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Ultrasonic and viscometric studies of molecular interactions in binary mixtures of tetrahydrofuran with some aromatic hydrocarbons at temperatures from 288.15 to 318.15 K

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Ultrasonic speed, u , and viscosity, η , of pure tetrahydrofuran (THF), benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, mesitylene and those of their binary mixtures with THF as a common component, over the entire composition range expressed by mole fraction, x_1 of THF ($0 \leq x_1 \leq 1$), were measured at temperatures 288.15, 298.15, 308.15 and 318.15 K. From the experimental data, the deviations in isentropic compressibility, Δk_s , in ultrasonic speed, Δu , and in viscosity, $\Delta \eta$ were calculated. The partial molar compressibilities, $\bar{K}_{m,1}$ and $\bar{K}_{m,2}$ of THF and aromatic hydrocarbons in the mixtures over the whole composition range and $\bar{K}_{m,1}^\infty$ and $\bar{K}_{m,2}^\infty$ at infinite dilution and excess partial molar compressibilities, $\bar{K}_{m,1}^E$ and $\bar{K}_{m,2}^E$, over the whole composition range and $\bar{K}_{m,1}^{E,\infty}$ and $\bar{K}_{m,2}^{E,\infty}$ at infinite dilution were calculated by using two different approaches. The variation of these parameters with composition and temperature of the mixtures are discussed in terms of molecular interaction in these mixtures. It is observed that the THF-aromatic hydrocarbon interaction in these mixtures follows the order: benzene > toluene > *p*-xylene > *m*-xylene > *o*-xylene > mesitylene. The effect of the number and position of the methyl groups in these aromatic hydrocarbons on the molecular interactions in these mixtures is also discussed.

Keywords: Ultrasonic speed; Viscosity; Tetrahydrofuran; Aromatic hydrocarbons; Excess functions; Partial molar compressibility; Molecular interactions

1. Introduction

The knowledge of physicochemical properties of non-aqueous binary liquid mixtures has relevance in theoretical and applied areas of research and such results are frequently used in the design process (flow, mass transfer or heat transfer calculations) of many chemical and industrial processes [1,2]. The binary mixtures containing aromatic hydrocarbons are interesting because they find applications in the studies of polymer phase diagrams and preferential interaction of polymers in mixed solvents [3–6].

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In continuation to our ongoing research [7–15] focussing on experimental and theoretical studies of acoustic, volumetric and transport properties of non-aqueous binary liquid mixtures, here we report the results of our study on the binary mixtures of tetrahydrofuran (THF) with six aromatic hydrocarbons (benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, and mesitylene) over the entire composition range at four different temperatures. THF is a very useful compound having applications as reaction solvent and also used commercially for the production of many useful compounds. It is polar (dipole moment and dielectric constant, $\mu=1.75$ D and $\epsilon=7.58$ at 298.15 K, respectively), aprotic and unassociated liquid [16]. The aromatic hydrocarbon molecules possess large quadrupole moments, causing an orientational order in these liquids. The orientational order is considered as a partial alignment of neighbouring segments or possibly of whole molecules [17]. The objective underlying the present work is to obtain information regarding molecular interactions in the mixtures of a polar liquid with non-polar liquids, which is essential for the understanding of many chemical and industrial processes in these media. A survey of literature indicates that there has been no study on these systems from the point of view of their ultrasonic and viscometric behaviour.

The present article reports the ultrasonic speeds, u and viscosities, η of the binary mixtures of THF with benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene and mesitylene, including those of pure liquids, at the temperatures 288.15, 298.15, 308.15 and 318.15 K, covering the entire composition range expressed by mole fraction, x_1 of THF ($0 \leq x_1 \leq 1$). The density, ρ data for the calculations was taken from our previous study [18]. The experimental values of ρ , u and η were used to calculate the deviations in isentropic compressibility, Δk_s , deviations in ultrasonic speed, Δu , deviations in viscosity, $\Delta \eta$ and excess molar compressibility, K_s^E . The partial molar compressibilities, $\bar{K}_{m,1}$ and $\bar{K}_{m,2}$ of THF and aromatic hydrocarbon in the mixture over the whole composition range and $\bar{K}_{m,1}^\infty$ and $\bar{K}_{m,2}^\infty$ at infinite dilution, and excess partial molar compressibilities, $\bar{K}_{m,1}^E$ and $\bar{K}_{m,2}^E$, over the whole composition range and $\bar{K}_{m,1}^{E,\infty}$ and $\bar{K}_{m,2}^{E,\infty}$ at infinite dilution were also calculated. The variation of these parameters with composition and temperature of the mixtures are discussed in terms of molecular interaction in these mixtures. The effect of the number and position of the methyl group in these aromatic hydrocarbons on molecular interactions in these mixtures is also discussed.

2. Experimental

THF and the aromatic hydrocarbons (benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene and mesitylene) used in the study were the products from SD Fine Chemicals, India and were purified by using the methods described in the literature [19,20]; the mass fraction purities as determined by gas chromatography are: THF > 0.996, benzene > 0.998, toluene > 0.998, *o*-xylene > 0.997, *m*-xylene > 0.997, *p*-xylene > 0.997 and mesitylene > 0.995. Before use, the pure chemicals were stored over 0.4 nm molecular sieves for 72 h to remove water content, if any, and were degassed at low pressure. The mixtures were prepared by mass and were kept in special airtight stopper glass bottles to avoid evaporation. The weighings were done on an electronic balance with a precision of ± 0.1 mg. The probable error in the mole fraction was estimated to be less than ± 0.0001 .

Table 1. Comparison of experimental values of ultrasonic speed, u and viscosity, η of pure liquids with the corresponding literature values at different temperatures.

| Liquid | T (K) | u (m s^{-1}) | | η ($10^{-3} \text{ N s m}^{-2}$) | |
|------------------|---------|---------------------------|---------------------|---|--|
| | | Expt. | Lit. | Expt. | Lit. |
| THF | 298.15 | 1276.6 | – | 0.4580 | 0.456 ^a |
| | 308.15 | 1231.7 | – | 0.4125 | – |
| | 318.15 | 1186.4 | – | 0.3762 | – |
| Benzene | 298.15 | 1303.5 | 1304.0 ^b | 0.6025 | 0.602 ^b , 0.6038 ^c |
| | 308.15 | 1257.4 | 1257.4 ^d | 0.5395 | 0.525 ^b |
| | 318.15 | 1207.2 | 1207.2 ^d | 0.4670 | 0.4670 ^c |
| Toluene | 298.15 | 1310.5 | 1309.0 ^b | 0.5531 | 0.552 ^b , 0.554 ^c |
| | 308.15 | 1266.2 | 1264.0 ^b | 0.5020 | 0.496 ^d |
| | 318.15 | 1221.0 | 1221.0 ^f | 0.4379 | 0.4379 ^e |
| <i>o</i> -Xylene | 298.15 | 1350.3 | 1350.3 ^f | 0.7576 | 0.7574 ^g |
| | 308.15 | 1321.4 | 1321.4 ^g | 0.6690 | 0.6690 ^e |
| | 318.15 | 1285.8 | 1285.8 ^f | 0.5972 | 0.5972 ^c |
| <i>m</i> -Xylene | 298.15 | 1326.6 | 1326.0 ^b | 0.5880 | 0.5892 ^c |
| | 308.15 | 1281.0 | 1283.0 ^b | 0.5229 | 0.519 ^b |
| | 318.15 | 1243.0 | 1243.0 ^f | 0.4684 | 0.4684 |
| <i>p</i> -Xylene | 298.15 | 1316.4 | 1316.4 ^f | 0.6110 | 0.6110 ^h |
| | 308.15 | 1268.0 | 1268.0 ^g | 0.5501 | 0.5470 ^j |
| | 318.15 | 1230.3 | 1230.3 ^f | 0.4912 | 0.4912 ^c |
| Mesitylene | 298.15 | 1369.8 | 1369.8 ^f | 0.6572 | 0.656 ^b |
| | 308.15 | 1325.2 | 1325.2 ^f | 0.5792 | 0.581 ^b |
| | 318.15 | 1279.0 | 1279.0 ^f | 0.5066 | 0.5066 ^c |

^aRef. [21]; ^bRef. [4]; ^cRef. [3]; ^dRef. [23]; ^eRef. [13]; ^fRef. [10]; ^gRef. [11]; ^hRef. [24].

The ultrasonic speeds in pure liquids and in their binary mixtures were measured using a single-crystal variable-path multifrequency ultrasonic interferometer operating at 3 MHz by the method described elsewhere [6–10]. The ultrasonic speed data were reproducible within $\pm 0.03\%$. The viscosities of pure liquids and their binary mixtures were measured by using Ubbelohde-type suspended level viscometer. The viscometer was calibrated with triply distilled water. The viscometer containing the test liquid was allowed to stand for about 30 min in a thermostatic water bath so that the thermal fluctuations in viscometer were minimised. The time of flow was recorded in triplicate with a digital stopwatch with an accuracy of ± 0.01 s. The viscosity data were reproducible within $\pm 5 \times 10^{-7} \text{ N s m}^{-2}$. The temperature of the test liquids during the measurements was maintained to an accuracy of ± 0.02 K in an electronically controlled thermostatic water bath (JULABO, Germany). The reliability of the experimental measurements of u and η were ascertained by comparing the experimental data of pure liquids with the corresponding values, which were available in the literature [3,4,10,11,13,21–23] at the studied temperatures. This comparison is given in table 1 and the agreement between the experimental and the literature values is found to be good.

