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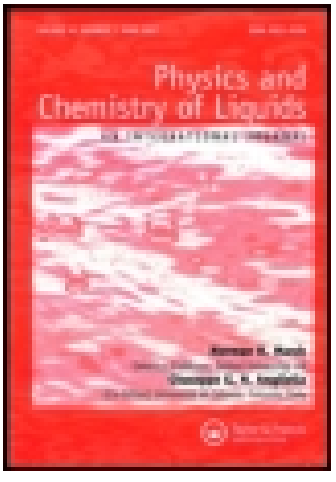

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Volumetric and transport properties of the ternary mixtures of toluene (1) + benzene (2) + butyl acetate (3) at different temperatures

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Volumetric and transport properties of the ternary mixtures of toluene (1) + benzene (2) + butyl acetate (3) at different temperatures

Alejandra Mariano[a,b]*, Lelia Mussari[a], Mirtha Orozco[c], Salvador Canzonieri[c] and Miguel Postigo[a]†

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Densities, ρ, speeds of sound, u, and viscosities, η, of ternary mixtures containing toluene, benzene and butyl acetate and binary mixtures formed by toluene and butyl acetate are reported in this paper. From experimental data, excess molar volumes, V^E, isentropic compressibilities, κ_s, and excess isentropic compressibilities, κ_s^E, were evaluated. The calculated magnitudes were fitted to different equations available on the literature, and geometrical models have been used to predict ternary magnitudes from the binary ones. Furthermore, viscosities were predicted by group contribution models. The results have been discussed in terms of molecular interactions among the components of the mixtures.

Keywords: density; speed of sound; viscosity; aromatic hydrocarbons; esters

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1. Introduction

Mixtures containing polar, non-polar, associated molecules or molecules with different sizes continue to be the interest of many investigations in the fields of Chemical Engineering, Physical Chemistry and Chemistry. One of the most important reasons for these studies is the need to have more knowledge about scientific and technical efficiency of processes of separation and purification of compounds. Another reason is trying to get theoretical values for the properties of pure fluids and mixtures, using the results in simulations and design in the field of chemical industry.

On the other hand, the results with which certain models predict the thermodynamic behaviour of mixtures depend mainly on the findings on the state equations used, the extensive knowledge we have about the intermolecular forces of substances involved and dependence on temperature and pressure. So, when you want to uncover the processes and mechanisms of molecular interactions involved in fluid mixtures, it is necessary to accurately assess the thermodynamic magnitudes, and in that sense, it is important to have experimental data of mixtures that could mean the goodness of theories or models.

The mixtures to study can contain polar, non-polar, associated molecules or molecules with different sizes. Particularly, the selection of the type of molecules to study is due to previous work that our research group has been doing for several years, studying the interactions between polar and non-polar molecules.[1–5] Within this type of mixtures,

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the literature reflects an important number of publications for systems containing normal hydrocarbons and different types of molecules, [6–12] but this is not the case for aromatic hydrocarbons. One of the lines of our research group conducted during the last years is the measurement of thermophysical properties of mixtures containing aromatic hydrocarbons and linear esters.[4,13,14]

Particularly, the experimental information presented on this work encloses density, ρ, speed of sound, u, and viscosity, η, for the ternary systems: toluene (1) + benzene (2) + butyl acetate (3) and the binary system toluene: (1) + butyl acetate (2).

From experimental information, the excess molar volume, V^E; isentropic compressibility, κ_s; and excess isentropic compressibility, κ_s^E, were calculated. These calculated properties were fitted to the expressions for ternary mixtures of Cibulka, [15] Singh *et al.* [16] and Nagata and Sakura.[17] The polynomial equation of Redlich and Kister [18] was used to calculate binary contributions. Standard deviations between experimental and calculated values were calculated.

The properties of the ternary system were estimated using symmetrical and asymmetrical models based on the contribution of the binary data: Kohler, [19] Jacob and Fitzner, [20] Rastogi *et al.* [21] and Tsao and Smith.[22] Also, the group contribution models of Wu [23] and GC-UNIMOD, Cao, [24] and the predictive model developed by Asfour *et al.* [25] and Nhaesi and Asfour [26] were applied to predict the viscosities of the ternary system at the seven temperatures.

The experimental information reported in this paper is original, and we did not find any viscosity, density or speed of sound data for this ternary mixture in the consulted literature.

