Journal of Applied Sciences

ISSN 1812-5654

science alert

ANSInet
an open access publisher
http://ansinet.com

Journal of Applied Sciences 12 (2): 136-144, 2012
ISSN 1812-5654 / DOI: 10.3923/jas.2012.136.144

Excess Properties of Binary Mixtures of o-xylene, m-xylene and p-xylene with Anisaldehyde at Different Temperatures

[1]K. Narendra, [2]Ch. Srinivasu and [3]P. Narayana Murthy
[1]Department of Physics, V.R. Siddhartha Engineering College, Vijayawada, Andhra Pradesh, India
[2]Department of Physics, Loyola College, Vijayawada, India
[3]Department of Physics, Acharya Nagarjuna University, Nagarjuna Nagar, Guntur, India

Abstract: The viscosities, densities and ultrasonic velocities of binary liquid mixtures of Anisaldehyde with o-xylene, m-xylene and p-xylene have been measured at temperatures (303.15, 308.15, 313.15 and 318.15) K over the entire range of mole fraction. These data have been used to evaluate adiabatic compressibility (β), free volume (V_f), free length (L_f), internal pressure (π) and enthalpy (H). Excess values of above parameters have also been calculated and fitted to the Redlich-Kister polynomial relation to estimate the binary coefficients and standard errors. The excess values of adiabatic compressibility and free volume are negative for all the binary mixtures. The results are interpreted in terms of molecular interactions present in the mixtures.

Key words: Adiabatic compressibility, free volume, free length, internal pressure, binary mixtures, xylenes

INTRODUCTION

The ultrasonic velocity measurements play an important role in understanding the physicochemical behavior of liquids. Being sensitive to very low population densities at high energy states, ultrasonic methods are reported to be complimentary to the other techniques like dielectric relaxation, infrared spectroscopy, nuclear magnetic resonance, etc. Thermodynamic properties derived from the measurement of ultrasonic velocity, density and viscosity for binary mixtures are useful in understanding the nature and type of intermolecular interactions between the component molecules (Saravanakumar *et al*., 2010; Singh *et al*., 2005). Excess thermodynamic properties of mixtures are useful in the study of molecular interactions and arrangements. Nain *et al*. (2010) and Singh *et al*. (2004) have carried out investigations of thermophysical properties of binary liquid mixtures containing aromatic ethers.

In order to study, the thermodynamic properties and molecular interactions in the mixture of anisaldehyde with o-xylene, m-xylene and p-xylene, the ultrasonic velocity (U), density (ρ) and viscosity (η) over the entire range of composition at (303.15, 308.15, 313.15 and 318.15) K are reported in the present study. The experimental values of u, ρ and η were used to calculate the adiabatic compressibility (β), free volume (V_f), free length (L_f), internal pressure (π) and enthalpy (H). From these results the excess parameters have been calculated and fitted to the Redlich-Kister type (Redlich and Kister, 1948) polynomial equation to derive the binary coefficients and the standard deviations between experimental and calculated results.

MATERIALS AND METHODS

The chemicals used were of analar grade and obtained from SRL Chemicals, Mumbai. They were purified by standard procedure (Perrin and Armarego, 1988). The purity of samples was checked by comparing the densities, ultrasonic velocities and viscosities of the pure compounds at 303.15 K with the available literature as shown in Table 1. Job's method of continuous variation was used to prepare the mixtures of required proportions. The prepared mixtures were preserved in well-stoppered conical flasks. After mixing the liquids thoroughly, the flasks were left undisturbed in order 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%. An electronic balance (Shimadzu AUY220, Japan), with precision of ±0.1 mg was used for the mass measurements. An average of 4-5 measurements was taken for each sample. Viscosities were measured at the desired temperature using Ostwald's viscometer, which was calibrated using water and benzene. The flow time has been measured after the attainment of bath temperature by each mixture. The flow measurements were

Corresponding Author: K. Narendra, Department of Physics, V.R. Siddhartha Engineering College, Kanuru, Vijayawada-520007, Andhra Pradesh, India Tel: +91-9885038074

made with an electronic stopwatch with a precision of 0.01 sec. The viscosities were obtained from the following relation:

$$\eta = k \cdot \rho \cdot t \quad (1)$$

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 mPa.s.

The ultrasonic velocities were measured by using a single crystal ultrasonic pulse echo interferometer (Model: F-80X Mittal enterprises, India) which 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 equipment was calibrated by measuring the velocity in carbon tetrachloride and benzene. The results are in good agreement with those reported in literature (Lide and Frederikse, 1995). The ultrasonic velocity has an accuracy of ±0.5 m sec^{-1}. The temperature was controlled by circulating water around the liquid cell from thermostatically controlled constant temperature water bath with an accuracy of ±0.01 K.

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

- Adiabatic compressibility:

$$\beta = \frac{1}{\rho U^2} \quad (2)$$

- Internal pressure:

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

where, b is a packing factor, K is a dimension less constant (Pandey *et al*., 1993a) 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:

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

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

- Intermolecular free length:

$$L_f = K_T \beta^{1/2} \quad (5)$$

where, K_T is the temperature dependent constant.

- Enthalpy:

$$H = V_m . \pi \quad (6)$$

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

- Excess Gibb's free energy of activation:

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

The strength of interaction between the component molecules of binary mixtures is well reflected in the deviation of the excess functions from ideality (Pandey *et al*., 1993b). The excess properties such as β^E, V_f^E, π^E, H^E and L_f^E have been calculated using the equation:

$$Y^E = Y_{mix} - [x_1 Y_1 + x_2 Y_2] \quad (8)$$

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.

The excess values of above parameters for each mixture have been fitted to Redlich-Kister polynomial equation:

$$Y^E = x_1(1 - x_1)\sum_{i=1}^{3} a_i (2x_1 - 1)^{i-1} \quad (9)$$

The values of the coefficients a_i were calculated by method of least squares along with the standard deviation $\sigma(Y^E)$. The coefficient is adjustable parameters for a better fit of the excess functions. The standard deviation values were obtained from:

$$\sigma(Y^E) = \left[\frac{\sum_{i=1}^{n}(Y_{expt}^E - Y_{cal}^E)^2}{m - n}\right]^{1/2} \quad (10)$$

where, m is the number of experimental points, n is the number of parameters, Y_{expt} and Y_{cal} are the experimental and calculated parameters, respectively.