3. Results and discussion

The experimental values of ultrasonic speeds and viscosities of binary mixtures of THF with benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene and mesitylene, with THF as a common component, over the whole composition range, expressed in mole fraction

x_1 of THF, at different temperatures are listed in table 2. The excess function such as Δk_s , $\Delta\eta$, Δu and K_s^E have been calculated by using the following standard relations:

$$\Delta k_s = k_s - (x_1 k_{s,1} + x_2 k_{s,2}) \quad (1)$$

$$\Delta u = u - (x_1 u_1 + x_2 u_2) \quad (2)$$

$$\Delta\eta = \eta - (x_1 \eta_1 + x_2 \eta_2) \quad (3)$$

$$K_s^E = K_s - (x_1 K_{s,1} + x_2 K_{s,2}) \quad (4)$$

Table 2. Values of ultrasonic speeds, u and viscosities, η as functions of mole fraction, x_1 of tetrahydrofuran (THF) for the binary mixtures at different temperatures.

| x_1 | u (m s ⁻¹) T (K) | | | | η (10 ⁻³ N s m ⁻²) T (K) | | | |
|------------------------|-------------------------------------|--------|--------|--------|---|--------|--------|--------|
| | 288.15 | 298.15 | 308.15 | 318.15 | 288.15 | 298.15 | 308.15 | 318.15 |
| THF + benzene | | | | | | | | |
| 0.0000 | 1352.4 | 1303.5 | 1257.4 | 1207.2 | 0.6930 | 0.6025 | 0.5395 | 0.4670 |
| 0.0754 | 1351.7 | 1302.5 | 1256.0 | 1206.1 | 0.6847 | 0.5973 | 0.5360 | 0.4667 |
| 0.1518 | 1350.7 | 1301.4 | 1254.7 | 1205.1 | 0.6762 | 0.5921 | 0.5330 | 0.4665 |
| 0.2230 | 1349.8 | 1300.6 | 1253.6 | 1204.3 | 0.6673 | 0.5863 | 0.5290 | 0.4659 |
| 0.2962 | 1348.5 | 1299.3 | 1252.2 | 1203.2 | 0.6573 | 0.5793 | 0.5237 | 0.4637 |
| 0.3556 | 1347.4 | 1298.4 | 1251.3 | 1202.5 | 0.6484 | 0.5728 | 0.5186 | 0.4609 |
| 0.4128 | 1346.3 | 1297.5 | 1250.3 | 1201.8 | 0.6394 | 0.5659 | 0.5128 | 0.4574 |
| 0.4812 | 1344.6 | 1296.0 | 1248.8 | 1200.7 | 0.6277 | 0.5568 | 0.5050 | 0.4522 |
| 0.5506 | 1342.7 | 1294.3 | 1247.1 | 1199.4 | 0.6151 | 0.5467 | 0.4961 | 0.4457 |
| 0.6219 | 1340.5 | 1292.4 | 1245.1 | 1197.8 | 0.6013 | 0.5353 | 0.4858 | 0.4379 |
| 0.6884 | 1338.0 | 1290.2 | 1243.0 | 1196.1 | 0.5875 | 0.5237 | 0.4752 | 0.4295 |
| 0.7512 | 1335.3 | 1287.9 | 1240.8 | 1194.4 | 0.5739 | 0.5120 | 0.4643 | 0.4207 |
| 0.8119 | 1332.7 | 1285.5 | 1238.6 | 1192.7 | 0.5600 | 0.4999 | 0.4529 | 0.4112 |
| 0.8792 | 1329.3 | 1282.7 | 1236.1 | 1190.7 | 0.5439 | 0.4857 | 0.4394 | 0.3996 |
| 0.9388 | 1326.3 | 1280.1 | 1233.8 | 1188.9 | 0.5289 | 0.4724 | 0.4265 | 0.3885 |
| 1.0000 | 1323.1 | 1277.6 | 1231.5 | 1187.2 | 0.5129 | 0.4580 | 0.4125 | 0.3762 |
| THF + toluene | | | | | | | | |
| 0.0000 | 1358.5 | 1310.5 | 1266.2 | 1221.0 | 0.6456 | 0.5531 | 0.5020 | 0.4379 |
| 0.0718 | 1357.7 | 1309.4 | 1264.6 | 1219.3 | 0.6406 | 0.5513 | 0.5013 | 0.4399 |
| 0.1498 | 1356.3 | 1307.9 | 1262.7 | 1217.3 | 0.6350 | 0.5491 | 0.5003 | 0.4415 |
| 0.2283 | 1354.6 | 1306.2 | 1260.7 | 1215.2 | 0.6285 | 0.5459 | 0.4980 | 0.4421 |
| 0.2902 | 1353.1 | 1304.8 | 1259.1 | 1213.5 | 0.6231 | 0.5431 | 0.4956 | 0.4418 |
| 0.3452 | 1351.7 | 1303.4 | 1257.6 | 1212.0 | 0.6176 | 0.5398 | 0.4929 | 0.4408 |
| 0.4005 | 1350.1 | 1302.0 | 1255.9 | 1210.4 | 0.6113 | 0.5357 | 0.4894 | 0.4388 |
| 0.4694 | 1347.8 | 1299.9 | 1253.7 | 1208.2 | 0.6027 | 0.5298 | 0.4840 | 0.4352 |
| 0.5368 | 1345.4 | 1297.7 | 1251.4 | 1205.9 | 0.5934 | 0.5230 | 0.4775 | 0.4307 |
| 0.6067 | 1342.8 | 1295.2 | 1248.8 | 1203.4 | 0.5834 | 0.5155 | 0.4704 | 0.4253 |
| 0.6704 | 1340.1 | 1292.8 | 1246.3 | 1200.9 | 0.5736 | 0.5080 | 0.4630 | 0.4196 |
| 0.7378 | 1337.0 | 1289.9 | 1243.5 | 1198.3 | 0.5626 | 0.4993 | 0.4544 | 0.4125 |
| 0.8018 | 1333.8 | 1287.0 | 1240.7 | 1195.7 | 0.5515 | 0.4903 | 0.4453 | 0.4050 |
| 0.8714 | 1330.2 | 1284.0 | 1237.6 | 1192.8 | 0.5387 | 0.4797 | 0.4346 | 0.3957 |
| 0.9368 | 1326.6 | 1280.7 | 1234.5 | 1190.0 | 0.5259 | 0.4690 | 0.4237 | 0.3861 |
| 1.0000 | 1323.1 | 1277.6 | 1231.5 | 1187.2 | 0.5129 | 0.4580 | 0.4125 | 0.3762 |
| THF + <i>o</i> -xylene | | | | | | | | |
| 0.0000 | 1388.5 | 1350.3 | 1321.4 | 1285.8 | 0.8623 | 0.7576 | 0.6690 | 0.5972 |
| 0.0764 | 1384.3 | 1345.1 | 1314.5 | 1277.9 | 0.8385 | 0.7380 | 0.6535 | 0.5850 |
| 0.1504 | 1380.0 | 1340.0 | 1307.8 | 1270.2 | 0.8155 | 0.7192 | 0.6384 | 0.5730 |

(Continued)

Table 2. Continued.

