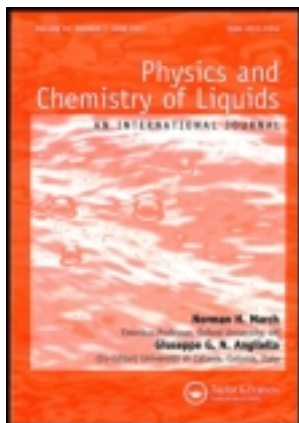


This article was downloaded by: [Lelia Mussari]

On: 25 April 2014, At: 09:50

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Physics and Chemistry of Liquids: An International Journal

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gpchl20>

Thermophysical properties for the ternary systems toluene (1) + benzene (2) + methyl acetate (3), at various temperatures from 288.15 K to 318.15 K

Alejandra Mariano ^{a b}, Lelia Mussari ^a, Alberto Camacho ^a, Salvador Canzonieri ^c & Miguel Postigo ^d

^a Departamento de Química, Facultad de Ingeniería, Universidad Nacional del Comahue, Buenos Aires, 1400- (8300), Neuquén, Argentina

^b CONICET - CCT Comahue, Argentina

^c Departamento de Física, Facultad de Ingeniería, Universidad Nacional del Comahue, Buenos Aires, 1400- (8300), Neuquén, Argentina

^d Deceased, December 2009

Published online: 26 Jul 2013.

To cite this article: Alejandra Mariano, Lelia Mussari, Alberto Camacho, Salvador Canzonieri & Miguel Postigo (2013) Thermophysical properties for the ternary systems toluene (1) + benzene (2) + methyl acetate (3), at various temperatures from 288.15 K to 318.15 K, Physics and Chemistry of Liquids: An International Journal, 51:6, 731-741, DOI: [10.1080/00319104.2013.812018](https://doi.org/10.1080/00319104.2013.812018)

To link to this article: <http://dx.doi.org/10.1080/00319104.2013.812018>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims,

proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>

Thermophysical properties for the ternary systems toluene (1) + benzene (2) + methyl acetate (3), at various temperatures from 288.15 K to 318.15 K

Alejandra Mariano^{a,b}, Lelia Mussari^{a*}, Alberto Camacho^a, Salvador Canzonieri^c
and Miguel Postigo[†]

^aDepartamento de Química, Facultad de Ingeniería, Universidad Nacional del Comahue, Buenos Aires 1400– (8300) Neuquén, Argentina; ^bCONICET – CCT Comahue, Argentina; ^cDepartamento de Física, Facultad de Ingeniería, Universidad Nacional del Comahue, Buenos Aires 1400– (8300) Neuquén, Argentina; [†]Deceased, December 2009

(Received 10 October 2012; final version received 2 June 2013)

Density, speed of sound and viscosity for the ternary system formed by toluene, benzene and methyl acetate and their corresponding binaries were measured at atmospheric pressure in the temperature range of 288.15 K to 318.15 K, every 5 K. Experimental data were used to calculate derived properties: excess molar volume, isentropic compressibility, isentropic compressibility deviation, viscosity deviation and excess free energy of activation for viscous flow. These magnitudes were fitted to different equations available in the literature. In addition, geometrical models have been used to predict ternary magnitudes. Predictions of viscosities for the ternary system were performed by group contribution models. Molecular interactions among the components of the mixtures were inferred from the sign of the excess and deviation properties.

Keywords: density; viscosity; speed of sound; toluene; benzene; esters

1. Introduction

The knowledge of the physical properties as much of pure compounds as of mixtures has been and continues being the centre of interest of many investigations in the fields of the Physics, Physical Chemistry and Chemical Engineering. The mixtures can contain polar molecules, non-polar, associated, or molecules with different sizes. In addition, orders of concentration, ranges of temperature and pressure are due to be considered. Our group of investigation has selected for several years to study systems that present interactions between polar and non-polar molecules. One of the lines of our research is the measurement of thermophysical properties of mixtures containing aromatic hydrocarbons and linear esters [1–5]. The literature reflects an important number of publications for binary systems with hydrocarbons and different types of molecules, but this is not the case for ternary systems. Particularly, the experimental information presented in this work includes density, ρ , speed of sound, u , and viscosity, η , for the ternary systems: toluene (1) + benzene (2) + methyl acetate (3) and the corresponding binary systems, except the toluene + methyl acetate system, that was already presented [3,4].

Using the experimental information, the excess molar volume, V^E ; isentropic compressibility, κ_s ; isentropic compressibility deviation, $\Delta\kappa_s$; viscosity deviation, $\Delta\eta$; and

*Corresponding author. Email: lmussari@yahoo.com

excess free energy of activation for viscous flow, ΔG^{*E} , were calculated. These properties were fitted to different expressions for ternary mixtures: Cibulka [6], Singh *et al.* [7], Nagata and Sakura [8], using Redlich and Kister [9] equation to calculate binary contributions. Standard deviations between experimental and calculated values were calculated.

As the behaviour of a ternary mixture depends strongly on the behaviour of the corresponding binaries, we used symmetrical and unsymmetrical geometrical models to estimate the properties of the ternary systems based on the contribution of the binary data: Tsao and Smith [10], Kohler [11], Jacob and Fitzner [12] and Rastogi *et al.* [13].

