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Influence of temperature on thermodynamic properties of substituted aromatic compounds

R. Gonzalez-Olmos^a; M. Iglesias^b; B. M. R. P. Santos^c; S. Mattedi^d; J. M. Goenaga^d; J. M. Resa^d

^a Departament d'Enginyeria Química, Escola Tècnica Superior d'Enginyeria Química, Universitat Rovira i Virgili, 43007 Tarragona, España ^b PF&PT Research Team, Department of Chemical Engineering, High Technical School of Engineering, University of Santiago de Compostela, E-15782 Santiago de Compostela, España ^c Departamento de Engenharia Química, Escola Politécnica, Universidade Federal da Bahia, 40210 Salvador-Bahia, Brasil ^d Departamento de Ingeniería Química, Universidad del País Vasco, Vitoria, España

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Influence of temperature on thermodynamic properties of substituted aromatic compounds

R. Gonzalez-Olmos^{a*}, M. Iglesias^b, B.M.R.P Santos^c, S. Mattedi^c,
J.M. Goenaga^d and J.M. Resa^d

^aDepartament d'Enginyeria Química, Escola Tècnica Superior d'Enginyeria Química, Universitat Rovira i Virgili, Avinguda Països Catalans 26, Campus Sescelades, 43007 Tarragona, España; ^bPF&PT Research Team, Department of Chemical Engineering, High Technical School of Engineering, University of Santiago de Compostela, Rúa Lope Gómez de Marzoa, E-15782 Santiago de Compostela, España; ^cDepartamento de Engenharia Química, Escola Politécnica, Universidade Federal da Bahia, 40210 Salvador – Bahia, Brasil; ^dDepartamento de Ingeniería Química, Universidad del País Vasco, Apto. 450, Vitoria, España

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This work presents experimental liquid densities and ultrasonic velocities for a collection of substituted aromatic compounds (isobutylbenzene, 1,3,5-trimethylbenzene, butylbenzene, isopropylbenzene, *p*-xylene, *m*-xylene and *o*-xylene) at the range of temperature 278.15–323.15 K and atmospheric pressure of a collection of halogenated and aromatic hydrocarbons. Fitting equations were applied to data in order to correlate for later computer-based design. The estimation of the studied properties was made by the application of different theoretical procedures. An equation of state based on the generalised Van der Waals theory which combines the Staverman–Guggenheim combinatorial term of lattice statistics with an attractive lattice gas expression and the free length theory (FLT) showed a good response at the studied conditions.

Keywords: density; ultrasonic velocity; equation of state; free length theory

1. Introduction

Reliable thermodynamic data of environmental pollutants are highly important from both practical and theoretical points of view. Environmental chemistry and engineering need this information for modelling the dispersion of organic pollutants in the environment, to solve the remediation of contaminated soils and surface waters, minimise the presence of hazardous pollutants in aqueous effluents and develop new strategies for cheap and effective cleaning procedures and then, adequate decisions and remediation policies. From a more fundamental point of view, thermodynamic information is necessary for the understanding of the complex molecular interactions and mechanisms of solution and dispersion. The test of models and the development of new prediction methods for these thermodynamic functions, have a particular significance because they are the only way to ensure accurate results.

*Corresponding author. Email: rafael.gonzalez@urv.net

Table 1. Densities (ρ) and ultrasonic velocities (u) of pure components.

Component	MW ^a (kg k mol ⁻¹)	ρ (298.15 K) (g cm ⁻³)		u (298.15 K) (m s ⁻¹)	
		Expt.	Lit. [6]	Expt.	Lit. [6]
<i>p</i> -Xylene	106.167	0.856589	0.85661	1305.39	1309.7
<i>m</i> -Xylene	106.167	0.859471	0.85999 ^b	1318.80	1320 ^b
<i>o</i> -Xylene	106.167	0.874708	0.87593 ^b	1347.26	1348 ^b
1,3,5-Trimethylbenzene	120.194	0.861148	0.86111	1330.12	1336.8
Isopropylbenzene	120.194	0.857518	0.85743	1305.07	1307.7
Butylbenzene	134.221	0.856214	0.85607	1321.33	1334.1
Isobutylbenzene	134.221	0.849058	0.84907	1294.98	1296.9

Notes: ^aRef. [4]. ^bRef. [7].