| x_1 | u (m s^{-1}) T (K) | | | | η ($10^{-3} \text{N s m}^{-2}$) T (K) | | | |
|------------------------|--------------------------------------|--------|--------|--------|---|--------|--------|--------|
| | 288.15 | 298.15 | 308.15 | 318.15 | 288.15 | 298.15 | 308.15 | 318.15 |
| 0.2243 | 1375.7 | 1335.0 | 1301.1 | 1262.7 | 0.7919 | 0.6998 | 0.6226 | 0.5602 |
| 0.2942 | 1371.4 | 1330.0 | 1294.8 | 1255.6 | 0.7690 | 0.6807 | 0.6067 | 0.5471 |
| 0.3660 | 1366.9 | 1324.9 | 1288.3 | 1248.4 | 0.7451 | 0.6606 | 0.5900 | 0.5331 |
| 0.4226 | 1363.4 | 1320.9 | 1283.2 | 1242.8 | 0.7260 | 0.6445 | 0.5764 | 0.5216 |
| 0.4801 | 1359.7 | 1316.7 | 1278.0 | 1237.1 | 0.7063 | 0.6277 | 0.5621 | 0.5094 |
| 0.5310 | 1356.3 | 1313.0 | 1273.4 | 1232.1 | 0.6888 | 0.6127 | 0.5493 | 0.4981 |
| 0.5850 | 1352.6 | 1309.0 | 1268.5 | 1226.8 | 0.6694 | 0.5959 | 0.5348 | 0.4856 |
| 0.6578 | 1347.6 | 1303.6 | 1262.0 | 1219.7 | 0.6432 | 0.5731 | 0.5150 | 0.4684 |
| 0.7322 | 1342.5 | 1298.0 | 1255.4 | 1212.5 | 0.6159 | 0.5493 | 0.4941 | 0.4498 |
| 0.8049 | 1337.4 | 1292.5 | 1248.9 | 1205.6 | 0.5887 | 0.5253 | 0.4729 | 0.4310 |
| 0.8708 | 1332.6 | 1287.5 | 1243.0 | 1199.3 | 0.5635 | 0.5030 | 0.4530 | 0.4130 |
| 0.9392 | 1327.7 | 1282.3 | 1236.9 | 1192.9 | 0.5370 | 0.4794 | 0.4319 | 0.3940 |
| 1.0000 | 1323.1 | 1277.6 | 1231.5 | 1187.2 | 0.5129 | 0.4580 | 0.4125 | 0.3762 |
| THF + <i>m</i> -xylene | | | | | | | | |
| 0.0000 | 1373.2 | 1326.6 | 1281.0 | 1243.0 | 0.6696 | 0.5880 | 0.5229 | 0.4684 |
| 0.0722 | 1370.9 | 1324.0 | 1278.1 | 1239.4 | 0.6615 | 0.5823 | 0.5193 | 0.4668 |
| 0.1486 | 1368.1 | 1321.0 | 1274.8 | 1235.5 | 0.6528 | 0.5762 | 0.5151 | 0.4647 |
| 0.2134 | 1365.6 | 1318.4 | 1272.1 | 1232.2 | 0.6449 | 0.5703 | 0.5110 | 0.4621 |
| 0.2804 | 1362.9 | 1315.6 | 1269.2 | 1228.7 | 0.6363 | 0.5638 | 0.5061 | 0.4587 |
| 0.3536 | 1359.7 | 1312.5 | 1265.9 | 1224.9 | 0.6263 | 0.5560 | 0.4999 | 0.4542 |
| 0.4255 | 1356.4 | 1309.3 | 1262.6 | 1221.1 | 0.6160 | 0.5477 | 0.4932 | 0.4489 |
| 0.4864 | 1353.5 | 1306.4 | 1259.7 | 1217.8 | 0.6068 | 0.5401 | 0.4869 | 0.4438 |
| 0.5476 | 1350.5 | 1303.4 | 1256.6 | 1214.4 | 0.5971 | 0.5321 | 0.4800 | 0.4382 |
| 0.6041 | 1347.5 | 1300.5 | 1253.7 | 1211.1 | 0.5879 | 0.5243 | 0.4732 | 0.4323 |
| 0.6751 | 1343.6 | 1296.7 | 1249.9 | 1206.9 | 0.5757 | 0.5139 | 0.4640 | 0.4241 |
| 0.7396 | 1339.8 | 1293.1 | 1246.4 | 1203.1 | 0.5642 | 0.5038 | 0.4550 | 0.4162 |
| 0.8005 | 1336.1 | 1289.6 | 1243.0 | 1199.5 | 0.5529 | 0.4939 | 0.4460 | 0.4080 |
| 0.8722 | 1331.6 | 1285.4 | 1238.9 | 1195.1 | 0.5392 | 0.4817 | 0.4347 | 0.3974 |
| 0.9378 | 1327.3 | 1281.4 | 1235.2 | 1191.1 | 0.5261 | 0.4699 | 0.4237 | 0.3870 |
| 1.0000 | 1323.1 | 1277.6 | 1231.5 | 1187.2 | 0.5129 | 0.4580 | 0.4125 | 0.3762 |
| THF + <i>p</i> -xylene | | | | | | | | |
| 0.0000 | 1357.5 | 1316.4 | 1268.0 | 1230.3 | 0.7084 | 0.6110 | 0.5501 | 0.4912 |
| 0.0840 | 1356.0 | 1314.1 | 1265.7 | 1227.2 | 0.6971 | 0.6047 | 0.5453 | 0.4891 |
| 0.1716 | 1354.2 | 1311.7 | 1263.2 | 1224.0 | 0.6842 | 0.5954 | 0.5385 | 0.4849 |
| 0.2322 | 1353.1 | 1310.1 | 1261.6 | 1221.9 | 0.6755 | 0.5895 | 0.5339 | 0.4819 |
| 0.2934 | 1351.7 | 1308.3 | 1259.9 | 1219.6 | 0.6656 | 0.5825 | 0.5280 | 0.4777 |
| 0.3548 | 1350.2 | 1306.5 | 1258.1 | 1217.3 | 0.6552 | 0.5748 | 0.5214 | 0.4727 |
| 0.4284 | 1348.1 | 1304.0 | 1255.7 | 1214.5 | 0.6420 | 0.5648 | 0.5127 | 0.4658 |
| 0.4896 | 1346.2 | 1301.8 | 1253.7 | 1212.0 | 0.6304 | 0.5558 | 0.5047 | 0.4592 |
| 0.5518 | 1344.1 | 1299.4 | 1251.5 | 1209.3 | 0.6181 | 0.5461 | 0.4959 | 0.4518 |
| 0.6201 | 1341.5 | 1296.6 | 1248.8 | 1206.2 | 0.6039 | 0.5347 | 0.4854 | 0.4428 |
| 0.6825 | 1338.9 | 1293.7 | 1246.2 | 1203.3 | 0.5904 | 0.5237 | 0.4751 | 0.4337 |
| 0.7414 | 1336.3 | 1290.9 | 1243.6 | 1200.4 | 0.5767 | 0.5127 | 0.4647 | 0.4245 |
| 0.8102 | 1333.1 | 1287.6 | 1240.6 | 1197.0 | 0.5609 | 0.4991 | 0.4518 | 0.4128 |
| 0.8756 | 1329.8 | 1284.3 | 1237.5 | 1193.7 | 0.5450 | 0.4855 | 0.4388 | 0.4009 |
| 0.9409 | 1326.4 | 1280.8 | 1234.4 | 1190.4 | 0.5284 | 0.4713 | 0.4250 | 0.3881 |
| 1.0000 | 1323.1 | 1277.6 | 1231.5 | 1187.2 | 0.5129 | 0.4580 | 0.4125 | 0.3762 |
| THF + mesitylene | | | | | | | | |
| 0.0000 | 1412.3 | 1369.8 | 1325.2 | 1279.0 | 0.7592 | 0.6572 | 0.5792 | 0.5066 |
| 0.0735 | 1406.8 | 1363.6 | 1318.5 | 1272.2 | 0.7428 | 0.6449 | 0.5698 | 0.5004 |
| 0.1513 | 1400.3 | 1356.6 | 1311.2 | 1264.9 | 0.7259 | 0.6321 | 0.5602 | 0.4943 |
| 0.2274 | 1393.5 | 1349.5 | 1303.9 | 1257.7 | 0.7089 | 0.6192 | 0.5502 | 0.4875 |
| 0.2986 | 1386.7 | 1342.4 | 1296.7 | 1250.6 | 0.6927 | 0.6066 | 0.5402 | 0.4805 |
| 0.3672 | 1379.7 | 1335.3 | 1289.6 | 1243.6 | 0.6767 | 0.5940 | 0.5301 | 0.4732 |

(Continued)

Table 2. Continued.

| x_1 | u (m s ⁻¹) T (K) | | | | η (10 ⁻³ N s m ⁻²) T (K) | | | |
|--------|-------------------------------------|--------|--------|--------|---|--------|--------|--------|
| | 288.15 | 298.15 | 308.15 | 318.15 | 288.15 | 298.15 | 308.15 | 318.15 |
| 0.4305 | 1373.5 | 1328.9 | 1283.1 | 1237.3 | 0.6616 | 0.5821 | 0.5203 | 0.4658 |
| 0.4912 | 1367.5 | 1322.9 | 1277.0 | 1231.5 | 0.6470 | 0.5703 | 0.5106 | 0.4583 |
| 0.5496 | 1361.9 | 1317.3 | 1271.4 | 1226.0 | 0.6326 | 0.5586 | 0.5008 | 0.4507 |
| 0.6055 | 1356.8 | 1312.0 | 1266.1 | 1220.8 | 0.6186 | 0.5472 | 0.4911 | 0.4429 |
| 0.6784 | 1350.4 | 1305.4 | 1259.4 | 1214.4 | 0.6000 | 0.5318 | 0.4779 | 0.4322 |
| 0.7516 | 1344.0 | 1298.8 | 1252.8 | 1207.9 | 0.5809 | 0.5159 | 0.4642 | 0.4208 |
| 0.8280 | 1337.4 | 1292.1 | 1246.0 | 1201.2 | 0.5609 | 0.4990 | 0.4494 | 0.4084 |
| 0.8790 | 1333.2 | 1287.7 | 1241.6 | 1196.9 | 0.5469 | 0.4872 | 0.4388 | 0.3992 |
| 0.9412 | 1328.2 | 1282.6 | 1236.4 | 1191.8 | 0.5299 | 0.4726 | 0.4258 | 0.3879 |
| 1.0000 | 1323.1 | 1277.6 | 1231.5 | 1187.2 | 0.5129 | 0.4580 | 0.4125 | 0.3762 |

where x is the mole fraction; subscripts 1 and 2 stand for the pure components, THF and aromatic hydrocarbon, respectively; k_s and K_s are the isentropic compressibility and molar isentropic compressibility, calculated by using the relations:

$$k_s = \frac{1}{u^2 \rho} \quad (5)$$

$$K_s = k_s V \quad (6)$$

where V is the molar volume. The excess functions Δk_s , Δu , $\Delta \eta$ and K_s^E were fitted to a Redlich–Kister-type polynomial equation:

$$Y^E = x_1(1 - x_1) \sum_{i=0}^n A_i(1 - 2x_1)^i \quad (7)$$

where Y^E is Δk_s or Δu or $\Delta \eta$ or K_s^E . The values of coefficients, A_i evaluated by using least-squares method with all points weighted equally, and the corresponding SDs, $\sigma(Y^E)$ are listed in table 3. The variations Δk_s , Δu and $\Delta \eta$ with composition of the mixtures, along with smoothed values using equation (7), at 298.15 and 318.15 K are presented graphically in figures 1–3.

