Available online at www.sciencedirect.com
SCIENCE DIRECT®
Thermochimica Acta 438 (2005) 9–15
thermochimica acta
www.elsevier.com/locate/tca

Volumetric and viscometric studies of molecular interaction of the ternary system toluene (1) + cyclohexane (2) + *n*-hexane (3) at 298.15 K

H. Iloukhani [*], M. Rezaei-Sameti, H.A. Zarei

Department of Chemistry, Faculty of Science, Bu-Ali Sina University, Hamadan 65174, Iran

Received 10 May 2005; received in revised form 21 July 2005; accepted 3 August 2005
Available online 2 September 2005

Abstract

The densities ρ, and viscosities η, of pure toluene, cyclohexane, and *n*-hexane and those of their binary and ternary mixtures have been measured at 298.15 K and atmospheric pressure over the entire range of compositions. Excess molar volumes V^{E}_{123}, viscosity deviations $\Delta\eta_{123}$, and excess Gibbs energy of activation G^{*E}_{123}, were obtained from the experimental results and those values for the binary and ternary systems were fitted to Redlich–Kister's and Cibulka's type function in terms of mole fractions. The V^{E}_{123} data were positive and $\Delta\eta_{123}$ and G^{*E}_{123}, values were negative. Several semi-empirical relations are used to predict the ternary excess molar volumes and viscosity deviations from experimental results on the constituted ternary and analyzed to discuss the nature and strength of intermolecular interactions in these mixtures.

Keywords: Excess molar volume; Viscosity; Toluene; Cyclohexane; *n*-Hexane

1. Introduction

A knowledge of the densities and viscosities of studied fluids and fluid mixtures is estimated to understand the molecular interactions between the molecules, to develop new theoretical models and also for the engineering applications of absorption heat pumps and heat transformers.

This paper, as part of a continuing study in our laboratory [1–4], reports the precise measurement of density and kinematic viscosity for the ternary system formed by toluene (1) + cyclohexane (2) + *n*-hexane (3), and constituted binary mixtures. Our results are compared with values of V^{E} for the binary mixtures (cyclohexane + *n*-hexane) and (toluene + *n*-hexane) which were reported earlier [5–8]. Excess molar volumes, deviation in viscosities and excess Gibbs energy of activation were calculated for the studied ternary mixtures on the excess properties are analyzed because of their importance for inferring which type of interactions predominate in liquid mixtures.

2. Experimental

The compounds used toluene (>99%); cyclohexane (99.5%); *n*-hexane (>99%) were obtained from Merck .Toluene and *n*-hexane used, were purified by distillation using a 1 m fractionation column. Cyclohexane was purified by the standard method described by Perrin and Armarego [9]. The purified compounds were stored in brown glass bottles and fractionally distilled immediately before use. Purity of each compound was ascertained by the accuracy of their density and viscosity values, which agreed as shown in Table 1 with the literature values [10–13]. Viscosities at 298.15 K were measured with an Ubbelohde viscometer. The equation for viscosity, according to Poiseuille's law, is

$$\eta = \rho v = \rho \left(kt - \frac{c}{t} \right) \qquad (1)$$

where k and c are the viscometer constants and t, η and v are the efflux time, dynamic viscosity and kinematic viscosity, respectively. The k and c were obtained by measurements on double distilled water and benzene at 298.15 K. The obtained parameters are $k = 0.010\ \mathrm{m^2\,s^{-2}}$ and $c = 1.095\ \mathrm{m^2}$. The dynamic viscosity was reproducible to

---

[*] Corresponding author. Tel.: +98 8118271061; fax: +98 8118271061.
E-mail address: iloukhani@basu.ac.ir (H. Iloukhani).

0040-6031/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2005.08.007

Table 1
Properties of the pure components at 298.15 K

Substance	ρ (kg m^{-3})		η (mPa s)	
	Observed	Literature	Observed	Literature
Toluene	862.19	862.17 [10]	0.5521	0.5516 [11]
Cyclohexane	773.93	773.89 [11]	0.8986	0.898 [11]
n-Hexane	655.08	655.04 [12]	0.2953	0.2949 [13]