Predictions of viscosities by the group contribution model of Wu [14] and the group contribution thermodynamics viscosity model (GC-UNIMOD), Cao [15] was performed at seven temperatures for the ternary system.

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

2. Experimental section

Toluene (Sigma-Aldrich, St. Louis, MO, USA, anhydrous, 99.8%, CAS 108-88-3), benzene (Merck, Darmstadt, Germany, puriss p.a., 99.7%, CAS 71-43-2) and methyl acetate (Merck-Schuchardt, Hohenbrunn, Germany, for synthesis, 99.0%, CAS 79-20-9). Their measured properties compared to those found in literature are presented in Table 1. All the liquids were dried over 0.4 nm Union Carbide molecular sieves from Fluka and partially degassed with an ultrasonic bath before use.

The procedure for mixtures preparation was described previously [3]. The uncertainty in mole fraction calculation is $\pm 1 \times 10^{-4}$.

Density and speed of sound were measured at 288.15 K, 293.15 K, 298.15 K, 303.15 K, 308.15 K, 313.15 K and 318.15 K (± 0.01 K) by a digital density/sound velocity analyser, automatically thermostated Anton Paar DSA 48 (estimated density measurement uncertainty, ± 0.01 kg m⁻³, speed of sound precision 0.05 m s⁻¹).

Viscosities were measured with a falling ball microviscometer Thermo Haake (Karlsruhe, Germany), model Microvisco 2, automatically thermostated (± 0.01 K) with a precision of 2×10^{-3} mPa s.

3. Results and discussion

Table 1 discloses measured density, speed of sound and viscosity, respectively, for pure compounds at seven temperatures as well as some literature values.

Densities, speeds of sound and viscosities for the binary mixtures toluene + benzene and benzene + methyl acetate are gathered in Tables 1S and 2S, respectively, presented as supplementary material, available online at <http://informahealthcare.com/doi/suppl/10.1080/00319104.2013.812018>. Data for the third binary has been published previously [3,4].

In Tables 2–4, we present density, speed of sound and viscosity, respectively, for ternary mixtures toluene (1) + benzene (2) + methyl acetate (3). Experimental values were measured over the entire composition range for the ternary compositions presented, at seven temperatures, 288.15 K, 293.15 K, 298.15 K, 303.15 K, 308.15 K, 313.15 K and 318.15 K (± 0.01 K).

Derived properties were calculated for the binary and ternary mixtures, with the following expressions:

Table 1. Density, ρ (kg m^{-3}), speed of sound, u (m s^{-1}), and viscosities of pure components, η (mPa s), experimental and literature values between 288.15 K and 318.15 K.

T (K)	288.15	293.15	298.15	303.15	308.15	313.15	318.15
ρ (kg m^{-3})							
Benzene							
Experimental	884.30	879.00	873.67	868.32	862.96	857.57	852.15
Literature		879.00 [16]	873.60 [16]	868.29 [16]	862.95 [20]	857.97 [20]	852.0 [21]
Toluene							
Experimental	871.66	867.00	862.34	857.65	852.96	848.24	843.51
Literature	871.3 [18]	866.93 [18]	862.29 [18]	857.54 [16]	852.85 [20]	848.15 [20]	
Methyl acetate							
Experimental	940.52	933.97	927.36	920.70	913.97	907.17	900.32
Literature		934.2 [16]	927.3 [17]	920.4 [17]		906.4 [17]	
u (m s^{-1})							
Benzene							
Experimental	1351.2	1327.0	1301.9	1277.7	1254.0	1230.6	1207.5
Literature			1304 [20]		1255 [21]		1227 [21]
Toluene							
Experimental	1352.4	1329.5	1306.3	1283.8	1262.0	1240.2	1218.9
Literature			1304.a	1285 [23]	1262.0 [20]		
Methyl acetate							
Experimental	1201.7	1178.2	1154.0	1130.3	1107.0	1083.7	1060.5
Literature			1150.6 [22]				
η (mPa s)							
Benzene							
Experimental	1351.2	1327.0	1301.9	1277.7	1254.0	1230.6	1207.5
Literature			1304 [20]		1255 [21]		1227 [21]
Toluene							
Experimental	1352.4	1329.5	1306.3	1283.8	1262.0	1240.2	1218.9
Literature			1304.a	1285 [23]	1262.0 [20]		
Methyl acetate							
Experimental	1201.7	1178.2	1154.0	1130.3	1107.0	1083.7	1060.5
Literature			1150.6 [22]				

Sources: Singh *et al.* [7], Riddick *et al.* [16], TRC – thermodynamic tables non-hydrocarbons [17], Palaiologou *et al.* [18], Cerdeir a *et al.* [19], George *et al.* [20], Sastry *et al.* [21], Canosa y col. [22], Krishnan y col. [23], Viswanath *et al.* [24], Shah *et al.* [25], Moumouzias *et al.* [26], Eysers *et al.* [27].