The results shown in figure 1 indicate that Δk_s values are negative over the entire mole fraction range ($0 \leq x_1 \leq 1$) and at each temperature for all the binary systems, except for THF + mesitylene which exhibit a sigmoid trend. The observed negative values of Δk_s for THF + aromatic hydrocarbon mixtures indicate the presence of specific interactions between THF and aromatic hydrocarbon molecules in these mixtures. The observed Δk_s values depend upon several contributions, which are of physical and/or chemical nature [24,25]. The physical contributions comprise of dispersion forces and non-specific physical (weak) interactions that lead to positive Δk_s values; physical contribution is also due to geometrical effect allowing the fitting of molecules of two different sizes into each other's structure resulting in negative Δk_s values. Chemical contributions involve breaking up of the hydrogen-bonded structure(s), resulting in positive Δk_s values and specific interactions such as the formation of hydrogen bonds, formation of charge transfer complex and strong dipole–dipole interactions between component molecules resulting in negative Δk_s values.

Table 3. Coefficients, A_i , of equation (7) and standard deviations, $\sigma(Y^E)$ for the binary mixtures at different temperatures.

| T (K) | A_0 | A_1 | A_2 | A_3 | A_4 | $\sigma(Y^E)$ |
|--|---------|---------|---------|---------|---------|---------------|
| THF + benzene | | | | | | |
| Δk_s ($10^{-11} \text{ m}^2 \text{ N}^{-1}$) | | | | | | |
| 288.15 | -3.2539 | 0.9180 | 0.3283 | -0.5053 | - | 0.0046 |
| 298.15 | -2.9557 | 0.9915 | 0.7611 | -0.6554 | - | 0.0060 |
| 308.15 | -2.6472 | 0.9250 | 1.0317 | -0.4889 | - | 0.0065 |
| 318.15 | -2.3992 | 0.8811 | 1.2061 | -0.6843 | - | 0.0077 |
| Δu (m s^{-1}) | | | | | | |
| 288.15 | 25.5700 | -5.5085 | -3.6459 | 5.2038 | - | 0.0522 |
| 298.15 | 20.1799 | -5.7678 | -6.7399 | 5.3122 | - | 0.0612 |
| 308.15 | 15.5462 | -4.5933 | -7.7506 | 2.6081 | - | 0.0569 |
| 318.15 | 12.4558 | -3.9392 | -7.4072 | 3.2042 | - | 0.0591 |
| $\Delta \eta$ ($10^{-4} \text{ N s m}^{-2}$) | | | | | | |
| 288.15 | 0.8596 | -0.0164 | -0.0418 | -0.0487 | - | 0.0007 |
| 298.15 | 0.9599 | -0.0199 | -0.0674 | -0.0720 | - | 0.0011 |
| 308.15 | 1.0719 | -0.0169 | -0.0777 | -0.1198 | - | 0.0015 |
| 318.15 | 1.1635 | -0.0208 | -0.1194 | -0.1546 | - | 0.0015 |
| K_s^E ($10^{-15} \text{ m}^5 \text{ N}^{-1} \text{ mol}^{-1}$) | | | | | | |
| 288.15 | -3.2954 | 0.9089 | 0.3227 | -0.4245 | - | 0.0038 |
| 298.15 | -3.0723 | 0.9914 | 0.7448 | -0.5989 | - | 0.0049 |
| 308.15 | -2.7973 | 0.9563 | 1.0362 | -0.5195 | - | 0.0057 |
| 318.15 | -2.6158 | 0.9274 | 1.0270 | -0.7524 | - | 0.0070 |
| THF + toluene | | | | | | |
| Δk_s ($10^{-11} \text{ m}^2 \text{ N}^{-1}$) | | | | | | |
| 288.15 | -2.6461 | 0.4942 | 0.0285 | -0.4860 | - | 0.0039 |
| 298.15 | -2.4129 | 0.5116 | 0.2690 | -0.3394 | - | 0.0064 |
| 308.15 | -2.1478 | 0.5157 | 0.4097 | -0.2675 | - | 0.0033 |
| 318.15 | -1.9071 | 0.4351 | 0.5163 | -0.2791 | - | 0.0038 |
| Δu (m s^{-1}) | | | | | | |
| 288.15 | 23.9590 | -0.9364 | -0.5666 | 4.3199 | - | 0.0419 |
| 298.15 | 19.4726 | -1.0110 | -2.3315 | 1.7778 | - | 0.0630 |
| 308.15 | 15.2799 | -0.8641 | -2.7675 | 0.2365 | - | 0.0272 |
| 318.15 | 12.1535 | -0.2008 | -2.6875 | -0.3791 | - | 0.0490 |
| $\Delta \eta$ ($10^{-4} \text{ N s m}^{-2}$) | | | | | | |
| 288.15 | 0.7775 | 0.0355 | -0.0517 | -0.1427 | - | 0.0012 |
| 298.15 | 0.8548 | 0.0350 | -0.0596 | -0.1421 | - | 0.0014 |
| 308.15 | 0.9601 | 0.0259 | -0.0639 | -0.1053 | - | 0.0014 |
| 318.15 | 1.0567 | 0.0487 | -0.0653 | -0.1378 | - | 0.0016 |
| K_s^E ($10^{-15} \text{ m}^5 \text{ N}^{-1} \text{ mol}^{-1}$) | | | | | | |
| 288.15 | -2.6469 | 0.4100 | 0.0764 | -0.5180 | - | 0.0038 |
| 298.15 | -2.4304 | 0.4751 | 0.3581 | -0.4219 | - | 0.0058 |
| 308.15 | -2.0441 | 0.5291 | 0.5521 | -0.3986 | - | 0.0043 |
| 318.15 | -1.7261 | 0.5026 | 0.7138 | -0.4972 | - | 0.0023 |
| THF + <i>o</i> -xylene | | | | | | |
| 288.15 | -1.4770 | 0.0956 | -0.0220 | 0.1048 | - | 0.0049 |
| 298.15 | -1.2817 | 0.1132 | 0.0940 | 0.0572 | - | 0.0031 |
| 308.15 | -1.0976 | 0.1061 | 0.0110 | 0.0494 | - | 0.0023 |
| 318.15 | -0.9499 | 0.1388 | 0.1554 | -0.0270 | - | 0.0036 |
| Δu (m s^{-1}) | | | | | | |
| 288.15 | 10.1447 | 1.2551 | -1.7958 | -1.1074 | 3.7747 | 0.0458 |
| 298.15 | 5.2299 | 0.7960 | -0.7908 | -0.6806 | 0.2793 | 0.0321 |
| 308.15 | -1.0432 | 0.4585 | 0.9643 | -0.3945 | -0.9400 | 0.0221 |
| 318.15 | -5.4309 | -0.2722 | -1.5275 | 0.2099 | 2.2257 | 0.0211 |

(Continued)

Table 3. Continued.