Table 2
Densities ρ (kg m^{-3}), dynamic viscosity η (mPa s), viscosity deviation $\Delta\eta$ (mPa s), excess molar volumes V^{E} (cm^3 mol^{-1}) and excess Gibbs energy of activation G^{*E} (J mol^{-1}) of viscous flow for the binary mixtures at 298.15 K

x	ρ	η	$\Delta\eta$	V^{E}	G^{*E}
x toluene + (1 − x) cyclohexane					
0.0721	853.16	0.8574	−0.0107	0.1368	−235
0.1813	843.41	0.7693	−0.0617	0.2772	−315
0.2798	834.61	0.7024	−0.0951	0.3890	−371
0.3613	827.33	0.6510	−0.1187	0.4809	−419
0.4416	820.17	0.6116	−0.1308	0.5410	−435
0.6003	806.00	0.5532	−0.1352	0.5600	−409
0.6784	799.02	0.5329	−0.1290	0.5220	−367
0.7615	791.60	0.5181	−0.1156	0.4720	−293
0.8396	784.63	0.5029	−0.1042	0.3280	−231
0.9202	777.43	0.4976	−0.0820	0.1090	−118
x toluene + (1 − x) n-hexane					
0.0406	657.47	0.2774	−0.0286	−0.0851	−184
0.2028	690.93	0.3073	−0.0404	−0.1049	−193
0.2804	706.95	0.3185	−0.0492	−0.3970	−226
0.3596	723.29	0.3272	−0.0608	−0.5948	−279
0.4423	740.35	0.3421	−0.0671	−0.7004	−297
0.5997	772.81	0.3812	−0.0685	−0.6411	−274
0.6757	788.50	0.4028	−0.0664	−0.5003	−255
0.7597	805.83	0.4300	−0.0607	−0.2667	−223
0.8412	822.63	0.4644	−0.0473	−0.0334	−160
0.9199	838.87	0.4990	−0.0329	−0.0388	−104
x cyclohexane + (1 − x) n-hexane					
0.0397	655.80	0.2833	−0.0360	0.2768	−183
0.2011	674.91	0.3282	−0.0875	0.7523	−258
0.2776	683.97	0.3485	−0.1128	0.8958	−315
0.3617	693.92	0.3778	−0.1337	0.9959	−344
0.4409	703.31	0.4077	−0.1511	1.0374	−370
0.5889	720.83	0.4815	−0.1657	0.9845	−364
0.6848	732.18	0.5355	−0.1689	0.8644	−362
0.7608	741.18	0.5994	−0.1504	0.7236	−296
0.8074	746.70	0.6444	−0.1333	0.6180	−248
0.9205	760.09	0.7507	−0.0945	0.3033	−182

within $\pm 2\times10^{-3}$ mPa s. The temperature in the cell was regulated to ±0.01 K.

The density of the compounds and their binary and ternary mixtures were measured with Anton Paar DMA 4500 oscillating U-tube densitometer, provided with automatic viscosity correction. The accuracy of density measurements was $\pm 5\times10^{-5}$ kg m^{-3}. The temperature in the cell was regulated to ±0.01 K with solid state thermostat. The apparatus was calibrated once in a day with dry air and double distilled freshly degassed water. Air-tight stoppered bottles were used for the preparation of the mixtures. The mass of the dry bottle was first determined. The less volatile component of the mixture was introduced in the bottle and the total mass was recorded. Subsequently, the other component was introduced and the mass of bottle along with the two components was determined. Ternary mixtures were prepared by mixing (toluene + cyclohexane) with pure liquid (n-hexane as a third component). Each mixture was immediately used after it was well mixed by shaking. All the weightings were preformed on an electronic balance (AB 204-N Mettler) accurate to 0.1 mg. The uncertainity in the mole fraction is estimated to be lower than $\pm 2\times10^{-4}$.

3. Results

3.1. Binary systems

In Table 2, we show values of densities, dynamic viscosities for binary systems as well as the molar excess volume, V^{E} and viscosity deviations, $\Delta\eta$ and excess Gibbs energy of activation, G^{*E} computed through the following equations:

$$V^{E}\,(\mathrm{cm^3\,mol^{-1}}) = \frac{\sum_{i=1}^{c} x_i M_i}{\rho} - \sum_{i=1}^{c} x_i \frac{M_i}{\rho_i} \tag{2}$$

$$\Delta\eta\,(\mathrm{mPa\,s}) = \eta - \sum_{i=1}^{c} x_i \eta_i \tag{3}$$

$$G^{*E}\,(\mathrm{J\,mol^{-1}}) = RT\left(\ln(vM) - \sum_{i=1}^{c} x_i\,\ln(v_i M_i)\right) \tag{4}$$

which are valid for ternary systems, as well. In the above equations the presence of the subindex i refers to the property of the pure component and the quantities without subindex refer to the property of the mixture. M is the molecular weight, x the mole fraction and c refers to the number of components in the mixture.

Figs. 1–3 show the variation with composition of V^{E}, $\Delta\eta$ and G^{*E} for the binary systems toluene + cyclohexane, toluene + n-hexane and cyclohexane + n-hexane, respectively. The V^{E} and $\Delta\eta$ values were correlated to composition, using the Redlich–Kister equation.

$$Y = x(1-x)\sum_{i=0}^{p} A_i (2x-1)^i \tag{5}$$

where $Y \equiv (V^{E}$ or $\Delta\eta)$ and x the mole fraction of the first component. The coefficients A_i were calculated by the unweighted least-square method and the computed values and standard deviation for each of the properties are shown in Table 3.

