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Excess thermo dynamical parameters of binary mixtures of toluene and mesitylene with anisaldehyde using ultrasonic technique at different temperatures

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Abstract The densities, viscosities, and ultrasonic velocities of the binary mixture of toluene and mesitylene with anisaldehyde have been measured at 303.15, 308.15, 313.15, and 318.15 K for the entire range of mole fraction of anisaldehyde. From the data the excess adiabatic compressibility (β^{E}), excess free volume (V_f^{E}), excess internal pressure (π^{E}), excess enthalpy (H^{E}), and excess Gibb's free energy of activation of flow (G^{*E}) for the binary mixture over the additive values were calculated. In light of these parameters molecular interactions involved between the component liquids have been discussed.

Keywords Adiabatic compressibility · Free volume · Free length · Internal pressure · Binary mixtures · Anisaldehyde

Introduction

Reliable and accessible reference data on the chemical and physical properties of a wide variety of liquid mixtures have demand in industry. These data are required in the developments of models for energy efficiency, in the evaluation of possible environmental impacts, molecular dynamics, and process design [1–3]. Anisaldehyde is used in perfume and pharmaceutical industries. Toluene is used as an industrial feedstock and as a solvent. Mesitylene is used as a solvent in research and industry. Ultrasonic methods have the added advantage of being less costly with efficiency comparable to other methods like dielectric relaxation, infrared spectroscopy, nuclear magnetic resonance, etc. The ultrasonic studies find extensive applications in characterizing aspects of physico-chemical behavior involving molecular interactions in liquids [4–7]. The deviation from ideality is expressed by many thermodynamic variables particularly by excess properties [8], and these are used for understanding the intermolecular interactions in liquid mixtures [9, 10]. The present work reports the experimental values of density (ρ), viscosity (η), and ultrasonic velocity (u) of the toluene and mesitylene with anisaldehyde measured at the temperatures 303.15, 308.15, 313.15, and 318.15 K. From these experimental results internal pressure (π), free volume (V_f), enthalpy (H), excess internal pressure (π^{E}), excess free volume (V_f^{E}), excess free length (L_f^{E}), excess enthalpy (H^{E}), and excess Gibb's free energy of activation of flow (G^{*E}) over the entire mole fraction range of anisaldehyde have been calculated. The intermolecular interactions have been estimated/suggested in the light of the excess parameters.

Experimental details

The chemicals used were of analytical grade and obtained from SRL Chemicals, Mumbai. The chemicals used were purified by standard procedure [11]. The purity of samples was checked by density and viscosity measurements [12]. Job's method of continuous variation was used to prepare

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the mixtures of required proportions. The prepared mixtures were preserved in well-Stoppard conical flasks. After mixing the liquids thoroughly, the flasks were left undisturbed to allow them to attain thermal equilibrium.

The densities of pure liquids and liquid mixtures were measured by using a specific gravity bottle with an accuracy of ±0.5%. Weights were measured with an electronic balance capable of measuring up to 0.1 mg. An average of 4–5 measurements was taken for each sample. Viscosities were measured at the desired temperature using Ostwald's viscometer, which is calibrated using water and benzene. After the mixture had attained bath temperature, flow time has been measured. The flow measurements were made with an electronic stopwatch with a precision of 0.01 s. The viscosity is determined using the relation

$$\eta = k\rho t \tag{1}$$

where k, ρ, and t are viscometric constant, density of liquid, and time of efflux for a constant volume of liquid, respectively. The values are accurate to ±0.001 cP.

The ultrasonic velocities were measured by using single crystal ultrasonic pulse echo interferometer (Mittal enterprises, India; Model: F-80X). It consists of a high frequency generator and a measuring cell. The measurements of ultrasonic velocities were made at a fixed frequency of 3 MHz. The capacity of the measuring cell is 12 mL. The calibration of the equipment was done by measuring the velocity in carbon tetrachloride and benzene. The results are in good agreement with the literature values [13]. The ultrasonic velocity has an accuracy of ±0.5 m s^{-1}. The temperature was controlled by circulating water around the liquid cell from thermostatically controlled constant temperature water bath (accuracy ±0.01 K).