| T (K) | A_0 | A_1 | A_2 | A_3 | A_4 | $\sigma(Y^E)$ |
|---|---------|---------|---------|---------|--------|---------------|
| $\Delta\eta$ (10^{-4} N s m $^{-2}$) | | | | | | |
| 288.15 | 0.4719 | -0.0177 | -0.0142 | -0.0323 | - | 0.0009 |
| 298.15 | 0.5601 | -0.0205 | -0.0441 | -0.0246 | - | 0.0011 |
| 308.15 | 0.6528 | -0.0188 | -0.0271 | -0.0225 | - | 0.0010 |
| 318.15 | 0.7320 | -0.0089 | -0.0207 | -0.0413 | - | 0.0011 |
| K_s^E (10^{-15} m 5 N $^{-1}$ mol $^{-1}$) | | | | | | |
| 288.15 | 0.2203 | -0.0785 | 0.0305 | 0.0735 | - | 0.0051 |
| 298.15 | 0.9951 | -0.0335 | 0.1782 | 0.0693 | - | 0.0036 |
| 308.15 | 2.2893 | -0.0126 | 0.1281 | 0.0549 | - | 0.0029 |
| 318.15 | 3.3913 | -0.0436 | 0.3246 | -0.0028 | - | 0.0045 |
| THF + <i>m</i> -xylene | | | | | | |
| Δk_s (10^{-11} m 2 N $^{-1}$) | | | | | | |
| 288.15 | -1.6803 | 0.2980 | -0.0059 | -0.2913 | - | 0.0027 |
| 298.15 | -1.4471 | 0.2791 | 0.2449 | -0.2674 | - | 0.0026 |
| 308.15 | -1.2283 | 0.2013 | 0.3541 | -0.1266 | - | 0.0036 |
| 318.15 | -1.0413 | 0.2446 | 0.4039 | -0.1972 | - | 0.0047 |
| Δu (m s $^{-1}$) | | | | | | |
| 288.15 | 18.8428 | -1.3841 | -0.8510 | 2.7224 | 1.4121 | 0.0273 |
| 298.15 | 14.6332 | -1.0457 | -3.9257 | 1.6959 | 3.4043 | 0.0185 |
| 308.15 | 11.0315 | -0.2230 | -4.5943 | -0.1818 | 4.1149 | 0.0287 |
| 318.15 | 7.7255 | -0.4792 | -4.7699 | -0.0688 | 5.1315 | 0.0297 |
| $\Delta\eta$ (10^{-4} N s m $^{-2}$) | | | | | | |
| 288.15 | 0.5369 | -0.0092 | -0.0068 | -0.0591 | - | 0.0007 |
| 298.15 | 0.6163 | -0.0059 | -0.0130 | -0.0559 | - | 0.0007 |
| 308.15 | 0.7090 | -0.0066 | -0.0108 | -0.0487 | - | 0.0005 |
| 318.15 | 0.8122 | -0.0216 | 0.0068 | -0.0360 | - | 0.0008 |
| K_s^E (10^{-15} m 5 N $^{-1}$ mol $^{-1}$) | | | | | | |
| 288.15 | -0.9126 | 0.1062 | 0.0307 | -0.3428 | - | 0.0031 |
| 298.15 | -0.5143 | 0.1559 | 0.3240 | -0.3165 | - | 0.0029 |
| 308.15 | -0.0157 | 0.1433 | 0.4852 | -0.2027 | - | 0.0031 |
| 318.15 | 0.8183 | 0.2543 | 0.6063 | -0.3289 | - | 0.0041 |
| THF + <i>p</i> -xylene | | | | | | |
| Δk_s (10^{-11} m 2 N $^{-1}$) | | | | | | |
| 288.15 | -1.9509 | 0.2789 | 0.3601 | 0.1076 | - | 0.0036 |
| 298.15 | -1.6998 | 0.2362 | 0.5917 | 0.1412 | - | 0.0047 |
| 308.15 | -1.4877 | 0.3061 | 0.6859 | -0.0191 | - | 0.0055 |
| 318.15 | -1.2771 | 0.2152 | 0.7483 | 0.1407 | - | 0.0059 |
| Δu (m s $^{-1}$) | | | | | | |
| 288.15 | 22.3174 | -2.0457 | -4.5515 | -1.3879 | 1.7568 | 0.0390 |
| 298.15 | 17.7281 | -1.5627 | -6.4264 | -1.6445 | 2.7418 | 0.0402 |
| 308.15 | 14.3690 | -2.2377 | -6.5199 | -0.1289 | 3.4542 | 0.0415 |
| 318.15 | 11.1896 | -1.5102 | -6.7011 | -1.2986 | 4.8974 | 0.0299 |
| $\Delta\eta$ (10^{-4} N s m $^{-2}$) | | | | | | |
| 288.15 | 0.7113 | 0.0105 | -0.0496 | -0.0749 | - | 0.0015 |
| 298.15 | 0.7887 | -0.0119 | -0.0052 | 0.0374 | - | 0.0021 |
| 308.15 | 0.8804 | 0.0055 | -0.0463 | 0.0233 | - | 0.0015 |
| 318.15 | 0.9753 | -0.0012 | -0.0307 | 0.0183 | - | 0.0013 |
| K_s^E (10^{-15} m 5 N $^{-1}$ mol $^{-1}$) | | | | | | |
| 288.15 | -1.9847 | -0.0391 | 0.4767 | 0.1628 | - | 0.0039 |
| 298.15 | -1.4104 | -0.0350 | 0.7581 | 0.2426 | - | 0.0049 |
| 308.15 | -1.1156 | 0.0715 | 0.9154 | 0.0989 | - | 0.0060 |
| 318.15 | -0.3095 | 0.0129 | 1.0613 | 0.2779 | - | 0.0057 |

(Continued)

Table 3. Continued.

| T (K) | A_0 | A_1 | A_2 | A_3 | A_4 | $\sigma(Y^E)$ |
|--|---------|---------|---------|---------|----------|---------------|
| THF + mesitylene | | | | | | |
| Δk_s ($10^{-11} \text{ m}^2 \text{ N}^{-1}$) | | | | | | |
| 288.15 | 0.6841 | -2.2435 | -1.0490 | 0.2832 | - | 0.0107 |
| 298.15 | 0.8690 | -2.1679 | -0.7822 | 0.0021 | - | 0.0124 |
| 308.15 | 1.0633 | -2.2080 | -0.6120 | -0.0472 | - | 0.0159 |
| 318.15 | 1.2743 | -2.1150 | -0.4318 | -0.5357 | - | 0.0215 |
| Δu (m s^{-1}) | | | | | | |
| 288.15 | -4.0794 | 14.7013 | 18.9752 | -3.2433 | -9.2064 | 0.0921 |
| 298.15 | -6.5656 | 11.5952 | 15.5816 | -1.0411 | -10.2185 | 0.0757 |
| 308.15 | -8.6267 | 9.8825 | 14.6195 | -1.4414 | -12.9710 | 0.0581 |
| 318.15 | -9.8679 | 7.2735 | 13.9649 | 1.5811 | -15.5819 | 0.0654 |
| $\Delta \eta$ ($10^{-4} \text{ N s m}^{-2}$) | | | | | | |
| 288.15 | 0.3501 | -0.0195 | -0.0048 | -0.0966 | - | 0.0010 |
| 298.15 | 0.4378 | -0.0107 | -0.0143 | -0.1078 | - | 0.0007 |
| 308.15 | 0.5309 | -0.0170 | -0.0068 | -0.1101 | - | 0.0008 |
| 318.15 | 0.6335 | -0.0258 | -0.0167 | -0.1135 | - | 0.0011 |
| K_s^E ($10^{-15} \text{ m}^5 \text{ N}^{-1} \text{ mol}^{-1}$) | | | | | | |
| 288.15 | 4.5494 | -3.0058 | -1.9166 | 0.0317 | - | 0.0139 |
| 298.15 | 5.5795 | -2.9590 | -1.6715 | -0.2417 | - | 0.0178 |
| 308.15 | 6.6995 | -3.0497 | -1.5228 | -0.2823 | - | 0.0238 |
| 318.15 | 7.7634 | -2.9989 | -1.3875 | -0.8177 | - | 0.0316 |

The curves in figure 1 indicate that Δk_s values are negative over entire mole fraction range and at all investigated temperatures for each binary system under study, except for THF + mesitylene which exhibit a sigmoid trend, with negative Δk_s value at lower THF concentration and then become positive as the concentration of THF increases in the mixture. The magnitude of negative deviations in Δk_s from linear dependence on mole fraction follows the sequence: benzene > toluene > *o*-xylene > *m*-xylene > *p*-xylene > mesitylene. This suggests that there is an increase in the compressibility of the mixtures as we move from benzene to mesitylene.

The behaviour of Δk_s with composition of the mixture can be qualitatively examined by considering the nature of the component molecules in the pure state and in the mixture. The molecules of THF are polar [16] and those of the aromatic hydrocarbons (benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene and mesitylene) are non-polar having large quadrupole moment [17], which causes molecular order in the pure state. THF on mixing with the aromatic hydrocarbons, would induce a decrease in the molecular order in the latter, resulting in an expansion in volume, and hence, positive Δk_s values. On the other hand, there is the possibility of the electron donor-acceptor-type (or charge-transfer) interactions [3] between highly electronegative oxygen of THF (acting as donor) and the π -electrons of ring of aromatic hydrocarbon molecules (acting as acceptor), resulting in negative Δk_s values. The observed negative Δk_s values suggest the presence of significant donor-acceptor interactions between THF and aromatic hydrocarbon molecules in these mixtures. 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 Ma *et al.* [3] recently.