RESULTS AND DISCUSSION

The experimental results of ultrasonic velocity, density and viscosity of the pure liquids at 303.15 K are compared with the published data in Table 1. The values of ultrasonic velocity, density and viscosity were taken for all the three mixtures at four different temperatures and

Table 1: Experimental and literature values of ultrasonic velocity (U), density (ρ) and viscosity (η) of pure liquid components at 303.15 K

	U (m sec^{-1})		ρx10^{-3} (kg m^{-3})		ηx10^{-3} (Nsm^{-2})	
Liquid	Expt*	Lit*	Expt*	Lit*	Expt*	Lit*
Anisaldehyde	1694.33	1684[a]	1.1252	1.1255[a]	3.2512	3.275[a]
o-xylene	1338.75	1328.30[b]	0.8707	0.8707[b]	0.7051	0.708[b]
m-xylene	1304.21	1300.34[b]	0.8557	0.8555[b]	0.5544	0.552[b]
p-xylene	1288.43	1289.68[b]	0.8528	0.8523[b]	0.5782	0.576[b]

*Expt: Experimental value, *Lit: Literature value, Bhaskaran and Kubendran (2008), Al-Kandary *et al.* (2006)

Table 2: Ultrasonic velocity (U), density (ρ) and viscosity (η) for the binary systems at varying temperatures

	U (m sec^{-1})				ρ×10^{-3} (kg m^{-3})				η×10^{-3} (Nsm^{-2})			
Mole fraction, X_1	303.15	308.15	313.15	318.15	303.15	308.15	313.15	318.15	303.15	308.15	313.15	318.15
anisaldehyde+o-xylene												
0.0000	1338.75	1315.00	1297.50	1278.15	0.8707	0.8694	0.8677	0.8659	0.7051	0.6652	0.6211	0.5691
0.1007	1381.73	1356.74	1335.25	1308.74	0.9189	0.9160	0.9133	0.9060	0.8305	0.7886	0.7383	0.6730
0.2012	1415.52	1390.01	1367.16	1335.85	0.9282	0.9257	0.9217	0.9168	0.9746	0.9254	0.8682	0.7802
0.3016	1450.79	1425.17	1400.10	1363.08	0.9385	0.9348	0.9303	0.9245	1.1473	1.0964	1.0423	0.9363
0.4018	1485.47	1460.20	1432.84	1390.89	0.9976	0.9930	0.9896	0.9827	1.3428	1.2817	1.1989	1.0874
0.5019	1520.00	1495.01	1465.95	1418.67	1.0006	0.9971	0.9942	0.9872	1.5873	1.5214	1.4223	1.2641
0.6018	1554.72	1529.88	1498.89	1446.25	1.0158	1.0127	1.0084	1.0029	1.8103	1.7308	1.6263	1.4619
0.7016	1596.41	1570.18	1534.84	1475.68	1.0424	1.0382	1.0343	1.0291	2.0867	2.0233	1.9108	1.7142
0.8012	1650.27	1620.04	1580.95	1514.86	1.0678	1.0593	1.0577	1.0529	2.7389	2.6372	2.4949	2.2620
0.9007	1673.45	1647.35	1608.08	1536.11	1.1067	1.0957	1.0914	1.0869	2.9809	2.8714	2.7171	2.4706
1.0000	1694.33	1670.67	1631.33	1557.00	1.1252	1.1116	1.1095	1.1047	3.2512	3.1306	2.9614	2.6822
anisaldehyde+m-xylene												
0.0000	1304.21	1285.27	1266.32	1244.21	0.8557	0.8487	0.8458	0.8405	0.5544	0.5229	0.4932	0.4684
0.1023	1353.73	1331.96	1309.17	1280.17	0.8900	0.8833	0.8812	0.8755	0.6669	0.6301	0.5950	0.5606
0.2040	1391.52	1369.06	1344.84	1310.57	0.9058	0.9006	0.8975	0.8927	0.8017	0.7603	0.7166	0.6716
0.3053	1429.79	1407.22	1381.10	1341.21	0.9213	0.9164	0.9134	0.9084	0.9653	0.9167	0.8584	0.8036
0.4060	1467.47	1445.58	1416.84	1372.28	0.9561	0.9534	0.9506	0.9444	1.1554	1.1019	1.0372	0.9617
0.5062	1505.00	1482.90	1452.69	1403.53	0.9825	0.9782	0.9755	0.9715	1.3887	1.3273	1.2481	1.1494
0.6060	1543.32	1520.41	1488.27	1434.52	1.0055	1.0008	1.0000	0.9979	1.6391	1.5702	1.4818	1.3626
0.7052	1589.41	1566.55	1529.75	1467.02	1.0361	1.0315	1.0295	1.0257	1.9248	1.8522	1.7494	1.6009
0.8040	1646.27	1617.88	1576.89	1510.24	1.0630	1.0575	1.0532	1.0479	2.7070	2.6098	2.4719	2.2452
0.9022	1671.45	1646.88	1606.93	1534.11	1.0983	1.0884	1.0839	1.0773	2.9363	2.8398	2.6905	2.4539
1.0000	1694.33	1670.67	1631.33	1557.00	1.1252	1.1116	1.1095	1.1047	3.2512	3.1306	2.9614	2.6822
anisaldehyde+p-xylene												
0.0000	1288.43	1275.79	1253.68	1234.73	0.8528	0.8460	0.8430	0.8369	0.5782	0.5501	0.5065	0.4912
0.1026	1341.85	1326.00	1299.15	1272.62	0.8866	0.8820	0.8791	0.8731	0.6933	0.6616	0.6090	0.5861
0.2046	1380.25	1362.85	1336.32	1304.10	0.9018	0.8987	0.8951	0.8903	0.8294	0.7945	0.7316	0.6993
0.3060	1420.21	1401.75	1373.68	1335.99	0.9168	0.9119	0.9080	0.9039	0.9937	0.9496	0.8763	0.8317
0.4068	1459.20	1440.79	1411.26	1367.67	0.9518	0.9484	0.9437	0.9389	1.1904	1.1388	1.0517	0.9902
0.5071	1498.58	1479.43	1448.01	1399.59	0.9789	0.9748	0.9703	0.9657	1.4278	1.3706	1.2786	1.1815
0.6068	1538.41	1518.25	1484.25	1431.32	0.9975	0.9938	0.9914	0.9871	1.6707	1.6079	1.4986	1.3886
0.7059	1586.12	1565.39	1528.61	1465.86	1.0305	1.0282	1.0267	1.0237	1.9594	1.8919	1.7712	1.6272
0.8045	1644.80	1616.73	1576.03	1510.38	1.0602	1.0554	1.0515	1.0468	2.7189	2.6212	2.4789	2.2523
0.9025	1670.82	1646.72	1606.85	1534.35	1.0949	1.0861	1.0834	1.0746	2.9578	2.8541	2.7092	2.4628
1.0000	1694.33	1670.67	1631.33	1557.00	1.1252	1.1116	1.1095	1.1047	3.2512	3.1306	2.9614	2.6822

