Study of Molecular Interactions in Binary Liquid Mixtures Containing Esters

M. SRI LAKSHMI[1,*], A. RATNAKAR[1], CH. KAVITHA[1], K. NARENDRA[2]

[1]Department of Chemistry, V.R. Siddhartha Engineering College (Autonomous), Vijayawada-07
[2]Department of Physics, V.R. Siddhartha Engineering College(Autonomous), Vijayawada-07
*e-mail ID: srilakshmi771977@gmail.com, narenk75@gmail.com

Abstract

Density, speed of sound and viscosity have been measured for binary liquid mixture containing o-anisidine + amyl acetate over the entire composition range at temperatures 303.15, 308.15, 313.15 and 318.15 K and at atmospheric pressure. By using these values various parameters like adiabatic compressibility (β), free volume (V), free length (L_f), internal pressure (π) and their excess values have been calculated. The intermolecular interactions and structural effects are analyzed on the basis of the measured and derived properties.

Key words: o-anisidine, amyl acetate, ultrasonic speed, viscosity, density

Introduction

In the estimation of structural properties of molecules, the study of molecular interaction in liquid mixtures is of considerable importance. Dielectric studies have been widely used to study the molecular interactions in liquid mixtures[1]. Since, acoustic parameters provide a better insight into molecular environments in liquid mixtures, it seemed important to study molecular interactions which motivated the authors to carry out the present investigations in binary liquid mixtures of o-anisidine with amyl acetate using ultrasonic technique. o-anisidine is used as an intermediate in the manufacture of dyes. The esters are commonly used as solvents in the production of lacquers and other products and also as synthetic fruit flavorings in food industry[2]. Literature survey showed that no data on thermodynamic and transport properties of mixtures containing o-anisidine with esters were reported. In this paper we report the ultrasonic speed, density and viscosity of o-anisidine with amyl acetate over the entire range of composition at temperatures 303.15, 308.15, 313.15 and 318.15 K. From these experimental values various acoustical parameters and some of their excess values have been evaluated.

Experimental

The mass fractions of o-anisidine and amyl acetate obtained from SDFCL are 0.98 & 0.90 respectively. All the liquids obtained from the suppliers were further purified by standard procedure[3]. A comparison of the experimental values of density, viscosity and ultrasonic velocity obtained in the present study with the values reported in literature shows good agreement.

Job's method of continuous variation was used to prepare the mixtures in the required proportions. The mixtures were preserved in well-stoppered conical flasks. After thorough mixing of the liquids, the flasks were left undisturbed to allow them to attain thermal equilibrium. An electronic balance

(Shimadzu AUY220 from Japan), with a precision of ± 0.1 mg was used for the mass measurements. The densities of pure liquids and liquid mixtures were measured by using a specific gravity bottle with an accuracy of ± 10^{-4} g/cm^3.

Viscosities were measured at the desired temperature using Ostwald's viscometer calibrated using water and benzene. The flow time has been measured after the attainment of bath temperature by each mixture. The flow measurements were made with an electronic stopwatch with a precision of 0.01 s. For all pure compounds and mixtures, 5 to 7 measurements were performed and the average of these values was used in all the calculations. The values are accurate to ± 10^{-3} mPa.s.

The ultrasonic speeds were measured by using a single crystal ultrasonic pulse echo interferometer (Model: F-80X Mittal enterprises, India), equipped with a high frequency generator and a measuring cell. The measurements of ultrasonic speeds were made at a fixed frequency of 3 MHz. The equipment was calibrated by measuring the velocity in carbon tetrachloride and benzene. The results are in good agreement with those reported in literature[4]. The error in velocity measurement is ± 0.5 %. The temperature was controlled through water circulation around the liquid cell using thermostatically controlled constant temperature water bath with an accuracy of ± 0.01 K.