Table 2. Densities, ρ (kg m^{-3}), of the ternary system toluene (1) + benzene (2) + methyl acetate (3) at different temperatures from 288.15 K to 318.15 K, as a function of molar fractions of components 1 and 2.

x_1	x_2	288.15	293.15	298.15	303.15	308.15	313.15	318.15
0.0909	0.8333	885.74	880.44	875.11	869.76	864.40	859.03	853.61
0.1982	0.7020	884.85	879.62	874.41	869.11	863.77	858.47	853.12
0.3011	0.6173	882.53	877.48	872.23	867.03	861.86	856.63	851.46
0.3977	0.4931	882.33	877.26	872.08	867.01	861.77	856.67	851.47
0.4970	0.4027	880.63	875.64	870.57	865.52	860.48	855.32	850.17
0.6260	0.2940	878.34	873.45	868.43	863.56	858.51	853.58	848.56
0.6931	0.2058	878.44	873.54	868.63	863.71	858.72	853.77	848.76
0.8391	0.0779	876.33	871.56	866.73	861.90	857.04	852.15	847.26
0.1026	0.6952	890.76	885.38	879.97	874.54	869.00	863.53	858.08
0.2089	0.6030	888.30	883.05	877.77	872.42	867.11	861.63	856.23
0.3024	0.4949	887.56	882.31	877.06	871.76	866.43	861.10	855.72
0.4112	0.4030	885.31	880.14	874.99	869.81	864.67	859.36	854.11
0.5010	0.2988	884.76	879.65	874.52	869.36	864.22	859.01	853.76
0.6169	0.1896	883.16	878.12	873.01	868.01	863.00	857.78	852.62
0.6989	0.0985	882.65	877.66	872.65	867.61	862.59	857.50	852.37
0.0907	0.6205	894.95	889.48	883.88	878.43	872.83	867.26	861.63
0.2061	0.4944	893.38	888.00	882.55	877.11	871.59	866.06	860.50
0.3043	0.4019	891.59	886.24	880.91	875.52	870.14	864.68	859.24
0.4160	0.3012	889.53	884.32	879.00	873.78	868.40	863.10	857.73
0.4976	0.2021	889.25	884.05	878.84	873.64	868.24	862.99	857.62
0.6166	0.0885	887.65	882.54	877.37	872.18	867.02	861.77	856.52
0.1003	0.5011	900.00	894.42	888.81	883.16	877.51	871.77	866.03
0.1985	0.3810	899.40	893.87	888.26	882.72	877.08	871.39	865.68
0.3061	0.2962	896.55	891.15	885.61	880.19	874.71	869.10	863.45
0.3984	0.2061	895.08	889.76	884.38	878.95	873.49	868.01	862.47
0.5051	0.0967	893.83	888.52	883.19	877.90	872.50	867.00	861.53
0.1034	0.3983	905.19	899.50	893.76	888.00	882.21	876.34	870.43
0.1992	0.3044	903.35	897.72	892.06	886.39	880.62	874.88	869.07
0.2970	0.2052	901.83	896.26	890.69	885.10	879.43	873.69	867.98
0.3989	0.0998	900.53	895.03	889.52	883.90	878.36	872.68	867.05
0.1006	0.3095	910.43	904.62	898.69	892.87	886.94	880.95	874.91
0.1975	0.1953	909.59	903.82	898.00	892.20	886.38	880.35	874.42
0.3022	0.1049	907.04	901.35	895.63	889.91	884.16	878.32	872.44
0.1013	0.2012	916.88	910.97	904.92	898.88	892.84	886.51	880.47
0.2018	0.0976	915.07	909.23	903.26	897.26	891.35	885.20	879.14
0.1021	0.1036	923.21	917.12	910.97	904.77	898.52	892.20	885.85

Excess molar volumes was calculated with Equation (1):

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

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

Isentropic compressibility, κ_s , was calculated with Equation (2) and isentropic compressibility deviation, $\Delta\kappa_s$, with Equation (3). The estimated uncertainty in κ_s ; isentropic compressibility is $\pm 0.1 \times 10^{-12} \text{ Pa}^{-1}$.

Table 3. Sound velocities, u (m s^{-1}), of the ternary system toluene (1) + benzene (2) + methyl acetate (3) at different temperatures from 288.15 K to 318.15 K, as a function of molar fractions of components 1 and 2.

