate.

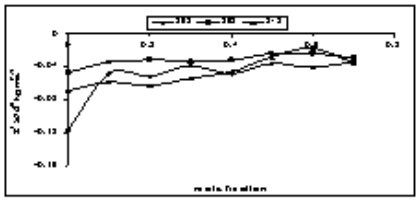

Fig. 10 Excess acoustical impedance versus mole fraction of ethyl benzoate.

As expected, Figs.7 & 8 shows the negative values of π_i^E indicate that only dispersion and dipolar forces are operating with complete absence of specific interaction [16].

A similar observation, arrived by Kannappan and Rajendran [15] supports this view. The excess acoustic impedance is completely negative for ethyl benzoate system whereas over the entire composition range except for small positive deviation at higher concentration. The negative Z^E values indicate weak interaction formed as a result of hydrogen bonding between the component molecules. Similar results have also been drawn in variety of liquid mixtures [17].

Conclusion

The trends in the variation of parameters derived from ultrasonic velocity, density and viscosity and the sign and magnitude of the excess functions suggest the presence of molecular interaction in the present ternary liquid mixtures. It may be concluded that the interaction between unlike components mainly due to hydrogen bonding through hydrogen atom of aniline and oxygen atom of esters. Moreover, dipole – induced dipole interaction also seen to exist between the component of the mixtures. The order of interaction is ethyl benzoate > ethyl acrylate.

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