From the experimental values of density, viscosity and speed of spound, various parameters are evaluated using the standard equations[5]. The strength of interaction between the component molecules of the binary mixtures is well reflected in the deviation of the excess functions from ideality. The excess properties such as β^E, V^E, L_f^E and π^E have been calculated using the equation

$$Y^E = Y_{mix} - [x_1Y_1 + x_2Y_2] \quad (1)$$

Where Y^E is β^E, V^E, L_f^E or π^E and x represents mole fraction of the component and subscript 1 and 2 for the components 1 and 2 respectively.

Results and discussion

The experimental values of density (ρ), viscosity (η) and speed of sound (*u*) for all the mixtures over the entire range of composition and at 303.15, 308.15, 313.15 and 318.15 K are presented in Table 1.

Table – I : Density (ρ), speed of sound (u) and viscosity (η) of binary mixtures.

x_1	ρ (Kg m^{-3})	u (m s^{-1})	η (m Pa.s)	ρ (Kg m^{-3})	u (m s^{-1})	η (m Pa.s)
	303.15 K			**308.15 K**		
0.0000	864.700	1137.14	7.1320	854.300	1120.38	6.7010
0.1287	882.500	1208.20	8.4320	879.100	1189.42	7.8530
0.2494	904.200	1261.80	9.4280	898.700	1240.16	8.8360
0.3629	927.600	1299.89	10.8590	920.800	1278.60	10.0957
0.4698	952.700	1357.80	12.5700	950.200	1330.20	11.6400

0.5706	972.600	1412.20	14.6570	968.900	1383.00	13.5240
0.6659	996.600	1454.60	17.0850	991.900	1426.00	15.8240
0.7562	1018.790	1488.64	19.8230	1012.390	1461.72	18.3900
0.8417	1038.280	1512.08	23.1000	1033.950	1482.81	21.5750
0.9228	1065.340	1523.80	27.1190	1058.870	1493.80	25.3040
1.0000	1087.074	1525.26	31.1250	1080.019	1500.00	29.0143
	313.15 K			**318.15 K**		
0.0000	849.600	1104.60	6.0920	846.030	1092.08	5.6150
0.1287	870.400	1173.64	7.1460	864.900	1159.04	6.3440
0.2494	890.700	1225.08	8.0915	885.800	1203.12	7.1890
0.3629	914.000	1263.00	9.2891	910.200	1239.60	8.2500
0.4698	946.800	1310.60	10.7290	942.000	1285.80	9.4750
0.5706	968.000	1360.40	12.4960	965.200	1335.00	11.0050
0.6659	985.500	1410.20	14.5964	982.600	1377.80	12.8410
0.7562	1009.500	1446.40	16.9260	1008.900	1419.60	14.8890
0.8417	1031.100	1467.96	19.9361	1027.070	1443.40	17.4140
0.9228	1054.900	1482.00	23.2903	1049.200	1464.20	20.1790
1.0000	1074.590	1494.84	26.8342	1066.500	1481.05	23.4630