In each case, the optimum number of coefficients were ascertained from an examination of the variation of standard deviations, σ with

$$\sigma = \left[\frac{\sum (Y_{\mathrm{exp}} - Y_{\mathrm{cal}})^2}{(n-p)}\right]^{1/2} \tag{6}$$

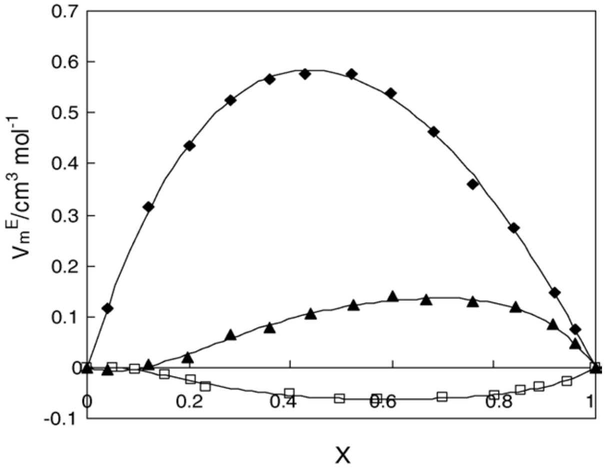

Fig. 1. Excess molar volumes of the binary mixtures against mole fraction x at T = 298.15 K. Experimental results: (⧫) x toluene + (1 − x) cyclohexane; (☐) x toluene + (1 − x) n-hexane; (▲) x cyclohexane + (1 − x) n-hexane; (—) Redlich–Kister's correlation at T = 298.15 K.

where Y_{exp} and Y_{cal} are the experimental and calculated values of the property Y, respectively, and n and p are the number of experimental points and number of parameters retained in the respective equations. The standard deviations, σ are also gathered in Table 3.

3.2. Ternary systems

The results for densities and excess molar volumes for the above ternary systems are reported in Table 4.

In Table 5 we show the densities and dynamic viscosities as well as the computed properties of viscosity deviations, $\Delta\eta_{123}$ and excess Gibbs energy of activation, G^{*E}_{123} for the system toluene (1) + cyclohexane (2) + n-hexane (3) at 298.15 K.

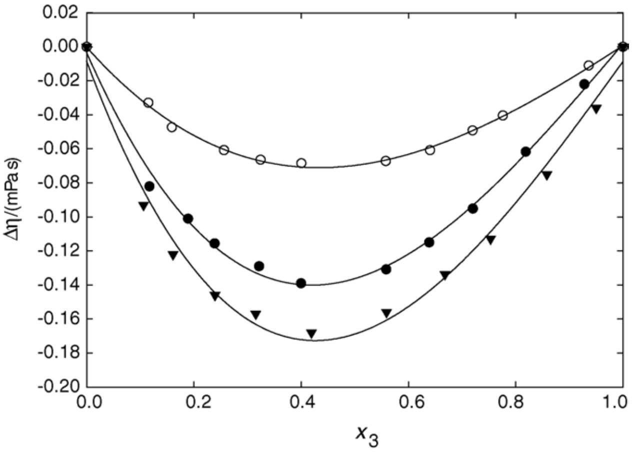

Fig. 2. Excess dynamic viscosity of the binary mixtures against mole fraction x. Experimental results: (●) x toluene + (1 − x) cyclohexane; (○) x toluene + (1 − x) n-hexane; (▼) x cyclohexane + (1 − x) n-hexane; Redlich–Kister fit curves (—) at 298.15 K.

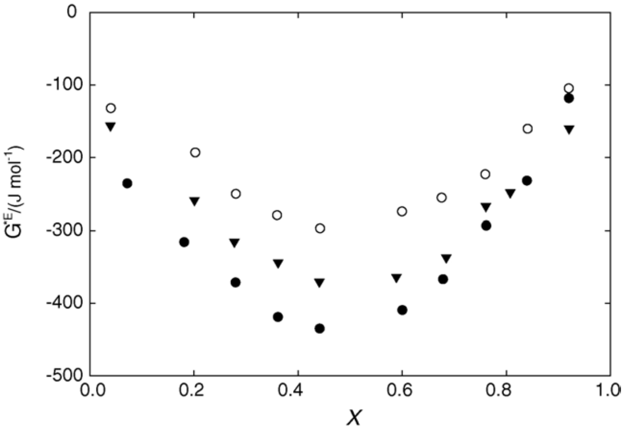

Fig. 3. Excess Gibbs free energies of activation of the binary mixtures against mole fraction x at 298.15 K. Experimental results: (●) x toluene + (1 − x) cyclohexane; (○) x toluene + (1 − x) n-hexane; (▼) x cyclohexane + (1 − x) n-hexane.