With these facts in mind, as a continuation of our scientific work investigating physical properties related to characterisation of pollutants [1,2], this work presents the temperature dependence of density and ultrasonic velocity at the range of temperature 278.15–323.15 K and atmospheric pressure of a collection of halogenated and aromatic hydrocarbons (isobutylbenzene, 1,3,5-trimethylbenzene, butylbenzene, isopropylbenzene, *p*-xylene, *m*-xylene and *o*-xylene). From the experimental data, temperature-dependent polynomials were fitted. Different derived properties were computed from density and ultrasonic velocity data, since they are important in the study of the thermodynamic trend and theoretical calculations. Because of the expense of the experimental measurement of such data and current processes design is strongly computer oriented, consideration was also given to how accurate different theoretical methods work by comparison with the experimental data. Different procedures were applied to the experimental data. A lattice type equation of state was applied to simultaneously correlate vapour pressure and densities in order to describe the non-ideal temperature dependence of these magnitudes at a wide range. The Equation of State (EOS) is based on the generalised Van der Waals theory and combines the Staverman–Guggenheim combinatorial term of lattice statistics with an attractive lattice gas expression [3]. The free length theory (FLT) was applied to estimate the ultrasonic velocity of these compounds [4]. Satisfactory results were obtained for both properties, a good accuracy being obtained for a wide range of temperatures.

2. Experimental section

2.1. Materials

All chemical solvents used in the preparation of samples were supplied by Merck with richness higher than 99.5 mol%. The pure components were stored in glass containers protected from sunlight at constant humidity and temperature. All products were degassed using ultrasound and dried on molecular sieves (pore diameter of 4×10^{-10} and 5×10^{-10} m from Fluka) before use. Densities and ultrasonic velocities of the pure substances were checked and listed in Table 1 and compared with literature values.

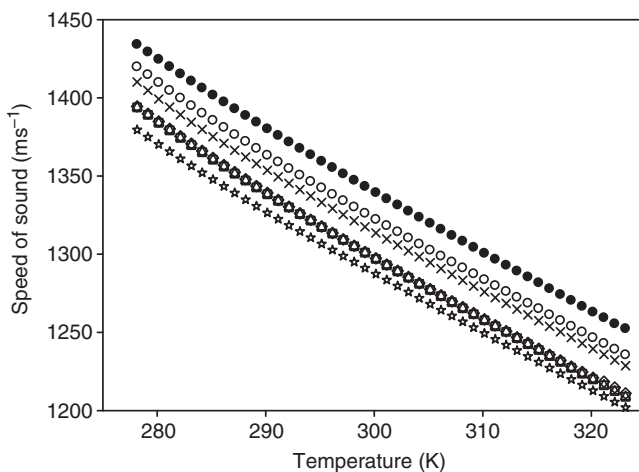


Figure 1. Curves of ultrasonic velocity (m s^{-1}) of *p*-xylene (\diamond), *m*-xylene (\square), *o*-xylene (\bullet), 1,3,5-trimethylbenzene (\circ), isopropylbenzene (\triangle), butylbenzene (\times) and isobutylbenzene (\star) at the range of temperature 278.15–323.15 K.

2.2. Apparatus and procedure

The ultrasonic velocities and densities were measured with an Anton Paar DSA-5000 device with a precision of $\pm 0.01 \text{ m s}^{-1}$ and $\pm 10^{-6} \text{ g cm}^{-3}$. The temperature was maintained at a constant with a precision of ± 0.01 . Calibration of the apparatus was performed periodically, in accordance with technical specifications, using Millipore quality water (resistivity, $18.2 \text{ M}\Omega \text{ cm}$) and ambient air.

2.3. Determination of the experimental uncertainty

The uncertainty of the experimental method was analysed in *m*-xylene. The density and speed of sound of *m*-xylene was measured three times at each temperature (181 temperatures). Then the uncertainty of each measurement was established as the SD of the mean and is represented in Figure 1 for each temperature for the two measured properties. The horizontal line is the mean of all SD and is considered as the uncertainty of the experimental measurement. In the case of the density we may establish that the uncertainty of the measurement is approximately $0.00002 \text{ g cm}^{-3}$ and in the case of speed of sound it is 0.55 m s^{-1} .

3. Results and discussion

3.1. Data correlation

For compact and smooth representation of the experimental data, the density and ultrasonic velocity of the chemicals were correlated as a function of temperature in accordance to Equation (1):

$$P = \sum_{i=0}^N A_i T^i, \quad (1)$$

where P is density (g cm^{-3}) or ultrasonic velocity (ms^{-1}), T is the absolute temperature in Kelvin degrees and A_i are fitting parameters. N stands for the extension of the mathematical series, which was optimised by means of the Bevington test. A summarised version of the densities and ultrasonic velocities data are given by Tables 2 and 3, respectively. The complete data used to correlate the thermodynamical properties have been submitted as supplementary material (181 points between 278.15 and 323.15 K). The fitting parameters were obtained by the unweighted least-squared method applying a fitting Marquardt algorithm. The root mean square deviations were computed using Equation (2)

$$\sigma = \left(\frac{\sum_{i=1}^{n_{\text{DAT}}} (z_{\text{exp}} - z_{\text{pred}})^2}{n_{\text{DAT}}} \right)^{1/2}, \quad (2)$$

where z is the value of the property, and n_{DAT} is the number of experimental data.

