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Journal of Solution Chemistry

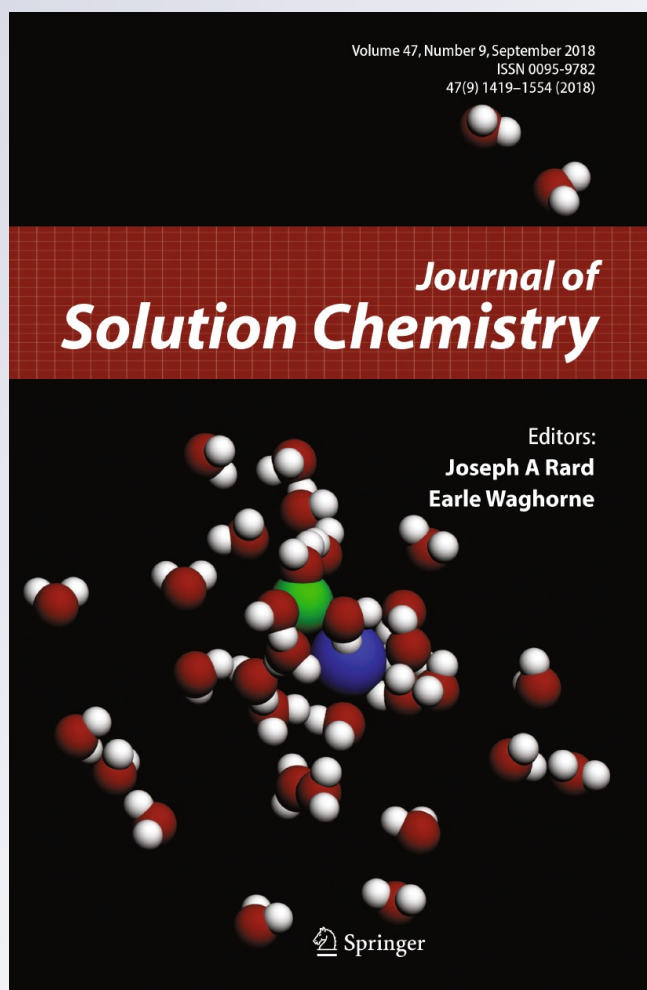
ISSN 0095-9782

Volume 47

Number 9

J Solution Chem (2018) 47:1529-1538

DOI 10.1007/s10953-018-0807-z



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Influence of Temperature on Liquid–Liquid Equilibrium of Methanol + Toluene + Hexane Ternary Systems at Atmospheric Pressure

Jonatán Hernán Veliz¹ · Alicia Marta Cases¹ · Constanza Geraldine Varas Gutiérrez¹ · Mónica Beatriz Gramajo¹

Received: 14 June 2017 / Accepted: 6 July 2018 / Published online: 10 September 2018
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Abstract

Phase equilibria of methanol + toluene + hexane ternary systems at (278.15, 283.15, 288.15 and 293.15) K at atmospheric pressure were investigated. The influence of temperature on the liquid–liquid equilibrium is discussed. All chemicals were quantified using gas chromatograph with a thermal conductivity detector coupled to a ChemStation and nitrogen as gas carrier, their mass fractions were higher than 0.999. From literature are found two articles from the same system at different temperatures studied here. Experimental data are compared with literature values. Values calculated using the NRTL and UNIQUAC equations are compared with the experimental data and it is found that the UNIQUAC equation fitted the experimental data better than the NRTL model for this ternary system.

Keywords Liquid–liquid · Methanol · Toluene · Hexane · Equilibrium

1 Introduction

There are increasing demands for the use of oxygenated compounds to produce reformulated gasoline. Thus, we have begun a systematic investigation into the phase equilibrium of systems containing oxygenated and hydrocarbons compounds. Oxygenated compounds such as ethers and ethanol are the most important but currently methanol is receiving much attention.

Methanol is partially miscible with aliphatic hydrocarbons, but not with aromatic hydrocarbons. Therefore, it is of great importance to study systems composed by methanol and representative hydrocarbons of gasoline. Many experiments have focused on establishing the concentration and temperature ranges where mixtures of hydrocarbons and methanol show no phase separation [1–7]. Schematic diagrams based on the temperature of (liquid + liquid)

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equilibria are very important because they show the temperature range in which the system becomes completely miscible.

