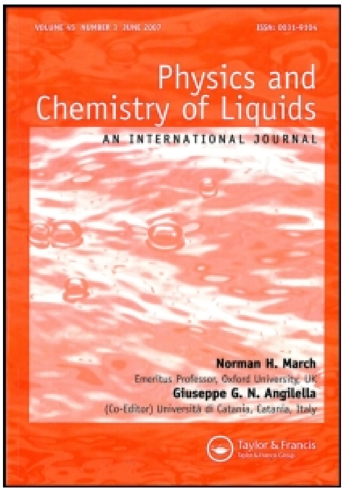

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Excess internal pressures, excess free volumes and excess thermodynamic parameters of some non-aqueous binary mixtures from ultrasonic speed, density and viscosity data

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Excess internal pressures, excess free volumes and excess thermodynamic parameters of some non-aqueous binary mixtures from ultrasonic speed, density and viscosity data

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The internal pressure, π_i; free volume, V_f; excess internal pressure, π_i^E; excess free volume, V_f^E; excess free energy, G^E; excess enthalpy, H^E and excess entropy, S^E of mixing for the binary mixtures of tetrahydorfuran (THF) with benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene and mesitylene have been calculated from experimental ultrasonic speed, density and viscosity data over the whole composition range at 298.15 K. The results have been discussed in terms of intermolecular interactions between the component molecules in the mixture. The variations of these excess functions with composition indicate that the THF-aromatic hydrocarbon interaction in these mixtures follows the order: benzene > toluene > *p*-xylene > *m*-xylene > *o*-xylene > mesitylene. Further, π_i of these binary mixtures are also evaluated theoretically by using various equations proposed in the literature. The results are compared with the experimental findings, and relative merits of these equations in predicting internal pressure are discussed.

Keywords: internal pressure; free volume; molecular interactions; tetrahydrofuran; aromatic hydrocarbons

1. Introduction

Internal pressure, free volume and the excess thermodynamic functions have been found to provide useful information regarding intermolecular interactions between the component molecules of the binary liquid mixtures. Whatever the model chosen for the liquid state, the cohesive forces are of primary importance. Internal pressure, π_i [$=(\partial E/\partial V)_T$] of a fluid is the volume derivative of the internal energy of the fluid at constant temperature. It is the resultant of the forces of attraction and repulsion between the constituents in a liquid medium. Internal pressure has gained significant interest by chemists, physicists and chemical engineers in past, as it provides a measure of explaining molecular interactions, internal structure, clustering phenomenon, ionic interactions and dipolar interactions. Internal pressure has been a subject of active

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interest among several researchers during recent past [1–5]. Several attempts have been made by a number of investigators [6–15] to calculate the internal pressure of liquids and liquid mixtures theoretically.

In the present study, the internal pressure, π_i; free volume, V_f; excess internal pressure, π_i^E; excess free volume, V_f^E; excess free energy, G^E; excess enthalpy, H^E and excess entropy, S^E of mixing for the binary mixtures of tetrahydrofuran (THF) with benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene and mesitylene have been evaluated from ultrasonic speed, u; density, ρ and viscosity, η data over the whole composition range expressed by mole fraction, x_1 of THF ($0 \leq x_1 \leq 1$) at 298.15 K. The required experimental u, ρ and η data of the binary mixtures have been taken from our previous studies [16,17]. The variations of these parameters with composition of the mixtures are discussed in terms of molecular interaction in these mixtures. Furthermore, the internal pressure of these binary mixtures have also been evaluated theoretically by using various equations and theories proposed in the literature [6–15]. The theoretical values have been compared with experimental findings.

2. Theory

The internal pressure of a fluid is related to the thermal pressure coefficient $(\partial P/\partial T)_V$ by the following well-known thermodynamic equation of state

$$\pi_i = \left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P = T\left(\frac{\alpha_p}{k_T}\right) - P, \tag{1}$$

where α_p is the isobaric expansivity and k_T is the isothermal compressibility of the mixture. For most of the liquids, the thermal pressure coefficient multiplied by absolute temperature, i.e. $T(\alpha_p/k_T)$ is very high so that the external pressure P becomes negligible in comparison [14], therefore it may be neglected in the Equation (1) in the present calculations. Thus, the internal pressure can be shown to be equal to [14]

$$\pi_{nt} = \frac{\alpha T}{k_T}. \tag{2}$$

The V_f of the mixtures are calculated from the relation [18,19]

$$V_f = \frac{RT}{(P + \pi_i)}, \tag{3}$$

since P is very small as compared to π_i, it has been neglected in Equation (3) in the present calculations. k_T, is calculated using the well-known thermodynamic relation

$$k_T = k_s + \frac{TV\alpha_T^2}{C_p}, \tag{4}$$

where k_s [$=1/(u^2\rho)$] is isentropic compressibility, V is the molar volume and C_p is the heat capacity of the mixture. The α_p values for the mixtures were evaluated from temperature dependence of density data and C_p values for the mixtures have been calculated by using the relation

$$C_p = x_1 C_{p,1} + x_2 C_{p,2}. \tag{5}$$

The $\pi_\mathrm{i}^\mathrm{E}$ and V_f^E of binary mixtures have been calculated using the relation

$$Y^\mathrm{E} = Y - (x_1 Y_1 + x_2 Y_2), \tag{6}$$

where Y is π_i or V_f and subscripts 1 and 2 refers to pure THF and aromatic hydrocarbons, respectively. The excess enthalpies, H^E and excess entropies, TS^E are calculated from π_i and V_f by using the following relations [18,19]

$$H^\mathrm{E} = \pi_\mathrm{i} V - \left[x_1 \pi_{\mathrm{i},1} V_1 + x_2 \pi_{\mathrm{i},2} V_2\right], \tag{7}$$

$$TS^\mathrm{E} = RT\left[x_1 \ln V_{\mathrm{f},1} + x_2 \ln V_{\mathrm{f},2} - \ln V_\mathrm{f}\right]. \tag{8}$$

