Research Article

LLE of methanol–methylcyclohexane–isooctane–benzene quaternary system

Abstract

A quaternary system {methanol+methylcyclohexane+isooctane+benzene} was studied at T=303.15 K. Only after all ternary equilibria data were determined experimentally, the quaternary binodal surface could be characterized fully. For this purpose, tie line data of {methanol+methylcyclohexane+benzene} ternary systems were obtained at the same temperature, while data for {methanol+isooctane+benzene}, and {methanol+isooctane+methylcyclohexane} were taken from literature. Experimental results show that the binodal surface with four quaternary sectional planes P_1, P_2, P_3, P_4 with several methylcyclohexane/isooctane in the solid diagram is small and that the highest benzene mass fraction values beyond which only one phase is present for the methanol–rich phase and hydrocarbon–rich one, respectively, are: 0.046 and 0.053 for P_1, 0.053 and 0.057 for P_2, 0.055 and 0.049 for P_3, 0.034 and 0.041 for P_4. So, if this quaternary system contains the correct methanol and hydrocarbons concentrations, this blend can be used as a reformulated gasoline because no phase separation should be observed. The distribution of benzene between both phases was also analysed. Ternary experimental results were correlated with the UNIQUAC and NRTL equation. The UNIQUAC equation is more accurate than the NRTL equation for the ternary systems studied here. The equilibria data of the three ternary systems were used to determine interactions parameters for the UNIQUAC equation. The UNIQUAC equation fitted to the experimental data is more accurate than the UNIFAC method for this quaternary system. The main reason for this is that F is fit in the size of the quaternary binodal surface.

Keywords: data, liquid–liquid equilibria, ternary system, quaternary system

Monica Beatriz Gramajo, Jonatan H Veliz, Alicia M Cases

Faculty of Exact Sciences and Technology, National University of Tucuman, Argentina

Correspondence: Monica Beatriz Gramajo, Department of Physics, Faculty of Exact Sciences and Technology, National University of Tucuman, Argentina, Email mgramajo@herrera.unt.edu.ar

Introduction

In recent years, there has been an increasing demand to use oxygenated compounds in the reformulation of gasoline in order to substantially reduce toxic emissions into the environment and simultaneously enhance the octane number of gasoline. This is the reason why we studied the phase equilibria of systems containing representative hydrocarbons of gasoline (benzene, isooctane, or cyclohexane) and oxygenated compounds (methanol, ethanol, or methyl tert–butyl ether).[1–8]

The US Environmental Protection Agency recommends the use of alcohols as gasoline additives to provide antiknock properties and to help reduce harmful combustion emissions. However, methanol presents partial miscibility with aliphatic hydrocarbons, but not with aromatic ones. Therefore, it is of great importance to study systems composed of methanol and representative hydrocarbons of gasoline.[7,8]

Keeping this in mind, a quaternary system containing methanol, methylcyclohexane, benzene and isooctane {$w_1CH_4O+w_2C_7H_{14}+w_3C_8H_{18}+w_4C_6H_6$} was also studied at 303.15K. Tie line data for the methanol–methylcyclohexane–benzene {$w_1CH_4O+w_2C_7H_{14}+w_3C_6H_6$} ternary system, where w is the mass fraction, were also investigated at temperature the same temperature, while data for methanol–isooctane–benzene, and methanol–isooctane– methylcyclohexane were taken from literature.[8] The fourth ternary subsystem methylcyclohexane–isooctane–benzene is completely miscible. This particular temperature was selected because it is representative of tropical and subtropical climates. Table 1 shows the respective Treybal[9] classification types for these systems.

Table 1 Ternary and quaternary systems, including their Treybal's classification type; w_i denotes mass fraction of component i.

n°	Type	System
1	1	w_1 CH$_4$O + w_2 C$_7$H$_{14}$ + (1- w_1-w_2) C$_6$H$_6$
2	2	w_1 CH$_4$O + w_2 C$_7$H$_{14}$ + w_3 C$_8$H$_{18}$ + (1- w_1-w_2-w_3) C$_6$H$_6$

The experimental data for the ternary systems studied here were correlated with the UNIQUAC (Universal Quasi–Chemical equation)[10] and NRTL (Non–Random, Two–Liquid) models.[11]

All the pairs of the UNIQUAC interaction parameters obtained from the three partially miscible ternary subsystems included in the quaternary system were averaged and they were then used to predict the quaternary LLE of this model. The original UNIFAC (UNIQUAC Functional–group Activity Coefficients) method was also used for this purpose.[12] To the best of our knowledge, there is no reference in the literature on the LLE of the quaternary system studied in this work.