To obtain the behavior of blends of hydrocarbons and methanol at different temperatures, liquid–liquid equilibrium data have been obtained for the methanol + toluene + hexane ternary system at $(278.15, 283.15, 288.15 \text{ and } 293.15) \pm 0.05$ K. The equilibrium concentration for each component was determined by gas chromatography. Experimental results are compared with those correlated with the NRTL [8] and UNIQUAC [9] models fitted to those experimental results. The plait point coordinates at each temperature are reported.

As far as we know, liquid–liquid equilibrium of methanol + toluene + hexane ternary systems only at 298.15 and 303.15 K have been investigated [10, 11].

2 Experimental Section

2.1 Materials

Methanol, toluene and hexane were provided by Merck. The purity of the chemicals was determined by chromatographically using a HP 6890 gas chromatograph with a ChemStation software, a TCD detector and nitrogen as gas carrier; their mass fractions were higher than 0.999. Therefore, chemicals were used without further purification.

2.2 Apparatus and Procedures

Ternary equilibrium data were obtained by preparing mixtures of known overall mass composition within the heterogeneous region, using a dual range Mettler Toledo (Switzerland) AG245 balance with precisions of ± 0.1 mg/0.01 mg. All mixtures were prepared simultaneously and placed in 16 mL screw-top sample vials (Agilent Technologies Inc., USA, HP 5183-4535) equipped with cap, septa, and a Teflon coated magnetic stirring bar to provide intense stirring for at least 7 d. A water bath thermostated at $(278.15, 283.15, 288.15 \text{ or } 293.15) \pm 0.05$ K was connected in series with two acrylic boxes having each six holes with o-ring seals to hold the sample vials. Uniformity of temperature within the vials was maintained by continuous agitation of the mixture samples with a multipoint magnetically coupled stirrer (SBS, model A-04, SBS Instruments S.A., Spain) placed under the boxes. Figure 1 shows a line drawing of the experimental device. After phase equilibrium was reached, the magnetic stirrers were turned off and the liquid phases were allowed to settle for 24 h. At the end of each experiment, samples were taken from both phases with hypodermic syringes and analyzed by means of gas chromatography. To prevent contamination of the lower phase with the upper during sampling, the needle of the hypodermic syringe was introduced through the upper phase while its piston was pushed gently. The same procedure was adopted to remove the needle. The needle was dried with a soft paper tissue before the sample was introduced into the 2 mL analysis vial (HP 5182-0714) containing the compound used as the internal standard.

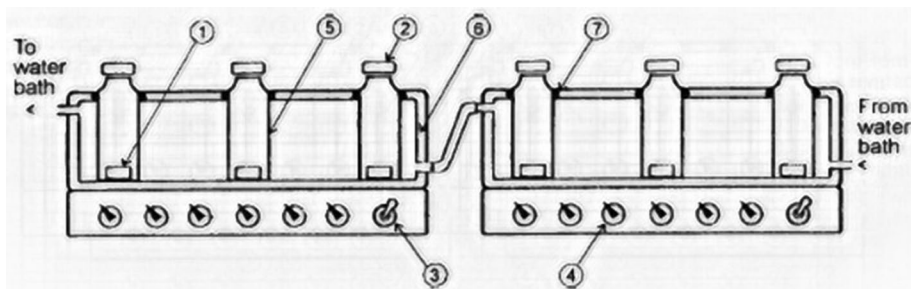


Fig. 1 Schematic of the experimental device. 1, Teflon coated magnetic bar; 2, screw caps with PTFE/white silicone septa; 3, power switch; 4, speed controls; 5, 16 mL screw sample vials (HP 5183-4535); 6, acrylic box (wall thickness: 10 mm); 7, O-Ring seals

3 Results and Discussion

Table 1 reports the liquid–liquid equilibrium (LLE) data, expressed in mass fraction, of (w_1 methanol + w_2 toluene + w_3 hexane) ternary systems at (278.15, 283.15, 288.15 and 293.15) \pm 0.05 K.