Table 3
Coefficients, A_i of Eq. (5) and standard deviation, σ for binary mixture at 298.15 K

System	A_0	A_1	A_2	A_3	σ
x toluene + (1 − x) cyclohexane					
V^E (cm^3 mol^{-1})	2.3031	−0.5556	0.2236	−0.0680	0.0050
$\Delta\eta$ (mPa s)	−0.5244	0.0892	−0.3764	0.4144	0.0042
x toluene + (1 − x) n-hexane					
V^E (cm^3 mol^{-1})	−0.1455	0.0006	0.0386	−0.1145	0.0052
$\Delta\eta$ (mPa s)	−0.2629	−0.0833	−0.1231	0.0529	0.0062
x cyclohexane + (1 − x) n-hexane					
V^E (cm^3 mol^{-1})	0.4692	0.5573	0.1277	0.0466	0.0045
$\Delta\eta$ (mPa s)	−0.6167	−0.2090	−0.5265	0.0915	0.0032

The excess molar volumes and viscosity deviations were correlated with ternary composition using the equation proposed by Cibulka [14].

$$Y_{123} = Y_{bin} + x_1x_2(1 - x_1 - x_2)(B_0 + B_1x_1 + B_2x_2) \qquad (7)$$

where $Y \equiv (V^E$ or $\Delta\eta)$ and $Y_{bin} = Y_{12} + Y_{13} + Y_{23}$ are the so-called "binary contribution".

The coefficients, B_p and standard deviations, σ (Eq. (6)) obtained by the least-squares method are gathered in Table 6. In Figs. 4 and 5 the isoline curves for V^E_{123} and $\Delta\eta_{123}$ for the ternary systems toluene (1) + cyclohexane (2) + n-hexane (3), are shown, respectively.

4. Correlating equations for the ternary system

Apart from expressing V^E_{123} and $\Delta\eta_{123}$ as a polynomial fit, several semi-empirical relations have been proposed to estimate V^E_{123} and $\Delta\eta_{123}$ of liquid mixtures in terms of pure component data. In this work, we applied the following models [15–22].

Table 4
Densities ρ (kg m^{-3}), excess molar volumes V^{E}_{123} (cm^3 mol^{-1}) for the ternary mixtures of toluene (1) + cyclohexane (2) + n-hexane (3) at 298.15 K

x_1	x_2	x_3	ρ	V^{E}_{123}
0.1762	0.5865	0.2373	753.69	0.3443
0.1604	0.5273	0.3123	742.84	0.3054
0.1538	0.4673	0.3789	734.11	0.2644
0.0653	0.2222	0.7125	689.32	0.0659
0.0301	0.0966	0.8733	680.17	0.0037
0.0098	0.0315	0.9586	669.97	0.0010
0.4582	0.4993	0.0426	803.56	0.5368
0.4382	0.4830	0.0788	796.71	0.5053
0.4046	0.4349	0.1604	782.60	0.4381
0.3674	0.3990	0.2336	769.75	0.3786
0.2816	0.3134	0.4050	741.12	0.2471
0.2400	0.2974	0.4626	730.85	0.2135
0.2129	0.2278	0.5593	717.54	0.1372
0.1704	0.1866	0.6430	704.85	0.0880
0.1339	0.1555	0.7106	694.68	0.0566
0.0951	0.1063	0.7985	682.40	0.0290
0.0581	0.0641	0.8777	671.53	0.0021
0.7033	0.2569	0.0398	826.50	0.3834
0.6760	0.2465	0.0775	818.57	0.3537
0.6176	0.2238	0.1586	801.93	0.2926
0.5609	0.2048	0.2343	786.66	0.2442
0.5011	0.1829	0.3160	770.84	0.1895
0.4478	0.1651	0.3871	757.38	0.1434
0.3871	0.1413	0.4715	742.00	0.1047
0.3289	0.1193	0.5518	727.81	0.0661
0.2700	0.0989	0.6311	714.00	0.0483
0.2088	0.0810	0.7103	700.49	0.0230
0.1510	0.0580	0.7910	687.38	0.0129
0.0918	0.0327	0.8755	674.19	0.0012
0.0298	0.0114	0.9587	661.29	0.0028

4.1. Tsao–Smith [15] model

$$Q^{\mathrm{E}}_{123} = \frac{x_2 Q^{\mathrm{E}}_{12}}{(1-x_1)} + \frac{x_3 Q^{\mathrm{E}}_{13}}{(1-x_1)} + (1-x_1) Q^{\mathrm{E}}_{23} \tag{8}$$

where $Q \equiv (V^{\mathrm{E}}$ or $\Delta\eta)$.