Theory

From the experimental data of density, viscosity, and ultrasonic velocity various thermodynamic parameters are evaluated using standard equations:Adiabatic compressibility

$$\beta = \frac{1}{\rho . u^2} \tag{2}$$

Internal pressure

$$\pi = bRT\left(\frac{k\eta}{u}\right)^{1/2}\left(\frac{\rho^{2/3}}{M^{7/6}}\right) \tag{3}$$

where b is a packing factor, k is a dimensionless constant [14] independent of temperature, and nature of liquids and its value is 4.28 × 10^9 and η is the viscosity. The other symbols have their usual meaning.

Free volume

$$V_f = \left(\frac{M_{eff}u}{K\eta}\right)^{3/2} \tag{4}$$

where M_{eff} is the effective molecular weight and K is proportionality constant, which is sensitive to molecular phenomenon.

Inter molecular free length

$$L_f = K_T\beta^{1/2} \tag{5}$$

where K_T is the temperature dependent constant.

Enthalpy

$$H = V_m.\pi \tag{6}$$

where V_m is the molar volume and π is the internal pressure.

Excess Gibb's free energy of activation

$$G^{*E} = RT\left[\ln\left(\frac{\eta V_m}{\eta_2 V_{m2}}\right) - x_1 \ln\left(\frac{\eta_1 V_{m1}}{\eta_2 V_{m2}}\right)\right] \tag{7}$$

The strength of interaction between the component molecules of binary mixtures is well reflected in the deviation of the excess functions from ideality [15]. The excess properties such as β^E, V_f^E, π^E, H^E, and L_f^E have been calculated using the equation

$$Y^E = Y_{mix} - [x_1Y_1 + x_2Y_2] \tag{8}$$

where Y^E is β^E or V_f^E or π^E or L_f^E or H^E and x represent mole fraction of the component and subscript 1 and 2 for the components 1 and 2.

Results and discussion

The experimental values of density, viscosity, and ultrasonic velocity for the binary systems over the entire range of composition and at temperatures 303.15, 308.15, 313.15, and 318.15 K are given in Tables 1 and 2. From these data various parameters like adiabatic compressibility, internal pressure, free volume, inter molecular free length, and enthalpy have been evaluated. Values of free volume and internal pressure are presented in Tables 3 and 4. Plots of respective excess parameters against mole fraction of anisaldehyde are given in Fig. 1a–f in case of anisaldehyde + toluene mixture and in Fig. 2a–f for anisaldehyde + mesitylene mixture. It is observed that as the concentration of anisaldehyde increases, free volume decreases whereas the internal pressure increases. This suggests close packing of the molecules inside the shield, which may be brought about by the increasing magnitude of interactions [16, 17].

The experimental data collected in the literature provide strong evidence that for mixtures in which strong attractive

Table 1 Density (ρ), viscosity (η), and ultrasonic velocity (u) for the binary mixture anisaldehyde + toluene at varying temperatures

X_1	$T = 303.15$ K			$T = 308.15$ K			$T = 313.15$ K			$T = 318.15$ K		
	ρ/g cm^{-3}	η/mPa s	u/m s^{-1}	ρ/g cm^{-3}	η/mPa s	u/m s^{-1}	ρ/g cm^{-3}	η/mPa s	u/m s^{-1}	ρ/g cm^{-3}	η/mPa s	u/m s^{-1}
0.0000	0.8567	0.5275	1273.50	0.8543	0.5011	1263.50	0.8510	0.4846	1253.50	0.8479	0.4524	1236.50
0.0899	0.9132	0.5703	1329.00	0.9105	0.5414	1304.00	0.9051	0.5120	1293.00	0.8958	0.4586	1269.00
0.1818	0.9134	0.6449	1368.00	0.9116	0.6128	1325.00	0.9114	0.5751	1315.00	0.9063	0.5216	1300.00
0.2759	0.9298	0.7185	1416.00	0.9296	0.6929	1386.67	0.9275	0.6448	1353.00	0.9252	0.5862	1317.99
0.3721	0.9902	0.9019	1444.33	0.9899	0.8502	1419.00	0.9861	0.7809	1398.00	0.9858	0.7004	1332.67
0.4706	0.9964	1.0986	1491.33	0.9951	1.0178	1434.00	0.9938	0.9332	1404.00	0.9905	0.8327	1366.67
0.5714	1.0061	1.3564	1530.66	1.0060	1.2584	1482.00	1.0008	1.1216	1416.00	1.0004	0.9898	1386.00
0.6747	1.0399	1.5508	1590.00	1.0387	1.3882	1530.00	1.0352	1.2586	1494.99	1.0305	1.0976	1442.00
0.7805	1.0794	2.6101	1644.67	1.0749	2.2175	1583.33	1.0718	2.0105	1569.67	1.0681	1.6497	1499.00
0.8889	1.0984	2.8567	1655.67	1.0954	2.5051	1640.67	1.0953	2.1654	1626.67	1.0908	1.8252	1544.33
1.0000	1.1252	3.2512	1694.33	1.1116	3.1306	1670.67	1.1095	2.9614	1631.33	1.1047	2.6822	1557.00