x_1	x_2	288.15	293.15	298.15	303.15	308.15	313.15	318.15
0.0909	0.8333	1338.1	1314.2	1289.2	1265.3	1241.8	1218.6	1195.7
0.1982	0.7020	1334.0	1310.3	1286.0	1262.0	1238.6	1215.7	1192.9
0.3011	0.6173	1336.9	1313.5	1289.1	1265.5	1242.4	1219.5	1196.9
0.3977	0.4931	1332.9	1309.7	1285.6	1262.0	1239.2	1216.2	1194.0
0.4970	0.4027	1334.4	1311.5	1287.6	1264.3	1241.6	1218.8	1196.8
0.6260	0.2940	1338.0	1315.1	1291.8	1268.6	1246.1	1223.7	1201.7
0.6931	0.2058	1335.5	1312.6	1289.4	1266.3	1244.0	1221.6	1199.8
0.8391	0.0779	1339.7	1316.7	1293.2	1270.8	1248.8	1226.6	1204.8
0.1026	0.6952	1317.9	1294.3	1269.7	1245.7	1222.3	1199.1	1176.1
0.2089	0.6030	1320.2	1296.8	1272.5	1248.7	1225.3	1202.3	1179.6
0.3024	0.4949	1318.4	1295.2	1270.9	1247.2	1224.3	1201.2	1178.7
0.4112	0.4030	1321.3	1298.4	1274.3	1251.1	1228.1	1205.3	1182.9
0.5010	0.2988	1320.0	1297.1	1273.2	1249.9	1227.3	1204.7	1182.4
0.6169	0.1896	1322.3	1299.2	1275.6	1252.3	1229.8	1207.9	1185.6
0.6989	0.0985	1321.4	1298.6	1275.4	1252.4	1230.1	1207.7	1185.9
0.0907	0.6205	1304.4	1280.7	1256.2	1232.2	1208.8	1185.4	1162.6
0.2061	0.4944	1303.2	1279.9	1255.5	1232.0	1208.7	1185.7	1162.8
0.3043	0.4019	1305.1	1281.6	1257.4	1233.9	1211.0	1188.1	1165.5
0.4160	0.3012	1307.3	1284.5	1260.5	1237.2	1214.4	1191.7	1169.3
0.4976	0.2021	1306.0	1282.7	1259.1	1236.0	1213.3	1190.7	1168.5
0.6166	0.0885	1307.9	1285.5	1261.5	1238.7	1216.0	1193.7	1171.9
0.1003	0.5011	1288.0	1263.8	1239.8	1215.9	1192.5	1169.4	1146.3
0.1985	0.3810	1285.4	1262.1	1237.8	1214.2	1190.7	1168.0	1145.2
0.3061	0.2962	1290.3	1266.6	1242.6	1219.3	1196.2	1173.3	1150.8
0.3984	0.2061	1291.3	1268.4	1244.5	1221.3	1198.4	1175.7	1153.1
0.5051	0.0967	1292.2	1269.7	1245.9	1222.5	1200.2	1177.5	1155.4
0.1034	0.3983	1272.7	1249.3	1225.3	1201.4	1178.0	1154.9	1132.0
0.1992	0.3044	1274.1	1250.9	1227.2	1203.6	1180.3	1157.4	1134.5
0.2970	0.2052	1275.7	1252.6	1228.7	1205.6	1182.2	1159.4	1136.7
0.3989	0.0998	1276.4	1253.9	1229.9	1208.0	1183.9	1161.2	1138.8
0.1006	0.3095	1259.5	1236.1	1211.9	1188.4	1165.4	1142.0	1118.8
0.1975	0.1953	1258.8	1235.3	1211.3	1187.7	1164.7	1141.8	1118.9
0.3022	0.1049	1262.9	1239.5	1215.2	1191.9	1169.0	1146.3	1123.6
0.1013	0.2012	1244.7	1221.4	1197.3	1173.5	1150.3	1127.0	1104.0
0.2018	0.0976	1246.4	1223.2	1199.3	1175.9	1152.6	1129.2	1106.3
0.1021	0.1036	1231.4	1207.9	1183.8	1160.2	1137.0	1113.8	1090.8

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

$$\Delta\kappa_s = \kappa_s - \sum_{i=1}^n x_i \kappa_{s_i} \quad (3)$$

where x_i is the mole fraction, and ρ and u are the pure component density and speed of sound, respectively.

Dynamic viscosity was indirectly determined from the kinematic viscosity and density of the mixture. The estimated uncertainty in the dynamic viscosity is ± 0.002 mPa s.

Deviation of dynamic viscosity was calculated with Equation (4):

Table 4. Viscosities, η (mPa s), of the ternary system toluene (1) + benzene (2) + methyl acetate (3) at different temperatures from 288.15 K to 318.15 K, as a function of molar fractions of components 1 and 2.