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2. Experimental section

The substances employed were toluene, benzene and butyl acetate. The specifications of the chemical used are detailed in Table S1. All the liquids were dried over 0.4 nm Union Carbide molecular sieves from Fluka and partially degassed before use with an ultrasonic bath. The experimental properties of pure liquids compared to those found in literature are presented in Table S2 at temperatures between 288.15 K and 313.15 K.

The mixtures were prepared by weighting. More details about the procedure were described previously.[27] The uncertainty in mole fraction calculation is $\pm 1\ 10^{-4}$.

Densities and speeds of sound of pure liquids and mixtures were measured at temperatures of 288.15, 293.15, 298.15, 303.15, 308.15, 313.15 and 318.15 K, and atmospheric pressure using digital density/sound velocity analyser Anton Paar DSA 48 automatically thermostated at ±0.01 K. The estimated measurement uncertainties were ±0.01 kg m^{-3} and ±0.05 m s^{-1} for density and the speed of sound, respectively.

Viscosities of pure liquids and mixtures were measured with a precision of $2 \cdot 10^{-3}$ mPa s using a falling ball microviscometer Thermo-Haake, model MicroVisco 2, automatically thermostatised at ±0.01 K.

3. Results and discussion

Experimental densities, ρ, speeds of sound, u, and viscosities, η, for the ternary mixtures of toluene (1) + benzene (2) + butyl acetate (3), measured at 288.15, 293.15, 298.15, 303.15, 308.15, 313.15 and 318.15 K over the entire composition range and atmospheric pressure, are gathered in Tables 1, 2 and 3, respectively. Data for the binary mixtures toluene (1) + butyl acetate (2) are gathered in Table S3, and the experimental data of the other two binary systems were published previously.[13,28,29]

Table 1. Experimental densities, ρ, of the ternary system toluene (1) + benzene (2) + butyl acetate (3) at different temperatures as a function of molar fractions of components 1 and 2.

T (K)		ρ (kg m^{-3})						
x_1	x_2	288.15	293.15	298.15	303.15	308.15	313.15	318.15
0.0920	0.8082	882.76	877.58	872.37	867.16	861.92	856.68	851.40
0.1976	0.7061	881.18	876.06	870.96	865.78	860.64	855.45	850.24
0.2909	0.6169	879.98	874.92	869.83	864.72	859.66	854.54	849.40
0.3975	0.5036	878.62	873.67	868.67	863.66	858.60	853.58	848.49
0.4987	0.4015	877.49	872.56	867.68	862.69	857.74	852.72	847.72
0.6152	0.2913	876.25	871.48	866.60	861.72	856.81	851.89	846.95
0.6973	0.2010	875.56	870.74	865.97	861.10	856.26	851.30	846.50
0.8140	0.0887	874.54	869.78	865.07	860.25	855.49	850.68	845.84
0.0965	0.7009	882.89	877.77	872.63	867.42	862.24	857.03	851.77
0.1984	0.6035	881.65	876.57	871.48	866.37	861.24	856.03	850.85
0.3009	0.4971	880.44	875.39	870.40	865.32	860.25	855.15	850.04
0.4091	0.3908	879.33	874.34	869.41	864.36	859.38	854.33	849.29
0.4951	0.3050	878.42	873.51	868.62	863.64	858.70	853.70	848.70
0.6007	0.2018	877.51	872.65	867.78	862.90	857.98	853.06	848.12
0.7032	0.0981	876.70	871.86	867.08	862.18	857.35	852.48	847.56
0.1034	0.5955	883.16	878.06	872.98	867.80	862.65	857.46	852.26
0.1968	0.5017	882.14	877.08	872.03	866.90	861.80	856.66	851.49
0.3106	0.3888	881.02	876.04	871.02	865.99	860.93	855.82	850.72
0.3921	0.3025	880.29	875.34	870.36	865.35	860.31	855.30	850.25
0.5034	0.1967	879.25	874.35	869.47	864.48	859.54	854.57	849.60
0.5982	0.1017	878.51	873.65	868.79	863.88	858.97	854.04	849.10
0.1030	0.5029	883.57	878.47	873.43	868.23	863.08	857.90	852.70
0.1986	0.3955	882.69	877.66	872.61	867.52	862.42	857.30	852.16
0.2956	0.2906	881.88	876.89	871.87	866.84	861.80	856.71	851.60
0.4087	0.1918	880.83	875.88	870.93	865.93	860.94	855.92	850.88
0.4988	0.1019	880.21	875.28	870.34	865.41	860.44	855.45	850.42
0.0968	0.4067	884.16	879.01	873.99	868.77	863.65	858.50	853.25
0.2028	0.2993	883.24	878.16	873.17	868.07	862.95	857.82	852.69
0.2990	0.2007	882.48	877.48	872.46	867.37	862.31	857.22	852.15
0.4009	0.1002	881.64	876.70	871.72	866.73	861.71	856.67	851.65
0.0873	0.2913	884.71	879.63	874.60	869.41	864.27	859.09	853.90
0.1962	0.1868	883.86	878.83	873.81	868.62	863.54	858.42	853.29
0.3047	0.0834	883.00	878.02	873.06	867.95	862.91	857.83	852.73
0.0992	0.2002	885.00	879.92	874.86	869.68	864.50	859.40	854.20
0.2018	0.0989	884.23	879.18	874.15	869.09	863.92	858.81	853.68
0.0910	0.0830	885.52	880.44	875.34	870.20	865.05	859.89	854.68

