Liquid−Liquid Equilibria for Monoethylene Glycol + Hexane and 2,2,4-Trimethylpentane, Water + Hexane and 2,2,4-Trimethylpentane, Monoethylene Glycol + Water + Hexane, and Monoethylene Glycol + Water + 2,2,4-Trimethylpentane in the Temperature Range between $T = 283.15$ K and $T = 323.15$ K

Antonio Razzouk,[†] Ramy Abou Naccoul,[†] Ilham Mokbel,*[,†] Pierre Duchet-Suchaux,[‡] Jacques Jose,[†] Evelyne Rauzy,[§] and Charles Berro[§]

Université Claude Bernard Lyon1, UMR 5180, Laboratoire “Thermodynamique Analyse et Procédés”, 43 bd du 11 Novembre 1918, 69622 Villeurbanne, France, Sté TOTAL, 2 place de la Coupole-La Défense 6, 92078 Paris La Défense Cedex, France, and UMR 6114, Département de Chimie, Faculté des Sciences de Luminy, 163 av. de Luminy, 13288 Marseille Cedex 9, France

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The authors declare that data presented in the article entitled “Liquid−Liquid Equilibria for Monoethylene Glycol + Water + Alkane Systems in the Range (273 to 313) K and Atmospheric Pressure” [*J. Chem. Eng. Data* **2004**, *49*, 1577−1580] are completely erroneous. In the present study, the authors report new solubility data for two of the eight ternary systems mentioned in the previously cited article: monoethylene glycol (MEG) + water + *n*-hexane/2,2,4-trimethylpentane. The experimental protocol was first validated by studying the liquid−liquid equilibria of four binary mixtures, MEG + *n*-hexane/2,2,4-trimethylpentane and water + *n*-hexane/2,2,4-trimethylpentane, under atmospheric pressure at $T = 283.15$ K, $T = 303.15$ K, and $T = 323.15$ K. The experimental results have been compared with the available literature data, and a good agreement has been found.

Introduction

Even though the data for the eight ternary systems reported in “Liquid−Liquid Equilibria for Monoethylene Glycol + Water + Alkane Systems in the Range (273 to 313) K and Atmospheric Pressure” [*J. Chem. Eng. Data* **2004**, *49*, 1577−1580] are completely erroneous, in the present study we carried out for a second time measurements on only two of these ternary systems, MEG (monoethylene glycol) + water + *n*-hexane and MEG + water + 2,2,4-trimethylpentane (isooctane), over the temperature range (273 to 323) K at atmospheric pressure. In addition to the two ternary systems mentioned previously, the following binary mixtures were studied too: water + hexane, water + 2,2,4-trimethylpentane, MEG + hexane, and MEG + 2,2,4-trimethylpentane at $T = 283.15$ K, $T = 303.15$ K, and $T = 323.15$ K.

The erroneous solubilities of hydrocarbon in the aqueous phase and of MEG and water in the hydrocarbon-rich phase (100 times higher for the mixture MEG + water + hexane) obtained in the previous study[1] could be explained by several assumptions:
(1) the phase separation step following the mixing phase was not achieved due to a too short settlement time, 2 h (presence of microemulsions);
(2) the external calibration is not recommended in gas chromatography when the analyses concern low quantity of solute;
(3) the thermal conductivity detector, TCD, of the gas chromatograph is not sensitive enough for water quantification (low concentration range).

In the present study, the experimental conditions were modified: the two-phase separation step is longer (8 h), and internal calibration was chosen for the MEG and hydrocarbon solubility determinations with a gas chromatograph equipped with a flame ionization detector (much more sensitive than TCD). The traces of water in the hydrocarbon-rich phase were analyzed by the Karl Fischer method.

Liquid−liquid equilibria (LLE) data for systems including MEG, water, and hydrocarbons are very scarce in the literature. Folas et al.[2] have studied binary and ternary systems containing MEG, aromatic hydrocarbons (benzene and toluene), and water. Derawi et al.[3] have reported experimental data for binary mixtures containing MEG + hydrocarbon (heptane, methylcyclohexane, and hexane). The experimental values of MEG + *n*-hexane were compared with the latter authors’ data. A single data point at 298.73 K for comparison was found in the literature for the binary system MEG + 2,2,4-trimethylpentane.[4] On the other hand, several authors studied the mixtures water + *n*-hexane or + 2,2,4-trimethylpentane. The agreement between the experimental results and those of the literature are good considering the low solubility values of the components. No literature data were found for comparison with the values obtained for the two ternary systems.