x_1	x_2	288.15	293.15	298.15	303.15	308.15	313.15	318.15
0.0934	0.8317	0.650	0.606	0.565	0.528	0.496	0.465	0.437
0.2053	0.6837	0.626	0.584	0.546	0.511	0.481	0.453	0.427
0.3004	0.6253	0.634	0.591	0.555	0.520	0.489	0.459	0.432
0.4012	0.4958	0.615	0.576	0.540	0.506	0.477	0.449	0.424
0.5068	0.3980	0.611	0.573	0.537	0.505	0.476	0.448	0.423
0.6126	0.3090	0.613	0.574	0.540	0.507	0.478	0.450	0.426
0.7394	0.1891	0.611	0.573	0.540	0.508	0.479	0.451	0.427
0.8060	0.1071	0.603	0.567	0.533	0.502	0.474	0.449	0.424
0.0851	0.7434	0.607	0.569	0.531	0.498	0.467	0.439	0.414
0.1975	0.6390	0.603	0.565	0.528	0.496	0.465	0.439	0.414
0.2965	0.5298	0.595	0.557	0.522	0.490	0.461	0.435	0.410
0.4163	0.4166	0.590	0.553	0.519	0.486	0.459	0.433	0.410
0.5208	0.2900	0.578	0.543	0.510	0.479	0.452	0.427	0.405
0.6386	0.1902	0.581	0.546	0.513	0.483	0.456	0.431	0.408
0.7396	0.0845	0.579	0.544	0.512	0.483	0.456	0.430	0.408
0.0865	0.6268	0.564	0.527	0.494	0.464	0.438	0.412	0.391
0.1941	0.5212	0.559	0.524	0.492	0.463	0.437	0.411	0.390
0.3111	0.4132	0.557	0.523	0.491	0.462	0.437	0.412	0.391
0.4206	0.2967	0.553	0.519	0.489	0.459	0.434	0.409	0.388
0.5210	0.1979	0.551	0.516	0.487	0.458	0.433	0.410	0.389
0.6369	0.0829	0.549	0.518	0.489	0.460	0.435	0.411	0.390
0.0834	0.5365	0.532	0.499	0.467	0.442	0.418	0.394	0.374
0.1938	0.4152	0.526	0.494	0.464	0.438	0.414	0.391	0.372
0.2886	0.3286	0.528	0.496	0.467	0.439	0.416	0.393	0.373
0.4035	0.1821	0.516	0.486	0.460	0.432	0.409	0.387	0.368
0.5099	0.1135	0.525	0.495	0.468	0.440	0.416	0.394	0.374
0.1079	0.3966	0.498	0.469	0.442	0.417	0.394	0.373	0.354
0.1862	0.2893	0.490	0.461	0.435	0.411	0.389	0.369	0.351
0.2909	0.2158	0.499	0.469	0.443	0.418	0.395	0.374	0.356
0.3942	0.1151	0.500	0.471	0.445	0.420	0.398	0.377	0.358
0.0842	0.2869	0.464	0.437	0.414	0.393	0.372	0.352	0.335
0.1933	0.1866	0.469	0.442	0.418	0.395	0.374	0.355	0.339
0.2990	0.1292	0.481	0.453	0.428	0.404	0.384	0.364	0.346
0.0871	0.1914	0.448	0.424	0.400	0.379	0.360	0.341	0.325
0.2080	0.1071	0.459	0.431	0.408	0.386	0.366	0.348	0.332
0.1000	0.1038	0.436	0.411	0.389	0.370	0.351	0.334	0.319

$$\Delta\eta = \eta - \sum_{i=1}^n x_i \eta_i \quad (4)$$

where η (mPa s) is the mixture dynamic viscosity, x_i is the mole fraction of component i in the mixture and η_i is the pure component viscosity.

The excess free energy of activation for viscous flow was calculated with Equation (5):

$$\Delta G^{*E} = RT(\ln(\eta \cdot V) - \sum_{i=1}^n x_i \ln(\eta_i V_i)) \quad (5)$$

where x_i , η_i and V_i represent the mole fraction, dynamic viscosity (mPa s) and molar volume ($\text{m}^3 \text{mol}^{-1}$) of the pure component i , respectively, and V is the molar volume of the mixture, R is the universal gas constant ($\text{J mol}^{-1} \text{K}^{-1}$), T is the absolute temperature and n is the number of components in the mixture. The symbols without subscript refer to the property of the mixture. The estimated uncertainty in excess free energy of activation for viscous flow is $\pm 10 \text{ J mol}^{-1}$.

3.1. Fitting equations

Binary data was adjusted to the polynomial expression of Redlich Kister [9], Equation (6):

$$Q = x_1 x_2 \sum_{i=0}^n a_i (2x_1 - 1)^i \quad (6)$$

where Q refers to every measured or derived property in this work. a_i are the adjustable coefficients, listed in Table 3S (supplementary material), together with standard deviation, calculated by Equation (7):

$$\sigma = \sqrt{\sum_{i=1}^n (Q(\text{exp})_i - Q(\text{calc})_i)^2 / (n - p)} \quad (7)$$

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

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

Cibulka [6],

$$Q = Q_{12^*} + Q_{13^*} + Q_{23^*} + x_1 x_2 x_3 (A + B x_1 + C x_2) \quad (8)$$

Singh *et al.* [7],

$$Q = Q_{12^*} + Q_{13^*} + Q_{23^*} + A x_1 x_2 x_3 + B x_1 (x_2 - x_3) + C x_1^2 (x_2 - x_3)^2 \quad (9)$$

Nagata and Sakura [8],

$$Q = Q_{12^*} + Q_{13^*} + Q_{23^*} + x_1 x_2 x_3 \Delta \quad (10)$$

In these expressions A , B , C and Δ are the adjustable parameters. The letter Q stands for ρ , V^E , $\Delta\kappa_s$, $\Delta\eta$ and ΔG^{*E} . The terms Q_{12^*} , Q_{13^*} and Q_{23^*} correspond to binary contributions. These terms were evaluated by Redlich and Kister [9] equation at the molar fractions of the ternary mixture. The star in Q_{ij^*} indicates that the sum $x_i + x_j$ it is not equal to one.

Fitting parameters for Cibulka, Nagata and Singh equations and standard deviation, σ , calculated with Equation (7) at various temperatures from 288.15 K to 318.15 K are gathered in Table 4S as supplementary material.

Figures 1(a)–4(a) show, at 298.15 K, experimental data and surfaces calculated from Equation (8), the fitting equation of Cibulka [6], of the properties excess molar volume, viscosity deviation, excess free energy of activation and isentropic compressibility deviation. In Figures 1(b)–4(b), the corresponding isolines for Cibulka surfaces are depicted, also at 298.15 K.

