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(Liquid + liquid) equilibria of methanol + isooctane + methylcyclohexane + ethylbenzene quaternary system at $T = 303.15$ K

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ABSTRACT

Tie line data of {methanol + isooctane + methylcyclohexane}, {methanol + ethylbenzene + methylcyclohexane}, and {methanol + ethylbenzene + isooctane} ternary systems were obtained at $T = 303.15$ K. A quaternary system {methanol + isooctane + methylcyclohexane + ethylbenzene} was also studied at the same temperature. In order to obtain the binodal surface of the quaternary system, four quaternary sectional planes with several methylcyclohexane/isooctane ratios were studied. Experimental results show that the binodal surface in the solid diagram is small and that the highest ethylbenzene mass fraction values beyond which only one phase is present for the methanol-rich phase and hydrocarbon-rich one, respectively, are: 0.0783 and 0.0864 for P1, 0.0791 and 0.0906 for P2, 0.0798 and 0.0805 for P3, 0.0812 and 0.0935 for P4. 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 ethylbenzene between both phases was also analysed. Ternary experimental results were correlated with the UNIQUAC and NRTL equation, and predicted with the original UNIFAC group contribution method. The equilibrium data of the three ternary systems were used to determine interactions parameters for the UNIQUAC equation. The UNIQUAC and NRTL equations are more accurate than the UNIFAC method for the ternary systems studied here, because this last model predicts an immiscibility region larger than the experimentally observed in the methanol-rich phase. The UNIQUAC equation fitted to the experimental data is more accurate than the UNIFAC method for this quaternary system.

1. Introduction

Presently, there is an increasing interest to adding oxygenated compounds in the reformulation of gasoline in order to substantially reduce toxic emissions into the environment and enhance the octane number of gasoline. Therefore, this is the reason for which we are studying the phase equilibrium of systems containing hydrocarbons (benzene, isooctane, or cyclohexane) and oxygenated compounds (methanol, ethanol, or methyl *tert*-butyl ether) [1–8].

The physical and chemical properties of methanol make it a candidate as an oxygenated fuel additive. However, methanol presents partial miscibility with aliphatic hydrocarbons, not so with aromatic ones. Therefore, it is of great importance to study systems composed by methanol and representative hydrocarbons of gasoline, establishing the concentration ranges of hydrocarbons and methanol in which the two-phase region does not exist [7,8].

Having this in mind, (liquid + liquid) equilibrium (LLE) measurements of {w_1 methanol + w_2 isooctane + w_3 methylcyclohexane + w_4 ethylbenzene}, named throughout the text as {w_1 CH_4O + w_2 C_8H_{18} + w_3 C_7H_{14} + w_4 C_8H_{10}}, quaternary system and its ternary subsystems: {w_1 CH_4O + w_2 C_8H_{10} + w_3 C_7H_{14}}, {w_1 CH_4O + w_2 C_8H_{10} + w_3 C_8H_{18}}, and {w_1 CH_4O + w_2 C_8H_{18} + w_3 C_7H_{14}} at $T = (303.15 \pm 0.05\ \text{K})$ and atmospheric pressure were performed. The fourth ternary subsystem {w_1 C_7H_{14} + w_2 C_8H_{10} + w_3 C_8H_{18}} is completely miscible. This particular temperature was selected because it is representative of tropical and subtropical climates. Table 1 shows for these systems their respective Treybal [9] classification types.

The experimental data for the ternary systems studied here were correlated with the UNIQUAC [10] and NRTL [11] models, and predicted with the original UNIFAC group contribution method [12].

All the pairs of the UNIQUAC interaction parameters obtained from the three partially miscible ternary subsystems included in the quaternary system were averaged and, after that, they were

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Nomenclature

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 Eqs. (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 Eqs. (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 Eqs. (1) and (2)
PP	plait point
Q	constant value in the penalty term Eqs. (1) and (2)
r.m.s.	root mean square deviation
w_i	mass fraction of component *i*
x_{ijk}	experimental mole fraction of the *i*th component in the *j*th phase on the *k*th tie line (Eqs. (2) and (3)
$\hat{x}_{ijk}$	calculated mole fraction of the *i*th component in the *j*th phase on the *k*th tie-line (Eqs. (2) and (3)
w'_i	mass fraction of the *i*th component in the ′ methanol phase
w''_i	mass fraction of the *i*th component in the ″ organic 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
″	organic phase

Greek letters

α_{ij}	non-randomness parameter for the NRTL equation

used to predict the quaternary LLE with this model. The original UNIFAC method was also used for this purpose.

To the best of our knowledge, there is no reference in the literature about of LLE either of the ternary or quaternary systems studied in this work.

2. Experimental

2.1. Materials

Methanol were supplied by Merck, while methylcyclohexane and ethylbenzene by Sigma–Aldrich and isooctane by Sintorgan (Argentina). The purity of the chemicals was verified chromatographically, showing that their mass fractions were higher than 0.998. Therefore, they were used without further purification.

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 $CH_4O + w_2$ $C_8H_{10} + (1 - w_1 - w_2)$ C_7H_{14}
2	1	w_1 $CH_4O + w_2$ $C_8H_{10} + (1 - w_1 - w_2)$ C_8H_{18}
3	2	w_1 $CH_4O + w_2$ $C_8H_{18} + (1 - w_1 - w_2)$ C_7H_{14}
4	2	w_1 $CH_4O + w_2$ $C_8H_{18} + w_3 C_7H_{14} + (1 - w_1 - w_2 - w_3)$ C_8H_{10}

2.2. Methods

The experimental procedure used is the same as that reported in a previous work [2]. Consequently, only its essential parts are reproduced here.

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 ChemStation (HP G2070AA) was used. Good separation of the five components was obtained on a 30 m long × 0.25 mm i.d. × 0.5 μm film thickness capillary column (INNOWax, cross-linked polyethylene glycol, HP 19091N-233). The temperature program used was: initial temperature 343 K for 2 min, ramp 50 K min^{-1}, and final temperature 393 K for another 2 min. The nitrogen carrier gas flow rate was electronically kept constant 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 by 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. On the other hand, 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 chromatographic calibration curves.

In order to obtain the uncertainty in the equilibrium mass fraction values, we prepare several ternary mixtures with very well known concentrations by mass. 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 Fig. 1). Fig. 1 shows a schematic

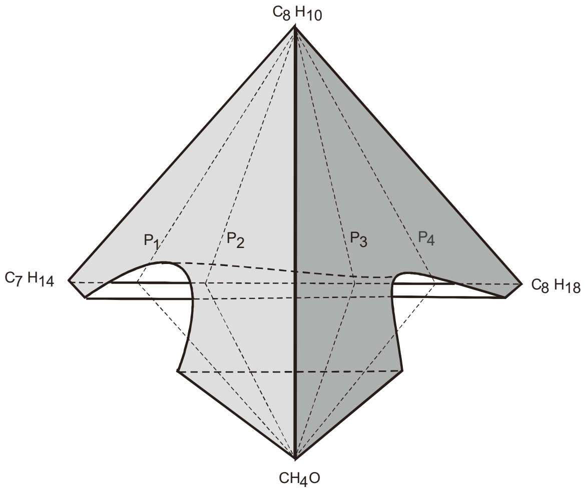

Fig. 1. Schematic representation of {w_1 $CH_4O + w_2$ $C_8H_{18} + w_3$ $C_7H_{14} + w_4$ C_8H_{10}} quaternary system at $T = 303.15$ K. P_1, P_2, P_3, and P_4 are sectional planes for the determination of the binodal surface.