Experimental Section

Materials. Monoethylene glycol was obtained from Sigma-Aldrich with a mass fraction purity of 0.998 and water content < 0.00003. *n*-Hexane and 2,2,4-trimethylpentane (isooctane) were purchased from Acros Organics with a mass fraction purity better than 0.99. Distilled and deionized water from a Millipore Milli-Q system was used in this work.

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* To whom correspondence should be addressed. E-mail: mokbel@univ-lyon1.fr.
[†] Université Claude Bernard Lyon1.
[‡] Sté TOTAL.
[§] Faculté des Sciences de Luminy.

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Table 1. Characteristics of the Two HP Gas Chromatographs Used in This Work

	GC-1	GC-2
type	HP 6890	HP 5890 series II
column type	Supelcowax-10	Restek Rtx-35 amine
column length	15 m	30 m
column i.d.	0.53 mm	0.32 mm
column film thickness	0.50 μm	1 μm
injector type	cool on-column	split
injection volume	1 μL	1 μL
detector type	FID	FID
carrier gas	He (flow: 4.4 $\text{mL}\cdot\text{min}^{-1}$)	He (flow: 3 $\text{mL}\cdot\text{min}^{-1}$)

Table 2. Mutual Solubility Data for the Binary Systems Monoethylene Glycol (1) + Alkane (2) and Water (1) + Alkane (2) Expressed in Molar Fractions (x_i)

T/K	$10^5\ x_1$ in the hydrocarbon-rich phase	$10^5\ x_2$ in the polar phase
	Monoethylene Glycol + *n*-Hexane	
283.15	4.55	139
303.15	13.0	177
323.15	43.1	231
	Monoethylene Glycol + 2,2,4-Trimethylpentane	
283.15	6.47	47.9
303.15	18.5	76.8
323.15	40.7	97.0
	Water + *n*-Hexane	
283.15	30.9	0.178
303.15	78.3	0.226
323.15	137	0.315
	Water + 2,2,4-Trimethylpentane	
283.15	38.8	0.0351
303.15	107	0.0378
323.15	196	0.0450

Apparatus and Procedure. To establish liquid−liquid equilibrium, a glass cell of about 300 mL was used. The cell was equipped with a magnetic stirrer and a jacket for a circulating fluid to keep constant the temperature of the liquid mixture. The temperature was controlled to within 0.1 K. The mixtures, contained in the glass cell, were vigorously agitated for 10 h, and then the two phases were left to settle for 8 h to obtain equilibrium.

Sampling and Analysis. The samples of the two phases were withdrawn from the equilibrium cell by means of two preheated sampling lines to avoid adsorption phenomena. The samples were collected in an auxiliary solvent (methanol or ethanol whose water content was about 20 $\text{mg}\cdot\text{L}^{-1}$) to maintain their homogeneity. The solvent contained previously an internal standard. Only the minor compounds of each phase were analyzed. Two different gas chromatography (GC) apparatuses with different columns and injectors and a coulometric Karl Fischer (KF) system were used to analyze the trace amounts of compounds involved in this study. The MEG in the hydrocarbon-rich phase was quantified using GC-1 with *n*-butylbenzene as the internal standard. The hydrocarbon in the aqueous phase was analyzed by means of GC-2, and *n*-heptane was used as an internal standard. Calibration curves were established by analyzing four different standard solutions containing known quantities of the component and the internal standard. The calibration curves covered the concentration range of the studied samples, with a good correlation coefficient (0.999). The characteristics of the two GC apparatuses used in this work are given in Table 1.