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From experimental data, derived properties for ternary mixtures were calculated using the following Equations (1)–(3).

Excess molar volumes, V^E,

$$V^E = V - \sum_{i=1}^{n} (x_i M_i / \rho_i) \tag{1}$$

where x_i is the mole fraction of component i in the mixture, and M_i and ρ_i are the molar mass and density of pure component, respectively. The estimated uncertainty in V^E is $\pm 2 \cdot 10^{-9}$ m^3 mol^{-1}.

Isentropic compressibility, κ_s,

Table 2. Experimental speeds of sound, u, of the ternary system toluene (1) + benzene (2) + butyl acetate (3) at different temperatures as a function of molar fractions of components 1 and 2.

T (K)		u (m s^{-1})						
x_1	x_2	288.15	293.15	298.15	303.15	308.15	313.15	318.15
0.0920	0.8082	1333.4	1309.5	1285.6	1262.1	1239.3	1216.4	1194.1
0.1976	0.7061	1334.3	1310.8	1286.6	1263.2	1240.5	1217.9	1195.6
0.2909	0.6169	1335.2	1312.1	1288.2	1264.9	1242.4	1219.9	1197.8
0.3975	0.5036	1334.7	1312.1	1288.4	1265.3	1242.9	1220.7	1198.5
0.4987	0.4015	1335.4	1312.9	1289.4	1266.4	1243.9	1221.8	1199.8
0.6152	0.2913	1337.2	1314.5	1290.9	1268.3	1245.7	1223.9	1202.2
0.6973	0.2010	1337.4	1314.8	1291.0	1268.6	1245.9	1224.1	1202.9
0.8140	0.0887	1338.9	1316.4	1292.7	1270.8	1248.3	1226.5	1205.2
0.0965	0.7009	1318.8	1295.9	1272.2	1249.1	1226.7	1204.4	1181.9
0.1984	0.6035	1319.7	1296.9	1273.3	1250.4	1228.1	1205.9	1184.0
0.3009	0.4971	1320.6	1297.9	1274.5	1251.7	1229.0	1206.8	1185.1
0.4091	0.3908	1321.5	1298.9	1275.6	1253.0	1230.6	1208.4	1187.1
0.4951	0.3050	1322.8	1300.3	1277.1	1254.6	1232.2	1210.3	1188.7
0.6007	0.2018	1324.0	1301.7	1278.6	1256.2	1234.4	1212.4	1191.1
0.7032	0.0981	1325.3	1303.1	1280.1	1257.8	1235.7	1214.1	1192.7
0.1034	0.5955	1305.4	1282.7	1259.4	1236.7	1214.6	1192.7	1171.0
0.1968	0.5017	1306.7	1284.1	1260.9	1238.3	1216.3	1194.1	1172.5
0.3106	0.3888	1307.9	1285.5	1262.4	1239.9	1218.0	1196.1	1174.7
0.3921	0.3025	1308.4	1286.1	1263.0	1240.6	1218.8	1197.1	1175.8
0.5034	0.1967	1310.2	1288.1	1265.1	1242.8	1221.2	1199.6	1178.4
0.5982	0.1017	1312.0	1290.0	1267.2	1245.0	1223.5	1202.0	1180.9
0.1030	0.5029	1293.4	1271.2	1248.2	1225.9	1204.1	1182.4	1161.0
0.1986	0.3955	1294.1	1271.9	1249.0	1226.7	1205.0	1183.4	1162.1
0.2956	0.2906	1294.8	1272.6	1249.8	1227.5	1205.9	1184.4	1163.2
0.4087	0.1918	1298.1	1276.1	1253.3	1231.2	1209.7	1188.3	1167.2
0.4988	0.1019	1301.4	1278.1	1255.3	1233.6	1211.8	1190.4	1169.2
0.0968	0.4067	1281.7	1260.5	1237.9	1215.8	1193.8	1172.2	1151.0
0.2028	0.2993	1283.5	1262.1	1239.9	1217.7	1195.9	1174.5	1153.5
0.2990	0.2007	1284.9	1263.9	1241.6	1219.5	1198.3	1176.5	1155.6
0.4009	0.1002	1288.2	1266.5	1243.9	1222.1	1200.2	1179.3	1158.4
0.0873	0.2913	1269.9	1248.1	1225.7	1203.9	1182.5	1161.3	1140.4
0.1962	0.1868	1272.8	1251.1	1228.6	1206.7	1185.4	1164.2	1143.3
0.3047	0.0834	1275.0	1253.3	1231.0	1209.2	1188.1	1167.0	1146.2
0.0992	0.2002	1260.9	1241.3	1218.5	1196.9	1176.0	1154.7	1134.2
0.2018	0.0989	1263.5	1243.4	1221.2	1199.6	1178.7	1157.5	1136.7
0.0910	0.0830	1251.9	1230.4	1208.4	1186.9	1165.9	1145.1	1124.5