It is interesting to note that Δk_s becomes less negative and finally turns positive as the number of $-\text{CH}_3$ group in the ring increase from benzene (without any $-\text{CH}_3$ group)

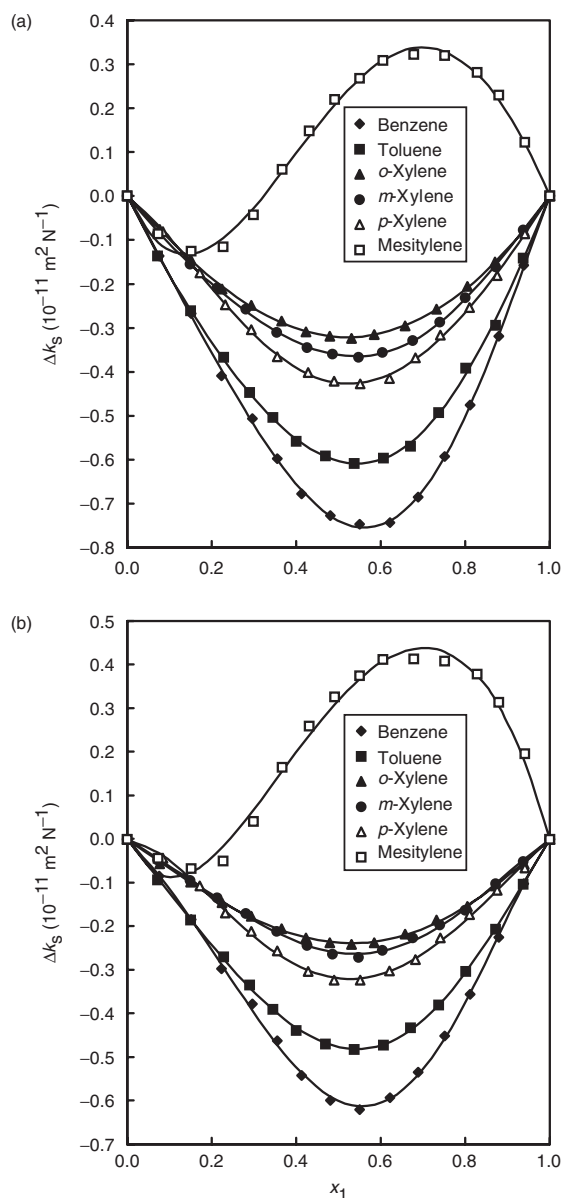


Figure 1. Plots of deviations in isentropic compressibility, Δk_s vs. mole fraction x_1 of tetrahydrofuran (THF) for the binary mixtures (a) at 298.15 K and (b) at 318.15 K. Points show experimental values and curves show smoothed values using equation (7).

to mesitylene (with three $-\text{CH}_3$ groups). This is due to the fact that methyl group ($-\text{CH}_3$) 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 ($-\text{CH}_3$) in the aromatic hydrocarbon molecule,

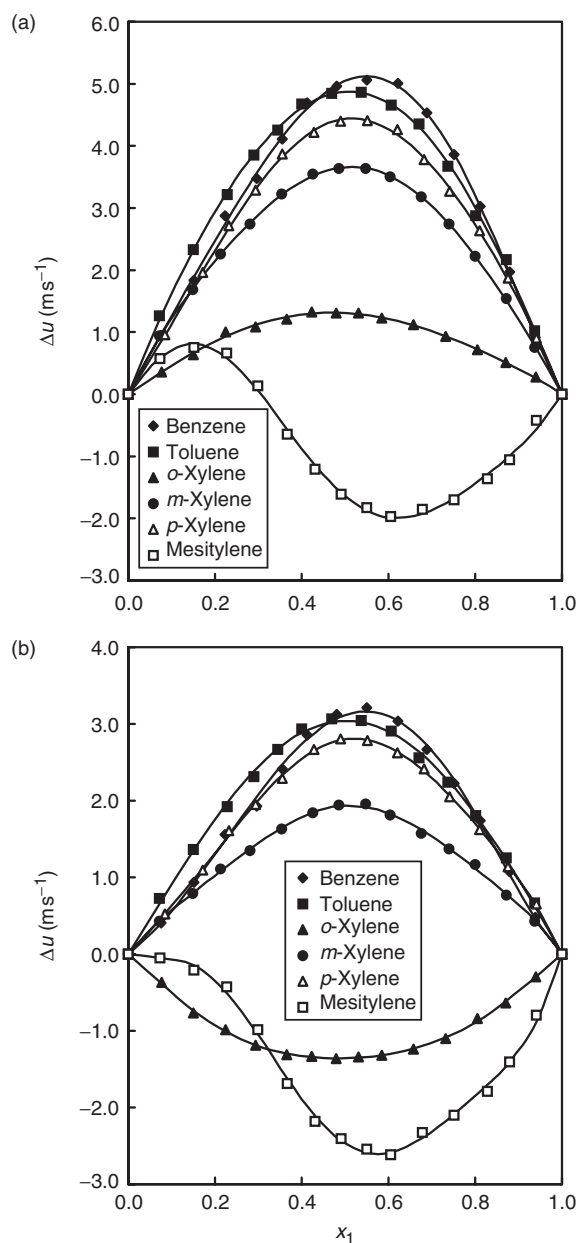


Figure 2. Plots of deviations in ultrasonic speed, Δu vs. mole fraction, x_1 of tetrahydrofuran (THF) for the binary mixtures (a) at 298.15 K and (b) at 318.15 K. Points show experimental values and curves show smoothed values using equation (7).

causing an expansion in volume of the mixture. This would cause an increase in Δk_s values in the sequence: benzene < toluene < xylenes < mesitylene, as we move from benzene to mesitylene.

Another factor that would cause an increase the Δk_s values is the steric hindrance due to $-\text{CH}_3$ groups of the rings. As the number of methyl group in the ring increases

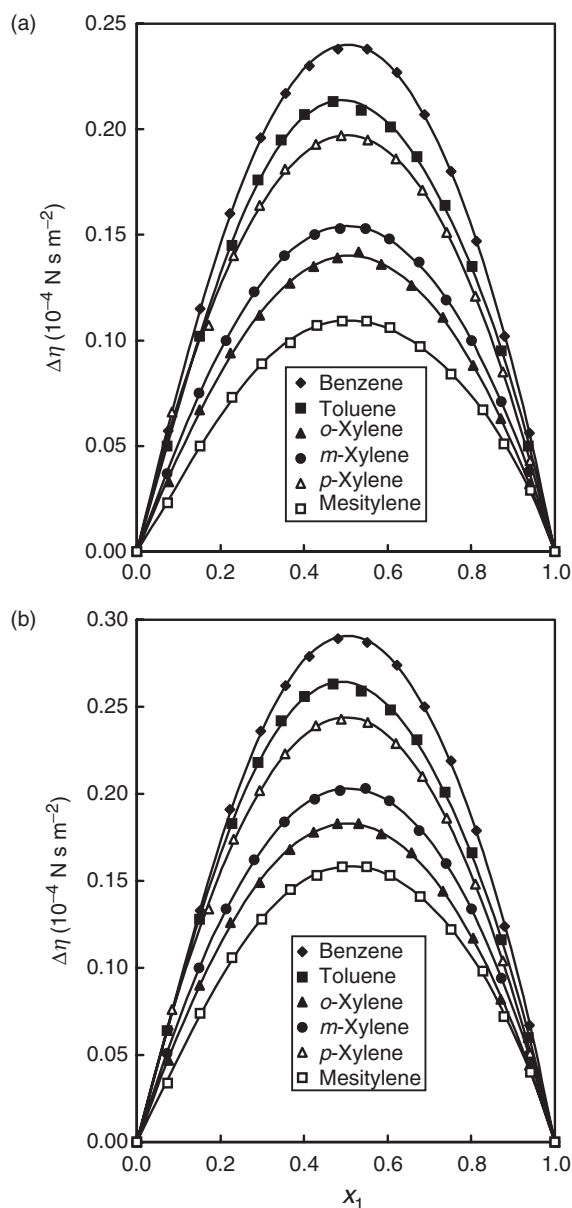


Figure 3. Plots of deviations in viscosity, $\Delta\eta$ vs. mole fraction, x_1 of tetrahydrofuran (THF) for the binary mixtures (a) at 298.15 K and (b) at 318.15 K. Points show experimental values and curves show smoothed values using equation (7).

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. Amongst the xylenes the magnitude of negative Δk_s values follows the order: *p*-xylene > *m*-xylene > *o*-xylene; which suggests that the position of $-\text{CH}_3$ groups on the aromatic ring plays a substantial role in deciding the magnitude of Δk_s and, hence, the order of interaction between the component

molecules of the mixtures. The more negative Δk_s values for THF + *p*-xylene are observed due to the fact that THF molecules could approach more closely to the ring of *p*-xylene from two directions as compared to *o*- and *m*-xylenes, showing maximum interaction of THF molecule with the former xylene than with the latter two xylenes. This is in good agreement with the results reported [26] for DMSO + xylenes.