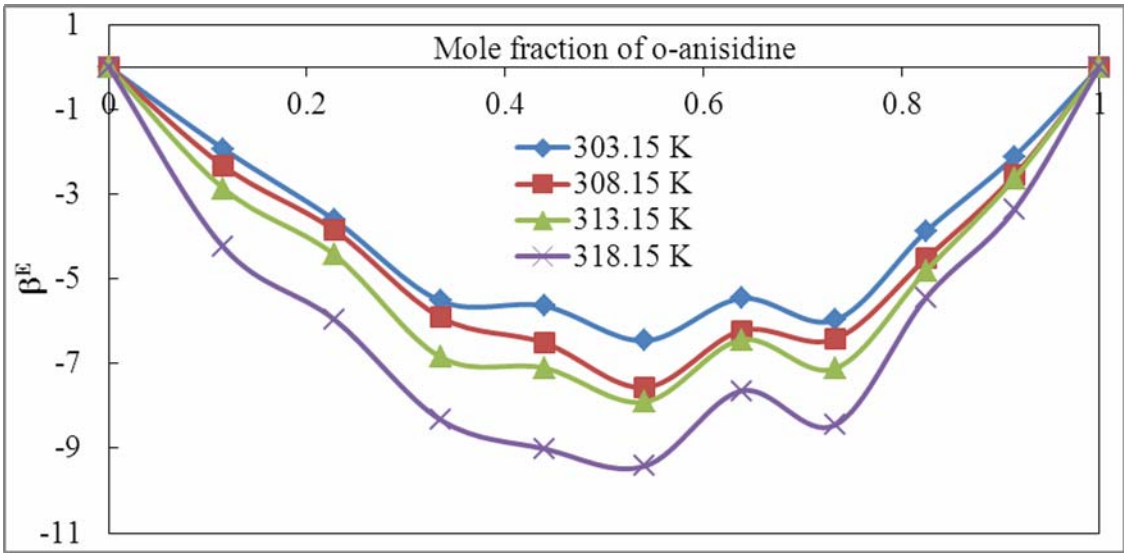

Figure 1 Curves of excess adiabatic compressibility (β^E) with mole fraction of o-anisidine for the binary mixtures at different temperatures.

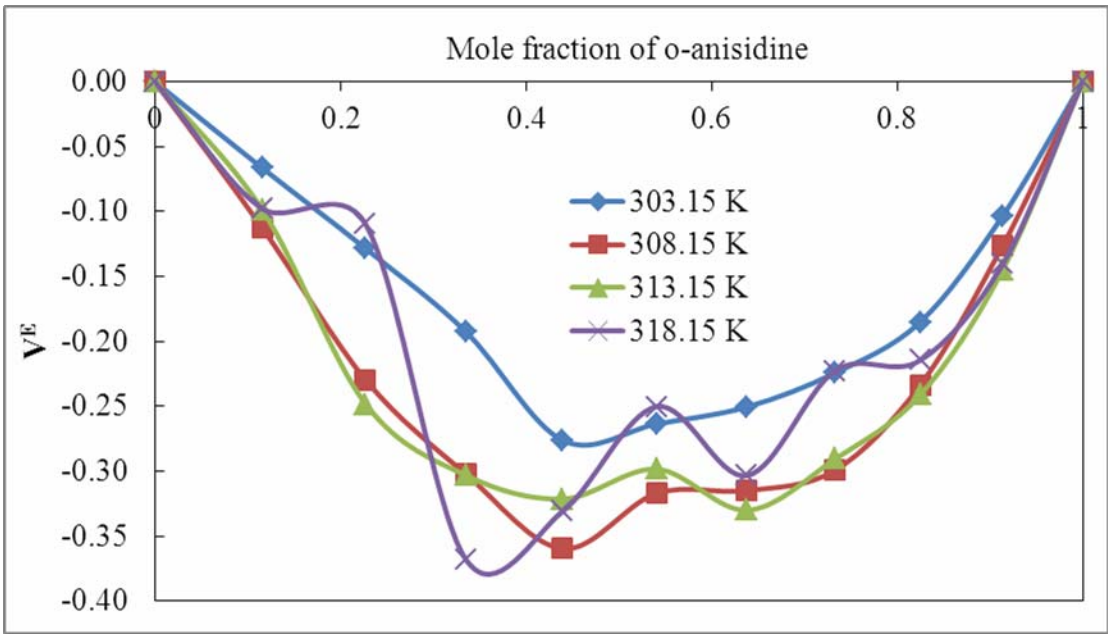

Figure- 2. Curves of excess free volume (V^E) with mole fraction of o-anisidine for the binary mixtures at different temperatures.