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$$\kappa_s = 1/\rho u^2 \tag{2}$$

where ρ and u are density and speed of sound, respectively. The estimated uncertainty in κ_s is $\pm 0.1 \cdot 10^{-12}$ Pa^{-1}.

Excess isentropic compressibility, κ_s^E,

$$\kappa_s^E = \kappa_s - \kappa_s^{id} \tag{3}$$

where κ_s^{id} is the isentropic compressibility of an ideal mixture and can be calculated from the properties of the pure components as follows:

Table 3. Experimental viscosities, η, of the ternary system toluene (1) + benzene (2) + butyl acetate (3) at different temperatures as a function of molar fractions of components 1 and 2.

T (K)		η (mPa s)						
x_1	x_2	288.15	293.15	298.15	303.15	308.15	313.15	318.15
0.0888	0.8219	0.6819	0.6356	0.5937	0.5558	0.5205	0.4884	0.4592
0.2044	0.6887	0.6723	0.6276	0.5869	0.5490	0.5153	0.4844	0.4562
0.2900	0.6237	0.6663	0.6211	0.5820	0.5447	0.5117	0.4812	0.4535
0.3953	0.4953	0.6587	0.6161	0.5771	0.5412	0.5091	0.4791	0.4522
0.5024	0.4069	0.6520	0.6092	0.5719	0.5353	0.5052	0.4762	0.4492
0.6081	0.2947	0.6478	0.6051	0.5690	0.5338	0.5028	0.4751	0.4484
0.7270	0.1750	0.6441	0.6030	0.5670	0.5331	0.5021	0.4746	0.4484
0.8401	0.0737	0.6419	0.6014	0.5656	0.5326	0.5019	0.4750	0.4490
0.0781	0.7337	0.6809	0.6358	0.5949	0.5567	0.5225	0.4908	0.4622
0.1849	0.6292	0.6746	0.6297	0.5896	0.5528	0.5187	0.4879	0.4598
0.2588	0.5713	0.6714	0.6254	0.5857	0.5492	0.5158	0.4858	0.4576
0.3990	0.4182	0.6627	0.6200	0.5816	0.5449	0.5128	0.4831	0.4560
0.5193	0.2860	0.6590	0.6155	0.5786	0.5427	0.5115	0.4826	0.4555
0.6145	0.1780	0.6577	0.6153	0.5779	0.5430	0.5118	0.4832	0.4567
0.7279	0.0766	0.6542	0.6129	0.5758	0.5418	0.5103	0.4830	0.4559
0.0816	0.6122	0.6846	0.6396	0.5996	0.5618	0.5280	0.4961	0.4680
0.2149	0.4913	0.6783	0.6349	0.5955	0.5576	0.5249	0.4938	0.4658
0.3043	0.4032	0.6756	0.6316	0.5924	0.5553	0.5229	0.4927	0.4648
0.4073	0.2770	0.6742	0.6303	0.5922	0.5554	0.5235	0.4936	0.4659
0.4938	0.1949	0.6720	0.6282	0.5900	0.5539	0.5219	0.4926	0.4651
0.6173	0.0715	0.6698	0.6270	0.5886	0.5540	0.5215	0.4926	0.4654