are shown in Table 2. From these values, various acoustical parameters like adiabatic compressibility, free length, free volume, internal pressure and enthalpy have been evaluated. The excess values of some of the acoustic parameters are also calculated and are presented in Table 3. The values of the Redlich-Kister polynomial coefficient, a_i evaluated by the method of least squares along with the standard deviation is given in Table 4. Plots of π^E, U^E, G^{*E} and H^E against mole fraction of anisaldehyde for all the three systems are given in Fig. 1-4, respectively.

From Table 2, it can be observed that the ultrasonic velocity (U) of binary mixtures at each mole fraction decreases with increase of temperature. Also it is observed that at each temperature, as anisaldehyde mole fraction increases, the ultrasonic velocity, density and viscosity of the mixtures increase. The order of interactions among the mixtures is observed as anisaldehyde+o-xylene>anisaldehyde+m-xylene> anisaldehyde+p-xylene.

Adiabatic compressibility, β is found to be decreased with increase in the concentration of anisaldehyde. It is primarily the compressibility that changes with structure, which leads to a change in ultrasonic velocity. The change in adiabatic compressibility in liquid mixtures indicates that there is a definite contraction on mixing and

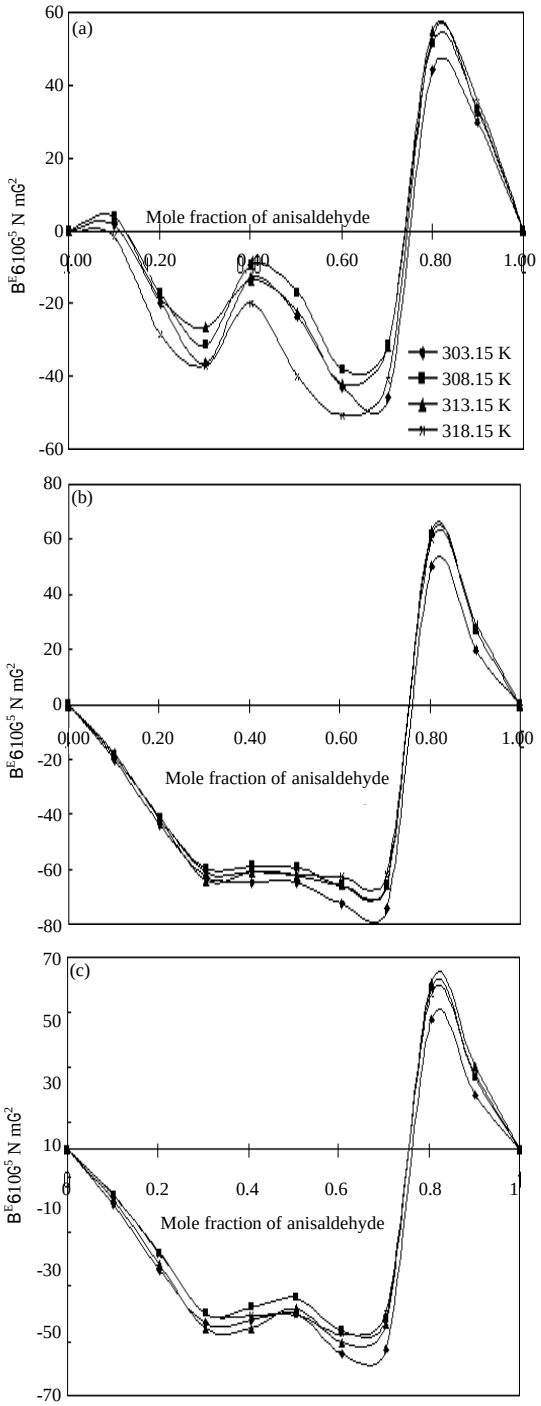

Fig. 1(a-c): Excess Internal pressure (π^E) as a function of mole fraction of anisaldehyde (x_1) for anisaldehyde+o-xylene (a), anisaldehyde+m-xylene (b) and anisaldehyde+p-xylene (c) at different temperatures