The water content in the organic phase was determined using coulometric Karl Fischer titration. To ensure the homogeneity of the sample, the organic phase was dissolved in dry ethanol before analysis. Prior to measurements, the KF determination of water was controlled by analyzing certified water standards "Hydranal-coulomat E" from Fluka (relative standard deviation (RSD) certified 1 %). As the RSD of the analysis of water was 2.5 %, the uncertainty in the water measurements was estimated to be 5 %. To obtain reliable data, three cells were prepared for each composition to be studied. Each cell was subject to one or two samplings. Each sample was analyzed four times. The obtained reproducibility of the GC analysis was good, as the mean variation coefficient of the measurements was less than 4 % for the different components analyzed.

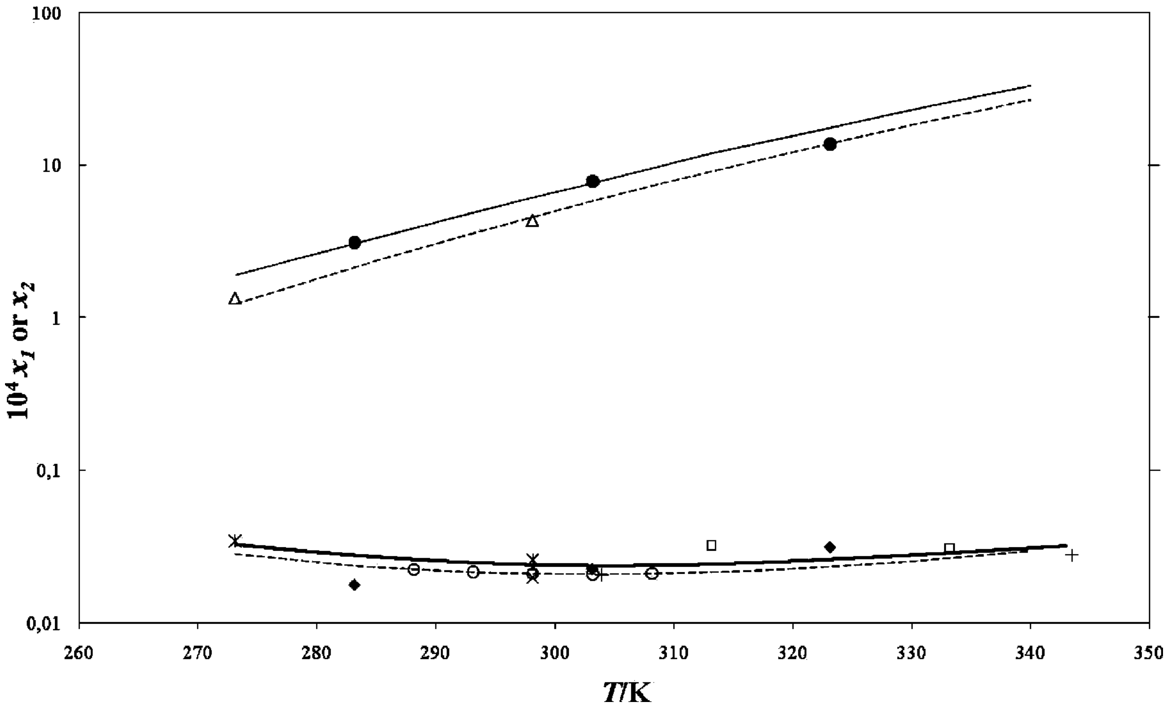

Figure 1. Mutual solubility of the water (1) + *n*-hexane (2) system. x_1 is the molar fraction of water in the hydrocarbon-rich phase: ●, this work; Δ, Polak and Lu,[6] ---, Tsonopoulos;[11] solid line, Maczynski et al.[7] x_2 is the molar fraction of *n*-C$_6$ in the aqueous phase: ◆, this work; □, Perada et al.;[5] *, Polak and Lu;[6] +, Marche;[8] ×, McAuliffe;[9] ○, Jonsson et al.;[10] ---, Tsonopoulos;[11] solid line, Maczynski et al.[7]