Experimental

a. Materials

Methanol was supplied by Merck, while methylcyclohexane and benzene by Sigma–Aldrich and isooctane by Sintorgan (Argentina). The purity of the chemicals was verified chromatographically, which showed that their mass fractions were higher than 0.998. Therefore, they were used without further purification. Methanol was maintained over 0.3 nm activated molecular sieves to prevent water absorption.

b. Methods

The experimental procedure used in the present study is the same as that reported in a previous work.[2] Quantification of all components in the conjugate phases was made by gas chromatography using the internal standard method. Acetone (C_3H_6O) (Merck, chromatographic quality) with a mass fraction purity >0.999 (GC) was the standard compound used for this purpose. A Hewlett Packard 6890 gas chromatograph with an automatic injector (Agilent G2613A) directly connected to a Chem Station (HP G2070AA) was used. Adequate separation of the five components was obtained on a 30m long×0.25mm id0.5µm film thickness capillary column (INN Wax, cross–linked polyethylene glycol, HP 19091N–233). The temperature program used was: initial temperature 343 K for two minutes, ramp 50 K·min⁻¹, and final temperature 473 K for another two minutes. The nitrogen carrier gas flow rate was electronically kept constantly working with a split ratio of 20:1 and with the injector maintained at 453 K. Detection was carried out by a thermal conductivity detector at 523 K. Three or four analyses were performed for each sample in order to obtain a mean mass fraction value with repeatability better than one percent.

In order to obtain a calibration curve for each component of the internal standard method, a Mettler AG245 dual range balance with an accuracy of ±0.1/0.01 mg was used to weigh the chemicals with the highest accuracy. Furthermore, to obtain overall mixtures for LLE studies, we weighed the components with the lowest balance accuracy. For the four components, linear correlations always provided the best fit for chromatography calibration curves.

To validate the reported mass fraction values, three samples of different known overall compositions (determined by mass) were analyzed. These mixtures were analysed with the chromatographic method and their chromatographic concentrations were compared with those obtained by mass. This comparison shows that the reported mass fraction values have an uncertainty of ± 0.001.

In order to determine the quaternary binodal surface, measurements were carried out at four different methylcyclohexane/isooctane ratios, which characterize four quaternary planes (named P_1, P_2, P_3, and P_4 in (Figure 1). Figure 1 shows a schematic representation of $\{w_1CH_4O+w_2C_7H_{14}+w_3C_8H_{18}+w_4C_6H_6\}$ quaternary system. The equilibria data for this system were obtained with the same procedure used in the ternary systems. In this work, the initial mixtures (corresponding to the P_1, P_2, P_3, and P_4 planes) were selected to determine tie lines within the whole heterogeneous region.
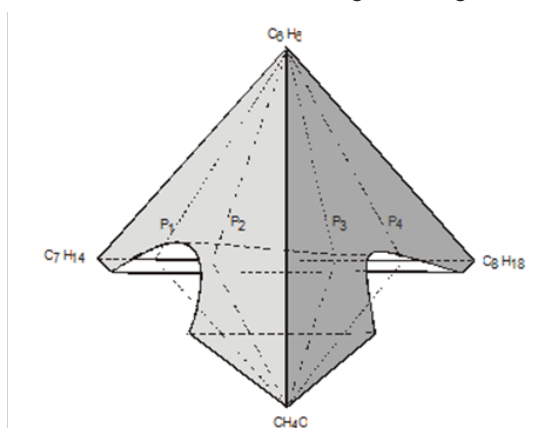

Figure 1 Schematic representation of $\{w_1 CH_4O + w_2 C_7H_{14} + w_3 C_8H_{18} + w_4 C_6H_6\}$ quaternary system at temperature 303.15 K. P_1, P_2, P_3, and P_4 are sectional planes or the determination of the binodal surface.