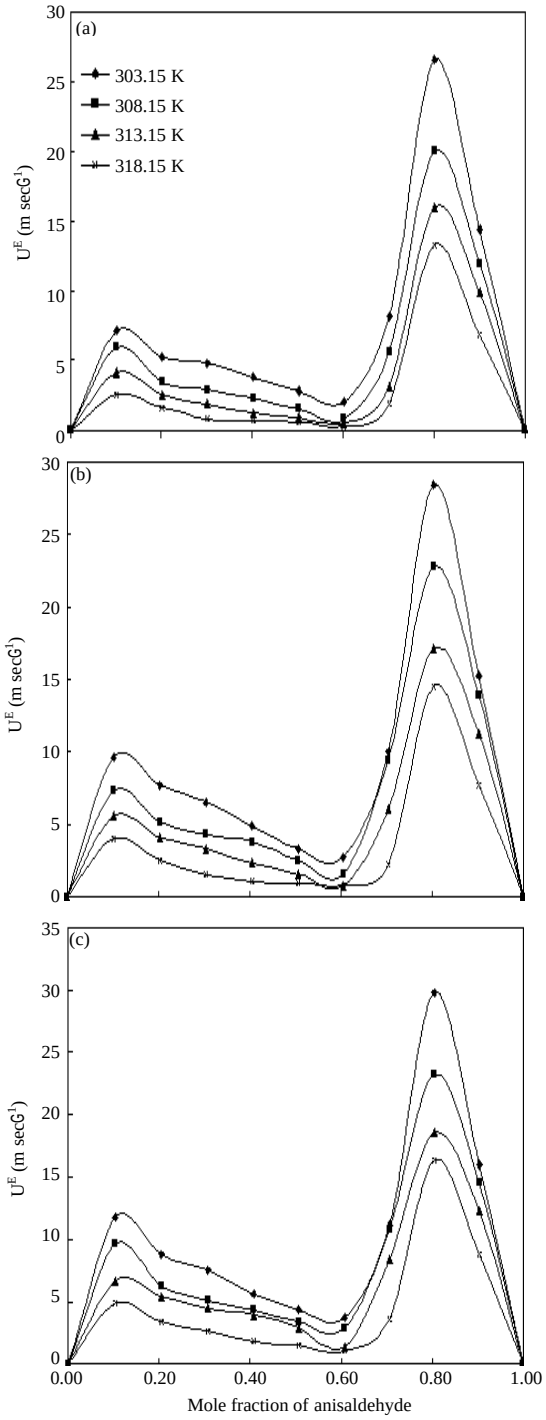

Fig. 2(a-c): Excess ultrasonic velocity (U^E) as a function of mole fraction of anisaldehyde (x_1) for anisaldehyde o-xylene (a), anisaldehyde+m-xylene (b) and anisaldehyde+p-xylene (c) at different temperatures

Table 3: Excess Free length (L_f^E), Excess adiabatic compressibility (β^E) and excess free volume (V_f^E) for the binary systems at varying temperatures

	L_f^E (A°)				β^E x10^{-11} (m^2 N^{-1})				V_f^E x10^{-6} (m^3 mol^{-1})			
Mole fraction, X_1	303.15	308.15	313.15	318.15	303.15	308.15	313.15	318.15	303.15	308.15	313.15	318.15
anisaldehyde+o-xylene												
0.0000	0.000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.000	0.0000	0.0000	0.0000	0.0000
0.1007	-0.013	-0.013	-0.012	-0.009	-3.745	-3.753	-3.561	-2.892	-2.095	-2.507	-2.946	-3.2553
0.2012	-0.011	-0.0113	-0.010	-0.008	-3.648	-3.705	-3.451	-2.856	-3.681	-4.126	-4.748	-4.7389
0.3016	-0.009	-0.0095	-0.008	-0.005	-3.467	-3.509	-3.189	-2.414	-4.749	-5.393	-6.521	-6.8997
0.4018	-0.017	-0.0181	-0.017	-0.015	-5.344	-5.508	-5.337	-4.689	-5.155	-5.698	-6.294	-7.0611
0.5019	-0.013	-0.0134	-0.013	-0.010	-4.200	-4.436	-4.292	-3.622	-5.362	-5.932	-6.489	-6.7750
0.6018	-0.009	-0.0106	-0.009	-0.007	-3.419	-3.692	-3.501	-2.951	-4.487	-4.888	-5.433	-5.9477
0.7016	-0.009	-0.0105	-0.009	-0.007	-3.199	-3.394	-3.147	-2.671	-3.537	-4.076	-4.613	-5.0335
0.8012	-0.012	-0.0109	-0.010	-0.008	-3.155	-3.076	-2.917	-2.583	-3.986	-4.352	-4.829	-5.4288
0.9007	-0.008	-0.007	-0.007	-0.006	-1.982	-2.005	-1.872	-1.612	-1.988	-2.167	-2.409	-2.7675
1.0000	0.000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.000	0.0000	0.0000	0.0000	0.0000
anisaldehyde+m-xylene												
0.0000	0.000	0.0000	0.000	0.000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1023	-0.0124	-0.011	-0.011	-0.009	-3.532	-3.516	-3.442	-3.118	-3.420	-3.822	-4.297	-4.333
0.2040	-0.0114	-0.012	-0.011	-0.009	-3.988	-4.110	-3.991	-3.574	-6.129	-6.849	-7.406	-7.5601
0.3053	-0.0107	-0.011	-0.010	-0.008	-4.086	-4.287	-4.164	-3.595	-7.815	-8.608	-9.006	-9.4221
0.4060	-0.0134	-0.015	-0.014	-0.012	-4.810	-5.261	-5.142	-4.583	-8.4060	-9.270	-9.955	-10.2073
0.5062	-0.0129	-0.014	-0.014	-0.012	-4.661	-5.046	-4.973	-4.596	-8.3934	-9.218	-9.852	-10.0536
0.6060	-0.0110	-0.012	-0.012	-0.011	-4.076	-4.411	-4.426	-4.213	-7.3473	-8.076	-8.710	-8.9675
0.7052	-0.0117	-0.013	-0.012	-0.010	-3.881	-4.252	-4.110	-3.687	-5.7259	-6.347	-6.889	-7.1299
0.8040	-0.0130	-0.013	-0.012	-0.010	-3.647	-3.768	-3.497	-3.246	-6.2003	-6.758	-7.304	-7.5995
0.9022	-0.0077	-0.008	-0.007	-0.006	-2.058	-2.178	-2.037	-1.762	-2.9899	-3.296	-3.572	-3.8045
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
anisaldehyde+p-xylene												
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1026	-0.0125	-0.013	-0.012	-0.010	-3.924	-3.996	-3.808	-3.446	-2.850	-3.2861	-3.748	-3.741
0.2046	-0.0122	-0.013	-0.012	-0.011	-4.313	-4.450	-4.398	-3.933	-5.214	-5.9419	-6.586	-6.554
0.3060	-0.0114	-0.011	-0.011	-0.009	-4.417	-4.453	-4.377	-3.833	-6.681	-7.3303	-8.174	-8.114
0.4068	-0.0141	-0.015	-0.014	-0.012	-5.152	-5.396	-5.342	-4.741	-7.383	-8.0299	-8.913	-8.823
0.5071	-0.0138	-0.015	-0.014	-0.012	-5.029	-5.269	-5.223	-4.703	-7.439	-8.1180	-9.232	-8.821
0.6068	-0.0109	-0.012	-0.011	-0.010	-4.201	-4.458	-4.442	-4.026	-6.414	-7.0293	-7.928	-7.783
0.7059	-0.0119	-0.013	-0.013	-0.011	-4.056	-4.418	-4.422	-3.945	-5.030	-5.5550	-6.315	-6.205
0.8045	-0.0135	-0.013	-0.012	-0.011	-3.850	-3.877	-3.714	-3.486	-5.561	-6.0210	-6.792	-6.785
0.9025	-0.0076	-0.008	-0.007	-0.006	-2.109	-2.214	-2.175	-1.812	-2.724	-2.9544	-3.377	-3.421
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table 4: Redlich-Kister Coefficients (a_i) and standard deviation (σ) for the binary systems at varying temperatures