0.0833	0.5058	0.6931	0.6481	0.6079	0.5698	0.5360	0.5038	0.4753
0.2103	0.3891	0.6881	0.6434	0.6036	0.5672	0.5332	0.5023	0.4738
0.3076	0.3014	0.6852	0.6411	0.6009	0.5650	0.5315	0.5002	0.4724
0.4035	0.2101	0.6825	0.6384	0.5990	0.5630	0.5297	0.4997	0.4719
0.5150	0.0743	0.6831	0.6398	0.6011	0.5645	0.5323	0.5021	0.4736
0.0889	0.4093	0.7033	0.6573	0.6169	0.5786	0.5443	0.5118	0.4827
0.2084	0.2999	0.7003	0.6543	0.6140	0.5764	0.5425	0.5105	0.4816
0.2976	0.1763	0.7031	0.6572	0.6160	0.5795	0.5456	0.5132	0.4846
0.4094	0.0737	0.7002	0.6554	0.6149	0.5775	0.5439	0.5127	0.4839
0.1087	0.2969	0.7154	0.6692	0.6267	0.5888	0.5537	0.5204	0.4913
0.1980	0.2115	0.7139	0.6669	0.6263	0.5879	0.5530	0.5202	0.4908
0.3078	0.1068	0.7108	0.6649	0.6237	0.5864	0.5523	0.5192	0.4903
0.1071	0.1998	0.7304	0.6819	0.6392	0.6004	0.5644	0.5306	0.5001
0.2053	0.0983	0.7287	0.6806	0.6390	0.6002	0.5639	0.5306	0.5001
0.1039	0.1027	0.7451	0.6955	0.6515	0.6111	0.5749	0.5404	0.5086

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$$\kappa_s^{id} = \sum_{i=1}^{n} \phi_i \left\{ \kappa_{s,i} + TV_i\alpha_{p,i}^2 \Big/ C_{p,i} \right\} - T\left(\sum_{i=1}^{n} x_i V_i\right)\left(\sum_{i=1}^{n} \phi_i \alpha_{p,i}\right)^2 \Big/ \left(\sum_{i=1}^{n} x_i C_{p,i}\right) \quad (4)$$

where n is the number of components in the mixture, T is the temperature, and Φ_i, x_i, $\kappa_{s,i}$, V_i, $\alpha_{p,i}$ and $C_{p,i}$ are the volume fraction, mole fraction, isentropic compressibility, molar volume, thermal expansion coefficient and molar heat capacity at constant pressure for the component i.

The values of C_p were obtained from literature.[30] The thermal expansion coefficient, $\alpha_{p,i}$, was estimated from Equation (5), using finite difference method.

$$\alpha_{p,i} = \frac{-1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p \tag{5}$$

Calculated values of α_p and used C_p values are listed in Table S4.

Dynamic viscosity, η, for each mixture was determined from the kinematic viscosity and density. The estimated uncertainty in the dynamic viscosity is ±0.002 mPa s.