Results and discussion

Table 2 lists the (liquid+liquid) equilibria data for the ternary systems $\{w_1 CH_4O+w_2 C_7H_{14}+w_3 C_6H_6\}$ at temperature (303.15±0.05) K. Figure 2 shows the corresponding LLE diagrams. Data correlated by the UNIQUAC and NRTL models are also shown.
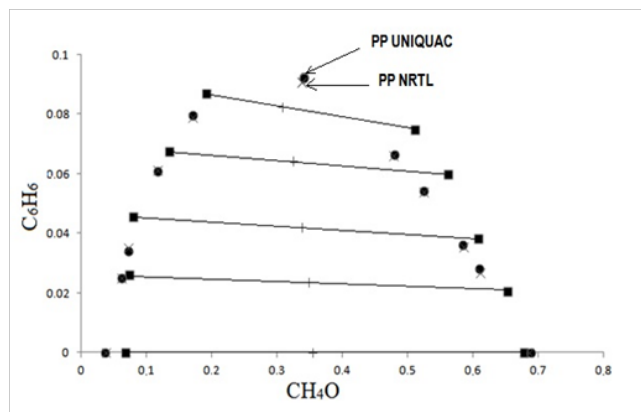

Figure 2 (Liquid + liquid) equilibrium of $\{w_1 CH_4O + w_2 C_7H_{14} + w_3C_6H_6\}$ ternary system at temperature 303.15 K. ■—■, Experimental; ✗, NRTL; ●, UNIQUAC; and +, global compositions.

Table 3 lists (liquid+liquid) equilibria data, expressed in mass fraction, of $\{w_1 CH_4O+w_2 C_7H_{14}+w_3 C_8H_{18}+w_4 C_6H_6\}$ quaternary system for each quaternary plane: P_1=(0.8067 C_7H_{14}+0.1933 C_8H_{18}), P_2=(0.6026 C_7H_{14}+0.3974 C_8H_{18}), P_3=(0.3996 C_7H_{14}+0.6004 C_8H_{18}), and P_4=(0.1926 C_7H_{14}+0.8074 C_8H_{18}). Experimental results reported in Table 2 & 3 satisfy the mass balance with a maximum deviation of 5 mass percent.

Since the concentrations of the four components were individually determined, the sums of the mass fractions for each phase shown in Table 3 may slightly differ from unity. The same consideration is applied to Table 2 for the ternary system (range±0.001, in mass fraction).

As can be seen in Table 3, we conclude that the benzene mass fractions values beyond which only one phase is present for the methanol–rich phase and hydrocarbon–rich are 0.046 and 0.053 for P_1, 0.053 and 0.057 for P_2, 0.055 and 0.049 for P_3, 0.034 and 0.041 for P_4. Since the binodal surface in the solid diagram is small, an adequate blend of these four components could be used as a reformulated gasoline, because no phase separation would occur.

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

$$F_a = \sum_{}^{k}\sum_{}^{i}\left\{\left(a_{ik}^{I}-a_{ik}^{II}\right)\Big/\left(a_{ik}^{I}+a_{ik}^{II}\right)\right\}^2 + Q\sum_{}^{n}P_n^2 , \qquad (1)$$

$$\min \sum_{}^{i}\sum_{}^{j}\left(x_{ijk}-\hat{x}_{ijk}\right)^2 + Q\sum_{}^{n}P_n^2 , \qquad (2)$$

Here, $a_{ik}^{I,II}$ 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 the calculated tie line lying close to the considered experimental line, respectively, where *i* represents the components, *j* 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. Table 4 shows

the structural parameters of the pure components taken from the literature[14] and the optimised binary interaction parameters of the UNIQUAC and NRTL models, for the ternary systems. The non–randomness parameter for the NRTL equation is also given.

Table 2 (Liquid+liquid) equilibrium data of {w_1 CH_4O + w_2 C_7H_{14} + w_3 C_6H_6} ternary system at temperature (303.15 ± 0.05) K; w_i denotes mass fraction of component i.

Global compositions			w_i w_i					
w_1	w_2	w_3	w_1	w_2	w_3	w_1	w_2	w_3
CH_4O	C_7H_{14}	C_6H_6	CH_4O	C_7H_{14}	C_6H_6	CH_4O	C_7H_{14}	C_6H_6
0.3537	0.6462	0	0.677	0.323	0	0.067	0.933	0
0.3479	0.6485	0.0236	0.651	0.328	0.021	0.072	0.902	0.026
0.3379	0.6199	0.0422	0.607	0.354	0.039	0.079	0.875	0.046
0.3245	0.6111	0.0643	0.56	0.38	0.06	0.133	0.799	0.069
0.3076	0.6098	0.0826	0.51	0.415	0.075	0.191	0.722	0.087
PP[a]			0.34	0.567	0.092	0.34	0.567	0.092
PP[b]			0.338	0.571	0.091	0.338	0.571	0.091

[a]: Estimated plait point by the UNIQUAC model.

[b]: Estimated plait point by the NRTL model.