Functions	a_1	a_2	a_3	σ	a_1	a_2	a_3	σ
anisaldehyde+o-xylene T = 303.15 K					**T = 308.15 K**			
L_f^E (A^0)	-0.0509	0.0355	-0.1025	0.003662	-0.0537	0.0348	-0.0955	0.003719
β^E (x10^{-11} m^2 N^{-1})	-16.8465	12.0621	-23.3232	0.888143	-17.7910	11.9560	-22.1242	0.910549
V_f^E (x10^{-6} m^3 mol^{-1})	-21.4516	0.5692	-1.9320	0.452904	-23.7357	2.1627	-3.4801	0.445764
U^E (m sec^{-1})	10.9244	50.8746	170.89	4.342786	5.8364	42.5185	146.76	3.226308
π^E (x10^{-5} N m^{-2})	-94.7441	193.8635	420.9190	25.46317	-68.5909	206.2432	431.6000	23.82163
G^{*E} (cal mol^{-1})	99.2609	310.3821	73.7259	21.99248	106.4214	299.6615	99.9784	21.80237
anisaldehyde+o-xylene T = 313.15 K					**T = 318.15 K**			
L_f^E (A^0)	-0.0509	0.0348	-0.0860	0.003866	-0.0413	0.0231	-0.0708	0.003479
β^E (x10^{-11} m^2 N^{-1})	-17.2118	11.5508	-20.2031	0.944018	-14.5199	8.3951	-16.7941	0.847455
V_f^E (x10^{-6} m^3 mol^{-1})	-25.9696	3.5144	-5.8893	0.476825	-27.1122	3.1551	-9.9012	0.518241
U^E (m sec^{-1})	3.4450	40.3513	116.8074	2.7979	2.1250	29.9778	77.6651	2.553136
π^E (x10^{-5} N m^{-2})	-94.7441	193.8635	420.9190	25.46317	-68.5909	206.2432	431.6000	23.82163
G^{*E} (cal mol^{-1})	99.2609	310.3821	73.7259	21.99248	106.4214	299.6615	99.9784	21.80237
anisaldehyde+m-xylene T = 303.15 K					**T = 308.15 K**			
L_f^E (A^0)	-0.0519	0.0231	-0.0834	0.002416	-0.0570	0.0189	-0.0754	0.002301
β^E (x10^{-11} m^2 N^{-1})	-18.7642	9.6319	-19.0228	0.634119	-20.2923	8.6652	-17.5543	0.606972
V_f^E (x10^{-6} m^3 mol^{-1})	-33.6046	2.1257	-3.0767	0.604456	-36.9137	2.7014	-4.0398	0.63636
U^E (m s^{-1})	12.6252	40.8534	196.9824	4.444837	9.4678	47.3886	169.7418	3.251656
π^E (x10^{-5} N m^{-2})	- 262.586	271.2076	412.1320	27.15016	-241.6701	319.6554	454.0950	28.07026
G^{*E} (cal mol^{-1})	70.3386	318.9747	244.4066	26.64186	63.8712	346.5720	272.1138	26.54153
anisaldehyde+m-xylene T = 313.15 K					**T = 318.15 K**			
L_f^E (A^0)	-0.0551	0.0225	-0.0672	0.002369	-0.0499	0.0234	-0.0535	0.002568
β^E (x10^{-11} m^2 N^{-1})	-20.0052	9.1434	-16.1281	0.623054	-18.4927	8.8622	-13.2993	0.673748
V_f^E (x10^{-6} m^3 mol^{-1})	-39.4619	4.0060	-6.5577	0.619671	-40.2518	2.6099	-7.6738	0.662907