3.1. *Fitting equations*

Ternary measured and calculated data were fitted to the following equations:

Cibulka,[15]

$$Q = Q_{12*} + Q_{13*} + Q_{23*} + x_1 x_2 x_3 (A + B x_1 + C x_2) \tag{6}$$

Singh *et al.*,[16]

$$\mathrm{Q} = \mathrm{Q}_{12*} + Q_{13*} + Q_{23*} + x_1 x_2 x_3 (A + B x_1 (x_2 - x_3) + C x_1^2 (x_2 - x_3)^2) \tag{7}$$

Nagata and Sakura,[17]

$$Q = Q_{12*} + Q_{13*} + Q_{23*} + x_1 x_2 x_3 \Delta \tag{8}$$

In these equations, *A, B, C* and Δ are the adjustable parameters. Q represents V^E, κ_s^E and η. The terms Q_{12*}, Q_{13*} and Q_{23*} correspond to binary contributions; the asterisk in Q_{ij*} indicates that the sum $x_i + x_j$ is not equal to one. The binary contributions were evaluated at the molar fractions of the ternary mixture by Redlich and Kister [18] polynomial equation:

$$Q = x_1 x_2 \sum_{i=0}^{n} a_i (2x_1 - 1)^i \tag{9}$$

where Q refers to V^Eor κ_s^E. a_i are the adjustable coefficients, listed in Table S5, together with standard deviation, calculated with Equation (10) for the binary systems toluene (1) + benzene (2), toluene (1) + butyl acetate (2) and benzene (2) + butyl acetate (2).

$$\sigma = \sqrt{\sum_{i=1}^{n} (Q(\exp)_i - \mathrm{Q(calc)}_i)^2 \Big/ (n - p)} \tag{10}$$

where n and p represent the number of data and the number of parameters, respectively.

To correlate viscosity data, the Redilich and Kister's polynomial equation as the form of Equation (11) was applied.

$$\eta = \eta_1 x_1 + \eta_2 x_2 + x_1 x_2 \sum_{i=0}^{n} a_i (2x_1 - 1)^i \tag{11}$$

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Fitting parameters for Cibulka, Nagata and Singh's equations and standard deviation σ, calculated with Equation (10), are gathered in Table S6 at various temperatures from 288.15 to 318.15 K.

Figures 1(a) and 2(a) show experimental data and surfaces calculated from the fitting equation of Cibulka [15] at 298.15 K, of the properties: excess molar volume and excess isentropic compressibility. In Figures 1(b) and 2(b), the corresponding isolines for Cibulka surfaces at 298.15 K are shown. Figure 1(a) and (b) evince positive and negative values of excess molar volumes for the ternary mixtures, whereas Figure 2(a) and (b) present the negative values of excess isentropic compressibility for the most compositions of the ternary mixtures.

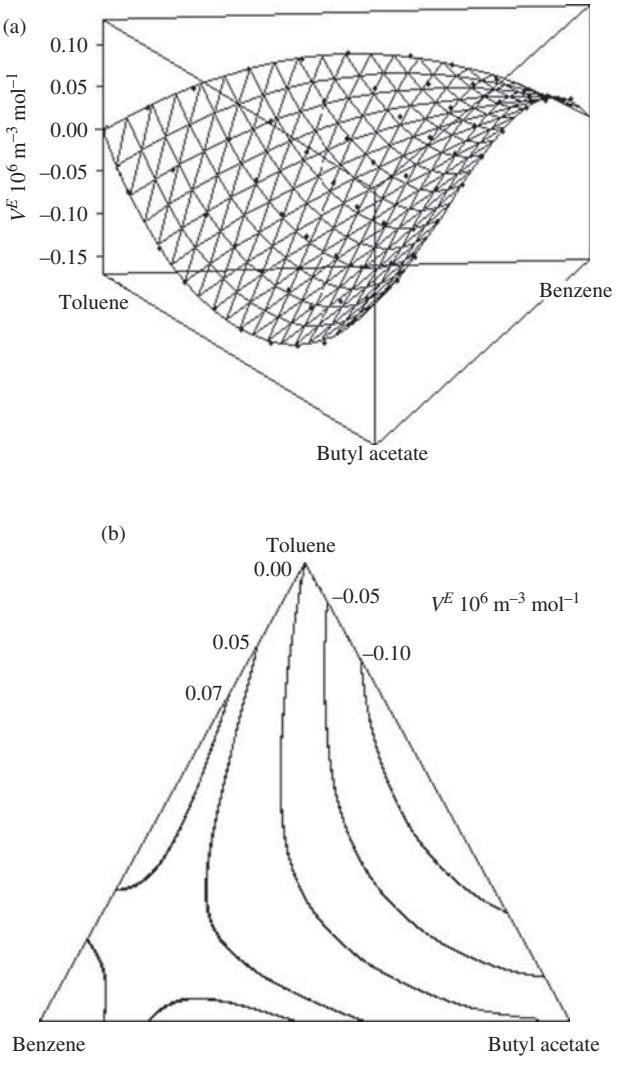

Figure 1. (a). Excess molar volume, V^E 10^6 m^{-3} mol^{-1}, for toluene (1) + benzene (2) + butyl acetate (3) at T = 298.15 K. Experimental data, ♦, and surface are calculated from Cibulka expression, Equation (6). (b). Excess molar volume, V^E 10^6 m^{-3} mol^{-1}, for toluene (1) + benzene (2) + butyl acetate (3) at T = 298.15 K. Isolines are calculated from Equation (6).