Table 2 Density (ρ), viscosity (η), and ultrasonic velocity (u) for the binary mixture anisaldehyde + mesitylene at varying temperatures

X_1	$T = 303.15$ K			$T = 308.15$ K			$T = 313.15$ K			$T = 318.15$ K		
	ρ/g cm^{-3}	η/mPa s	u/m s^{-1}	ρ/g cm^{-3}	η/mPa s	u/m s^{-1}	ρ/g cm^{-3}	η/mPa s	u/m s^{-1}	ρ/g cm^{-3}	η/mPa s	u/m s^{-1}
0.0000	0.8563	0.6213	1314.15	0.8523	0.5480	1306.00	0.8484	0.4376	1290.00	0.8446	0.3678	1278.89
0.1142	0.8911	0.6860	1365.03	0.8880	0.6450	1343.00	0.8830	0.4380	1324.00	0.8805	0.3920	1313.00
0.2248	0.8920	0.7660	1401.00	0.8891	0.7130	1363.62	0.8840	0.4870	1348.56	0.8804	0.4350	1339.00
0.3321	0.9189	0.8250	1439.46	0.9159	0.7707	1403.00	0.9094	0.5470	1372.00	0.8986	0.5000	1350.00
0.4361	0.9628	1.0440	1474.21	0.9590	0.9600	1434.00	0.9541	0.6760	1413.00	0.9503	0.6140	1371.00
0.5370	0.9810	1.2830	1514.98	0.9760	1.1480	1461.00	0.9745	0.8250	1432.01	0.9680	0.7330	1398.60
0.6350	0.9980	1.5810	1543.17	0.9920	1.3950	1493.00	0.9869	1.0000	1469.00	0.9826	0.9000	1429.00
0.7302	1.0300	1.7700	1588.59	1.0243	1.5820	1571.00	1.0201	1.0940	1513.00	1.0163	1.0000	1460.00
0.8227	1.0713	2.8260	1643.93	1.0640	2.4520	1623.00	1.0595	1.8590	1589.00	1.0545	1.5170	1516.00
0.9126	1.0910	2.9630	1671.11	1.0841	2.6650	1645.00	1.0794	1.9690	1623.00	1.0750	1.7130	1552.00
1.0000	1.1252	3.2512	1694.33	1.1116	3.1306	1670.67	1.1095	2.9614	1631.33	1.1047	2.6822	1557.00

Table 3 Free volume (V_f) and internal pressure (π) for the binary mixture anisaldehyde + toluene at varying temperatures

X_1	$T = 303.15$ K		$T = 308.15$ K		$T = 313.15$ K		$T = 318.15$ K	
	V_f/cm^3 mol^{-1}	$\pi/10^{-5}$ Nm^{-2}	V_f/cm^3 mol^{-1}	$\pi/10^{-5}$ Nm^{-2}	V_f/cm^3 mol^{-1}	$\pi/10^{-5}$ Nm^{-2}	V_f/cm^3 mol^{-1}	$\pi/10^{-5}$ Nm^{-2}
0.0000	37.4689	977.71	39.9929	970.66	41.5545	971.38	45.1351	957.74
0.0899	37.8463	988.73	39.7677	986.64	42.6957	975.31	48.9703	940.12
0.1818	34.9660	987.78	35.9834	993.22	39.1318	981.36	44.5312	951.42
0.2759	33.2731	989.18	34.0480	997.66	36.5550	988.63	40.5450	968.72
0.3721	25.8722	1092.42	27.5273	1087.50	30.5801	1064.34	33.5071	1048.67
0.4706	21.4136	1138.25	22.6422	1134.72	24.9848	1114.93	28.4676	1082.11
0.5714	17.1970	1201.21	18.3341	1195.16	20.3495	1169.01	23.7706	1127.42
0.6747	15.7668	1232.39	17.5728	1207.31	19.6611	1179.17	22.8699	1135.68
0.7805	8.0361	1542.59	9.6934	1468.94	11.0833	1424.82	13.9158	1338.72
0.8889	7.4937	1558.48	9.0017	1487.54	11.0579	1411.40	13.2183	1347.42
1.0000	6.7498	1600.38	6.9945	1594.61	7.3355	1592.96	7.9352	1572.00