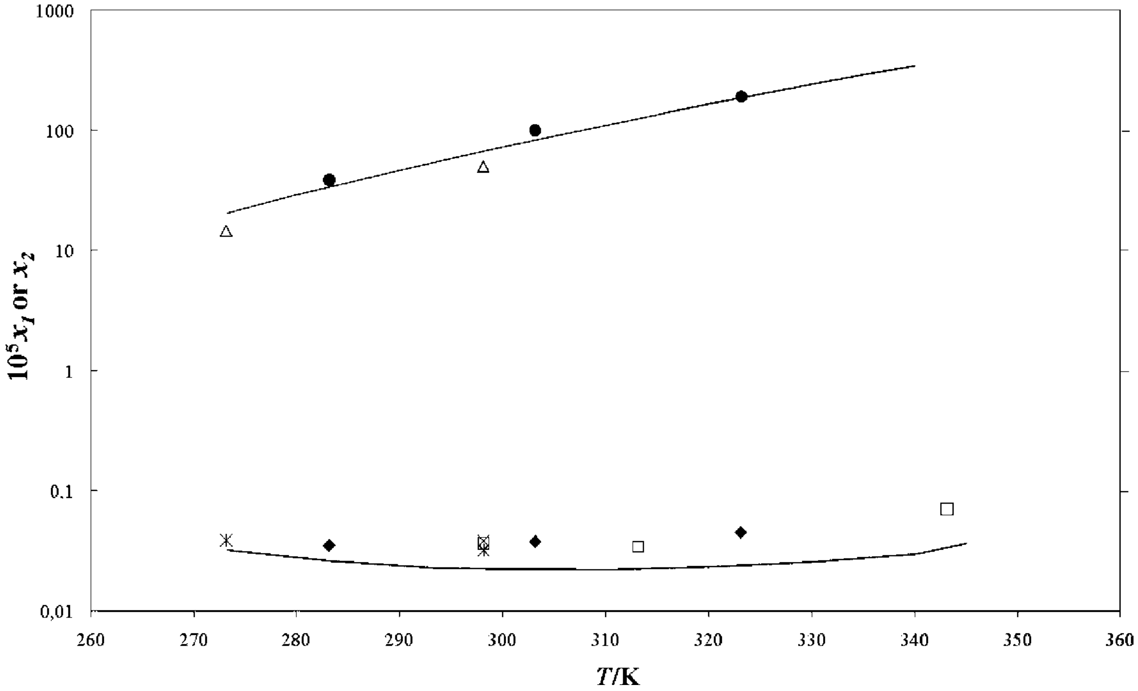

Figure 2. Mutual solubility of the water (1) + 2,2,4-trimethylpentane (2) system. x_1 is the molar fraction of water in the hydrocarbon-rich phase: ●, this work; Δ, Polak and Lu;[6] solid line, Maczynski et al.[7] x_2 is the molar fraction of 2,2,4-trimethylpentane in the aqueous phase: ◆, this work; ×, McAuliffe;[9] □, Perada et al.;[5] *, Polak and Lu;[6] solid line, Maczynski et al.[7]