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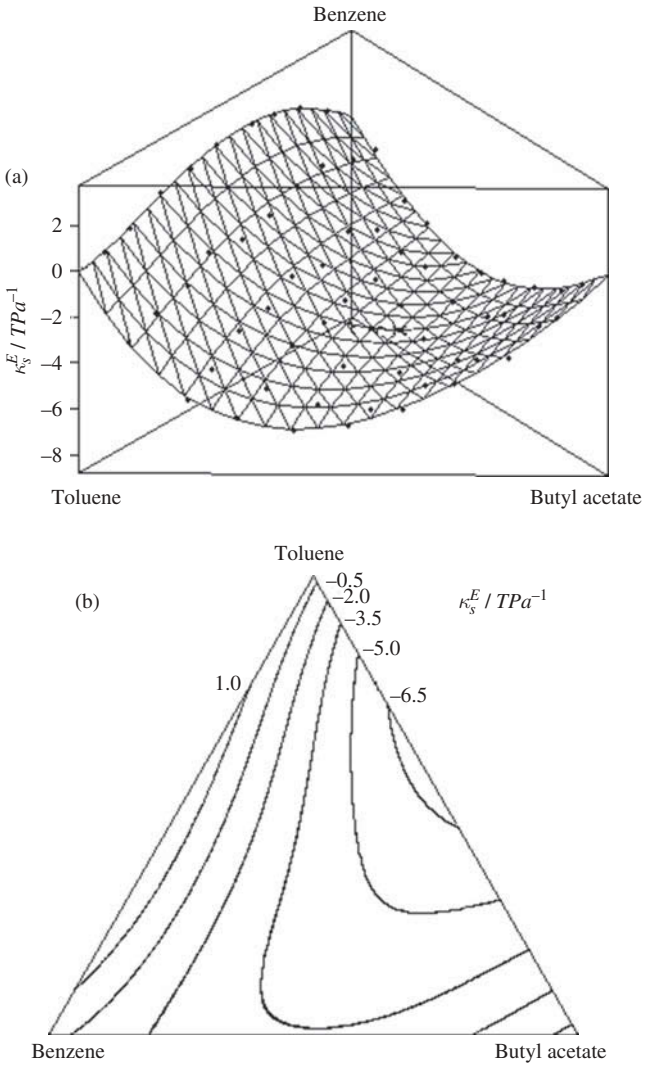

Figure 2. (a). Isentropic compressibility deviation, κ_s^E/TPa^{-1}, for toluene (1) + benzene (2) + butyl acetate (3) at T = 298.15 K. Experimental data, ♦, and surface are calculated from Cibulka expression, Equation (6). (b). Isentropic compressibility deviation, κ_s^E/TPa^{-1}, for toluene (1) + benzene (2) + butyl acetate (3) at T = 298.15 K. Isolines are calculated from Equation (6).

In a wide region of this ternary mixture, the V^E are positive, finding the negative values in the region close to the binary toluene + butyl acetate. Among the factors that produce negative value of excess molar volume is the fact that the interactions occurring between different molecules are stronger than that present between like molecules. Moreover, a complex formation between the free electrons of group COO of the ester and the π electrons of the aromatic ring could increase the negative contribution.[31] The dipole–dipole interaction, caused by the strong polar character of the ester carbonyl group, and toluene molecules could also enhance these negative values.[32] The general behaviour of this ternary mixture indicates that dispersive forces predominate and there are no

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strong specific interactions between the components of this ternary mixture. The excess molar volumes for this ternary mixture were significantly lower than the ternary toluene (1) + benzene (2) + methyl acetate (3) previously published [29]; this could be due to the presence of butyl acetate instead of methyl acetate. In these systems, an increment in the chain length of the ester reduces dispersion forces, while the specific interaction increments, leading to a decrease in excess molar volumes.[33,34]