Table 4 Free volume (V_f) and internal pressure (π) for the binary mixture anisaldehyde + mesitylene at varying temperatures

X_1	$T = 303.15$ K		$T = 308.15$ K		$T = 313.15$ K		$T = 318.15$ K	
	V_f/cm^3 mol^{-1}	$\pi/10^{-5}$ Nm^{-2}	V_f/cm^3 mol^{-1}	$\pi/10^{-5}$ Nm^{-2}	V_f/cm^3 mol^{-1}	$\pi/10^{-5}$ Nm^{-2}	V_f/cm^3 mol^{-1}	$\pi/10^{-5}$ Nm^{-2}
0.0000	45.7775	765.83	54.7496	731.09	75.3192	665.98	96.4871	621.14
0.1142	42.7234	796.72	45.7313	789.87	79.9945	663.68	93.3055	639.35
0.2248	38.4692	817.76	41.1344	811.13	71.6656	682.41	83.9916	655.79
0.3321	36.5902	840.42	38.9946	834.53	63.0662	719.07	70.4356	698.55
0.4361	27.1705	949.06	29.5614	935.50	48.9330	800.93	54.0272	785.20
0.5370	21.1730	1035.56	23.6905	1010.50	37.7354	878.39	43.4906	847.39
0.6350	16.2032	1136.01	18.6039	1098.34	29.9164	949.44	33.6172	925.12
0.7302	14.5373	1193.63	16.9192	1149.22	27.8073	986.91	30.1617	973.44
0.8227	7.7134	1502.36	9.3621	1425.14	13.7387	1270.86	17.3680	1190.34
0.9126	7.4827	1525.27	8.5675	1475.76	13.2209	1294.04	15.2354	1250.58
1.0000	6.7498	1600.38	6.9945	1594.61	7.3355	1592.96	7.9352	1572.00

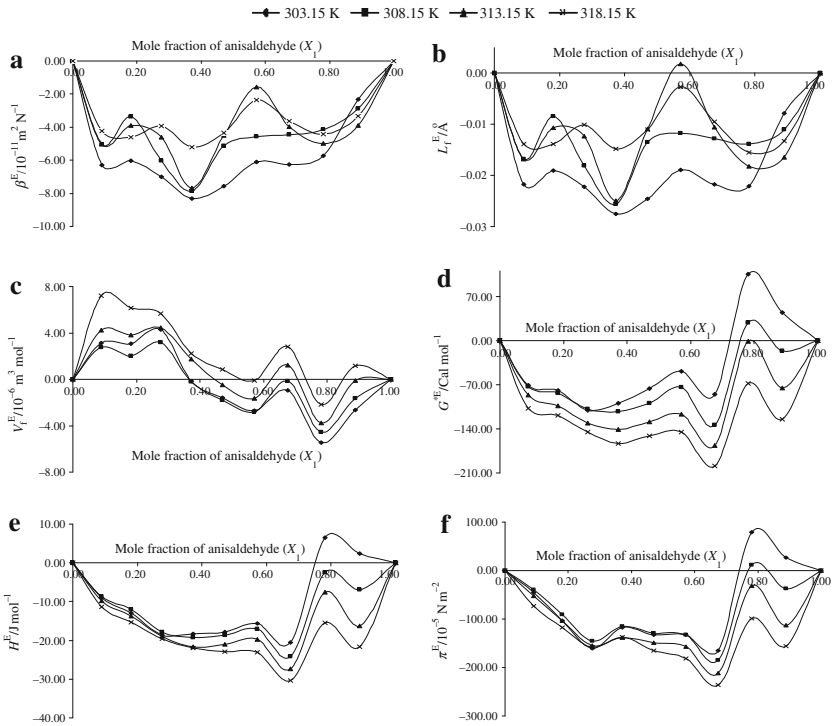

Fig. 1 Variation of excess parameters with mole fraction of anisaldehyde for anisaldehyde + toluene mixture. **a** Excess adiabatic compressibility; **b** excess intermolecular free length; **c** excess free volume; **d** excess Gibb's free energy; **e** excess enthalpy; **f** excess internal pressure