Table 4: Continued

Functions	a_1	a_2	a_3	σ	a_1	a_2	a_3	σ
U^E (m sec^{-1})	5.7893	41.1702	137.6178	2.554452	3.5361	26.5902	96.1709	2.71084
π^E (x10^{-5} N m^{-2})	-253.887	310.8779	483.7135	27.31739	-252.9021	327.9681	501.4045	25.73112
G^{*E} (cal mol^{-1})	53.7459	368.9131	315.8617	27.75695	34.1844	403.7281	360.0868	28.71552
anisaldehyde+p-xylene T = 303.15 K					**T = 308.15 K**			
L_f^E (A^0)	-0.0556	0.0318	-0.0869	0.002951	-0.0592	0.0303	-0.0865	0.003019
β^E (x10^{-11} m^2 N^{-1})	-20.2848	11.8664	-20.4274	0.760773	-21.2442	11.6112	-20.4661	0.787695
V_f^E (x10^{-6} m^3 mol^{-1})	-29.7651	0.0191	-1.8609	0.587401	-32.4971	1.3562	-3.3482	0.589559
U^E (m sec^{-1})	16.7878	31.8370	216.0144	4.60949	13.0603	35.4891	190.7487	3.106281
π^E (x10^{-5} N m^{-2})	-245.048	273.3291	388.2955	27.58187	-220.8306	297.1040	436.6086	27.27429
G^{*E} (cal mol^{-1})	88.2186	337.2531	253.7260	25.13176	82.1559	347.1295	259.9321	25.33885
anisaldehyde+p-xylene T = 313.15 K					**T = 318.15 K**			
L_f^E (A^0)	-0.0568	0.0262	-0.0783	0.002689	-0.0496	0.0300	-0.0625	0.002846
β^E (x10^{-11} m^2 N^{-1})	-21.0414	10.6015	-18.8373	0.714691	-18.9651	10.6851	-15.7897	0.739478
V_f^E (x10^{-6} m^3 mol^{-1})	-36.9575	1.4992	-4.0487	0.657527	-35.3047	1.1682	-6.9562	0.626509
U^E (m s^{-1})	10.6788	40.3728	149.6002	2.578684	5.3369	28.3134	110.2170	2.857757
π^E (x10^{-5} N m^{-2})	-237.999	333.3466	488.7546	28.19423	-245.9407	298.1271	488.9928	25.04555
G^{*E} (cal mol^{-1})	86.1977	394.6831	279.1507	27.71634	50.2570	406.0278	340.8629	27.72395

the variation may be due to complex formation. It clearly shows that there are some significant interactions between the molecules of the mixtures taken under study. Intermolecular free length (L_f) shows a similar behavior as reflected by adiabatic compressibility. The decrease in compressibility brings the molecules closer, resulting in a decrease of intermolecular free length. Intermolecular free length is a predominant factor in determining the variation of ultrasonic velocity in the mixtures. The decrease in the values of adiabatic compressibility and the free length with increase in ultrasonic velocity further strengthens the strong molecular interactions between the unlike molecules through hydrogen bonding.

It is also observed that there is decrease in free volume and increase in internal pressure with increase in mole fraction of anisaldehyde for all the three systems. It shows the presence of strong interactions and hence, supports the present investigation. In order to understand in a better way, the nature of molecular interactions between the components of the liquid mixtures, the discussion can be extended to excess parameters.

The results of excess values of compressibility, β^E of anisaldehyde+o-xylene, anisaldehyde+m-xylene and anisaldehyde+p-xylene are shown in Table 3 and are observed to be negative. The negative values of β^E suggest that the mixtures are less compressible than the corresponding ideal mixtures which signifies chemical effect including charge transfer forces, formation of H bonds and other complex forming interactions making negative contributions towards β^E and positive contributions towards G^{*E} (Parveen *et al*., 2009a). Also it is observed that in case of all the mixtures at each temperature, as mole fraction of anisaldehyde increases, the β^E values of the binary mixtures attain a minimum value at the mole fraction 0.5. Beyond this, the β^E values of the mixture increases with the increase of mole fraction of anisaldehyde. However, the change in β^E with temperature has been observed to be small for the mixtures anisaldehyde+p-xylene. Similar behaviour was reported by Gupta *et al*. (2006) and Iloukhani *et al*. (2005), who worked on binary mixtures.

The excess properties of the mixtures are influenced by three main contributions, viz. (1) physical : due to non-specific Vander Waals type forces, (2) chemical : due to hydrogen bonding, dipole-dipole and donar-acceptor interactions between unlike molecules and (3) structural: due to the fitting of smaller molecules into the voids created by the bigger molecules. The first effect leads to contraction in volume and hence, leads to positive contribution towards H^E and negative contribution towards U^E and π^E. In case of all the three mixtures, the Π^E values are found to be negative for the mole fraction range of 0.0 to 0.7. The negative contribution of π^E value (Fig. 1) is an evidence of presence of stronger molecular interactions between the components present in the mixture. Further, the values of π^E are more negative in anisaldehyde+m-xylene and anisaldehyde+p-xylene when compared to anisaldehyde+o-xylene mixtures.

V_f^E is found to be negative for all the mixtures over the entire composition range of anisaldehyde. As temperature rises, V_f^E values decreases in the mixtures. The negative values of V_f^E suggest the existence of strong dipole-dipole interactions due to hydrogen bonding among the molecules (Parveen *et al*., 2009b).

The plots (Fig. 2) of deviation in ultrasonic velocity, U^E with mole fraction at all the four temperatures for all the three mixtures exhibit positive values. The positive values of U^E decrease with increase in temperature which indicates the decrease of strength of interactions with temperature in all the systems. The higher positive values of U^E are observed in case of the anisaldehyde+p-xylene when compared with other two mixtures. It confirms that anisaldehyde+p-xylene exhibits higher molecular interactions when compared to other two mixtures. Similar results of U^E have been observed by Chorazewski (2007).