The excess free energy, G^E of mixtures is given by the relation

$$G^\mathrm{E} = H^\mathrm{E} - TS^\mathrm{E}. \tag{9}$$

The values of $\pi_\mathrm{i}^\mathrm{E}$, V_f^E, H^E, TS^E and G^E were fitted to a Redlich–Kister-type polynomial Equation [20]

$$Y^\mathrm{E} = x_1(1 - x_1) \sum_{i=0}^{n} A_i (1 - 2x_1)^i, \tag{10}$$

where Y^E is $\pi_\mathrm{i}^\mathrm{E}$ or V_f^E or H^E or TS^E or G^E. The values of coefficients, A_i in Equation (10) were evaluated by using least-squares method with all points weighted equally.

The internal pressures of these mixtures have also been calculated theoretically by using Flory's statistical theory

$$(\pi_i)_\mathrm{Flory} = \frac{(\alpha_p)_\mathrm{Flory} T}{(k_T)_\mathrm{Flory}}, \tag{11}$$

where $(\alpha_p)_\mathrm{Flory}$ and $(k_T)_\mathrm{Flory}$ are the isobaric thermal expansivity and isothermal compressibility of liquid mixtures, computed using Flory's statistical theory [21–26] from the knowledge of the α_p and k_T of pure liquids as

$$(\alpha_p)_\mathrm{Flory} = \frac{3(\tilde{V}^{1/3} - 1)}{[1 - 3(\tilde{V}^{1/3} - 1)]T}, \tag{12}$$

and

$$(k_T)_\mathrm{Flory} = \frac{(\alpha_p)_\mathrm{Flory} T \tilde{V}^2}{P^*}. \tag{13}$$

The details pertaining to the calculation of various parameters used in Equations (12) and (13) can be obtained from the literature [21–26].

The internal pressure of a liquid can also be evaluated theoretically using the equation of the state proposed by Buehler *et al.* [27,28]

$$(\pi_\mathrm{i})_\mathrm{Beuhler} = \frac{2^{1/6}RT}{2^{1/6}V - dN^{1/3}V^{2/3}}, \tag{14}$$

where *d* the molecular diameter has been calculated using the relation [29]

$$d = \left(\frac{V\sigma^{1/4}}{7.21 \times 10^{19} T_\mathrm{c}^{1/4}}\right)^{2/5}, \tag{15}$$

where, σ is surface tension and T_c is critical temperature. The surface tension, σ of the mixtures has been calculated using the following relation [30]

$$\sigma = 6.3 \times 10^{-4} \rho u^{3/2}, \tag{16}$$

where ρ is in $\mathrm{g\,cm^{-3}}$ and u is in $\mathrm{m\,s^{-1}}$.

The internal pressure of a liquid can also be evaluated by using the equation proposed by Suryanarayana [31,32]

$$\pi_i = bRT\left(\frac{k\eta}{u}\right)^{1/2} \frac{\rho^{2/3}}{M_\mathrm{eff}^{7/6}}, \tag{17}$$

where *b* is the packing fraction of the liquid which is taken equal to 2 for most of the liquids, *k* is a constant equal to 4.28×10^9, M_eff $(=x_1M_1 + x_2M_2)$ is the effective molecular mass and *M* is the molar mass of the mixture of pure liquid.

3. Results

The experimental *u* and ρ data of THF + benzene/toluene/*o*-xylene/*m*-xylene/*p*-xylene/mesitylene binary mixtures have been taken from our previous studies [16,17]. The values of u, ρ, η, π_i, V_f, $\pi_\mathrm{i}^\mathrm{E}$, V_f^E, G^E, H^E and TS^E as functions of mole fraction, x_1 of THF at 298.15 K are listed in Table 1. The values of coefficients, A_i of Equation (10) for the excess functions, evaluated by using least-squares method with all points weighted equally, and the corresponding standard deviations, $\sigma(Y^\mathrm{E})$ are listed in Table 2. The variations $\pi_\mathrm{i}^\mathrm{E}$, V_f^E, G^E, H^E and TS^E with composition of the mixtures, along with smoothed values using Equation (10) at 298.15 K are presented graphically in Figures 1–5. The values of various parameters of pure liquids used in the theoretical calculation of internal pressure, π_i from Equations (11), (14) and (17) are listed in Table 3. The comparison of theoretically calculated values of π_i with the experimental values in terms of average percentage deviation (APD) is presented in Table 4.