3.2. *Predictions models*

Symmetrical and asymmetrical solution models were used to predict the derived properties of the ternary mixtures, and the results obtained were analysed by the standard deviations, calculated with Equation (10). The expressions used for the geometrical solution models are listed below:

Kohler,[19]

$$Q_{123} = (x_1 + x_2)^2 Q_{12} + (x_1 + x_3)^2 Q_{13} + (x_2 + x_3)^2 Q_{23} \tag{12}$$

Jacob and Fitzner,[20]

$$Q_{123} = \frac{x_1 x_2 Q_{12}}{[(x_1 + x_3/2)(x_2 + x_3/2)]} + \frac{x_1 x_3 Q_{13}}{[(x_1 + x_2/2)(x_3 + x_2/2)]} + \frac{x_2 x_3 Q_{12}}{[(x_2 + x_1/2)(x_3 + x_1/2)]} \tag{13}$$

Rastogi *et al.*,[21]

$$Q_{123} = [(x_1 + x_2)Q_{12} + (x_1 + x_3)Q_{13} + (x_2 + x_3)Q_{23}] \Big/ 2 \tag{14}$$

Tsao and Smith,[22] asymmetrical model

$$Q_{123} = \frac{x_2 Q_{12}}{1 - x_1} + \frac{x_3 Q_{13}}{1 - x_1} + (1 - x_1)Q_{23} \tag{15}$$

where Q_{123} represents V^E, κ_s^E and η for the ternary mixture. The terms Q_{12}, Q_{13} and Q_{23} correspond to binary contributions. The binary contributions of the calculated properties were evaluated by Redlich and Kister [18] at molar fractions calculated by arbitrary-chosen combination of ternary molar fractions, as was described on a previous work.[27] For asymmetrical model, three sets of possible combination of ternary molar fractions were considered as options (a), (b) or (c).

The results gathered in Table S7 for standard deviations indicate that all the symmetrical and asymmetrical predictive models were able to represent the behaviour of the ternary mixture with more or less precision, with a standard deviation lesser than 0.017 $m^3\ mol^{-1}$, 1.0 TPa^{-1} and 0.004 mPs s for V^E, κ_s^E and η, respectively. However, the predictions with Rastogi *et al.* [21] model presented higher deviations for all the temperatures studied for viscosities predictions. These high deviations are related to the failure of the Rastogi *et al.*'s model to describe mathematically the behaviour of the

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binary systems. As it can be seen in Equation (14), the prediction does not go to the properties of the binary mixture as the third component goes to zero; the prediction goes to a half value of the property. This limitation of the model was already noticed by Bertrand *et al.*[35,36]

Viscosities were predicted by applying group contribution models for the ternary system. The Wu [23] approach has two values for the parameter A, 1 and 2.45, being $A = 2.45$ the best option, presenting a percentage average absolute deviation (%AAD), lower than 1.5%. The GC-UNIMOD group contribution model, Cao, [24] was also applied, exhibiting AAD in the order of 2.5%. The results obtained with the generalised McAllister three-body interaction model, Nhaesi and Asfour, [26] were successful, with AAD lower than 2.2%. All the results of predictive models are presented in Table S8.

4. Conclusions

In this paper, densities, speeds of sound and viscosities of the ternary system toluene (1) + benzene (2) + butyl acetate (3) and the binary system toluene (1) + butyl acetate (2) are reported at 288.15, 293.15, 298.15, 303.15, 308.15, 313.15 and 318.15 K. From these experimental data, excess molar volume, excess isentropic compressibility and dynamic viscosity were computed and successfully correlated by Cibulka's, Singh *et al.'s* and Nagata and Sakura's equations. Symmetrical and asymmetrical solution models were used to predict these properties. We have obtained no significant differences in function of temperature on the behaviour of the geometrical models applied. The model of Rastogi *et al.* predicted the viscosity of the ternary mixtures with significatively higher deviations. The experimental viscosity results were employed to test the predictive capability of three widely used viscosity models, the Wu model, the GC-UNIMOD model and the generalised McAllister three-body interaction model. The analysis showed that the %AAD obtained was lower than 2.5%.

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Supplemental data

Supplemental data for this article can be accessed here.

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