Table 3 Liquid + liquid equilibrium data of {w_1 CH_4O + w_2 C_7H_{14} + w_3 C_8H_{18}+ w_4 C_6H_6} quaternary system at temperature (303.15 ± 0.05) K; w_i denotes mass fraction of component i

Global compositions	w_i	w_i
w_1 w_2 w_3 w_4	w_1 w_2 w_3 w_4	w_1 w_2 w_3 w_4
CH_4O C_7H_{14} C_8H_{18} C_6H_6	CH_4O C_7H_{14} C_8H_{18} C_6H_6	CH_4O C_7H_{14} C_8H_{18} C_6H_6
P1 = (0.8067 C_7H_{14} + 0.1933 C_8H_{18})		
0.3803 0.4999 0.1198 0	0.636 0.296 0.068 0	0.056 0.760 0.184 0
0.3957 0.4775 0.1144 0.0124	0.615 0.303 0.070 0.012	0.085 0.723 0.179 0.013
0.3626 0.4833 0.1167 0.0374	0.514 0.364 0.086 0.036	0.133 0.663 0.165 0.039
0.3678 0.4707 0.1136 0.0479	0.452 0.406 0.096 0.046	0.155 0.635 0.157 0.053
P2 = (0.6026 C_7H_{14} + 0.3974 C_8H_{18})		
0.3848 0.3707 0.2445 0	0.602 0.248 0.150 0	0.090 0.535 0.375 0
0.3811 0.3653 0.2412 0.0124	0.578 0.254 0.156 0.012	0.092 0.531 0.364 0.013
0.3715 0.3553 0.2343 0.0389	0.510 0.273 0.180 0.037	0.135 0.497 0.326 0.042
0.3649 0.3542 0.2338 0.0471	0.484 0.283 0.187 0.046	0.152 0.482 0.318 0.048
0.3754 0.3445 0.2263 0.0538	0.435 0.304 0.203 0.053	0.192 0.452 0.298 0.057
P3 = (0.3996 C_7H_{14} + 0.6004 C_8H_{18})		
0.3706 0.2515 0.3779 0		
0.3730 0.2408 0.3619 0.0243	0.616 0.153 0.231 0	0.078 0.368 0.554 0
0.3763 0.2359 0.3545 0.0333	0.539 0.174 0.262 0.025	0.105 0.348 0.524 0.023
0.3593 0.2377 0.3571 0.0459	0.527 0.175 0.263 0.035	0.108 0.344 0.517 0.031
0.3741 0.2288 0.3437 0.0534	0.482 0.189 0.283 0.046	0.126 0.331 0.497 0.046
	0.448 0.199 0.298 0.055	0.153 0.319 0.479 0.049
P4 = (0.2009 C_7H_{14} + 0.7991 C_8H_{18})		
0.3673 0.1219 0.5108 0	0.600 0.077 0.323 0	0.098 0.174 0.728 0
0.3845 0.1168 0.4897 0.0090	0.583 0.079 0.329 0.009	0.100 0.172 0.720 0.008
0.3852 0.1136 0.4763 0.0249	0.563 0.079 0.331 0.027	0.125 0.164 0.689 0.022
0.3688 0.1145 0.4800 0.0367	0.520 0.086 0.360 0.034	0.150 0.156 0.653 0.041

Table 4 Residuals F and Δ*m* for UNIQUAC and NRTL optimised parameters of the UNIQUAC and NRTL equations, and non-randomness parameter (α_{ij}), for the system $\{w_1\,CH_4O + w_2\,C_7H_{14} + (1 - w_1 - w_2)\,C_6H_6\}$ at temperature 303.15 K[a].

F%	%μ	i,j	a_{ij} b	a_{ji} b	φια
UNIQUAC					
0.4	17.9	1.2	-1.5929	706.08	
		1.3	345.14	-98.318	
		2.3	606.45	-274.16	
NRTL					
0.3	50.7	1.2	499.24	564.43	0.3
		1.3	995.17	-515	
		2.3	1021.7	-562.3	

[a]: The following UNIQUAC structural parameters were used : for CH_4O, $r = 1.4311$ and $q = 1.4320$; for C_7H_{14}, $r = 4.7200$ and $q = 3.7760$; and for C_6H_6, $r = 3.1878$ and $q = 2.4000$.