4. Discussion

The results shown in Figure 1 indicate that $\pi_\mathrm{i}^\mathrm{E}$ values are positive for THF + benzene and negative for THF + *o*-xylene/*m*-xylene/*p*-xylene/mesitylene mixtures over the entire

Table 1. The values of u, ρ, η, π_i, V_f, π_i^E, V_f^E, G^E, H^E and TS^E as a function of mole fraction, x_1 of THF for the binary mixtures at 298.15 K.

x_1	u ($m\,s^{-3}$)	ρ ($kg\,m^{-3}$)	η ($10^{-3}\,N s\,m^{-2}$)	π_i ($10^8\,N\,m^{-2}$)	V_f ($10^{-6}\,m^3\,mol^{-1}$)	π_i^E ($10^6\,N\,m^{-2}$)	V_f^E ($10^{-8}\,m^3\,mol^{-1}$)	G^E ($J\,mol^{-1}$)	H^E ($J\,mol^{-1}$)	TS^E ($J\,mol^{-1}$)
THF + benzene										
0.0000	1303.5	873.61	0.6025	3.778	6.561	0.000	0.000	0.00	0.00	0.00
0.0754	1302.5	874.68	0.5973	3.805	6.514	1.128	−2.070	100.32	92.71	−7.62
0.1518	1301.4	875.78	0.5921	3.832	6.469	2.164	−3.920	188.24	173.73	−14.51
0.2230	1300.6	876.77	0.5863	3.856	6.428	3.138	−5.603	269.81	248.92	−20.89
0.2962	1299.3	877.80	0.5793	3.879	6.390	3.870	−6.835	325.44	299.82	−25.62
0.3556	1298.4	878.60	0.5728	3.898	6.360	4.461	−7.796	369.92	340.55	−29.37
0.4128	1297.5	879.30	0.5659	3.914	6.333	4.937	−8.546	405.57	373.22	−32.35
0.4812	1296.0	880.13	0.5568	3.932	6.304	5.255	−9.008	423.59	389.33	−34.26
0.5506	1294.3	880.81	0.5467	3.948	6.279	5.353	−9.094	425.97	391.23	−34.74
0.6219	1292.4	881.41	0.5353	3.962	6.257	5.261	−8.859	413.32	379.33	−33.99
0.6884	1290.2	881.87	0.5237	3.972	6.241	4.860	−8.131	375.71	344.41	−31.30
0.7512	1287.9	882.12	0.5120	3.978	6.231	4.226	−7.036	323.51	296.37	−27.15
0.8119	1285.5	882.28	0.4999	3.983	6.223	3.429	−5.685	259.13	237.15	−21.98
0.8792	1282.7	882.31	0.4857	3.986	6.218	2.337	−3.862	174.37	159.41	−14.95
0.9388	1280.1	882.23	0.4724	3.988	6.216	1.197	−1.977	87.77	80.11	−7.66
1.0000	1277.6	882.05	0.4580	3.989	6.215	0.000	0.000	0.00	0.00	0.00
THF + toluene										
0.0000	1310.5	862.36	0.5531	3.535	7.013	0.000	0.000	0.00	0.00	0.00
0.0718	1309.4	863.77	0.5513	3.566	6.951	−0.075	−0.532	55.39	54.66	−0.73
0.1498	1307.9	865.42	0.5491	3.601	6.883	−0.135	−1.023	101.68	100.24	−1.44
0.2283	1306.2	867.09	0.5459	3.636	6.817	−0.168	−1.441	139.42	137.30	−2.12
0.2902	1304.8	868.44	0.5431	3.665	6.764	−0.128	−1.799	166.48	163.55	−2.92
0.3452	1303.4	869.66	0.5398	3.690	6.717	−0.093	−2.050	183.56	180.04	−3.52
0.4005	1302.0	870.86	0.5357	3.716	6.670	−0.009	−2.326	201.01	196.69	−4.32
0.4694	1299.9	872.38	0.5298	3.748	6.614	0.034	−2.469	207.13	202.39	−4.74
0.5368	1297.7	873.89	0.5230	3.779	6.559	0.112	−2.579	207.00	201.78	−5.22
0.6067	1295.2	875.35	0.5155	3.811	6.504	0.145	−2.517	197.34	192.12	−5.22
0.6704	1292.8	876.67	0.5080	3.841	6.454	0.203	−2.427	183.65	178.40	−5.25
0.7378	1289.9	877.95	0.4993	3.871	6.404	0.142	−2.046	153.71	149.37	−4.34

(continued)

Table 1. Continued.