Binary contributions were evaluated at $x_i^0 = x_1$ and $x_j^0 = 1 - x_i^0$ for 1–2 and 1–3 binaries, and $x_2^0 = x_2/(x_2 + x_3)$ and $x_3^0 = x_3/(x_2 + x_3)$, for 2–3 binary (option ‘a’ in Table 7). As this model is asymmetric, we evaluated binary contributions alternatively at $x_i^0 = x_2$ and $x_j^0 = 1 - x_i^0$ for 2–1 and 2–3 binaries and $x_3^0 = x_3/(x_1 + x_3)$ and $x_1^0 = x_1/(x_1 + x_3)$, for the 3–1 binary (option ‘b’ in Table 7). The third alternative (option ‘c’ in Table 7), was using $x_i^0 = x_3$ and $x_j^0 = 1 - x_i^0$ for 3–1 and 3–2 binaries and $x_2^0 = x_2/(x_2 + x_1)$ and $x_1^0 = x_1/(x_2 + x_1)$, for the 1–3 binary.

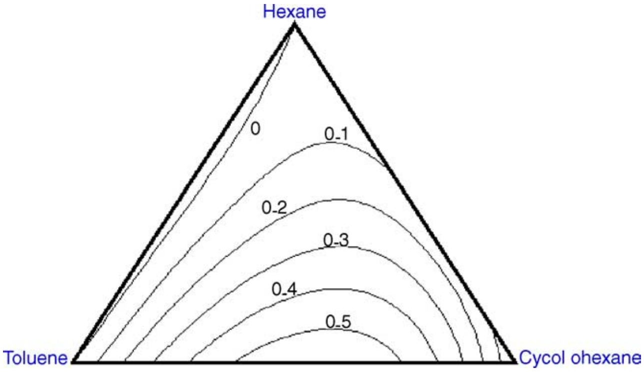

Fig. 4. Isolines for excess molar volumes V^{E}_{123} from Ciubulka’s Eq. (7) toluene (1) + cyclohexane (2) + n-hexane (3) at 298.15 K.

Table 5
Densities ρ (kg m^{-3}), dynamic viscosity η (mPa s), viscosity deviation $\Delta\eta$ (mPa s), and excess Gibbs energy of activation $G^{*\mathrm{E}}$ (J mol^{-1}) of viscous flow for the ternary mixtures of toluene (1) + cyclohexane (2) + n-hexane (3) at 298.15 K

x_1	x_2	x_3	ρ	η	$\Delta\eta_{123}$	$G^{*\mathrm{E}}_{123}$
0.2245	0.6975	0.0780	655.56	0.6994	−0.1383	−158
0.1991	0.6453	0.1556	668.49	0.6316	−0.1574	−204
0.1797	0.5852	0.2351	679.29	0.5619	−0.1684	−275
0.1619	0.5247	0.3134	695.05	0.5096	−0.1709	−326
0.1422	0.4656	0.3921	711.42	0.4207	−0.1655	−446
0.1049	0.3413	0.5538	724.33	0.3789	−0.1441	−475
0.0905	0.2791	0.6304	744.31	0.3332	−0.1251	−496
0.0687	0.2119	0.7195	755.12	0.3040	−0.1016	−441
0.0473	0.1563	0.7964	767.47	0.2923	−0.0787	−344
0.0099	0.0312	0.9589	779.26	0.2781	−0.0341	−234
0.4407	0.4794	0.0799	655.69	0.6246	−0.1469	−120
0.4031	0.4385	0.1584	677.14	0.5745	−0.1578	−161
0.3646	0.3967	0.2387	691.50	0.5213	−0.1559	−230
0.3254	0.3540	0.3206	706.71	0.4770	−0.1483	−275
0.2883	0.3137	0.3980	725.37	0.4334	−0.1424	−346
0.2103	0.2334	0.5563	744.36	0.3802	−0.1201	−416
0.1727	0.1916	0.6357	756.62	0.3432	−0.1067	−412
0.1272	0.1411	0.7317	769.59	0.3194	−0.0844	−380
0.0842	0.0934	0.8224	782.30	0.3032	−0.0643	−308
0.0189	0.0208	0.9604	794.74	0.2767	−0.0277	−234
0.6721	0.2471	0.0809	824.75	0.5971	−0.0945	−49
0.6171	0.2269	0.1560	819.31	0.5790	−0.1045	−71
0.5574	0.2049	0.2377	804.73	0.5351	−0.1155	−120
0.5033	0.1850	0.3117	793.66	0.4970	−0.1143	−191
0.4435	0.1630	0.3935	772.31	0.4455	−0.1102	−246
0.3264	0.1259	0.5477	746.55	0.3865	−0.0950	−334
0.2672	0.1030	0.6298	732.58	0.3588	−0.0836	−375
0.2090	0.0762	0.7149	711.21	0.3294	−0.0697	−364
0.1498	0.0546	0.7957	683.80	0.3078	−0.0568	−244
0.0912	0.0300	0.8788	671.55	0.2965	−0.0418	−206