Figure 2 shows the experimental ternary equilibrium data at the four temperatures studied here, together with LLE data reported by literature [10, 11].

As can be seen, there is good agreement at all temperatures. In this plot the binodal curve and tie lines are omitted in order to avoid confusion.

Figure 2 shows that this ternary system can be classified as type 1 in the Treybal's classification [12].

The upper critical solution temperature (UCST) for methanol + hexane binary system was determined using the constant-composition method [12]. The heterogeneous binary liquid sample was prepared in 16 mL sample vials equipped with cap, septa and a Teflon coated magnetic bar to provide intense stirring. The sample was brought into thermal equilibrium in a water bath and subjected to changes in temperature with heating rates of about 0.1 K \cdot min $^{-1}$. The temperature was read when the transition was achieved. Repeated measurements of the temperature at which the opalescence of sample disappeared gave the same value within \pm 0.1 K.

Figure 3 shows the solubility curve of the methanol + hexane binary system, the upper critical solution temperature (UCST) at 308.3 K, together with bibliographic data for comparison [13].

Using these experimental results, a triangular prism can be constructed at constant pressure, as can be seen in Fig. 4.

Schematic binodal curves of methanol + toluene + hexane ternary systems are shown at different temperatures ($T_1, T_2, T_3, T_4, T_5, T_6$), the binary UCST at T_7 is observed. As can be observed, this ternary system does not have a ternary UCST.

Since the concentrations of the three components were individually determined, the sums of the mass fractions for each phase in Table 1 may slightly differ from unity. Material balances [14] were performed for each tie line at each temperature in order to check the consistency of the equilibrium experimental data reported in Table 1. These calculations show that our data satisfy the mass balance within an average absolute deviation of 1.8, 2.0, 1.8 and 0.3% at (278.15, 283.15, 288.15 and 293.15) K with a greatest deviations of (2.3, 2.8, 2.4 and 0.5)%, respectively.

Table 1 Experimental data of (w_1 methanol + w_2 toluene + w_3 hexane) ternary system at four temperatures; w_i denotes mass fraction

T (K)	Overall compositions			Methanol rich phase			Hexane rich phase		
	w_1	w_2	w_3	w_1	w_2	w_3	w_1	w_2	w_3
278.15	0.4603	0	0.5397	0.775	0	0.225	0.049	0	0.951
	0.4294	0.0421	0.5285	0.717	0.036	0.247	0.058	0.050	0.892
	0.4213	0.0580	0.5207	0.703	0.046	0.251	0.069	0.073	0.858
	0.4119	0.0809	0.5072	0.669	0.065	0.266	0.083	0.101	0.816
	0.3895	0.1233	0.4872	0.577	0.116	0.307	0.113	0.134	0.753
	0.3550	0.1530	0.4920	0.520	0.145	0.335	0.148	0.163	0.689
PP ^a				0.296	0.202	0.502	0.296	0.202	0.502
PP ^b				0.303	0.201	0.496	0.303	0.201	0.496
283.15	0.3354	0	0.6646	0.731	0	0.269	0.062	0	0.938
	0.3042	0.0362	0.6595	0.696	0.023	0.281	0.076	0.044	0.880
	0.2886	0.0645	0.6469	0.674	0.037	0.290	0.098	0.079	0.823
	0.2657	0.0947	0.6396	0.588	0.067	0.346	0.113	0.109	0.779
	0.2536	0.1232	0.6232	0.533	0.108	0.359	0.119	0.131	0.750
	0.2414	0.1540	0.6046	0.440	0.143	0.418	0.167	0.158	0.675
PP ^a				0.267	0.184	0.549	0.267	0.184	0.549
PP ^b				0.271	0.168	0.561	0.271	0.168	0.561
288.15	0.3111	0	0.6889	0.702	0	0.298	0.074	0	0.926
	0.3184	0.0347	0.6469	0.660	0.023	0.317	0.093	0.043	0.864
	0.2939	0.0660	0.6401	0.625	0.045	0.330	0.119	0.076	0.805
	0.2937	0.0918	0.6145	0.582	0.071	0.347	0.145	0.103	0.752
	0.2725	0.1236	0.6039	0.503	0.106	0.391	0.189	0.130	0.681
	PP ^a				0.327	0.151	0.522	0.327	0.151
PP ^b				0.328	0.151	0.521	0.328	0.151	0.521
293.15	0.3237	0	0.6763	0.660	0	0.340	0.084	0	0.916
	0.3031	0.0244	0.6725	0.628	0.017	0.355	0.098	0.029	0.873
	0.2995	0.0451	0.6554	0.587	0.036	0.377	0.116	0.051	0.833
	0.2778	0.0540	0.6682	0.570	0.042	0.388	0.130	0.060	0.810
	0.2976	0.0782	0.6242	0.493	0.071	0.436	0.169	0.083	0.748
	PP ^a				0.310	0.105	0.585	0.310	0.105
PP ^b				0.307	0.106	0.587	0.307	0.106	0.587