x_1	u $(\mathrm{m\,s^{-3}})$	ρ $(\mathrm{kg\,m^{-3}})$	η $(10^{-3}\,\mathrm{N\,s\,m^{-2}})$	π_i $(10^{8}\,\mathrm{N\,m^{-2}})$	V_f $(10^{-6}\,\mathrm{m^3\,mol^{-1}})$	$\pi_\mathrm{i}^\mathrm{E}$ $(10^{6}\,\mathrm{N\,m^{-2}})$	V_f^E $(10^{-8}\,\mathrm{m^3\,mol^{-1}})$	G^E $(\mathrm{J\,mol^{-1}})$	H^E $(\mathrm{J\,mol^{-1}})$	TS^E $(\mathrm{J\,mol^{-1}})$
0.8018	1287.0	879.03	0.4903	3.899	6.358	0.046	−1.552	119.33	116.23	−3.10
0.8714	1284.0	880.16	0.4797	3.931	6.306	0.098	−1.191	89.48	86.89	−2.59
0.9368	1280.7	881.13	0.4690	3.960	6.260	−0.019	−0.511	41.45	40.54	−0.91
1.0000	1277.6	882.05	0.4580	3.989	6.215	0.000	0.000	0.00	0.00	0.00
THF + *o*-xylene										
0.0000	1350.3	875.57	0.7576	3.612	6.863	0.000	0.000	0.00	0.00	0.00
0.0764	1345.1	876.13	0.7380	3.632	6.825	−0.852	1.123	−11.28	−6.36	4.92
0.1504	1340.0	876.74	0.7192	3.653	6.786	−1.556	2.027	−21.16	−12.22	8.94
0.2243	1335.0	877.31	0.6998	3.675	6.745	−2.109	2.699	−22.28	−10.25	12.02
0.2942	1330.0	877.87	0.6807	3.696	6.706	−2.614	3.347	−33.04	−18.14	14.90
0.3660	1324.9	878.46	0.6606	3.720	6.664	−2.977	3.780	−38.10	−21.20	16.90
0.4226	1320.9	878.89	0.6445	3.739	6.629	−3.166	3.985	−38.22	−20.32	17.91
0.4801	1316.7	879.36	0.6277	3.760	6.593	−3.304	4.137	−42.14	−23.49	18.64
0.5310	1313.0	879.73	0.6127	3.778	6.561	−3.350	4.170	−42.48	−23.63	18.85
0.5850	1309.0	880.08	0.5959	3.799	6.526	−3.355	4.165	−44.05	−25.20	18.85
0.6578	1303.6	880.54	0.5731	3.828	6.476	−3.203	3.950	−42.42	−24.48	17.94
0.7322	1298.0	880.97	0.5493	3.859	6.424	−2.891	3.545	−39.69	−23.55	16.14
0.8049	1292.5	881.32	0.5253	3.891	6.371	−2.404	2.932	−33.59	−20.20	13.39
0.8708	1287.5	881.63	0.5030	3.922	6.320	−1.764	2.133	−24.53	−14.74	9.79
0.9392	1282.3	881.88	0.4794	3.957	6.265	−0.910	1.085	−11.58	−6.57	5.01
1.0000	1277.6	882.05	0.4580	3.989	6.215	0.000	0.000	0.00	0.00	0.00
THF + *m*-xylene										
0.0000	1326.6	860.02	0.5880	3.425	7.238	0.000	0.000	0.00	0.00	0.00
0.0722	1324.0	861.31	0.5823	3.456	7.173	−0.949	0.849	28.26	33.04	4.78
0.1486	1321.0	862.78	0.5762	3.490	7.103	−1.858	1.681	47.55	56.94	9.39
0.2134	1318.4	864.04	0.5703	3.520	7.042	−2.515	2.264	62.85	75.52	12.67
0.2804	1315.6	865.40	0.5638	3.552	6.979	−3.081	2.753	75.01	90.48	15.47
0.3536	1312.5	866.96	0.5560	3.589	6.907	−3.518	3.067	88.71	106.22	17.51
0.4255	1309.3	868.50	0.5477	3.626	6.836	−3.825	3.288	97.04	115.97	18.93
0.4864	1306.4	869.87	0.5401	3.659	6.774	−3.988	3.408	97.22	116.89	19.67
0.5476	1303.4	871.29	0.5321	3.693	6.712	−4.020	3.399	95.58	115.32	19.74
0.6041	1300.5	872.57	0.5243	3.726	6.654	−3.978	3.365	89.86	109.38	19.52