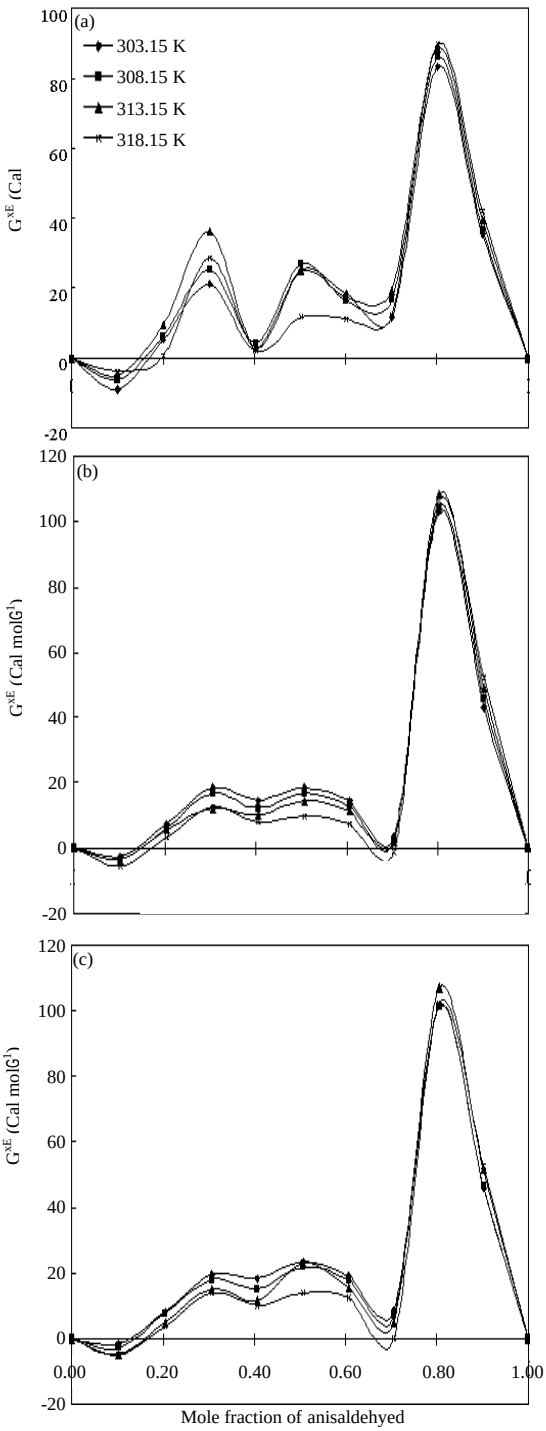

Fig. 3(a-c): Excess Gibb's free energy of activation (G^{*E}) as a function of mole fraction of anisaldehyde (x_1) for anisaldehyde+o-xylene (a), anisaldehyde+m-xylene (b) and anisaldehyde +p-xylene (c) at different temperatures

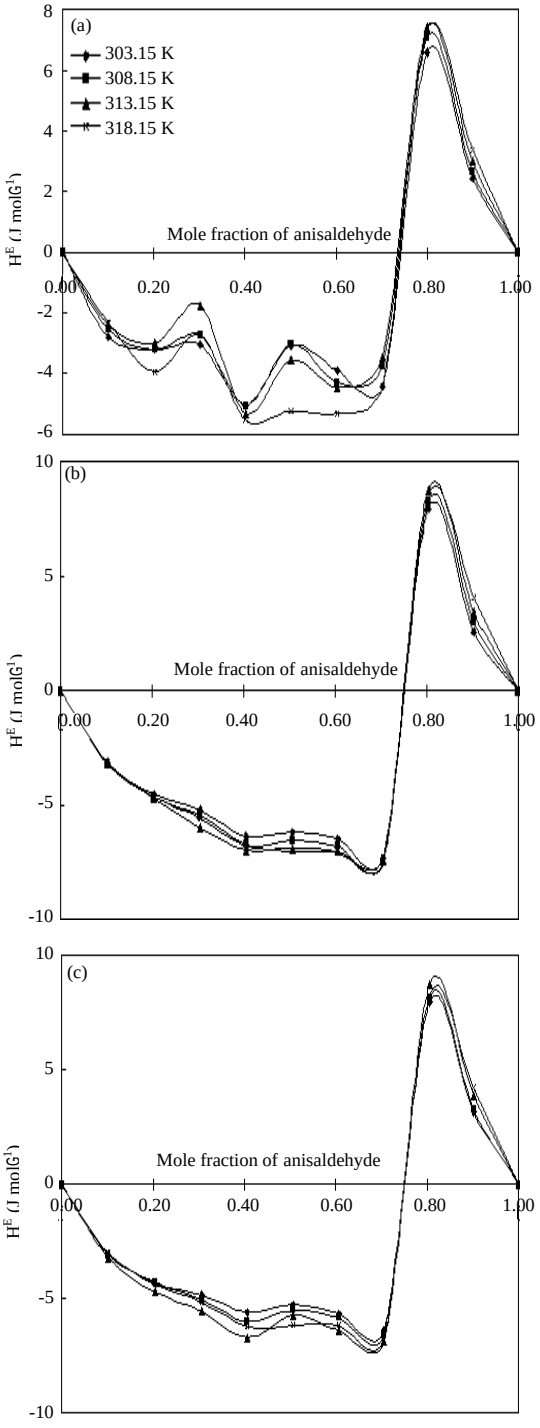

Fig. 4(a-c): Excess Enthalpy (H^E) as a function of mole fraction of anisaldehyde (x_1) for anisaldehyde+o-xylene (a), anisaldehyde+m-xylene (b) and anisaldehyde+p-xylene (c) at different temperatures

Figure 3 indicates the variation of G^{*E} with mole fraction of anisaldehyde at different temperatures for all the mixtures, respectively. In case of all the three mixtures, G^{*E} values are almost positive. It indicates the presence of strong intermolecular interactions through hydrogen bonding between the molecules of the mixtures. Subha *et al.* (2004) made the similar results. The positive values of G^{*E} in each system attain a maximum value at all temperatures at the mole fraction of 0.8. It suggests that an increase in intermolecular interaction between unlike molecules is due to thermal energy. However, G^{*E} value with temperature is small in anisaldehyde+o-xylene mixture when compared to other two mixtures.

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 o-xylene, m-xylene or p-xylene. In case of all the three mixtures, the H^E values (Fig. 4) are found to be negative for the mole fraction range of 0.0-0.7. The negative values of H^E in the mixtures indicate the presence of stronger interactions between unlike molecules. However, as mole fraction of anisaldehyde increases from 0.7-1.0, the H^E values are found to be positive. The positive values of H^E indicate that the interactions among the molecules lead to weak dispersion type of forces arrived due to rupture of hydrogen bonding in the structure. Similar variations in H^E with change in composition has also been reported by Misra *et al.* (2007).