Positive excess molar volumes, Figures 1(a) and (b), indicate that dispersive forces predominate and there are no strong specific interactions between the components of this mixture. This is also reinforced by negative values of viscosity deviation and excess free energy of activation for viscous flow, Figures 2(a) and (b) and Figures 3(a) and (b), respectively. Isentropic compressibility deviations were positive for almost all compositions except for the region close to the binary mixture (toluene + methyl acetate) in the

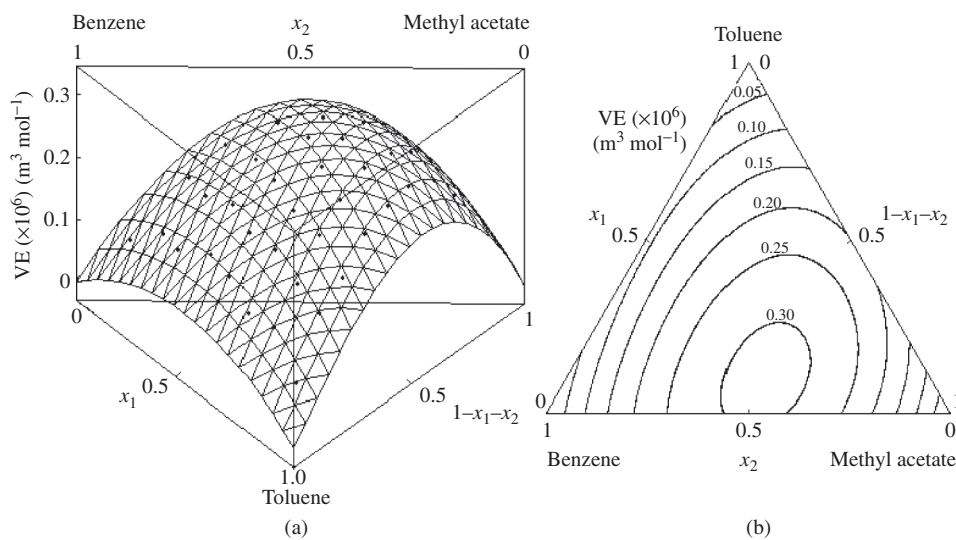


Figure 1. Excess molar volume, V^E , $10^6 \text{ m}^3 \text{ mol}^{-1}$, for toluene (1) + benzene (2) + methyl acetate (3) at $T = 298.15 \text{ K}$. (a) Experimental data, \diamond , and surface calculated from Cibulka expression, Equation (8). (b) Isolines calculated from Equation (8).

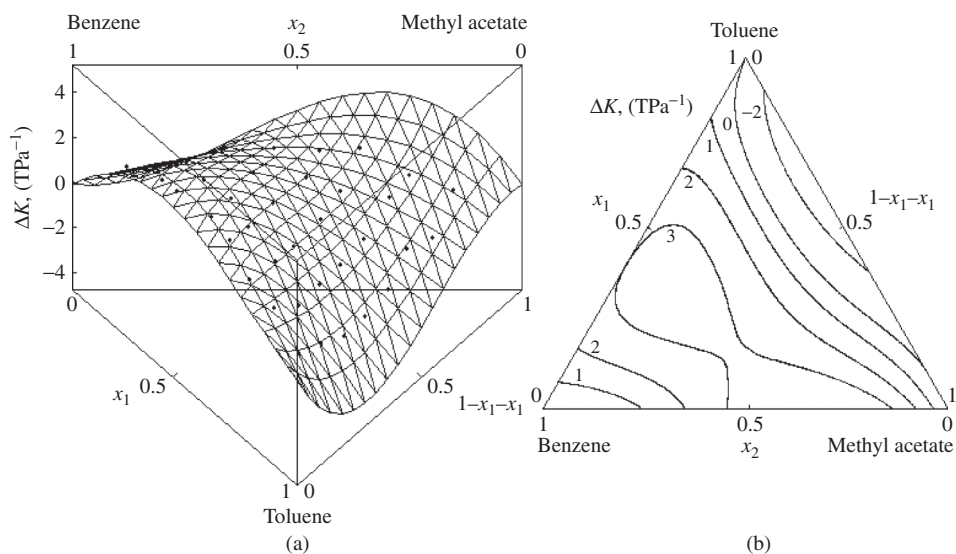


Figure 2. Isentropic compressibility deviation, $\Delta\kappa_s/\text{TPa}^{-1}$, for toluene (1) + benzene (2) + methyl acetate (3) at $T = 298.15 \text{ K}$. (a) Experimental data, \diamond , and surface calculated from Cibulka expression, Equation (8). (b) Isolines calculated from Equation (8).