0.6751	1296.7	874.25	0.5139	3.768	6.579	−3.758	3.172	78.64	97.05	18.40
0.7396	1293.1	875.76	0.5038	3.808	6.510	−3.419	2.902	64.75	81.50	16.75
0.8005	1289.6	877.17	0.4939	3.847	6.444	−2.951	2.530	49.93	64.42	14.49
0.8722	1285.4	878.89	0.4817	3.895	6.364	−2.142	1.839	32.94	43.44	10.50
0.9378	1281.4	880.48	0.4699	3.942	6.289	−1.191	1.044	14.31	20.18	5.88
1.0000	1277.6	882.05	0.4580	3.989	6.215	0.000	0.000	0.00	0.00	0.00
THF + *p*-xylene										
0.0000	1316.4	856.82	0.6110	3.426	7.234	0.000	0.000	0.00	0.00	0.00
0.0840	1314.1	858.60	0.6047	3.463	7.157	−1.038	0.870	35.69	40.81	5.13
0.1716	1311.7	860.59	0.5954	3.504	7.074	−1.878	1.459	73.68	82.73	9.05
0.2322	1310.1	861.99	0.5895	3.534	7.014	−2.302	1.667	103.39	114.24	10.86
0.2934	1308.3	863.44	0.5825	3.565	6.954	−2.682	1.885	124.62	137.15	12.53
0.3548	1306.5	864.95	0.5748	3.597	6.892	−2.920	1.932	146.89	160.29	13.41
0.4284	1304.0	866.74	0.5648	3.635	6.819	−3.195	2.113	157.69	172.33	14.64
0.4896	1301.8	868.28	0.5558	3.669	6.757	−3.308	2.171	162.04	177.15	15.11
0.5518	1299.4	869.89	0.5461	3.703	6.694	−3.332	2.177	159.99	175.16	15.18
0.6201	1296.6	871.64	0.5347	3.742	6.624	−3.261	2.145	151.64	166.49	14.85
0.6825	1293.7	873.27	0.5237	3.778	6.560	−3.161	2.184	130.13	144.70	14.57
0.7414	1290.9	874.82	0.5127	3.814	6.499	−2.928	2.093	109.00	122.61	13.61
0.8102	1287.6	876.65	0.4991	3.857	6.426	−2.445	1.778	85.70	97.10	11.40
0.8756	1284.3	878.47	0.4855	3.901	6.355	−1.793	1.315	59.37	67.74	8.37
0.9409	1280.8	880.31	0.4713	3.945	6.283	−0.982	0.755	27.27	31.91	4.64
1.0000	1277.6	882.05	0.4580	3.989	6.215	0.000	0.000	0.00	0.00	0.00
THF + mesitylene										
0.0000	1369.8	861.45	0.6025	3.600	6.886	0.000	0.000	0.00	0.00	0.00
0.0735	1363.6	862.72	0.5973	3.618	6.851	−1.029	1.453	−12.52	−6.40	6.13
0.1513	1356.6	864.01	0.5921	3.637	6.816	−2.184	3.154	−44.12	−30.99	13.13
0.2274	1349.5	865.04	0.5863	3.654	6.783	−3.373	4.961	−82.12	−61.68	20.44
0.2986	1342.4	865.86	0.5793	3.670	6.754	−4.600	6.891	−135.62	−107.51	28.11
0.3672	1335.3	866.64	0.5728	3.685	6.727	−5.761	8.735	−193.31	−157.91	35.40
0.4305	1328.9	867.40	0.5659	3.701	6.698	−6.622	10.076	−231.17	−190.42	40.75
0.4912	1322.9	868.20	0.5568	3.718	6.666	−7.230	10.996	−253.90	−209.42	44.48
0.5496	1317.3	869.11	0.5467	3.738	6.631	−7.550	11.436	−261.08	−214.73	46.35
0.6055	1312.0	870.05	0.5353	3.759	6.595	−7.668	11.562	−260.07	−213.10	46.97

(*continued*)

Table 1. Continued.

x_1	u ($\mathrm{m\,s^{-3}}$)	ρ ($\mathrm{kg\,m^{-3}}$)	η ($10^{-3}\,\mathrm{N\,s\,m^{-2}}$)	π_i ($10^{8}\,\mathrm{N\,m^{-2}}$)	V_f ($10^{-6}\,\mathrm{m^3\,mol^{-1}}$)	$\pi_\mathrm{i}^\mathrm{E}$ ($10^{6}\,\mathrm{N\,m^{-2}}$)	V_f^E ($10^{-8}\,\mathrm{m^3\,mol^{-1}}$)	G^E ($\mathrm{J\,mol^{-1}}$)	H^E ($\mathrm{J\,mol^{-1}}$)	TS^E ($\mathrm{J\,mol^{-1}}$)
0.6784	1305.4	871.47	0.5237	3.790	6.541	−7.386	11.032	−236.51	−191.47	45.04
0.7516	1298.8	873.18	0.5120	3.825	6.481	−6.699	9.903	−204.48	−163.84	40.65
0.8280	1292.1	875.27	0.4999	3.867	6.410	−5.440	7.944	−155.54	−122.73	32.81
0.8790	1287.7	876.96	0.4857	3.899	6.357	−4.234	6.126	−116.13	−90.71	25.42
0.9412	1282.6	879.29	0.4724	3.943	6.287	−2.277	3.246	−53.61	−40.03	13.58
1.0000	1277.6	882.05	0.4580	3.989	6.215	0.000	0.000	0.00	0.00	0.00

Table 2. Coefficients, A_i of Equation (10) and standard deviations, $\sigma(Y^E)$ for THF + aromatic hydrocarbon binary mixtures at different temperatures.