The fitting parameters and the corresponding deviations are gathered in Table 4. In Figures 2 and 3, the temperature trend of density and ultrasonic velocity are gathered.

3.2. Derived properties

A frequently applied derived magnitude for chemicals is the temperature dependence of volumetry, which is expressed as isobaric expansibility or thermal expansion coefficient (α). The data reported in literature normally give only values of thermal expansion coefficients both of pure compounds and its mixtures, showing the relative changes in density, calculated by means of $-(\Delta\rho/\rho)$ as a function of temperature and assuming that α remains constant in any thermal range. This fact is due to the scarce availability of accurate density data in a wide temperature range. As in the case of pure chemicals or substances it can be computed at a molar fraction by way of the expression:

$$\alpha = - \left(\frac{\partial \ln \rho}{\partial T} \right)_{P,x}, \quad (3)$$

taking into account the temperature dependence of density. As shown in Figure 4, it is important to point out the rapid decreasing values of α when temperature raises at any compounds having the highest values for *p*-xylene and the lowest for butylbenzene. As expected similar values were measured for those chemicals of analogous structure.

The isentropic compressibility (κ_s) of pure compounds was also calculated from the density and ultrasonic velocity data using Equation (4):

$$\kappa_s = \left(\frac{1}{u^2 \rho} \right). \quad (4)$$

Figure 5 indicates the behaviour of this magnitude as temperature function. As expected, this evolution is in opposition to the density and ultrasonic velocity. The compound with higher isentropic compressibility is isobutylbenzene and the lower is *o*-xylene and the other compounds are between them with similar values. This is due to the same aromatic nature of all compounds.

Table 2. Densities (g m^{-3}) of the studied chemicals at the range of temperature 278.15–323.15 K.

T (K)	<i>p</i> -Xylene	<i>m</i> -Xylene	<i>o</i> -Xylene	1,3,5-Trimethylbenzene	Isopropylbenzene	Butylbenzene	Isobutylbenzene
278.15	0.873823	0.876481	0.891360	0.877333	0.874405	0.872090	0.865216
279.15	0.872966	0.875565	0.890498	0.876498	0.873541	0.871282	0.864386
280.15	0.872070	0.874702	0.889621	0.875641	0.872650	0.870432	0.863535
281.15	0.871196	0.873825	0.888750	0.874792	0.871766	0.869603	0.862689
282.15	0.870312	0.872958	0.887891	0.873956	0.870896	0.868774	0.861842
283.15	0.869418	0.872071	0.887036	0.873123	0.870038	0.867955	0.861013
284.15	0.868536	0.871222	0.886192	0.872298	0.869188	0.867151	0.860191
285.15	0.867683	0.870358	0.885338	0.871484	0.868313	0.866340	0.859373
286.15	0.866803	0.869506	0.884506	0.870667	0.867488	0.865540	0.858567
287.15	0.865930	0.868642	0.883678	0.869847	0.866625	0.864753	0.857748
288.15	0.865069	0.867813	0.882856	0.869043	0.865782	0.863959	0.856951
289.15	0.864211	0.866962	0.882032	0.868243	0.864943	0.863169	0.856147
290.15	0.863348	0.866114	0.881216	0.867439	0.864100	0.862378	0.855344
291.15	0.862495	0.865279	0.880375	0.866641	0.863266	0.861599	0.854553
292.15	0.861638	0.864446	0.879574	0.865853	0.862451	0.860818	0.853756
293.15	0.860797	0.863604	0.878761	0.865058	0.861606	0.860052	0.852974
294.15	0.859949	0.862778	0.877947	0.864270	0.860795	0.859278	0.852189
295.15	0.859100	0.861935	0.877134	0.863488	0.859963	0.858505	0.851395
296.15	0.858259	0.861129	0.876317	0.862705	0.859146	0.857741	0.850623
297.15	0.857426	0.860294	0.875523	0.861929	0.858332	0.856976	0.849844
298.15	0.856589	0.859471	0.874708	0.861148	0.857518	0.856214	0.849058
299.15	0.855757	0.858655	0.873909	0.860378	0.856704	0.855455	0.848286
300.15	0.854927	0.857837	0.873111	0.859605	0.855891	0.854699	0.847507
301.15	0.854107	0.857020	0.872307	0.858839	0.855084	0.853936	0.846743

(continued)

Table 2. Continued.