[b]: $a_{ij} = (u_{ij} - u_{jj})/(R/K)$ for the UNIQUAC equation, where u_{ij} is the UNIQUAC binary interaction parameter (J-mol⁻¹) and R = 8.31451 J-K⁻¹-mol⁻¹. $a_{ij} = (g_{ij} - g_{jj})/(R/K)$ for the NRTL equation, where g_{ij} is the energy of interaction between an i-j pair of molecules (J-mol⁻¹).

Goodness of fit, as measured by the r.m.s. deviation in mole fraction F, is given by

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

Where n is the number of components in the system. The r.m.s. relative error in the solute distribution ratio Δ*m* is given by

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

Table 4 shows the UNIQUAC structural parameters for the pure components taken from the literature.[14] The calculated values of the residuals F and Δ*m*, the optimized non–randomness parameter for the NRTL equation $_{ij}$, and the optimized binary interaction parameters for UNIQUAC and NRTL models are also listed in Table 4. Here, x_{ijk} is the experimental mole fraction of the ith component in the jth phase on the kth 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''/w_2'.

Figure 2 shows the NRTL and UNIQUAC equations. The UNIQUAC equation fitted to the experimental results is considerably more accurate than NRTL equation taking into account overall errors, F and Δ*m*, listed in Table 4.

Table 5 lists the residuals for the UNIFAC and UNIQUAC models of $\{w_1\,CH_4O + w_2\,C_7H_{14} + w_3\,C_8H_{18} + w_4\,C_6H_6\}$ quaternary system. The fit was poor in terms of Δ*m* for both models, due to the large relative error associated with the very low concentrations of benzene in both phases, while the goodness of fit in terms of F was satisfactory, particularly for the UNIQUAC model. Therefore, the UNIQUAC equation fitted to the experimental data is more accurate than the UNIFAC method of this quaternary system.

Table 5 Residuals F and Δ*m* of $\{w_1\,CH_4O + w_2\,C_7H_{14} + w_3\,C_8H_{18} + w_4\,C_6H_6\}$ quaternary system at temperature 303.15 K[a].

Planes	F%	Δ*m*%
UNIFAC		
P_1	17.2	39.5
P_2	16.4	34.6
P_3	14.6	40.6
P_4	11.7	33.6
UNIQUAC		
P_1	3.4	46.7
P_2	4.6	74
P_3	3	81.1
P_4	1.5	66.5

[a]: The values of Δ*m* were calculated only for C_6H_6. The distribution coefficient for this compound is defined as m = mass fraction of C_6H_6 in the II phase (w_4'')/mass fraction of C_8H_{10} in the I phase (w_4').

The average of all the binary interaction parameters, calculated from their respective ternary subsystems, was chosen in order to obtain a unique set of binary parameters suitable for prediction of the quaternary equilibria data using the UNIQUAC model, as previously done.[3] They are reported in Table 6.

Table 6 Average UNIQUAC interaction parameters for the prediction of the quaternary system.

i-j	a_{ij}	a_{ji}
1-2	-4.6795	664.945
1-3	-19.3145	647.465
1-4	183.0015	22.481
2-3	-17.974	27.111
2-4	606.45	-274.16
3-4	-5.2652	-5.5424

Conclusion

(Liquid+liquid) equilibria of $\{w_1CH_4O + w_2C_7H_{14} + w_3C_6H_6\}$ ternary systems and of $\{w_1CH_4O + w_2C_8H_{18} + w_3C_7H_{14} + w_4C_8H_{10}\}$ quaternary system were investigated at temperature 303.15 K, and the highest concentrations of hydrocarbons and methanol beyond which only one phase is present were established.

The UNIQUAC equations fitted to the experimental data is considerably more accurate than the NRTL equations taking into account both overall errors F and Δ*m*. These residuals also show that the UNIQUAC model is better than the NRTL one Table 4 for the ternary systems.

The quaternary equilibria was predicted by the UNIQUAC and UNIFAC models, showing that the fit was poor in terms of m for both models, due to the large relative error associated with the very low concentrations of benzene in both phases, while the goodness of fit in terms of F was satisfactory, particularly for the UNIQUAC model. Therefore, The UNIQUAC equation fitted to the experimental data is

more accurate than the UNIFAC method of this quaternary system. The main reason for this is that F is fit in the size of the quaternary binodal surface.

List of symbols

a : Activity obtained directly from the model by insertion of the experimental concentrations; eq. (1)

a_{ij}, a_{ji} : Parameters of the UNIQUAC and NRTL models

F : r.m.s. deviation in mole fraction given by eq. (3)

F_a, F_x : Objective function given by equations (1) and (2).