4.2. Jacob–Fitzner [16] model

$$Q^{\mathrm{E}}_{123} = \frac{x_1 x_2 Q^{\mathrm{E}}_{12}}{[(x_1 + x_3/2)(x_2 + x_3)/2]} + \frac{x_1 x_3 Q^{\mathrm{E}}_{13}}{[(x_1 + x_2/2)(x_3 + x_2)/2]} + \frac{x_1 x_3 Q^{\mathrm{E}}_{23}}{[(x_2 + x_1/2)(x_3 + x_1)/2]} \tag{9}$$

Table 6
Coefficients B_p of Eq. (7) and standard deviation σ for ternary mixture of toluene (1) + cyclohexane (2) + n-hexane (3) at 298.15 K

System	B_0	B_1	B_2	σ
V^{E} (cm^3 mol^{-1})	0.3680	−0.8569	−0.6656	0.0050
$\Delta\eta$ (mPa s)	0.2641	0.4179	0.2453	0.0065

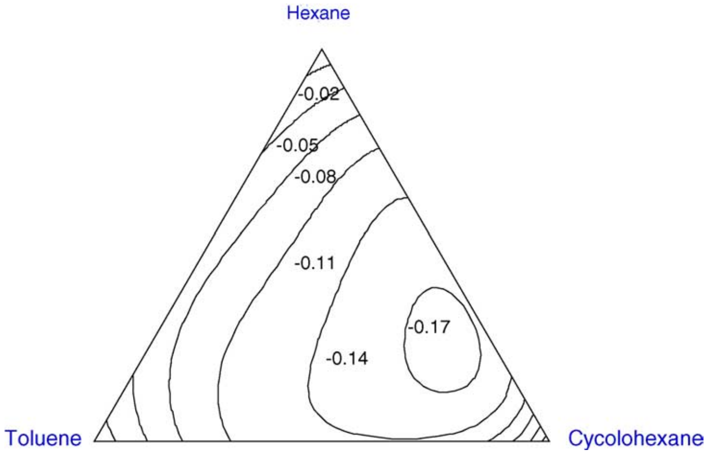

Fig. 5. Isolines for the deviation of dynamic viscosity, $\Delta\eta_{123}$ from Ciubulka's Eq. (7) toluene (1) + cyclohexane (2) + n-hexane (3) at 298.15 K.

Binary contributions were evaluated at mole fraction calculated by $x_i^0 = (1 - x_j^0) = (1 + x_i - x_j)/2$.

4.3. Kohler [17] model

$$Q_{123}^{\mathrm{E}} = (x_1 + x_2)^2 Q_{12}^{\mathrm{E}} + (x_1 + x_3)^2 Q_{13}^{\mathrm{E}} + (x_2 + x_3)^2 Q_{23}^{\mathrm{E}} \tag{10}$$

Binary contributions were evaluated at mole fraction calculated by $x_i^0 = (1 - x_j^0) = x_i/(x_i + x_j)$.

4.4. Rastogi [18] model

$$Q_{123}^{\mathrm{E}} = \frac{[(x_1 + x_2)Q_{12}^{\mathrm{E}} + (x_1 + x_3)Q_{13}^{\mathrm{E}} + (x_2 + x_3)Q_{23}^{\mathrm{E}}]}{2} \tag{11}$$

Binary contributions were evaluated at mole fraction calculated by $x_i^0 = (1 - x_j^0) = x_i/(x_i + x_j)$.

Table 7
Standard deviation, σ in the predictions, V_{123}^{E} and $\Delta\eta_{123}$ of different models for the ternary mixture of toluene (1) + cyclohexane (2) + n-hexane (3) at 298.15 K

	σ (V_{123}^{E}) (cm^3 mol^{-1})	σ ($\Delta\eta_{123}$) (mPa s)
Kohler	0.0240	0.0291
Radojkovic	0.0183	0.0699
Rastogi	0.1249	0.0296
Taso and Smith[a]	0.1079	0.0647
Taso and Smith[b]	0.0793	0.0779
Taso and Smith[c]	0.0517	0.0785
Toop[a]	0.0728	0.0381
Toop[b]	0.0827	0.0803
Toop[c]	0.0546	0.0349
Scatchad[a]	0.0809	0.0131
Scatchad[b]	0.0729	0.1439
Scatchad[c]	0.0799	0.2028
Jacob and Fitzner	0.0190	0.4670
Colinet	0.1117	0.2830

[a] Toluene is the asymmetric component.
[b] Cyclohexane is the asymmetric component.
[c] n-Hexane is the asymmetric component.