Excess property	A_0	A_1	A_2	A_3	A_4	$\sigma(Y^E)$
THF + benzene						
π_i^E (10^7 Nm^{-2})	2.1240	−0.5318	−0.3097	0.3222	−0.0628	0.0025
V_f^E (10^{-7} m^3 mol^{-1})	−3.6315	0.6614	0.4858	−0.4730	0.0930	0.0042
G^E (kJ mol^{-1})	1.7080	−0.2472	−0.2536	0.2347	−0.0502	0.0026
H^E (kJ mol^{-1})	1.5695	−0.2177	−0.2319	0.2161	−0.0497	0.0024
TS^E (kJ mol^{-1})	−0.1383	0.0296	0.0197	−0.0186	0.0028	0.0002
THF + toluene						
π_i^E (10^7 Nm^{-2})	0.0329	−0.1977	−0.1703	0.1730	0.0800	0.0028
V_f^E (10^{-7} m^3 mol^{-1})	−1.0211	0.2830	0.3371	−0.2791	−0.1763	0.0046
G^E (kJ mol^{-1})	0.8373	−0.0151	−0.2143	0.0848	0.1963	0.0025
H^E (kJ mol^{-1})	0.8171	−0.0032	−0.2025	0.0748	0.1897	0.0023
TS^E (kJ mol^{-1})	−0.0202	0.0123	0.0115	−0.0108	−0.0049	0.0002
THF + *o*-xylene						
π_i^E (10^7 Nm^{-2})	−1.3339	0.2520	−0.1282	−0.0164	0.0551	0.0014
V_f^E (10^{-7} m^3 mol^{-1})	1.6675	−0.2403	0.1723	0.0436	−0.0894	0.0025
G^E (kJ mol^{-1})	−0.1695	0.0622	−0.0322	−0.0368	0.0087	0.0016
H^E (kJ mol^{-1})	−0.0944	0.0495	−0.0240	−0.0353	0.0042	0.0015
TS^E (kJ mol^{-1})	0.0750	−0.0122	0.0078	0.0004	−0.0043	0.0001
THF + *m*-xylene						
π_i^E (10^7 Nm^{-2})	−1.5992	0.2403	−0.2221	0.1423	0.0876	0.0009
V_f^E (10^{-7} m^3 mol^{-1})	1.3605	−0.1122	0.3543	−0.2216	−0.2054	0.0016
G^E (kJ mol^{-1})	0.3915	0.0235	−0.1969	0.0785	0.1729	0.0009
H^E (kJ mol^{-1})	0.4703	0.0145	−0.1820	0.0684	0.1640	0.0008
TS^E (kJ mol^{-1})	0.0787	−0.0094	0.0147	−0.0088	−0.0075	0.0001
THF + *p*-xylene						
π_i^E (10^7 Nm^{-2})	−1.3222	0.2335	−0.3721	−0.0205	0.1021	0.0020
V_f^E (10^{-7} m^3 mol^{-1})	0.8605	−0.1773	0.6251	0.1193	−0.1719	0.0035
G^E (kJ mol^{-1})	0.6528	0.0293	−0.3219	−0.0969	0.1231	0.0019
H^E (kJ mol^{-1})	0.7130	0.0186	−0.2977	−0.0933	0.1145	0.0018
TS^E (kJ mol^{-1})	0.0602	−0.0107	0.0243	0.0033	−0.0079	0.0001
THF + mesitylene						
π_i^E (10^7 Nm^{-2})	−2.9149	1.5442	0.6230	0.0262	−0.6808	0.0034
V_f^E (10^{-7} m^3 mol^{-1})	4.4307	−2.2791	−1.4428	0.0060	1.2271	0.0062
G^E (kJ mol^{-1})	−1.0215	0.5395	0.9579	−0.0086	−0.5736	0.0040
H^E (kJ mol^{-1})	−0.8421	0.4461	0.9089	−0.0094	−0.5271	0.0037
TS^E (kJ mol^{-1})	0.1794	−0.0933	−0.0499	−0.0012	0.0480	0.0002

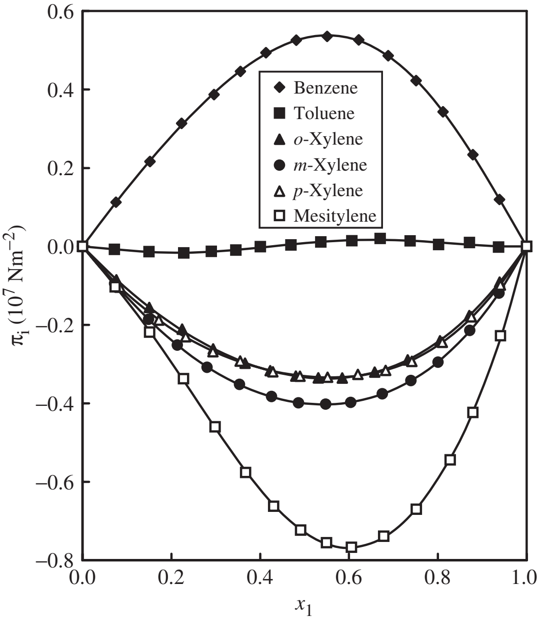

Figure 1. Plots of excess internal pressure, π_i^E *vs*. mole fraction, x_1 of tetrahydrofuran (THF) for the binary mixtures at 298.15 K. Points show experimental values and curves show smoothed values using Equation (10).

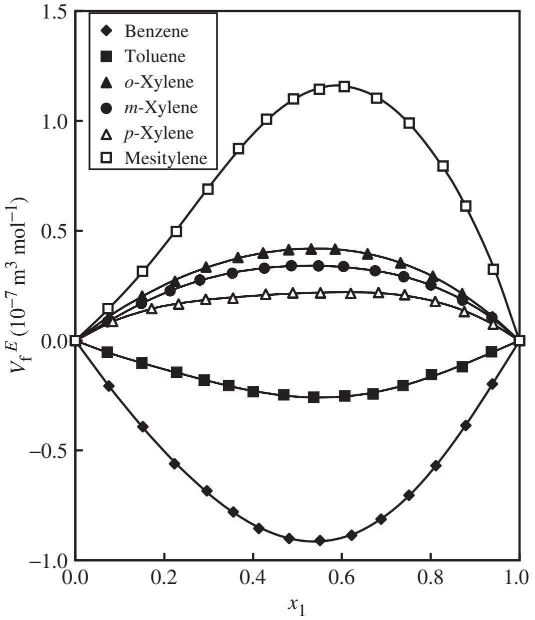

Figure 2. Plots of excess free volume, V_f^E *vs*. mole fraction, x_1 of tetrahydrofuran (THF) for the binary mixtures at 298.15 K. Points show experimental values and curves show smoothed values using Equation (10).