<i>T</i> (K)	<i>p</i> -Xylene	<i>m</i> -Xylene	<i>o</i> -Xylene	1,3,5-Trimethylbenzene	Isopropylbenzene	Butylbenzene	Isobutylbenzene
302.15	0.853281	0.856221	0.871515	0.858073	0.854282	0.853183	0.845972
303.15	0.852467	0.855417	0.870733	0.857311	0.853480	0.852428	0.845210
304.15	0.851658	0.854617	0.869932	0.856548	0.852686	0.851687	0.844454
305.15	0.850847	0.853821	0.869168	0.855793	0.851900	0.850941	0.843697
306.15	0.850042	0.853026	0.868385	0.855046	0.851107	0.850200	0.842950
307.15	0.849233	0.852234	0.867608	0.854298	0.850325	0.849474	0.842207
308.15	0.848442	0.851443	0.866846	0.853557	0.849541	0.848732	0.841468
309.15	0.847647	0.850659	0.866084	0.852812	0.848763	0.848010	0.840719
310.15	0.846840	0.849879	0.865319	0.852082	0.847984	0.847304	0.839978
311.15	0.846075	0.849099	0.864571	0.851353	0.847225	0.846582	0.839251
312.15	0.845285	0.848332	0.863806	0.850612	0.846480	0.845868	0.838530
313.15	0.844506	0.847574	0.863076	0.849894	0.845703	0.845172	0.837825
314.15	0.843752	0.846822	0.862335	0.849186	0.844952	0.844466	0.837096
315.15	0.842980	0.846058	0.861604	0.848484	0.844212	0.843770	0.836401
316.15	0.842217	0.845314	0.860874	0.847763	0.843471	0.843079	0.835681
317.15	0.841472	0.844572	0.860157	0.847075	0.842739	0.842417	0.834994
318.15	0.840714	0.843847	0.859442	0.846376	0.842008	0.841739	0.834312
319.15	0.839966	0.843104	0.858728	0.845695	0.841294	0.841063	0.833627
320.15	0.839246	0.842400	0.858033	0.845030	0.840584	0.840426	0.832965
321.15	0.838615	0.841679	0.857338	0.844365	0.839892	0.839769	0.832302
322.15	0.837917	0.840969	0.856628	0.843704	0.839197	0.839126	0.831645
323.15	0.837226	0.840290	0.855997	0.843060	0.838533	0.838509	0.831003

Table 3. Ultrasonic velocities (m s^{-1}) of the studied chemicals at the range of temperature 278.15–323.15 K.

T (K)	<i>p</i> -Xylene	<i>m</i> -Xylene	<i>o</i> -Xylene	1,3,5-Trimethylbenzene	Isopropylbenzene	Butylbenzene	Isobutylbenzene
278.15	1394.50	1407.54	1434.11	1419.73	1393.90	1410.16	1379.52
279.15	1389.79	1402.56	1429.30	1414.75	1389.17	1404.70	1374.98
280.15	1384.85	1397.86	1424.58	1409.76	1384.08	1399.22	1370.25
281.15	1380.10	1393.09	1419.92	1404.64	1379.17	1394.10	1365.66
282.15	1375.40	1388.40	1415.23	1399.81	1374.41	1389.18	1361.05
283.15	1370.67	1383.60	1410.66	1394.93	1369.73	1384.40	1356.54
284.15	1366.06	1379.04	1406.21	1390.15	1365.21	1379.82	1352.11
285.15	1361.56	1374.46	1401.69	1385.55	1360.46	1375.18	1347.79
286.15	1356.95	1369.95	1397.35	1381.04	1356.06	1370.83	1343.44
287.15	1352.44	1365.45	1392.95	1376.43	1351.51	1366.46	1339.15
288.15	1347.94	1361.08	1388.64	1372.09	1347.05	1362.16	1334.91
289.15	1343.55	1356.65	1384.38	1367.65	1342.69	1357.88	1330.74
290.15	1339.16	1352.26	1380.08	1363.26	1338.36	1353.63	1326.50
291.15	1334.70	1347.97	1375.88	1358.93	1334.10	1349.48	1322.44
292.15	1330.37	1343.77	1371.73	1354.73	1329.93	1345.34	1318.43
293.15	1326.13	1339.55	1367.61	1350.58	1325.63	1341.31	1314.52
294.15	1321.93	1335.37	1363.51	1346.45	1321.52	1337.20	1310.59
295.15	1317.72	1331.16	1359.36	1342.33	1317.28	1333.14	1306.61
296.15	1313.54	1327.07	1355.32	1338.21	1313.19	1329.20	1302.73
297.15	1309.47	1322.92	1351.29	1334.17	1309.12	1325.26	1298.85
298.15	1305.39	1318.80	1347.26	1330.12	1305.07	1321.33	1294.98
299.15	1301.34	1314.75	1343.27	1326.15	1301.00	1317.49	1291.14
300.15	1297.35	1310.65	1339.30	1322.16	1296.98	1313.59	1287.32
301.15	1293.37	1306.64	1335.34	1318.21	1292.96	1309.76	1283.54

(continued)

Table 3. Continued.