4.5. Radojkovic [19] model

$$Q_{123}^{\mathrm{E}} = Q_{12}^{\mathrm{E}} + Q_{13}^{\mathrm{E}} + Q_{23}^{\mathrm{E}} \tag{12}$$

Binary contributions V_{ij}^{E} were evaluated using the ternary mole fraction directly.

4.6. Colinet [20] model

$$\begin{aligned} Q_{123}^{\mathrm{E}} = 0.5 \Bigg[&\frac{x_2 Q_{12}^{\mathrm{E}}(x_1, 1 - x_1)}{(1 - x_1)} \\ &+ \frac{x_1 Q_{12}^{\mathrm{E}}(1 - x_2, x_2)}{(1 - x_2)} + \frac{x_3 Q_{13}^{\mathrm{E}}(x_1, 1 - x_1)}{(1 - x_1)} \Bigg] \\ &+ 0.5 \Bigg[\frac{x_1 Q_{12}^{\mathrm{E}}(1 - x_3, x_3)}{(1 - x_3)} + \frac{x_3 Q_{23}^{\mathrm{E}}(x_2, 1 - x_2)}{(1 - x_2)} \\ &+ \frac{x_2 Q_{23}^{\mathrm{E}}(1 - x_3, x_3)}{1 - x_3} \Bigg] \end{aligned} \tag{13}$$

4.7. Toop [21] model

The same argument is applied as Section 4.1

$$\begin{aligned} Q_{123}^{\mathrm{E}} = &\frac{x_2 Q_{12}^{\mathrm{E}}(x_1^0, x_2^0)}{(1 - x_1)} + \frac{x_3 Q_{12}^{\mathrm{E}}(x_1^0, x_3^0)}{(1 - x_1)} \\ &+ (1 - x_1)^2 Q_{23}^{\mathrm{E}}(x_2^0, x_3^0) \end{aligned} \tag{14}$$

4.8. Scatchard [22] model

Binary contributions were evaluated as Section 4.1

$$Q_{123}^{\mathrm{E}} = \frac{x_2 Q_{12}^{\mathrm{E}}(x_1^0, x_2^0)}{(1 - x_1)} + \frac{x_3 Q_{12}^{\mathrm{E}}(x_1^0, x_3^0)}{(1 - x_1)} + Q_{23}^{\mathrm{E}}(x_2^0, x_3^0) \tag{15}$$

Standard deviations σ, presented in Table 7 were determined for all models as:

$$\sigma = \sqrt{\sum_{i=1}^{n} \frac{(Q^{\mathrm{E}}_{(\mathrm{exp})_i} - Q^{\mathrm{E}}_{(\mathrm{cal})_i})^2}{(n-p)}} \qquad (16)$$

where p is the number of parameters and n is the number of experimental data.

5. Discussion

Comparison of V^{E} (Fig. 1) for different binary systems reveal several interesting features. Excess molar volumes for the binary systems formed by toluene with cyclohexane and cyclohexane with *n*-hexane are positive. This would indicate that molecule interactions between different molecules are weaker than interactions between molecules in the same pure liquid and that repulsive forces dominate the behavior of the solutions. The negative values of excess molar volumes for the binary systems of toluene with *n*-hexane means that the mixtures are less compressible than the corresponding ideal mixture. Therefore, in the systems, a compression in free volume is considered to occur, making the mixtures less compressible than the ideal mixture, which ultimately culminates into the negative value of V^{E}.

Experimental data for V^{E} (Table 4) of the ternary systems of toluene (1) + cyclohexane (2) + *n*-hexane (3) is positive over the whole range of composition.

The values of $\Delta\eta$ and $G^{*\mathrm{E}}$ (Figs. 2 and 3) were negative over the whole composition range for all the binary systems herein studied. The sign of $\Delta\eta$ is in agreement with the conclusion by Fort and Moore [23] who proposed that the negative values of this property are characteristic of systems where dispersion forces are predominated. According to Meyer et al. [24] the observed negative values of $G^{*\mathrm{E}}$ correspond to the existence of solute–solute association.

The ternary viscosity deviation, $\Delta\eta_{123}$ and excess Gibbs energy of activation, $G^{*\mathrm{E}}_{123}$ (Table 5) are negative over the whole composition range.

According to Kauzman and Eyring [25], the viscosity of a mixture strongly depends on entropy of mixture, which is related with liquid's structure and enthalpy (and consequently with molecular interactions between the components of the mixture). So, the viscosity deviations are function of molecular interactions as well as size and shape of molecules. Vogel and Weiss [26] affirm that mixtures with strong interactions between different molecules ($H^{\mathrm{E}} < 0$ and negative deviation from Raoult's law) present positive viscosity deviations; whereas, for mixtures with positive deviation of Raoult's law and without strong specific interactions, the viscosity deviations are negative. In this way, Meyer et al. [24] state that excess Gibbs energy of activation of viscous flow, like viscosity deviations, can be used to detect molecular interactions. The negative values observed for $\Delta\eta_{123}$ and G^{*E}_{123} of the ternary system under study point out the easier flow of mixture compared with the behavior of pure liquids. This is also in accordance with the conclusions of Fort and Moore [23] about the behavior of systems containing an associated component.