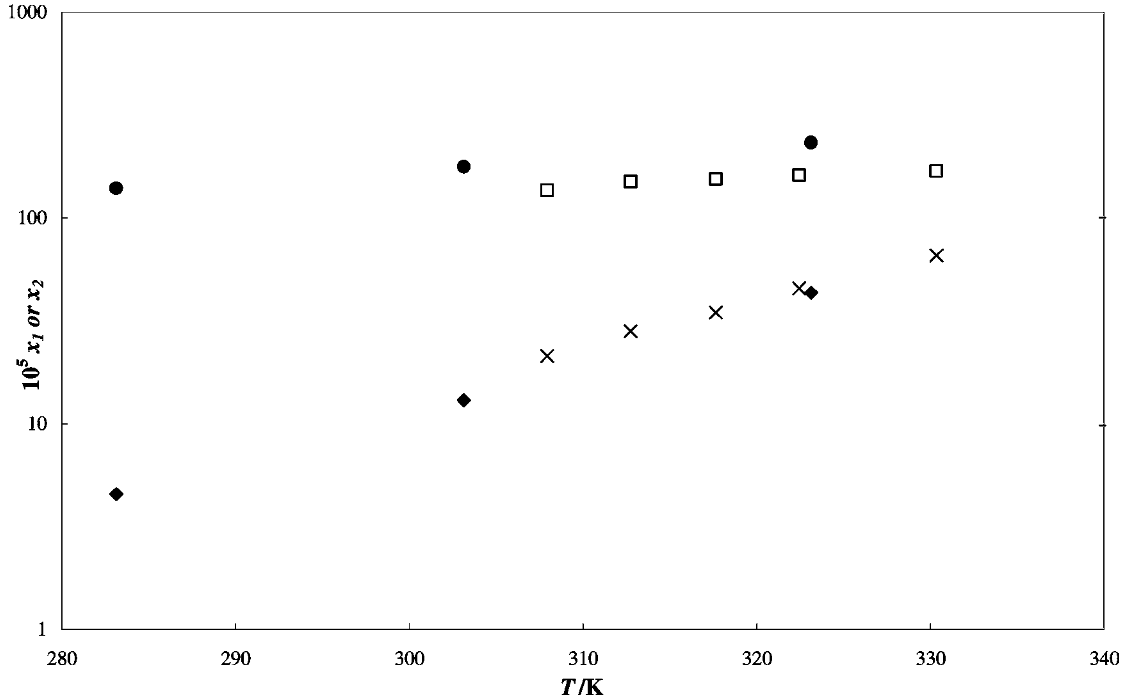

Figure 3. Mutual solubility of the MEG (1) + n-hexane (2) system. x_1 is the molar fraction of MEG in the hydrocarbon-rich phase: ●, this work; □, Derawi et al.[3] x_2 is the molar fraction of n-hexane in the aqueous phase: ◆ this work; ×, Derawi et al.[3]

Results and Discussion

Binary Systems. The obtained mutual solubility data for the binary systems MEG + n-hexane, MEG + 2,2,4-trimethylpentane, water + n-hexane, and water + 2,2,4-trimethylpentane at $T = 283.15$ K, $T = 303.15$ K, and $T = 323.15$ K are presented in Table 2. As shown in Figures 1 to 4, the experimental results were compared to the existing literature data. The solubility data of n-hexane in water obtained in this work are in good agreement with those of Perada et al.[5] and Polak and Lu[6] and are close to the values calculated from the Mazynski et al. equation.[7] On the other hand, our measurements are higher than the values of Marche,[8] McAuliffe,[9] Jonsson et al.,[10] and those calculated with the Tsonopoulos[11] correlation. Concerning the solubility of water in n-hexane, our measurements are quite higher than the values of Polak and Lu[6] and in excellent agreement with the calculated values from Maczynski et al.[7] at $T = 283.15$ K and $T = 303.15$ K, as well as the correlated values of Tsonopoulos[11] at $T = 323.15$ K.

The experimental solubility of 2,2,4-trimethylpentane in water is lower than the values of Perada et al.,[5] Polak and Lu,[6] and