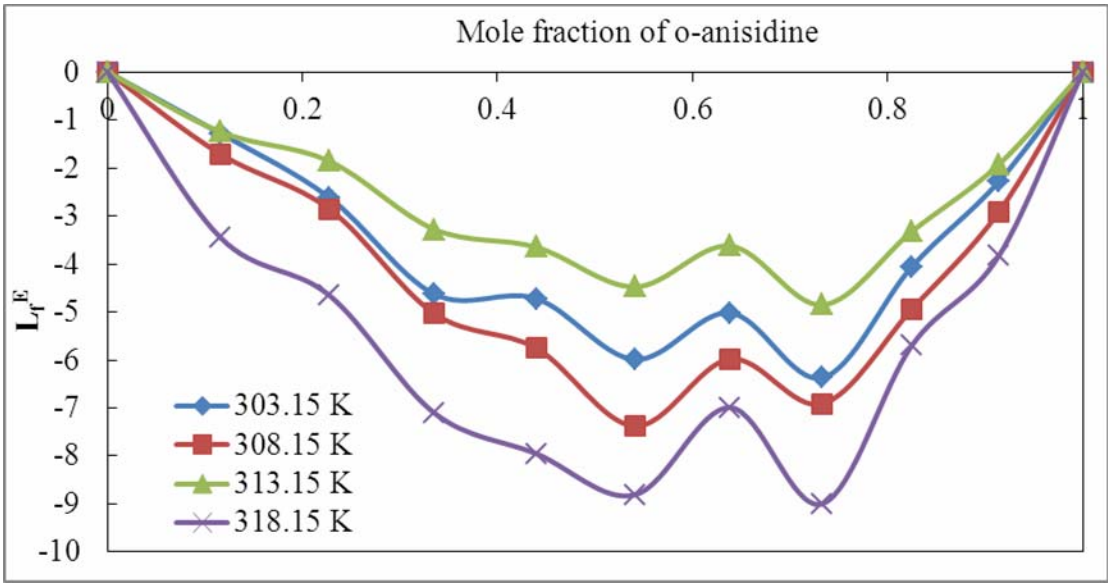

Figure- 3. Curves of excess intermolecular free length (L_f^E) with mole fraction of o-anisidine for the binary mixtures at different temperatures.

Curves of β^E, V^E, L_f^E, and π^E against mole fraction of o-anisidine at temperatures 303.15 to 313.15 K are given in Figs. 1 to 4, respectively. The values of β^E, V^E, L_f^E, and π^E for the binary mixtures of o-anisidine with amyl acetate may be explained on the basis of various types of intermolecular interactions between the components. The excess thermodynamic properties of the mixtures are influenced by three main types of contribution, viz., (i) physical: due to non-specific Vander Walls type

forces (ii) chemical: due to hydrogen bonding, dipole–dipole, and donor–acceptor interaction between unlike molecules and (iii) structural: due to the fitting of smaller molecules into the voids created by the bigger molecules.