<i>T</i> (K)	<i>p</i> -Xylene	<i>m</i> -Xylene	<i>o</i> -Xylene	1,3,5-Trimethylbenzene	Isopropylbenzene	Butylbenzene	Isobutylbenzene
302.15	1289.39	1302.64	1331.42	1314.27	1288.98	1305.95	1279.70
303.15	1285.42	1298.66	1327.50	1310.31	1285.02	1302.11	1275.79
304.15	1281.49	1294.65	1323.57	1306.43	1281.06	1298.43	1271.89
305.15	1277.60	1290.73	1319.72	1302.58	1277.16	1294.57	1268.06
306.15	1273.71	1286.79	1315.88	1298.76	1273.23	1290.75	1264.28
307.15	1269.92	1282.86	1311.98	1294.93	1269.36	1287.02	1260.56
308.15	1266.13	1278.99	1308.24	1291.22	1265.48	1283.26	1256.83
309.15	1262.28	1275.02	1304.34	1287.37	1261.65	1279.53	1253.09
310.15	1258.30	1271.12	1300.50	1283.65	1257.73	1275.92	1249.36
311.15	1254.51	1267.26	1296.73	1279.86	1253.97	1272.22	1245.65
312.15	1250.68	1263.39	1292.88	1276.07	1250.32	1268.56	1241.96
313.15	1246.85	1259.58	1289.17	1272.36	1246.33	1264.92	1238.36
314.15	1243.21	1255.76	1285.42	1268.62	1242.50	1261.23	1234.60
315.15	1239.48	1251.85	1281.68	1265.07	1238.77	1257.49	1231.01
316.15	1235.64	1248.04	1277.86	1261.20	1234.92	1253.87	1227.20
317.15	1232.02	1244.22	1274.15	1257.54	1231.14	1250.34	1223.62
318.15	1228.14	1240.47	1270.40	1253.85	1227.38	1246.69	1219.97
319.15	1224.64	1236.55	1266.59	1250.21	1223.62	1242.98	1216.37
320.15	1220.96	1232.87	1262.93	1246.55	1219.92	1239.45	1212.73
321.15	1218.46	1228.99	1259.28	1242.85	1216.19	1235.88	1209.12
322.15	1214.69	1225.18	1255.43	1239.22	1212.47	1232.29	1205.50
323.15	1211.00	1221.79	1252.33	1235.62	1208.82	1228.70	1201.92

Table 4. Parameters of Equation (2) in the range 283.15–323.15 K and root mean square deviations (σ).

	A_0	A_1	A_2	A_3	σ
	Density (g cm^{-3})				
<i>p</i> -Xylene	0.698203	3.7936×10^{-3}	-1.7302×10^{-5}	2.1330×10^{-8}	24×10^{-6}
<i>m</i> -Xylene	0.877140	1.9668×10^{-3}	-1.1039×10^{-5}	1.4232×10^{-8}	14×10^{-6}
<i>o</i> -Xylene	0.822278	2.6403×10^{-3}	-1.3249×10^{-5}	1.6714×10^{-8}	19×10^{-6}
1,3,5-Trimethylbenzene	0.956771	1.1228×10^{-3}	-8.1552×10^{-6}	1.1113×10^{-8}	22×10^{-6}
Isopropylbenzene	0.832606	2.4034×10^{-3}	-1.2550×10^{-5}	1.5994×10^{-8}	20×10^{-6}
Butylbenzene	0.835707	2.2656×10^{-3}	-1.1945×10^{-5}	1.5352×10^{-8}	23×10^{-6}
Isobutylbenzene	0.854171	2.0344×10^{-3}	-1.1214×10^{-5}	1.4532×10^{-8}	22×10^{-6}
	Ultrasonic velocity (ms^{-1})				
<i>p</i> -Xylene	7559.66	-50.1212	0.1389	-1.3791×10^{-4}	0.22
<i>m</i> -Xylene	9342.50	-68.7034	0.2038	-2.1338×10^{-4}	0.08
<i>o</i> -Xylene	8732.94	-62.6080	0.1842	-1.9205×10^{-4}	0.09
1,3,5-Trimethylbenzene	12,127.88	-95.5887	0.2903	-3.0567×10^{-4}	0.13
Isopropylbenzene	10,119.48	-76.3388	0.2282	-2.3929×10^{-4}	0.11
Butylbenzene	13,768.18	-112.3444	0.3467	-3.6853×10^{-4}	0.25
Isobutylbenzene	9883.26	-74.9433	0.2259	-2.3869×10^{-4}	0.17