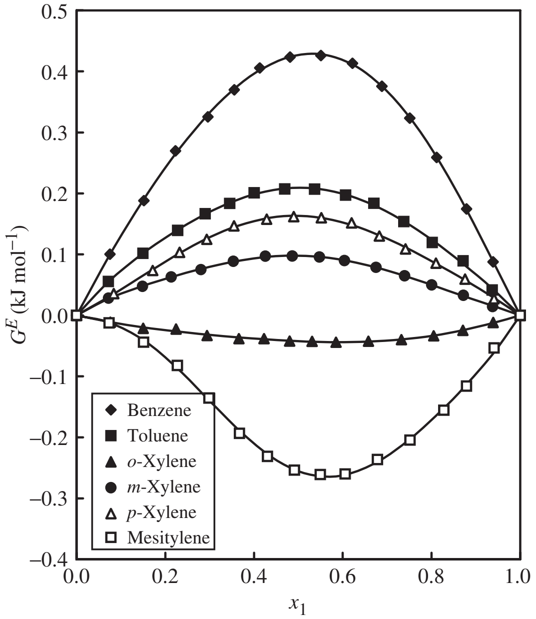

Figure 3. Plots of excess free energy, G^E *vs.* mole fraction, x_1 of THF for THF + aromatic hydrocarbon mixtures at 298.15 K. Points show experimental values and curves show smoothed values using Equation (10).

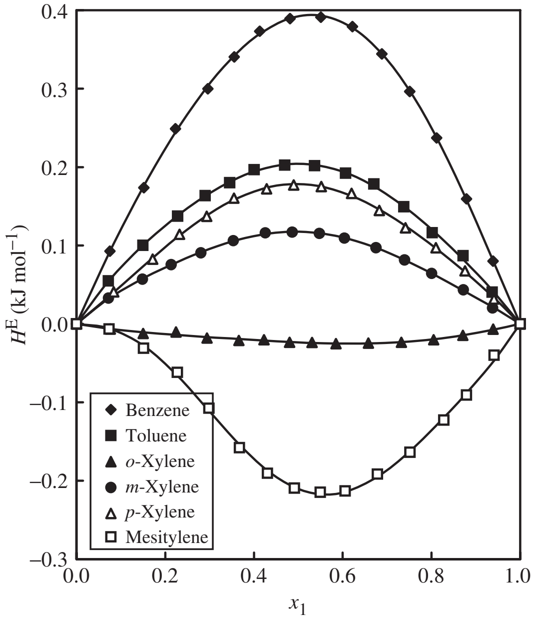

Figure 4. Plots of excess enthalpy, H^E *vs.* mole fraction, x_1 of THF for THF + aromatic hydrocarbon mixtures at 298.15 K. Points show experimental values and curves show smoothed values using Equation (10).

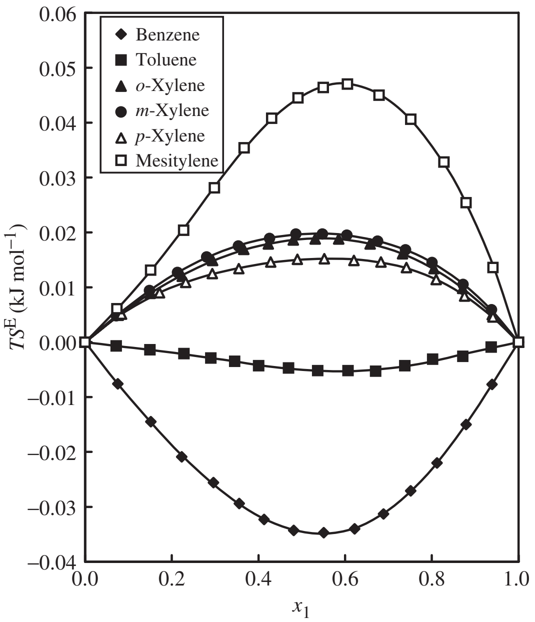

Figure 5. Plots of TS^{E} *vs.* mole fraction, x_1 of THF for THF + aromatic hydrocarbon mixtures at 298.15 K. Points show experimental values and curves show smoothed values using Equation (10).

Table 3. The values of various parameters of pure liquids at 298.15 K used in the theoretical calculations of internal pressure.

Parameter	THF	Benzene	Toluene	*o*-Xylene	*m*-Xylene	*p*-Xylene	Mesitylene
C_p (J mol^{-1} K^{-1})	177.03	136.78	157.3	186.1	183.0	181.5	209.3
α (10^{-3} K^{-1})	1.190	1.223	1.081	0.989	0.982	1.015	0.975
k_s (10^{-10} m^2 N^{-1})	6.946	6.737	6.752	6.264	6.607	6.735	6.187
k_T (10^{-10} m^2 N^{-1})	8.896	9.651	9.119	8.164	8.545	8.832	8.078
V (10^{-5} m^3 mol^{-1})	8.1753	8.9411	10.6846	12.1258	12.3451	12.3912	13.9532
$\tilde{V}$	1.2854	1.2917	1.2641	1.2454	1.2439	1.2508	1.2426
V^* (10^{-5} m^3 mol^{-1})	6.3601	6.9219	8.4525	9.7361	9.9245	9.9068	11.2291
P^* (10^6 J m^{-3})	659.01	630.39	564.78	560.24	529.91	5.3604	555.83
T_{c} (K)	540.1	562.05	591.72	630.25	617.0	591.72	692.35