CONCLUSIONS

In the present investigation, the excess adiabatic compressibility β^E, excess free volume V_f^E exhibit negative values over the entire range of composition in case of all the three mixtures. It clearly indicates the presence of strong hydrogen bonding interactions between unlike molecules (Fort and Moore, 1965). This also may be quantitatively interpreted in terms of closer approach of unlike molecules leading to reductions in compressibility and volume (Jayakumar *et al.*, 1996). Further, π^E which is usually discussed in terms of molecular interactions, whose negative excess values for all the systems suggests that strong molecular association between the unlike molecules. The positive values of G^{*E} and U^E in case of all the three mixtures supports the interpretation given above in terms of strong interactions. On comparing the above results for the three mixtures, the strengths of interactions are observed in the following order anisaldehyde+m-xylene>anisaldehyde+p-xylene> anisaldehyde+o-xylene.

REFERENCES

Al-Kandary, J.A., A.S. Al-Jimaz and A.H.M. Abdul-Latif, 2006. Viscosities, densities and speeds of sound of binary mixtures of benzene, toluene, o-xylene, m-xylene, p-xylene and Mesitylene with anisole at (288.15. 293.15, 298.15 and 303.15) K. J. Chem. Eng. Data, 51: 2074-2082.

Bhaskaran, R. and T.R. Kubendran, 2008. Thermophysical properties of para-anisaldehyde (1) + chlorobenzene (2) at temperatures of (303.15, 313.15 and 323.15) K and a pressure of 0.1 MPa. J. Chem. Eng. Data, 53: 978-982.

Chorazewski, M., 2007. Thermo physical and acoustical properties of the binary mixtures 1,2-dibromoethane + heptane with in the temperature range from 293.15 K to 313.15 K. J. Chem. Eng. Data, 52: 154-163.

Fort, R.J. and W.R. Moore, 1965. Adiabatic compressibilities of binary mixtures. Trans. Faraday Soc., 61: 2102-2114.

Gupta, M., I. Vibhu and J.P. Shukla, 2006. Ultrasonic velocity, viscosity and excess properties of binary mixture of tetrahydrofuran with 1-propanol and 2-propanol. Fluid Phase Equilib., 244: 26-32.

Iloukhani, H., N. Zoorasna and R. Soleimani, 2005. Excess molar volumes and speed of sound of tetrahydrofuran with chloroethane or chloroethenes at 298.15 K. Phys. Chem. Liq., 43: 391-401.

Jayakumar, A., S. Karunanithi and V. Kannappan, 1996. Ultrasonic velocity and other acoustical parameters in binary mixtures of o-cresol, p-cresol, o-chloro phenol and p-chlorophenol with CCl_4 at 303.15 K. Indian J. Pure Applied Phys., 34: 761-763.

Lide, D.R. and H.P.R. Frederikse, 1995. CRC Handbook of Chemistry and Physics: A Ready-Reference Book of Chemical and Physical Data. 76th Edn., CRC Press, Florida, USA., ISBN: 9780849304767, Pages: 2576.

Misra, A., I. Vibhu, R.K. Singh, M. Gupta and J.P. Shukla, 2007. Acoustic, viscometric and optical properties of binary mixture of tetrahydrofuran with 1-propanol and 2-propanol. Phys. Chem. Liq., 45: 93-104.

Nain, A.K., R. Sharma, A. Ali and S. Gopal, 2010. Densities and volumetric properties of binary mixtures of butyl acrylate with benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene and mesitylene at temperatures from 288.15 K to 318.15 K. Int. J. Thermophys., 31: 1073-1091.

Pandey, J.D., B.P. Sukhla and S.N. Dubey, 1993a. Study of variation of internal pressure with temperature. Indian J. Pure Applied Ultrason., 15: 33-39.

Pandey, J.D., R.D. Rai, R.K. Shukla, A.K. Shukla and N. Mishra, 1993b. Ultrasonic and thermodynamic properties of quaternary liquid system at 298.15 K. Indian J. Pure Applied Phys., 31: 84-90.

Parveen, S., D. Shukla, S. Singh, K.P. Singh, M. Gupta and J.P. Shukla, 2009a. Ultrasonic velocity, density, viscosity and their excess parameters of the binary mixtures of tetrahydrofuran with methanol and o-cresol at varying temperatures. Applied Accoustics, 70: 507-513.

Parveen, S., S. Singh, D. Shukla, K.P. Singh, M. Gupta and J.P. Shukla, 2009b. Molecular interaction study of binary mixtures of THF with Methanol and o-cresol: An optical and ultrasonic study. Acta Phys. Pol. A., 116: 1011-1017.

Perrin, D.D. and W.L.F. Armarego, 1988. Purification of Laboratory Chemistry. 3rd Edn., Pregamon Press, Oxford, UK., ISBN: 9780080347158, Pages: 391.

Redlich, O. and A.T. Kister, 1948. Algebric representation of thermodynamic properties and classification of solutions. Indian Eng. Chem., 40: 345-348.

Saravanakumar, K., R. Baskaran and T.R. Kubendran, 2010. Acoustic and thermodynamic properties of binary liquid mixtures of acetophenone and benzene. J. Applied Sci., 10: 1616-1621.

Singh, S., B.P.S. Sethi, R.C. Katyal and V.K. Rattan, 2004. Viscosities, densities and speed of binary mixtures of *o*-xylene, *m*-xylene, *p*-xylene and isopropylbenzene with 4-methylpentan-2-one at 298.15 K. J. Chem. Eng. Data, 49: 1373-1375.

Singh, S., V.K. Rattan, S. Kapoor, R. Kumar and A. Rampal, 2005. Thermophysical properties of binary mixtures of cyclohexane + nitrobenzene, cyclohexanone + nitrobenzene, and cyclohexane + cyclohexanone at (298.15, 303.15 and 308.15) K. J. Chem. Eng. Data, 50: 288-292.

Subha, M.C.S., G.N. Swamy, M.E. Bal and K.S.K.V. Rao, 2004. Excess volume and viscosity of ethoxy ethanol with *n*-butylamine, *sec*-butylamine, *tert*-butylamine, *n*-hexylamine, *n*-octylamineand cyclohexylamine. Indian J. Chem. Sect. A, 43: 1876-1881.