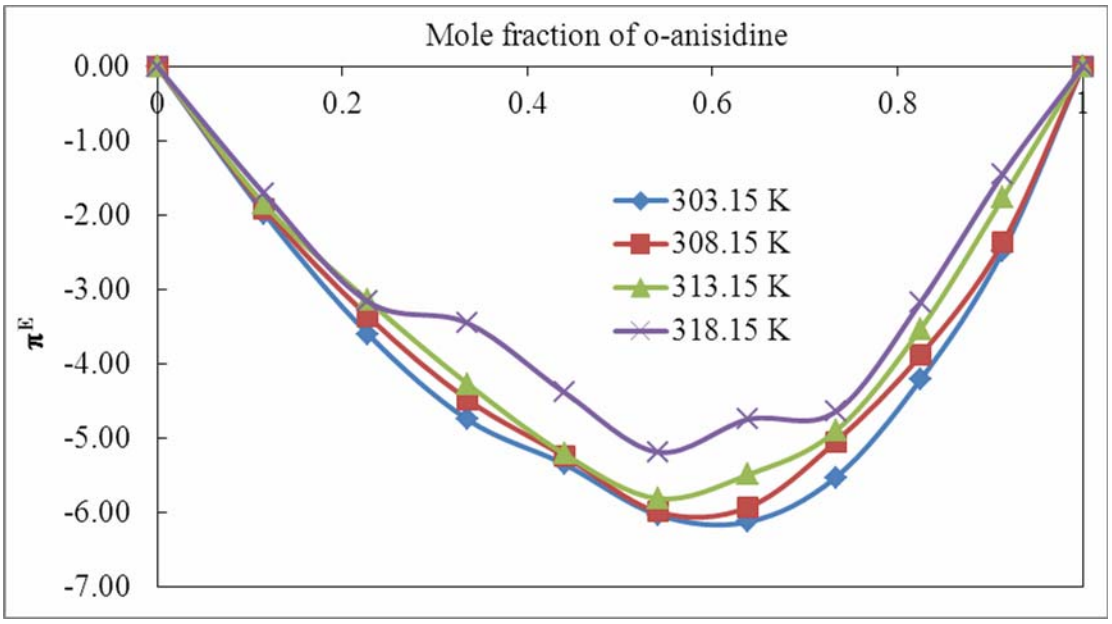

Figure- 4. Curves of excess internal pressure (π^E) with mole fraction of o-anisidine for the binary mixtures at different temperatures.

The excess adiabatic compressibility (β^E) versus mole fraction (x_1) is plotted and presented in Figure 1 over the entire composition range and at T = (303.15, 308.15, 313.15 and 318.15) K. The β^E values are found to be negative over the entire range of composition. The negative values of β^E suggest that the mixtures are less compressible than the corresponding ideal mixture. The liquids of different molecular sizes usually mix with decrease in volume results negative β^E values as suggested by Fort and Moore[6]. The strength of the interaction between the component molecules increase, when excess values tend to become increasingly negative. This also may be quantitatively interpreted in terms of closer approach of unlike molecules leading to reductions in compressibility and volume[7].

The excess free volume (V^E) versus mole fraction (x_1) is plotted and is presented in Figure 2 over the entire range of composition at different temperatures. The V^E values are observed to be negative over the entire mole fraction range at all temperatures studied. Similar results that are observed are presented in figure 3 for excess intermolecular free length (L_f^E) also.

In the present investigation, the excess adiabatic compressibility (β^E), the excess free volume (V^E), excess free length (L_f^E) exhibit negative values over the entire range of composition at all

temperatures studied clearly indicate the presence of strong interactions[8] between o-anisidine and amyl acetate.

Further, the excess internal pressure (π^E) which is usually explained in terms of molecular interaction, whose negative excess values suggest that strong molecular interaction between the unlike molecules[9].

Conclusions

From the data of ultrasonic speed, density and viscosity, various acoustical parameters and their excess values for the binary liquid mixture of o-anisidine with amyl acetate was measured at (303.15, 308.15, 313.15 and 318.15) K, it is obvious that there exist strong molecular interactions between o-anisidine and amyl acetate.

References

1. P.J. Singh and K.S. Shrama. *Pramana*. 46, 259, (1996).
2. J.M. Resa, C. Gonzalez, J.M. Goenaga, M. Iglesias. *J. Solution Chem*. 33, 169, (2004).
3. J.D. Pandey, R.D. Rai, R.K. Shukla, A.K. Shukla, N. Mishra, *Indian J Pure Appl. Phys*. 31, 84, (1993).
4. D. Das and D.K. Hazra. *Indian J Phys*.77B, 519, (2003).
5. K. Narendra, Ch. Srinivas, Sk. Fakruddin, P. Narayanamurthy. *J.Chem.Thermodynamics*. 43, 1604, (2011).
6. R.J. Fort and M.W.R. Moore. *Trans Faraday Soc*. 61, 2102, (1965).
7. A. Jayakumar, S. Karunanithi and V. Kannappan. *Ind. J. Pure Appl. Phys*. 34, 761, (1996).
8. S.N. Gour, J.S. Tomar and R.P. Varma. *Ind. J. Pure Appl. Phys*. 24, 602, (1986).
9. R. Singh, J.P. Mishra and M.C. Shukla. *J.Mol. Liq*. 26, 29, (1983).