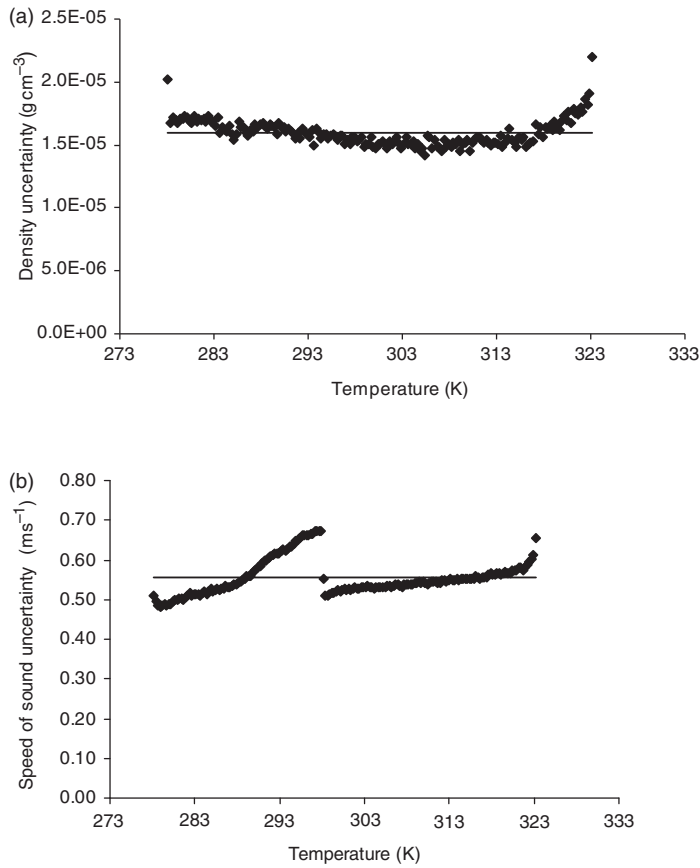


Figure 2. (a) Uncertainty of the density measurements for *m*-xylene (g cm^{-3}) and (b) uncertainty of the speed of sound measurements for *m*-xylene (m s^{-1}).

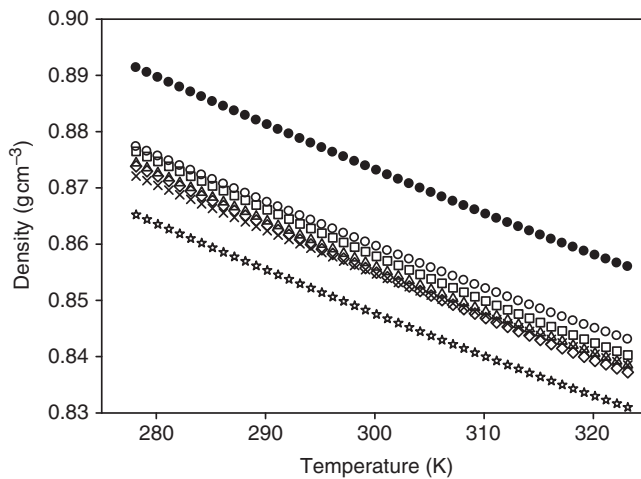


Figure 3. Curves of density (g cm^{-3}) of *p*-xylene (◇), *m*-xylene (□), *o*-xylene (●), 1,3,5-trimethylbenzene (○), isopropylbenzene (△), butylbenzene (×) and isobutylbenzene (☆) at the range of temperature 278.15–323.15 K.

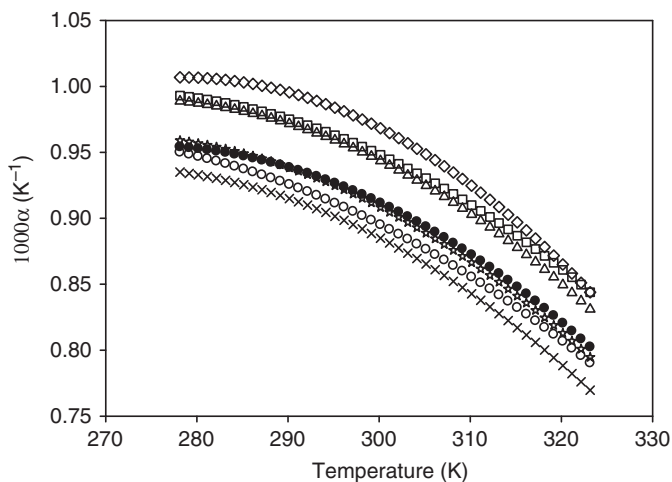


Figure 4. Curves of isobaric expansibility (α , K^{-1}) of *p*-xylene (\diamond), *m*-xylene (\square), *o*-xylene (\bullet), 1,3,5-trimethylbenzene (\circ), isopropylbenzene (\triangle), butylbenzene (\times) and isobutylbenzene (\star) at the range of temperature 278.15–323.15 K.