“Zero” means that the component is absent

^aEstimated plait point by the UNIQUAC model

^bEstimated plait point by the NRTL model

The LLE data for the ternary system studied here were correlated by the UNIQUAC and NRTL activity coefficient models, using an iterative computer program developed by Sørensen and Arlt [13] that minimizes the values of the following objective functions:

$$F_a = \sum^k \sum^i \left(\frac{a_{ik}^I - a_{ik}^{II}}{a_{ik}^I + a_{ik}^{II}} \right)^2 + Q \sum^n P_n^2, \quad (1)$$

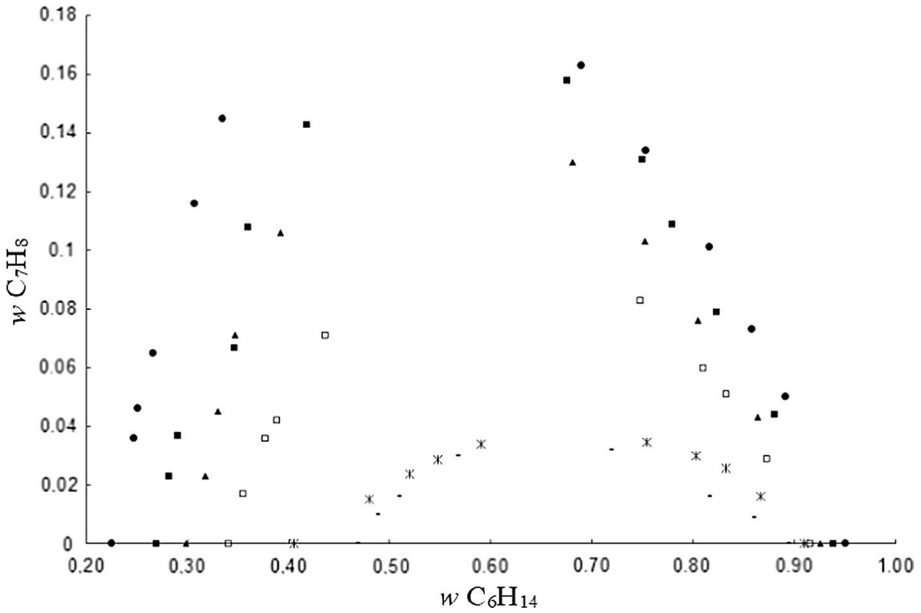


Fig. 2 (Liquid+liquid) equilibrium of $\{w_1 \text{CH}_4\text{O} + w_2 \text{C}_7\text{H}_8 + w_3 \text{C}_6\text{H}_{14}\}$ ternary system at $T = \{278.15$ (filled circle), 283.15 (filled square), 288.15 (filled triangle), 293.15 (open square), 298.15 (asterisk), 303.15 (hyphen) $\}$ K. Experimental data at 298.15 and 303.15 K were taken from the literature [10, 11]