LLE : Liquid–liquid equilibria

m_k : Experimental solute distribution ratio; eq. (4)

$\hat{m}_k$: Calculated solute distribution ratio; eq. (4)

Δm : r.m.s. relative error in the solute distribution ratio given by eq. (4)

M : Number of tie lines; equations (3) and (4)

n : Number of the components in the system (3) or (4)

P_i : Quaternary planes for the construction of the binodal surface

P_n : Parameter in the penalty term; equations (1) and (2)

PP : Plait point

Q : Constant value in the penalty term; equations (1) and (2)

r.m.s. : Root mean square deviation

w_i : Mass fraction of component *i*

x_{ijk} : Experimental mole fraction of the ith component in the jth phase on the kth tie line (Equations (2) and (3))

$\hat{x}_{ijk}$: Calculated mole fraction of the ith component in the jth phase on the kth tie–line (Equations (2) and (3))

w_i' : Mass fraction of the ith component in the methanol (') phase

w_i'' : Mass fraction of the ith component in the hydrocarbon ('') phase

Subscripts

i : lower index–denoting components (1–4)

j : lower index–denoting phases (' or '')

k : lower index denoting tie lines (1 to M)

' : methanol phase

'' : hydrocarbon phase

Greek letters

α_{ij} : Non–randomness parameter for the NRTL equation

Conflict of interest

References

1. Gramajo MB, Bonatti CM, Barnes N, et al. (Liquid + liquid) equilibria of ternary and quaternary systems including 2,2,4–trimethylpentane, benzene, methanol, and water at *T*=303.15 K**.** *Chem Thermodyn*. 2001;33(12):1663–1677.

2. Gramajo MB, Bonatti CM, Barnes N, et al. *Sci Technol*. 2002;37:245–260.

3. Gramajo MB, Bonatti CM, Sólimo HN. Liquid–liquid equilibria of ternary and quaternary systems with two hydrocarbons, an alcohol, and water at 303.15 K:Systems containing 2,2,4–trimethylpentane, toluene, methanol, and water, or 2,2,4–trimethylpentane, toluene, ethanol, and water. *Fluid Phase Equilib*. 2003;205(1):53–67.

4. Gramajo MB, Bonatti CM, Barnes N, et al. Water Tolerance and Ethanol Concentration in Ethanol–Gasoline Fuels at Three Temperatures. *Energy & Fuels*. 2004;18(2):334–337.

5. Gramajo MB, Bonatti CM, Sólimo HN. Liquid–liquid equilibria for the quaternary system water plus methyl tert–butyl ether plus benzene plus cyclohexane and its constituent partially miscible ternary systems at 303.15 K. *Energy & Fuels*. 2005;19(5):1977–1983.

6. Gramajo MB, Cases AM, Sólimo HN. (Liquid + liquid) equilibria for the quaternary system water+methyltert–butyl ether+ethanol+benzene at 303.15 K**.** *Fluid Phase Equilib*. 2006;249(1–2):109–114.

7. García Flores BE, Gramajo de Doz MB, Trejo A. Liquid–liquid equilibria for pseudoternary systems:isooctane–benzene–(methanol + water). *Fluid Phase Equilib*. 2005;230(1–2):121–130.

8. Gramajo MB, Cases AM. (Liquid + liquid) equilibria of methanol + isooctane + methylcyclohexane + ethylbenzene quaternary system at *T* = **303.15 K.** *Fluid Phase Equilib*. 2011;304(1–2):68–73.

9. Treybal RE. Liquid Extraction. 2nd edn. New York: McGraw–Hill; 1963.

10. Abrams DS, Prausnitz JM. Statistical thermodynamics of liquid mixtures:A new expression for the excess Gibbs energy of partly or completely miscible systems. *AIChE J*. 1975;21 (1):116–128.

11. H Renon JM, Prausnitz JM. Local compositions in thermodynamic excess functions for liquid mixtures. *AIChE J*. 1968;14(1):135–144.

12. Fredenslund, Gmehling J, Rasmussen P. Vapour–Liquid Equilibria Using UNIFAC, Amsterdam, Netherland, 1977.

13. Sørensen JM. Phase Equilibria and Separation Processes. MAN 8106. ESTM:Estimation of UNIQUAC and NRTL Parameters from Ternary LLE Data, Lyngby. Denmark, 1980.

14. Sørensen JM, Arlt W. Liquid–Liquid Equilibrium Data Collection. *Ternary and Quaternary Systems*. Frankfurt, Germany; 1980.