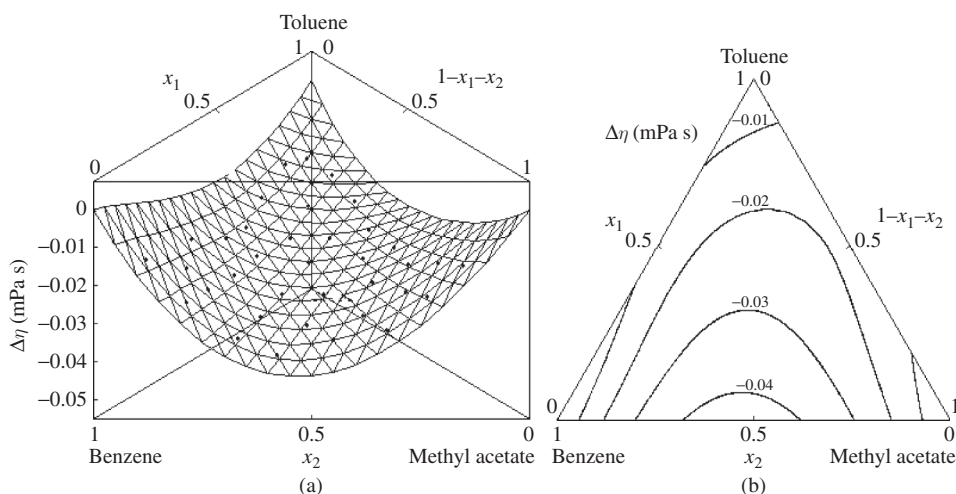


Figure 3. Viscosity deviation, $\Delta\eta/\text{mPa} \cdot \text{s}$, for toluene (1) + benzene (2) + methyl acetate (3) at $T = 298.15$ K. (a) Experimental data, \blacklozenge , and surface calculated from Cibulka expression, Equation (8). (b) Isolines calculated from Equation (8).

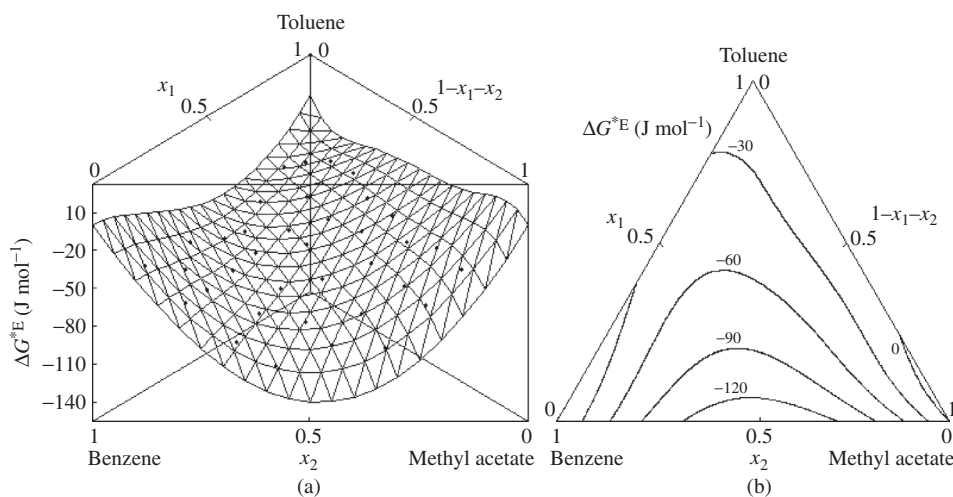


Figure 4. Excess free energy of activation for viscous flow, $\Delta G^*E/\text{J mol}^{-1}$, for toluene (1) + benzene (2) + methyl acetate (3) at $T = 298.15$ K. (a) Experimental data, \blacklozenge , and surface calculated from Cibulka expression, Equation (8). (b) Isolines calculated from Equation (8).

toluene rich zone, Figures 4(a) and (b). This behaviour could be imputable to complex interactions between the aromatic ring and the COO group [28].

3.2. Predictions models

Symmetrical and unsymmetrical solution models were used to predict measured and derived properties of the ternary mixtures. The results of the application of these geometrical models were analysed by the standard deviations, calculated with Equation (8). The expressions used for the geometrical solution models are listed further down.

Kohler [11],

$$Q_{123}^E = (x_1 + x_2)^2 Q_{12}^E + (x_1 + x_3)^2 Q_{13}^E + (x_2 + x_3)^2 Q_{23}^E \quad (11)$$

Jacob and Fitzner [12],

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

Rastogi *et al.* [13],

$$Q_{123}^E = [(x_1 + x_2)Q_{12}^E + (x_1 + x_3)Q_{13}^E + (x_2 + x_3)Q_{23}^E]/2 \quad (13)$$

Tsao and Smith [10], asymmetrical model

$$Q_{123}^E = \frac{x_2 Q_{12}^E}{1 - x_1} + \frac{x_3 Q_{13}^E}{1 - x_1} + (1 - x_1)Q_{23}^E \quad (14)$$

These models use binary contributions evaluated by Redlich and Kister [9] equations at molar fractions calculated by arbitrary chosen combination of ternary molar fractions, as were described on a previous work [1].

As it is shown in Table 5S, presented as supplementary material, all the symmetrical predictive models were able to represent the behaviour of the ternary mixture with more or less precision evaluated on the basis of the mean standard deviation. However, Rastogui predictions presented higher deviations. For the Tsao-Smith, asymmetrical model the option (a) presented smaller standard deviation.

Predictions of viscosities by group contribution models for the ternary system were performed, using Wu [14] approach with parameter $A = 1$ and $A = 2.45$, being A equal 2.45, the best option presenting smaller percentage relative error, $E_r\%$. The GC-UNIMOD [15] group contribution model was also applied, exhibiting errors in the order of 4%. The results are presented in Table 6S (supplementary material).