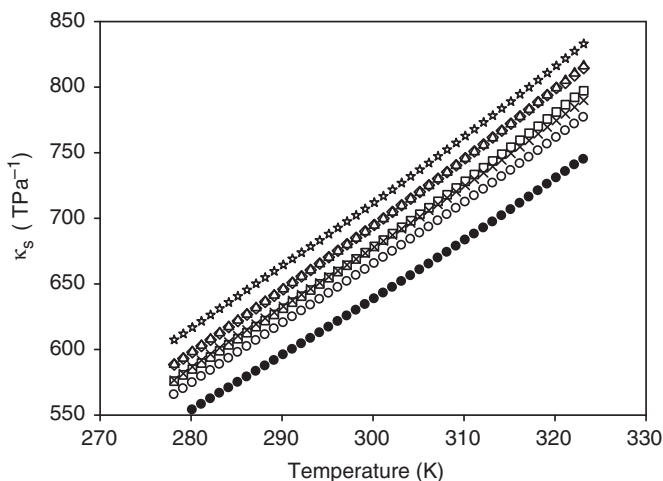


Figure 5. Curves of isentropic compressibility (TPa^{-1}) of *p*-xylene (\diamond), *m*-xylene (\square), *o*-xylene (\bullet), 1,3,5-trimethylbenzene (\circ), isopropylbenzene (\triangle), butylbenzene (\times) and isobutylbenzene (\star) at the range of temperature 278.15–323.15 K.

The values of κ_s and the values of isobaric expansibility computed from the measured densities and ultrasonic velocities are gathered in the supplementary material.

3.3. Estimation of density – MTC Lattice Gas EOS

In the last few years, many researchers have applied and modified cubic equations of state to almost any situation for thermodynamic studies of pure chemicals and

mixtures, although the success is always strongly dependent on a wide understanding of how molecules interact in terms of space and energy [7]. However, in the last few years the interest related to non-cubic theoretically based EOS for prediction of fluid phase equilibria or others thermodynamical properties has increased. In this work, the Lattice Gas EOS developed by Mattedi *et al.* [3] was also used to describe volumetric trend of these chemicals. Although, the EOS is normally written in group contribution form, in this work a molecular approach was used, and so the EOS is written as:

$$z = \tilde{v}r \ln \left[\frac{\tilde{v}}{\tilde{v}-1} \right] + \frac{Z}{2} \tilde{v}r \ln \left[\frac{\tilde{v}-1+(q/r)}{\tilde{v}} \right] + \ell - \frac{\tilde{v}\Psi(q/r) \quad q(\exp(-u/RT) - 1)}{\tilde{v}-1+(q/r) \quad \tilde{v}-1+(q/r)\exp(-u/RT)}, \quad (5)$$

where z is the compressibility factor, q is the surface area of the molecule, Z is the lattice coordination number which is set equal to 10, r is the average number of segments occupied by a molecule in the lattice, $\ell = (Z/2)(r - q) - (r - 1)$, u is the interaction energy between molecules and Ψ is a constant of the lattice structure set to 1. The reduced molar volume (\tilde{v}) is given by:

$$\tilde{v} = \frac{v}{rv^*}, \quad (6)$$

v is the molar hard-core volume parameter for a molecule. The fugacity coefficient for a pure component, derived for the model is:

$$\ln \phi = -r \ln \left[\frac{\tilde{v}-1}{\tilde{v}-1+(q/r)} \right] + (1-\ell) \ln \left[\frac{\tilde{v}}{\tilde{v}-1+(q/r)} \right] + \frac{\Psi(q/r)(q-r)}{\tilde{v}-1+(q/r)} + \Psi q \ln \left[\frac{\tilde{v}-1+(q/r)}{\tilde{v}-1+(q/r)\exp(-u/RT)} \right] - \frac{\Psi}{r} q \frac{(q \exp(-u/RT) - r)}{\tilde{v}-1+(q/r)\exp(-u/RT)} - \ln z. \quad (7)$$

It was assumed here, as in previous works, that u is given by:

$$\frac{u}{R} = \frac{u_0}{R} \left(1 + \frac{B}{T} \right). \quad (8)$$

More details about the EOS could be found in the original work [3].

In summary, the equation of state has four parameters for each pure compound (v , q , u_0/R and B). The cell volume v^* is fixed in $5 \text{ cm}^3 \text{ mol}^{-1}$ was used as suggested by Mattedi *et al.* [3]. Pure parameters were fitted using the simplex algorithm of Nelder and Mead (given in [8]), in order to minimise the objective function:

$$F = \frac{\sum_{i=1}^N \left[\left(\frac{P_{i,\text{cal}}^{\text{sat}} - P_{i,\text{pex}}^{\text{sat}}}{P_{i,\text{pex}}^{\text{sat}}} \right)^2 + \left(\frac{\rho_{i,\text{cal}}^{\text{liq-sat}} - \rho_{i,\text{pex}}^{\text{liq-sat}}}{\rho_{i,\text{pex}}^{\text{liq-sat}}} \right)^2 \right]}{N}, \quad (9)$$

where P^{sat} is the vapour pressure and $\rho^{\text{liq-sat}}$ is the saturated molar liquid density. The subscripts cal and pex indicate calculated and pseudo-experimental values and N is the number of data points used. The applicability of the model is wider if vapour