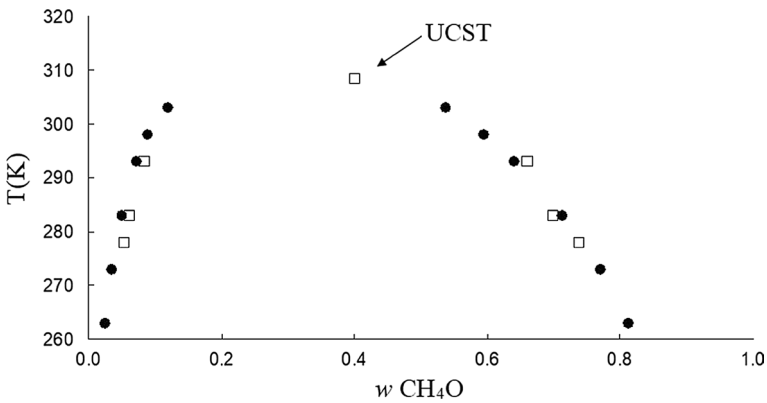
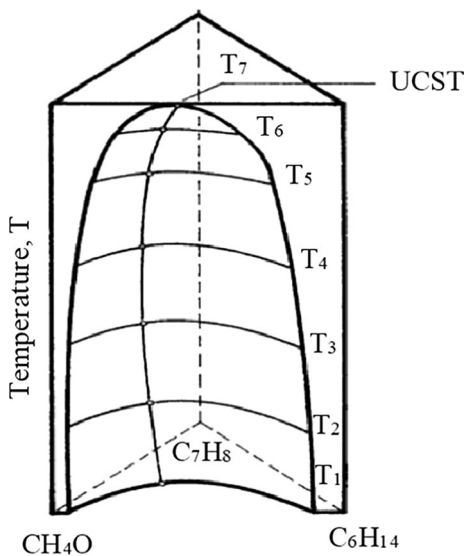


Fig. 3 Experimental coexistence temperature–composition (mass fraction of methanol) curve for the $\{w \text{CH}_4\text{O} + w \text{C}_6\text{H}_{14}\}$ binary system and the upper critical solution temperature, open square, and filled circle from Ref. [13]

$$F_x = \sum^k \min \sum^i \sum^j (x_{ijk} - \hat{x}_{ijk})^2 + Q \sum^n P_n^2, \quad (2)$$

Here, a_{ik}^{II} are the activities obtained from the experimental concentrations, I and II are the phases, x_{ijk} and \hat{x}_{ijk} are the experimental mole fraction values of the liquid phase and of the calculated tie line lying close to the experimental line, respectively, where i represents

Fig. 4 Schematic diagram based on the temperature of (liquid + liquid) equilibrium of $\{w_1 \text{CH}_4\text{O} + w_2 \text{C}_7\text{H}_8 + w_3 \text{C}_6\text{H}_{14}\}$ where ($T_1=278.15 \text{ K}$, $T_2=283.15 \text{ K}$, $T_3=288.15 \text{ K}$, $T_4=293.15 \text{ K}$, $T_5=298.15 \text{ K}$, $T_6=303.15 \text{ K}$) and binary UCST at $T_7=308.3 \text{ K}$ is observed. As can be observed, this ternary system does not have a ternary UCST



the components, j (I, II) the phases, and k the tie lines. P_n and Q are the parameter and the constant values in the penalty term, respectively.

This penalty term was established to reduce the risk of multiple solutions associated with high parameter values. The values of the penalty terms were chosen taking into account Sorensen's recommendation [13]. Table 2 shows the structural parameters of the pure components taken from the literature [15] and the optimized binary interaction parameters of the UNIQUAC and NRTL models for the ternary system. The non-randomness parameter for the NRTL equation is also given.

Experimental, correlated results at 283.15 K are shown in Fig. 5 for comparison. For the other temperatures, similar plots were obtained. Therefore, they are not shown.