interactions are likely to occur between the components, the excess volumes and excess adiabatic compressibilities are negative [18], while for mixtures with only weak London type interactions between the components, both excess volumes and excess adiabatic compressibilities are positive. But, however, in some systems that there is no simple correlation between the strength of the interactions and the observed properties. In the present investigations, the excess adiabatic compressibility (β^E), the excess free length (L_f^E), and excess free volume (V_f^E) exhibit negative values over the entire range of composition clearly indicating the presence of strong hydrogen bonding interactions between unlike molecules [19–21]. The internal pressure is the result of the forces of attraction or repulsion between the molecules in a liquid. The π values of the liquid mixture decreases and V_f values increases with the increase in temperature. The values of H^E can be interpreted in terms of the formation of intermolecular hydrogen bonding and the breaking of associated structures of anisaldehyde with toluene and mesitylene. In all the two systems the H^E values are found to be negative for the entire mole fraction range. The negative values of H^E in the mixtures indicates the presence of strong interactions between unlike molecules. Similar variations in H^E with

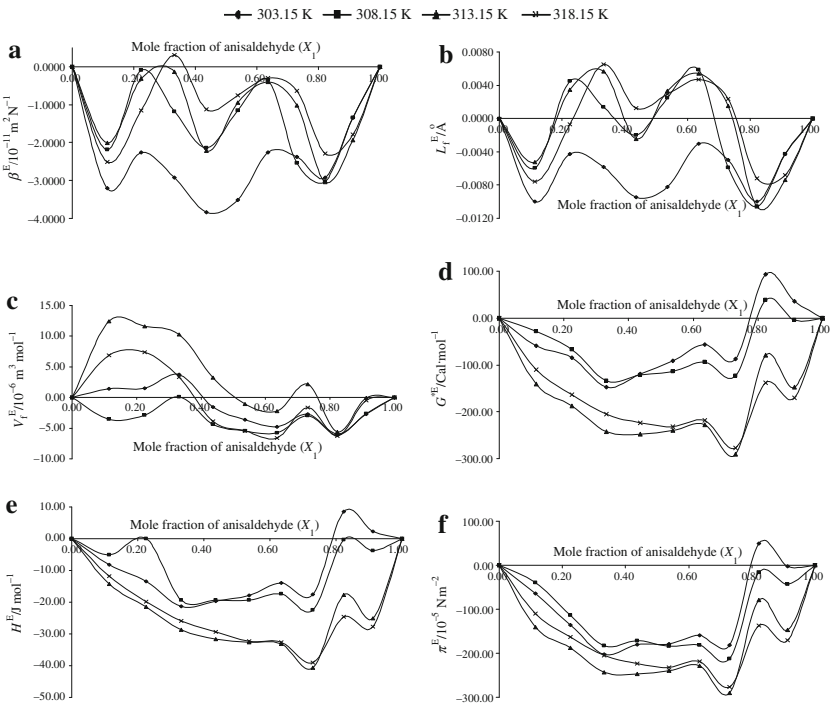

Fig. 2 Variation of excess parameters with mole fraction of anisaldehyde for anisaldehyde + mesitylene mixture. **a** Excess adiabatic compressibility; **b** excess intermolecular free length; **c** excess free volume; **d** excess Gibb's free energy; **e** excess enthalpy; **f** excess internal pressure

composition as reported earlier [22]. In all the two systems π^E and G^E values are almost negative. It indicates the presence of strong intermolecular interactions through hydrogen bonding between the molecules of the mixture. Similar reports [23] are made by several workers.

Conclusions

In the present investigation, the excess thermodynamic parameters β^E, G^{*E}, π^E, H^E, and V_f^E all exhibit negative values over the entire range of composition in all the two systems. It clearly indicates the presence of strong hydrogen bonding interactions between unlike molecules. This is in conformity with earlier workers [24, 25]. This also may be quantitatively interpreted in terms of closer approach of unlike molecules leading to reductions in compressibility and volume [26]. Further π^E, which is usually discussed in terms of molecular interactions, having negative values for all the systems under study, suggests strong molecular associations between the unlike molecules.

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