mole fraction range, and exhibit a sigmoid trend for THF + toluene mixtures, wherein π_i^{E} values change sign from negative to positive as amount of THF increases in the mixture. The magnitude of $\pi_{\mathrm{i}}^{\mathrm{E}}$ values follows the sequence: benzene > toluene > *p*-xylene ≈ *o*-xylene > *m*-xylene > mesitylene. The observed trends in $\pi_{\mathrm{i}}^{\mathrm{E}}$ values for THF + aromatic hydrocarbon mixtures indicate that the interactions between THF and aromatic hydrocarbon molecules in these mixtures follows the order: benzene > toluene > xylenes > mesitylene. Figure 2 indicates that $V_{\mathrm{f}}^{\mathrm{E}}$ values are negative for THF + benzene/toluene and positive for THF + *o*-xylene/*m*-xylene/*p*-xylene/mesitylene

Table 4. The average percentage deviation (APD) between theoretically calculated values of π_i and the experimental values for THF + aromatic hydrocarbon binary mixtures at 298.15 K.

	Average percentage deviation (APD)		
Mixture	Equation (11)	Equation (14)	Equation (17)
THF + benzene	0.902	12.084	2.338
THF + toluene	0.506	6.604	7.627
THF + *o*-xylene	0.054	7.369	9.019
THF + *m*-xylene	0.283	6.646	12.816
THF + *p*-xylene	0.390	6.681	11.695
THF + mesitylene	0.336	11.939	20.082

mixtures over the entire mole fraction range. The observed trends in V_f^E values for THF + aromatic hydrocarbon mixtures indicate the presence of specific interactions between THF and aromatic hydrocarbon molecules in these mixtures. The magnitude of V_f^E values follows the sequence: benzene > toluene > *p*-xylene > *m*-xylene > *o*-xylene > mesitylene, which in turn indicates the interactions in the same order.

The most probable interaction in THF + aromatic hydrocarbon mixtures can be the electron donor–acceptor-type (or charge-transfer) interactions [33] between highly electronegative oxygen of THF (acting as donor) and the π-electrons in ring of aromatic hydrocarbon molecules (acting as acceptor). Similar type of donor–acceptor interactions between oxygen atom of sulpholane and π-electrons of the aromatic hydrocarbons (benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene and *p*-xylene), had also been reported by Yang *et al.* [33] recently. It is interesting to note that π_i^E values decrease and turns negative (whereas V_f^E values increase and turn positive) as the number of $-CH_3$ group attached to the aromatic ring increases from benzene (without any $-CH_3$ group) to mesitylene (with three $-CH_3$ groups). This is due to the fact that methyl group ($-CH_3$) being an electron-releasing group would enhance the electron density of the benzene ring of the aromatic molecules, but the electron-accepting tendency of the aromatic ring would however decrease as we move from benzene to mesitylene, resulting in decreased donor–acceptor interaction between unlike molecules with increase in number of methyl group ($-CH_3$) in the aromatic hydrocarbon molecule.

Another factor that would cause a decrease in interactions is the steric hindrance due to $-CH_3$ groups of the rings. As the number of methyl group in the ring increases from benzene to mesitylene the closer approach of THF molecule to the aromatic ring becomes increasingly difficult, resulting in decreased interaction between THF and aromatic hydrocarbon molecules. The above view regarding interactions in these mixtures clearly justify the trends exhibited by π_i^E and V_f^E values with composition of the mixtures.

The values of G^E and H^E values are positive for THF + benzene/toluene/*m*-xylene/*p*-xylene and negative for THF + *o*-xylene/mesitylene mixtures over the entire mole fraction range. The magnitude of G^E and H^E values follows the sequence: benzene > toluene > *p*-xylene > *m*-xylene > *o*-xylene > mesitylene, which in turn indicate the interactions in the same order. The TS^E values are negative for THF + benzene/toluene and positive for THF + *o*-xylene/*m*-xylene/*p*-xylene/mesitylene mixtures over the entire mole fraction range, and follow the order: benzene < toluene < *p*-xylene < *m*-xylene < *o*-xylene < mesitylene. These trends in TS^E also indicate that the order of interactions in these mixtures follow the sequence: benzene > toluene > *p*-xylene > *m*-xylene > *o*-xylene > mesitylene. This further supports the trends exhibited by π_i^E, V_f^E, G^E and H^E values with composition of the mixtures.

A close perusal of the Table 4 indicates that Equation (11) provides satisfactory results for all the systems under study with low values of APD, whereas Equations (14) and (17) show larger APDs. The possible reason for the type of deviations in these methods could be that these relations are derived based upon some adjustments, and the approaches use more than one empirical relation. This shows that these equations in the present forms cannot be recommended strongly in most of the cases under investigation. As expected while aiming the present study, Flory's theory is found to give excellent results. The very low APD values in internal pressure calculated from Flory theory proves the applicability of the Flory's statistical theory for the evaluation of internal pressure of the liquid mixtures. The present study can also be considered as an authentication for the method of computing internal pressure using Flory's statistical theory completely, i.e. without the use of any empirical relation.

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