Among the semi-empirical equations used to predict V^{E}_{123} and $\Delta\eta_{123}$ for the studied system, the best for prediction of V^{E}_{123} were those of Radojkovic et al. [19], and Jacob and Fitzner [16], the predictions of equations of Rastogi et al. [18], and Colinet [20] for V^{E}_{123} erred significantly (Table 7). For $\Delta\eta_{123}$, the best prediction were those of the equations of Scatchard et al. [22], Kohler [17] and Rastogi et al. [18] although the equations of Jacob and Fitzner [16], Scatchard et al. [22], and Colinet [20] are the worst overall.

Thus, it is up to the design engineer to consider, the advantages of relying on these relations for the description of these properties as continuous models for the whole range of ternary compositions.

Acknowledgements

The authors thank the University authorities for providing the necessary facilities to carry out the work and thanks are due to Mr. Samei for his help with the manuscript.

References

[1] H. Iloukhani, M. Rezaei-Sameti, J. Chem. Thermodyn. 37 (2005) 1151–1161.
[2] H. Iloukhani, Z. Rostami, J. Solution Chem. 32 (2003) 451–462.
[3] H. Iloukhani, H.A. Zarei, J. Chem. Eng. Data 47 (2002) 195–197.
[4] H.A. Zarei, H. Iloukhani, Thermochim. Acta 405 (2003) 123–128.
[5] C.P. Menaut, J.M. Pico, E. Jimenez, C. Franjo, L. Segade, M.I. Paz Andrade, Fluid Phase Equilib. 142 (1998) 185–191.
[6] E. Mascato, L. Mosteiro, M.M. Pieiro, J. Garcia, T.P. Iglesias, J.L. Legid, J. Chem. Eng. Data 45 (2000) 1154–1159.
[7] T.M. Aminabhavi, V.B. Patil, M.I. Aralaguppi, H.T.S. Phayde, J. Chem. Data 41 (1996) 521–525.
[8] M. Caceres Alonso, J.L. Poveda Vilches, R.G. Sanchez-Pajares, J. Nunez Delgado, J. Chem. Thermodyn. 15 (1983) 913–917.
[9] D.D. Perrin, W.L.F. Armarego, Purification of Laboratory Chemicals, seventh ed., Pergamon Press, New York, 1970.
[10] M. Fermeglia, R. Lapasin, J. Chem. Eng. Data 33 (1988) 415–417.
[11] J.A. Riddick, W.B. Bunger, T.K. Sakano, Organic Solvents, Techniques of Chemistry, vol. 2, fourth ed., Wiley/Interscience, New York, 1986.
[12] A.D. Matilla, G. Tardajos, E. Junqueraz, E. Alicart, J. Solution Chem. 20 (1991) 805.
[13] J.H. Dymond, H.A. Oye, J. Phys. Chem. Ref. Data (1994) 23–41.
[14] I. Cibulka, Collect. Czech. Chem. Commun. 47 (1982) 1414–1419.
[15] C.C. Tsao, J.M. Smith, Chem. Eng. Prog. Symp. Ser. 49 (1953) 107–117.
[16] K.T. Jacob, K. Fitzner, Thermochim. Acta 18 (1977) 197–206.
[17] F. Kohler, Monatsh. Chem. 91 (1960) 738–740.
[18] R.P. Rastogi, J. Nath, S.S. Das, J. Chem. Eng. Data 22 (1977) 249–252.

[19] N. Radojkovic, A. Tasic, D. Grozdanic, B. Djordjevic, M. Malic, J. Chem. Thermodyn. 9 (1977) 349–356.
[20] C. Colinet, Ph.D. thesis, University of Grenoble, France, 1967.
[21] G.W. Toop, Trans. TMS-AIME 223 (1965) 850–855.
[22] G. Scatchard, L.B. Ticknor, J.R. Goates, E.R. McCartney, J. Am. Chem. Soc. 74 (1952) 3721–3724.
[23] R. Fort, W.R. Moore, Trans. Faraday Soc. 62 (1966) 1112–1119.
[24] R. Meyer, M. Meyer, J. Metyger, A. Peneloam, J. Chem. Phys. 62 (1971) 406–410.
[25] W. Kauzman, H. Eyring, J. Am. Chem. Soc. 62 (1940) 3113–3125.
[26] H. Vogel, A. Weiss, Ber. Bunsenges, Phys. Chem. 86 (1982) 193–198.