As expected, the Δu values are positive (figure 2) over entire mole fraction range and at all temperatures investigated for all the four binary system under study, except for THF + *o*-xylene which exhibit negative Δu values, and THF + mesitylene which exhibit a sigmoid trend, with positive Δk_s value at lower THF concentration and then become negative as the concentration of THF increases in the mixture. The Δu values at the equimolar compositions of the mixtures follow the order: benzene > toluene > *o*-xylene > *m*-xylene > *p*-xylene > mesitylene. In general, positive deviations in Δu indicate the presence of significant interactions between the component molecules in the present mixtures. Kawaizumi *et al.* [27] and Prakash and Sinha [28] suggested that the concentration at which Δu versus x_1 curve exhibits maximum indicates maximum interaction between the component molecules, leading to the formation of complex. Thus, the trends of Δu with x_1 (figure 2) support the behaviour of Δk_s for these mixtures. The values of Δk_s increase and those of Δu decrease with increase in temperature of the mixture for all the six binary systems under study. The increase in Δk_s (and decrease in Δu) is attributed to the breaking of donor–acceptor interactions between unlike molecules with rise in temperature, leading to an expansion in volume, hence, resulting in an increase in Δk_s (and decrease in Δu) values.

The curves in figure 3 indicate that $\Delta \eta$ values are positive over the whole composition range for all the six binary systems under study at all the studied temperatures, however, $\Delta \eta$ values are very small in magnitude (0.01×10^{-3} to 0.028×10^{-3} N s m⁻²). The positive $\Delta \eta$ values for THF + aromatic hydrocarbon mixtures suggest the presence of significant donor–acceptor interactions [29,30] between unlike molecules. Also, the positive deviations in $\Delta \eta$ follows the order: benzene > toluene > *o*-xylene > *m*-xylene > *p*-xylene > mesitylene, which in turn reflects the order of interaction between THF and aromatic hydrocarbon molecules in these mixtures. The $\Delta \eta$ values decrease with increase in temperature for all the six binary systems under study. This suggests that the donor–acceptor interactions decrease with rise in temperature, resulting in an increase in the viscosity of the mixture, and hence lower $\Delta \eta$ values are observed at higher temperatures. The observed trends of $\Delta \eta$ values with composition and temperature, further reinforces our earlier conclusion (from the variations of Δk_s and Δu values with composition and temperature) regarding intermolecular interactions in these binary mixtures.

The partial molar compressibilities, $\bar{K}_{m,1}$ of component 1 (THF) and $\bar{K}_{m,2}$ of component 2 (aromatic hydrocarbon) in these mixtures over entire composition range at 298.15 K were calculated adopting a new approach (that has been used earlier [8,31] for the calculation of partial molar volumes), in which $\bar{K}_{m,1}$ and $\bar{K}_{m,2}$ are given by the following relations

$$\bar{K}_{m,1} = K_s^E + K_{s,1}^* + x_2 \left(\frac{\partial K_s^E}{\partial x_1} \right)_{T,p} \quad (8)$$

$$\bar{K}_{m,2} = K_s^E + K_{s,2}^* - x_1 \left(\frac{\partial K_s^E}{\partial x_1} \right)_{T,p} \quad (9)$$

where $K_{s,1}^*$ and $K_{s,2}^*$ are the molar isentropic compressibilities of pure components, THF and aromatic hydrocarbon, respectively. The derivative, $(\partial K_s^E/\partial x_1)_{T,p}$ in equations (8) and (9) was obtained by differentiation of equation (7) on substituting K_s^E for Y^E , which leads to the following equations for $\bar{K}_{m,1}$ and $\bar{K}_{m,2}$

$$\bar{K}_{m,1} = K_{s,1}^* + x_2^2 \sum_{i=0}^n A_i(1-2x_1)^i - 2x_1x_2^2 \sum_{i=1}^n A_i(1-2x_1)^{i-1} \quad (10)$$

$$\bar{K}_{m,2} = K_{s,2}^* + x_1^2 \sum_{i=0}^n A_i(1-2x_1)^i + 2x_1^2x_2 \sum_{i=1}^n A_i(1-2x_1)^{i-1}. \quad (11)$$

The excess partial molar compressibilities, $\bar{K}_{m,1}^E$ and $\bar{K}_{m,2}^E$ over the whole composition range were calculated by using the following relations

$$\bar{K}_{m,1}^E = \bar{K}_{m,1} - K_{s,1}^* \quad (12)$$

$$\bar{K}_{m,2}^E = \bar{K}_{m,2} - K_{s,2}^*. \quad (13)$$

The variations of $\bar{K}_{m,1}^E$ and $\bar{K}_{m,2}^E$ with composition at 298.15 K are presented in figures 4 and 5, respectively. A close perusal of figures 4 and 5 indicates that the values of $\bar{K}_{m,1}^E$ and $\bar{K}_{m,2}^E$ are negative for THF + benzene/toluene/*m*-xylene/*p*-xylene and positive for THF + *o*-xylene/mesitylene binary mixtures over the whole composition range

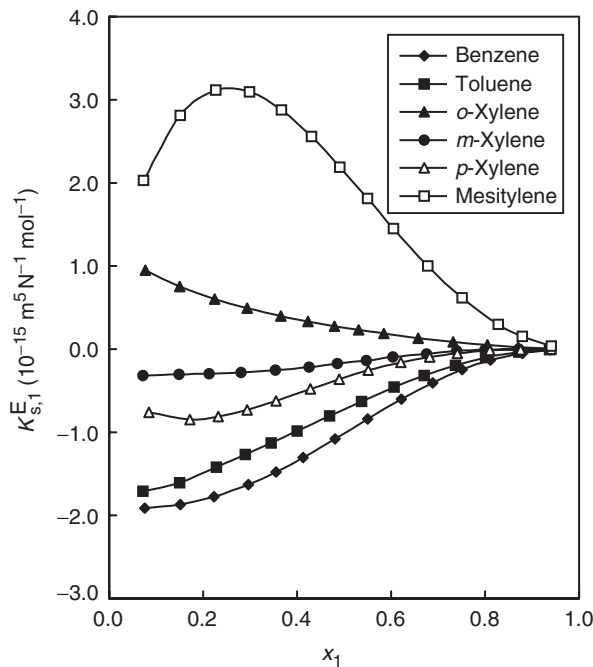


Figure 4. Plots of excess partial molar compressibility, $\bar{K}_{m,1}^E$ of THF vs. mole fraction, x_1 of tetrahydrofuran (THF) in the binary mixtures at 298.15 K.

binary mixtures. This suggests that the molar compressibilities of each component in the mixture are less than their respective molar compressibilities in the pure state, i.e. there is a decrease in the molar compressibility on mixing THF with benzene/toluene/*m*-xylene/*p*-xylene. In case of THF + *o*-xylene/mesitylene mixtures, the values of $\bar{K}_{m,1}^E$ and $\bar{K}_{m,2}^E$ (figures 4 and 5) are positive suggesting that the molar compressibilities of each component in the mixture are more than their respective molar compressibilities in the pure state, i.e. there is an increase in molar compressibility on mixing. In general, the negative $\bar{K}_{m,1}^E$ and $\bar{K}_{m,2}^E$ values indicate the presence of significant solute–solvent interactions between unlike molecules [32], whereas the positive $\bar{K}_{m,1}^E$ and $\bar{K}_{m,2}^E$ values indicate presence of solute–solute/solvent–solvent interactions between like molecules [32] in the mixture. The magnitude of $\bar{K}_{m,1}^E$ and $\bar{K}_{m,2}^E$ values at equimolar compositions follow the order: benzene < toluene < *p*-xylene < *m*-xylene < *o*-xylene < mesitylene, which is also the order of solute–solvent interactions between THF and aromatic hydrocarbon molecules in the mixture. These trends further support the trends observed in Δk_s , Δu and $\Delta \eta$ values for the binary mixtures under study. The values of partial molar compressibilities, $\bar{K}_{m,1}$ and $\bar{K}_{m,2}$ of THF and aromatic hydrocarbon at infinite dilution were also calculated by using the equations (8)–(11), and the excess partial molar compressibilities, $\bar{K}_{m,1}^E$ and $\bar{K}_{m,2}^E$ at infinite dilution were calculated by using equations (12) and (13) by substituting the values of $\bar{K}_{m,1}$ and $\bar{K}_{m,2}$ in place of $\bar{K}_{m,1}^E$ and $\bar{K}_{m,2}^E$, respectively.