Goodness of fit, as measured by the root-mean-square deviation in mole percent F , is given by

$$F = 100 \left\{ \sum_k \sum_i \sum_j \frac{(x_{ijk} - \hat{x}_{ijk})^2}{2nM} \right\}^{1/2}, \quad (3)$$

where n is the number of components in the system. The root mean square relative error in the solute distribution ratio Δm is given by

$$\Delta m = 100 \sum_k \left[\frac{((m_k - \hat{m}_k)/m_k)^2}{M} \right]^{1/2}, \quad (4)$$

These residuals are listed in Table 2 for these two models. Here, x_{ijk} is the experimental mole fraction of the i th component in the j th phase on the k th tie line, \hat{x}_{ijk} is the corresponding calculated value and m_k and \hat{m}_k are the experimental and calculated solute distribution ratios, respectively, given by $w_2^{\text{II}}/w_2^{\text{I}}$ and M is the number of tie lines.

The goodness of fit in terms of the residuals F and Δm was satisfactory for the UNIQUAC and NRTL models, although this last residual shows relatively high values due to

Table 2 Residuals F and Δm for the UNIQUAC and NRTL models, optimized parameters of the UNIQUAC and NRTL equations, and non-randomness parameter (α_{ij}), of the ternary system (w_1 methanol + w_2 toluene + w_3 hexane at $T=(278.15, 283.15, 288.15$ and $293.15)$ K

F (%)	Δm (%)	i, j	a_{ij} (K) ^a	a_{ji} (K) ^a	α_{ij}
$T=(278.15 \pm 0.05)$ K					
UNIQUAC					
0.3	9.8	1.2	216.42	98.078	
		1.3	21.889	636.69	
		2.3	224.34	-31.410	
NRTL					
0.2	11.5	1.2	552.60	-1141.3	0.1
		1.3	394.45	424.43	
		2.3	-856.88	-658.88	
$T=(283.15 \pm 0.05)$ K					
UNIQUAC					
0.6	18.4	1.2	274.31	205.19	
		1.3	21.601	586.20	
		2.3	1301.4	-123.13	
NRTL					
0.6	18.0	1.2	-68.795	2506.4	0.3
		1.3	515.76	430.57	
		2.3	-569.32	372.79	
$T=(288.15 \pm 0.05)$ K					
UNIQUAC					
0.1	5.7	1.2	-428.31	114.27	
		1.3	9.5820	593.57	
		2.3	-211.16	-302.51	
NRTL					
0.1	7.8	1.2	49.276	-482.29	0.2
		1.3	450.80	367.88	
		2.3	-772.96	-109.00	
$T=(293.15 \pm 0.05)$ K					
UNIQUAC					
0.1	2.6	1.2	-352.42	133.69	
		1.3	5.2664	601.32	
		2.3	-262.20	-84.490	
NRTL					
0.1	7.7	1.2	-1047.9	-1.3223	0.3
		1.3	484.92	435.17	
		2.3	-548.73	-738.08	

The following UNIQUAC structural parameters were used [15]: for CH_3O , $r=1.4311$ and $q=1.4320$; for C_7H_8 , $r=3.9228$ and $q=2.9680$; for C_6H_{14} , $r=4.4998$ and $q=3.8560$

^a $a_{ij}=(u_{ij}-u_{ji})/(R/K)$ for the UNIQUAC equation, where u_{ij} is the UNIQUAC binary interaction parameter ($\text{J}\cdot\text{mol}^{-1}$), $R=8.31451 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, and $a_{ij}=(g_{ij}-g_{ji})/(R/K)$ for the NRTL equation, where g_{ij} is the energy of interaction between an i - j pair of molecules ($\text{J}\cdot\text{mol}^{-1}$)