4. Conclusions

In this article, densities, speed of sound and viscosities of the binary and ternary mixtures containing toluene, benzene and methyl acetate are reported at 288.15 K, 293.15 K, 298.15 K, 303.15 K, 308.15 K, 313.15 K and 318.15 K. From these data, excess molar volume, isentropic compressibility, isentropic compressibility deviation, viscosity deviation and excess free energy of activation for viscous flow were computed and successfully correlated by Cibulka, Singh *et al.* and Nagata and Sakura equations. Symmetrical and unsymmetrical solution models were used to predict these properties. We have obtained no significant differences between the symmetrical geometrical models applied except for Rastogui predictions with higher deviations. For the Tsao Smith asymmetrical model, the set of ternary molar fractions chosen arbitrarily to evaluate binary contributions that presented smaller standard deviation was option (a), as was described on a previous

work [1]. Predictions of viscosities by group contribution models for the ternary system were performed, using Wu and GC-UNIMOD both exhibiting errors in the order of 4–6%.

Acknowledgment

The authors are grateful to the Argentinian National Research Council (CONICET) and to Universidad Nacional del Comahue (UNComa) for their financial support.

References

- [1] A. Mariano, M. Postigo, D. González-Salgado, and L. Romani, *J. Chem. Thermodyn.* **39**, 218–224 (2007).
- [2] A. Mariano, S. Canzonieri, A. Camacho, and M. Postigo, *Innovación*. **18**, 25–33 (2006–2007).
- [3] M. Postigo, S. Canzonieri, and A. Mariano, *J. Mol. Liq.* **143**, 115–118 (2008).
- [4] A. Camacho, A. Mariano, L. Mussari, R. Tabarrozzi, and S. Canzonieri, *Av. Cienc. Ingeniería* **3**, 41–50 (2012).
- [5] A. Mariano, S. Canzonieri, A. Camacho, A. Mainar, and M. Postigo, *Phys. Chem. Liq.* **49**, 720–728 (2011).
- [6] I. Cibulka, *Coll. Czech. Commun.* **47**, 1414–1419 (1982).
- [7] P. Singh, P.R. Nigam, S. Sharma, and S. Aggarwal, *Fluid Phase Equilib.* **18**, 333–344 (1984).
- [8] M. Nagata and J.J. Sakura, *Chem. Soc. Faraday Trans.* **83**, 2449–2457 (1987).
- [9] O. Redlich and A.T. Kister, *Ind. Eng. Chem.* **40**, 345–348 (1948).
- [10] C.C. Tsao and J.M. Smith, *Chem. Eng. Prog. Symp.* **7**, 107–117 (1953).
- [11] F. Kohler, *Monatsh. Chem.* **91**, 738–740 (1960).
- [12] K.T. Jacob, and K. Fitzner, *Thermochim. Acta.* **18**, 197–206 (1977).
- [13] R.P. Rastogi, J. Nath, S.S. Das, *J. Chem. Eng. Data.* **22**, 249–252 (1977).
- [14] D.T. Wu, *Fluid Phase Equilibria.* **30**, 149–156 (1986).
- [15] W. Cao, K. Knudsen, A. Fredenslund, and P. Rasmussen, *Ind. Eng. Chem. Res.* **32**, 2088–2092 (1993).
- [16] J.A. Riddick, W.B. Bunger, *Organic Solvents-Techniques of Chemistry*, 3rd ed. (Wiley-Interscience, New York, 1970).
- [17] *TRC – Thermodynamic Tables Non Hydrocarbons* (Thermodynamic Research Center, Texas A&M University, College Station, TX, 1966).
- [18] M.M. Palaologou and I.E. Molinou, *J. Chem. Eng. Data.* **40**, 880–882 (1995).
- [19] C.A. Cerdeiriña, C.A. Tovar, D. González-Salgado, E. Carballo, and L. Romani, *Phys. Chem. Chem. Phys.* **3**, 5230–5236 (2001).
- [20] J. George and N.V. Sastry, *J. Chem. Eng. Data.* **48**, 977–989 (2003).
- [21] N.V. Sastry, A. George, N.J. Jain, and P. Bahadur, *J. Chem. Eng. Data.* **44**, 456–464 (1999).
- [22] J. Canosa, A. Rodríguez, and J.J. Tojo, *Chem. Eng. Data.* **43**, 961–966 (1998).
- [23] K.M. Krishanan, K. Rambabu, P. Venkateswarlu, and G.K.J. Raman, *Chem. Eng. Data.* **40**, 132–135 (1995).
- [24] D.S. Viswanath and G. Natarajan, *Data Book on the Viscosity of Liquids* (Hemisphere Publishing Corporation, New York, 1989).
- [25] J. Shah, M.M. Vakharia, M.V. Pandya, A.T. Patel, J.H. Partiwalla, P.P. Palsanawala, and S.L. Oswal, *Ind. J. Technol.* **27**, 306–312 (1989).
- [26] G. Moumouzias and G.J. Ritzoulis, *J. Chem. Eng. Data.* **37**, 482–483 (1992).
- [27] C.H. Evers' and D.F. Williams, *J. Chem. Eng. Data.* **32**, 344–348 (1987).
- [28] J.P.E. Grolrier, D. Ballet, and A. Villard, *J. Chem. Thermodyn.* **6**, 895–908 (1974).