Furthermore, the apparent molar compressibilities, $K_{\phi,1}$ and $K_{\phi,2}$ of THF and aromatic hydrocarbons, respectively, in these mixtures, at each investigated

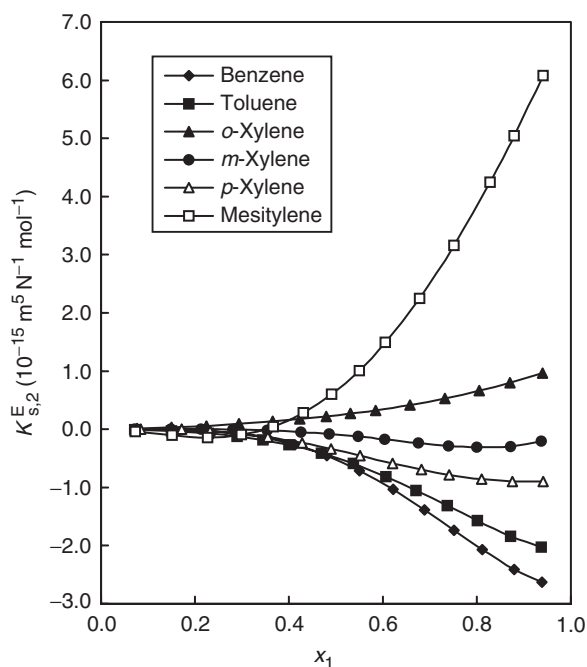


Figure 5. Plots of excess partial molar compressibility, $\bar{K}_{m,2}^E$ of aromatic hydrocarbon vs. mole fraction, x_1 of tetrahydrofuran (THF) in the binary mixtures at 298.15 K.

temperature, have been calculated by using another approach that involves of the following relations [33,34]:

$$K_{\phi,1} = K_{s,1}^* + \frac{K_s^E}{x_1} \quad (14)$$

$$K_{\phi,2} = K_{s,2}^* + \frac{K_s^E}{x_2}. \quad (15)$$

Equations (14) and (15) allow easy calculation of apparent molar compressibilities from experimental K_s^E values and corresponding mole fractions. Using the linear regression of $K_{\phi,1}$ versus x_1 for dilute solutions of THF in aromatic hydrocarbons and of $K_{\phi,2}$ versus x_2 for dilute solutions of aromatic hydrocarbons in THF, values of apparent molar compressibilities, $\bar{K}_{\phi,1}^{\circ}$ and $\bar{K}_{\phi,2}^{\circ}$ at infinite dilution are obtained. These are also called partial molar compressibilities at infinite dilution, represented as $\bar{K}_{m,1}^{\circ}$ and $\bar{K}_{m,2}^{\circ}$ earlier. The values of $\bar{K}_{\phi,1}^{\circ E}$ and $\bar{K}_{\phi,2}^{\circ E}$ have also been calculated by using the equations (12) and (13).

Table 4. The values of $\bar{K}_{m,1}^{\circ}$, $\bar{K}_{\phi,1}^{\circ}$, $K_{s,1}^*$, $\bar{K}_{m,1}^{\circ E}$, $\bar{K}_{\phi,1}^{\circ E}$, $\bar{K}_{m,2}^{\circ}$, $\bar{K}_{\phi,2}^{\circ}$, $K_{s,2}^*$, $\bar{K}_{m,2}^{\circ E}$ and $\bar{K}_{\phi,2}^{\circ E}$ for the binary mixtures at different temperatures.

| T (K) | $\bar{K}_{m,1}^{\circ}$ | $\bar{K}_{\phi,1}^{\circ}$ | $K_{s,1}^*$ | $\bar{K}_{m,1}^{\circ E}$ | $\bar{K}_{\phi,1}^{\circ E}$ | $\bar{K}_{m,2}^{\circ}$ | $\bar{K}_{\phi,2}^{\circ}$ | $K_{s,2}^*$ | $\bar{K}_{m,2}^{\circ E}$ | $\bar{K}_{\phi,2}^{\circ E}$ |
|------------------------|---|----------------------------|-------------|---------------------------|------------------------------|-------------------------|----------------------------|-------------|---------------------------|------------------------------|
| | (10 ⁻¹⁴ m ⁵ N ⁻¹ mol ⁻¹) | | | | | | | | | |
| THF + benzene | | | | | | | | | | |
| 288.15 | 4.429 | 4.429 | 5.177 | -0.249 | -0.248 | 5.116 | 5.113 | 5.461 | -0.345 | -0.348 |
| 298.15 | 5.485 | 5.485 | 5.678 | -0.193 | -0.193 | 5.752 | 5.747 | 6.024 | -0.272 | -0.277 |
| 308.15 | 6.119 | 6.118 | 6.251 | -0.132 | -0.133 | 6.415 | 6.410 | 6.635 | -0.220 | -0.225 |
| 318.15 | 6.765 | 6.765 | 6.882 | -0.117 | -0.117 | 7.227 | 7.219 | 7.379 | -0.152 | -0.159 |
| THF + toluene | | | | | | | | | | |
| 288.15 | 4.912 | 4.912 | 5.177 | -0.267 | -0.265 | 6.323 | 6.320 | 6.569 | -0.246 | -0.249 |
| 298.15 | 5.476 | 5.477 | 5.678 | -0.202 | -0.201 | 7.002 | 6.998 | 7.214 | -0.212 | -0.216 |
| 308.15 | 6.115 | 6.115 | 6.251 | -0.136 | -0.136 | 7.738 | 7.734 | 7.900 | -0.162 | -0.166 |
| 318.15 | 6.781 | 6.782 | 6.882 | -0.101 | -0.100 | 8.585 | 8.581 | 8.687 | -0.102 | -0.106 |
| THF + <i>o</i> -xylene | | | | | | | | | | |
| 288.15 | 5.202 | 5.201 | 5.177 | 0.025 | 0.024 | 7.071 | 7.072 | 7.046 | 0.025 | 0.026 |
| 298.15 | 5.799 | 5.793 | 5.678 | 0.121 | 0.115 | 7.709 | 7.710 | 7.596 | 0.113 | 0.114 |
| 308.15 | 6.497 | 6.496 | 6.251 | 0.246 | 0.245 | 8.326 | 8.325 | 8.088 | 0.238 | 0.237 |
| 318.15 | 7.249 | 7.248 | 6.882 | 0.367 | 0.366 | 9.089 | 9.088 | 8.713 | 0.376 | 0.375 |
| THF + <i>m</i> -xylene | | | | | | | | | | |
| 288.15 | 5.066 | 5.067 | 5.177 | -0.111 | -0.110 | 7.398 | 7.396 | 7.463 | -0.065 | -0.067 |
| 298.15 | 5.643 | 5.664 | 5.678 | -0.035 | -0.014 | 8.154 | 8.151 | 8.157 | -0.003 | -0.006 |
| 308.15 | 6.292 | 6.292 | 6.251 | 0.041 | 0.041 | 8.977 | 8.975 | 8.925 | 0.052 | 0.050 |
| 318.15 | 7.017 | 7.017 | 6.882 | 0.135 | 0.135 | 9.822 | 9.818 | 9.672 | 0.150 | 0.146 |
| THF + <i>p</i> -xylene | | | | | | | | | | |
| 288.15 | 5.039 | 5.036 | 5.177 | -0.138 | -0.141 | 7.528 | 7.527 | 7.691 | -0.163 | -0.164 |
| 298.15 | 5.634 | 5.630 | 5.678 | -0.044 | -0.048 | 8.259 | 8.258 | 8.345 | -0.086 | -0.087 |
| 308.15 | 6.248 | 6.243 | 6.251 | -0.003 | -0.008 | 9.143 | 9.138 | 9.180 | -0.037 | -0.042 |
| 318.15 | 6.986 | 6.981 | 6.882 | 0.104 | 0.099 | 10.001 | 10.000 | 9.955 | 0.046 | 0.045 |
| THF + mesitylene | | | | | | | | | | |
| 288.15 | 5.143 | 5.151 | 5.177 | -0.034 | -0.026 | 8.536 | 8.539 | 7.975 | 0.561 | 0.564 |
| 298.15 | 5.749 | 5.758 | 5.678 | 0.071 | 0.080 | 9.343 | 9.344 | 8.632 | 0.711 | 0.712 |
| 308.15 | 6.436 | 6.440 | 6.251 | 0.185 | 0.189 | 10.244 | 10.240 | 9.393 | 0.851 | 0.847 |
| 318.15 | 7.138 | 7.149 | 6.882 | 0.256 | 0.267 | 11.291 | 11.287 | 10.271 | 1.020 | 1.016 |

The values $\bar{K}_{m,1}^{\circ}$, $\bar{K}_{\phi,1}^{\circ}$, $K_{s,1}^*$, $\bar{K}_{m,1}^E$, $\bar{K}_{\phi,1}^E$, $\bar{K}_{m,2}^{\circ}$, $\bar{K}_{\phi,2}^{\circ}$, $K_{s,2}^*$, $\bar{K}_{m,2}^E$ and $\bar{K}_{\phi,2}^E$ for all the six binary systems at each investigated temperature are listed in table 4. A close perusal of table 4 indicates that the values of $\bar{K}_{m,1}^E$ and $\bar{K}_{m,2}^E$, and $\bar{K}_{\phi,1}^E$ and $\bar{K}_{\phi,2}^E$ calculated using equations (12) and (13) are nearly same in magnitudes for both the components in each mixture and exhibit similar trends. The magnitude of $\bar{K}_{m,1}^E$, $\bar{K}_{m,2}^E$, $\bar{K}_{\phi,1}^E$ and $\bar{K}_{\phi,2}^E$ values for these mixtures follow the order: benzene < toluene < *p*-xylene < *m*-xylene < *o*-xylene < mesitylene, which is also the order of solute–solvent interactions between THF and aromatic hydrocarbon molecules in the mixture. Also, the $\bar{K}_{m,1}^E$, $\bar{K}_{m,2}^E$, $\bar{K}_{\phi,1}^E$ and $\bar{K}_{\phi,2}^E$ values increase with increase in temperature (table 4) for each binary mixtures under study. These trends further support the trends observed in Δk_s , Δu , $\Delta \eta$, $\bar{K}_{m,1}^E$ and $\bar{K}_{m,2}^E$ values for the binary mixtures under study.

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