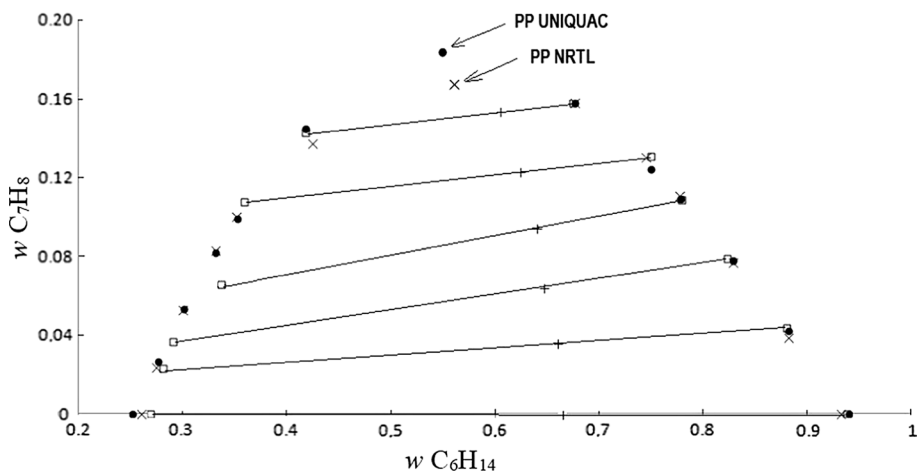


Fig. 5 (Liquid+liquid) equilibrium of $\{w_1 \text{CH}_4\text{O} + w_2 \text{C}_7\text{H}_8 + w_3 \text{C}_6\text{H}_{14}\}$ ternary system at $T=283.15$ K: open square, experimental; times symbol, NRTL; filled circle, UNIQUAC; plus symbol, global compositions

the large relative error associated with low concentrations of toluene in both phases. Taking into account both residuals, the UNIQUAC equation fitted the experimental data more accurately than the NRTL model for this ternary system for all temperatures studied here, as can be seen in Table 2.

In any case, the overall magnitudes of the r.m.s. values suggest that the NRTL and UNIQUAC models provide an adequate representation of the phase behavior of the ternary system methanol + toluene + hexane at all studied temperatures. These correlated parameters of these models are recommended to be used in the simulation and design of the liquid–liquid separation for this ternary system.

4 Conclusions

Liquid–liquid equilibrium (LLE) of the ternary system methanol + toluene + hexane was investigated at (278.15, 283.15, 288.15 and 293.15) K.

From LLE results, we conclude that mutual solubility of methanol in hexane is larger than that of hexane in methanol at the four temperatures. Additionally, this ternary system shows that the solubility increases when the temperature increases. Therefore, the heterogeneous region becomes smaller when temperature increases as can be seen in Fig. 2.

The temperature at which system becomes homogeneous corresponds to the upper critical solution temperature (UCST) of binary mixture methanol + hexane. Consequently, this blend cannot be used as a reformulated gasoline since it would show phase separation at temperatures lower at 308.3 K as can be seen in Fig. 3.

As can be seen, the solubility of this ternary system is extremely sensitive to changes in temperature. A plausible explanation to this thermal behavior can be obtained keeping in mind the chemical nature of the blended species. Methanol is a highly self-associated compound, while hydrocarbons are non-polar and non-associated chemical species. When hydrocarbons are added to methanol, the disruption of the hydrogen-bonded structure of methanol occurs with the consequent absorption of heat (endothermic

system) that provides excess molar enthalpy and excess molar entropy values greater than zero, because it is necessary to absorb heat to break hydrogen bonds and this produces greater molecular disorder.

Although no measurement of heat of mixing was performed for the ternary system studied here, it is reasonable to accept the stated behavior. This could cause the entropic term ($T\Delta S$) to be decisive in the mixing process and, since it is extremely sensitive to changes in temperature, small increase of temperature would produce big variations of solubility.

On the other hand, the asymmetric pattern observed in binodal curves at the four temperatures studied here (see Fig. 2) could be attributed to configurational differences between both hydrocarbons in this ternary system together with the mixing effect produced when the three components are mixed.

The UNIQUAC and NRTL models show low values of both residuals, particularly for the residual F , although Δm is high at 283.15 K (see Table 2) due to low concentrations of toluene in both phases. Furthermore, taking into account both residuals, the UNIQUAC equation is more accurate than the NRTL one, except at 283.15 K. These correlated parameters of models are recommended to be used in the simulation and design of the liquid–liquid separation for this ternary system.

Acknowledgements Financial support from the Consejo de Investigaciones de la Universidad Nacional de Tucumán, Argentina (CIUNT) Cod. E621 and Secretaria de Políticas Universitarias (SPU) de la Nación Argentina “Universidades Agregando Valor” RESOL-2017-5157-APN-SECPU#ME are gratefully acknowledged.

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