pressure data is also used for parameter estimation and so saturation pressures were also used to obtain EOS parameters. There were pseudo-experimental data used for saturated densities and vapour pressure generated through DIPPR correlation [9] to 180 points with temperature ranging from 278.15 to 323.15 K. Parameters from this EOS have physical meaning and the numerical values for the obtained parameters presented in Table 5 are coherent. As expected, similar parameters for all substances have the same magnitude, except for the parameter of temperature dependence of group-group energy which is a fitting parameter and so could vary in a larger range. In Table 6, the root mean square deviations and the relative deviation for vapour pressure (pseudo-experimental data) and liquid density data obtained in this work are shown. Densities were calculated with the EOS at 101.3 kPa. From the presented results for vapour pressure deviations it could be seen that a very good correlation was obtained. Moreover, for densities the EOS were compared with this work data and the presented results show a very good agreement between experimental and calculated values.

3.4. Estimation of ultrasonic velocity – free length theory

The FLT estimates the isentropic compressibility attending to the free displacement of molecules as a main function of temperature [4]. In the last few years, FLT has

Table 5. Obtained parameters for EOS.

Compound	v (cm ³ mol ⁻¹)	q	B (K)	u_0/R (K)
<i>p</i> -Xylene	89.179	12.165	0.387	-446.743
<i>m</i> -Xylene	89.109	12.212	-0.425	-456.025
<i>o</i> -Xylene	87.492	12.041	-0.020	-460.228
1,3,5-Trimethylbenzene	102.493	13.649	16.051	-441.332
Isopropylbenzene	100.181	13.690	0.346	-434.025
Butylbenzene	113.802	15.371	0.322	-436.329
Isobutylbenzene	113.748	15.160	0.269	-424.654

Table 6. Relative deviations between saturated pressure from [9] and calculated with the EOS, relative deviations between liquid density data obtained in this work and calculated by the EOS at 101.3 kPa and root mean square deviations for predictive ultrasonic velocity by means of FLT.

Compound	P^{sat}	ρ^{liq}	FLT (σ)
	$\Delta P/P$ (%)	$\Delta \rho/\rho$ (%)	
<i>p</i> -Xylene	0.32	0.13	37.39
<i>m</i> -Xylene	0.24	0.12	41.80
<i>o</i> -Xylene	0.24	0.15	38.14
1,3,5-Trimethylbenzene	0.21	0.09	43.80
Isopropylbenzene	0.34	0.20	39.79
Butylbenzene	0.38	0.15	31.47
Isobutylbenzene	0.37	0.23	31.71

proved its applicability for molecules of different nature. The experimental data for the speed of sound of the chemicals studied here were compared with values determined by the theoretical procedure. This model is expressed as follows:

$$\kappa_S = \left(\frac{L_f^2}{K^2} \right), \quad (10)$$

where K is a temperature-dependent constant [$K = (93.875 + 0.375 \cdot T) \cdot 10^{-8}$] and L_f is the intermolecular free length calculated by the following expression:

$$L_f = \left(\frac{2 \cdot (V - V_0)}{Y} \right), \quad (11)$$

where V is the molar volume, V_0 is the molar volume at absolute zero and Y is the molar surface area. V_0 and Y are calculated by the following equations:

$$Y = 408402519.1 \cdot (V_0)^{(2/3)} \quad (12)$$

$$V_0 = V \cdot \left(1 - \frac{T}{T_c} \right)^{0.3}, \quad (13)$$

where T_c is the critical temperature and values published in literature [10] were used.

Applying Equation (4) in Equation (10), the final expression to calculate the ultrasonic velocity through the FLT is:

$$u = \sqrt{\left(\frac{K^2}{L_f^2 \rho} \right)}. \quad (14)$$

The deviations between the predicted and the experimental data for the studied compounds are gathered in Table 6, giving the FLT acceptable results in terms of quantity and sign at every studied case.

4. Conclusions

It is well known that thermodynamic properties govern the behaviour and dispersion of contaminants in the environment. Values of such basic magnitudes as density, ultrasonic velocities and isentropic compressibilities can thus be applied to model and predict the displacement, distribution and fate of contaminants into natural media. In this article, original data for the temperature dependence of density and ultrasonic velocity at the range of temperature 278.15–323.15 K and atmospheric pressure of a collection of ethers (isobutylbenzene, 1,3,5-trimethylbenzene, butylbenzene, isopropylbenzene, *p*-xylene, *m*-xylene and *o*-xylene), have been measured. In order to provide correlative methods to be used in computer-aided design, data were directly correlated with polynomial functions. Density and vapour pressures were simultaneously correlated by a lattice equation of state and then the EOS was used to predict our experimental density data. Experimental ultrasonic velocities were compared with the predicted by the FLT. Satisfactory results were obtained with both models.

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