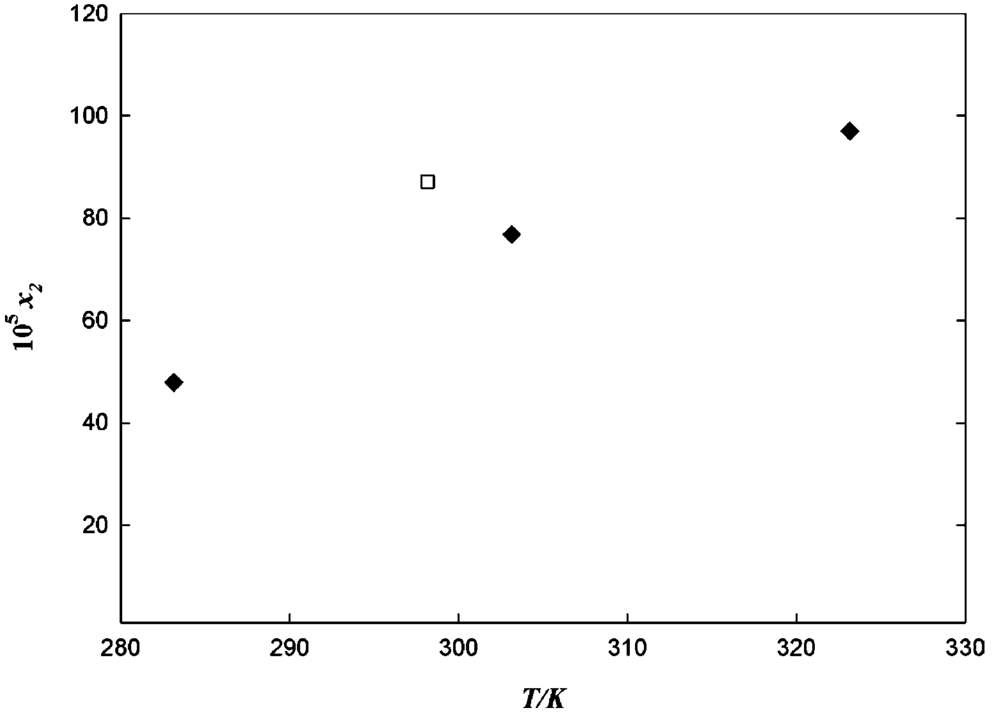

Figure 4. Molar fraction of the MEG (1) + 2,2,4-trimethylpentane (2) system. x_2 is the molar fraction of 2,2,4-trimethylpentane in the MEG phase: ◆, this work □, Arancibia and Catoggio.[4]

Table 3. Experimental Liquid−Liquid Equilibrium Data for the Ternary System Monoethylene Glycol (1) + Water (2) + *n*-Hexane (3) Expressed in Molar Fractions (x_i)

aqueous phase			hydrocarbon-rich phase	
x_1	x_2	$10^5\,x_3$	$10^5\,x_1$	$10^5\,x_2$
		283.15 K		
0.1107	0.8893	0.466	0.18	27.8
0.1500	0.8500	0.531	0.87	27.3
0.2250	0.7750	0.772	0.89	24.7
0.3000	0.7000	1.92	1.62	18.8
0.4038	0.5961	5.42	1.82	18.5
0.5000	0.5000	5.67	2.89	16.7
0.6997	0.2999	46.5	3.98	12.8
0.8494	0.1499	75.0	4.38	11.7
		303.15 K		
0.1107	0.8893	0.599	1.53	67.9
0.1500	0.8500	1.51	1.57	66.6
0.2250	0.7750	1.90	3.05	59.6
0.3000	0.7000	3.94	3.66	57.9
0.4038	0.5961	8.64	6.41	47.2
0.4999	0.4999	17.9	6.57	46.2
0.6996	0.2998	62.3	9.50	37.9
0.8491	0.1498	111	11.1	23.6
		323.15 K		
0.1107	0.8893	0.955	3.68	116
0.1500	0.8500	1.95	5.58	113
0.2250	0.7750	3.33	8.27	97.9
0.3000	0.7000	6.37	11.2	94.2
0.4038	0.5961	13.3	17.7	81.0
0.4999	0.4999	26.0	20.3	72.8
0.6995	0.2998	74.1	29.7	57.3
0.8487	0.1498	153	34.7	39.7

McAuliffe,[9] but it is close to the values calculated by the equation of Maczynski et al.[7] For the hydrocarbon-rich phase, the solubilities of water are in good agreement with the calculated values of Maczynski et al.[7] and are higher than the values of Polak and Lu.[6]

The solubility data of MEG in *n*-hexane of the present study are in very good agreement with the values of Derawi et al.,[3] whereas the solubilities of hexane in the MEG of the latter are lower than the values reported in this work.

Table 4. Experimental Liquid−Liquid Equilibrium Data for the Ternary System Monoethylene Glycol (1) + Water (2) + 2,2,4-Trimethylpentane (3) Expressed in Molar Fractions (x_i)

aqueous phase			hydrocarbon-rich phase	
x_1	x_2	$10^5\,x_3$	$10^5\,x_1$	$10^5\,x_2$
		283.15 K		
0.1500	0.8500	0.131	0.594	37.3
0.3000	0.7000	0.639	1.41	32.2
0.5000	0.5000	3.09	2.18	27.0
0.6999	0.3000	13.5	3.37	24.3
0.8498	0.1500	27.4	5.24	20.1
		303.15 K		
0.1500	0.8500	0.217	2.48	97.2
0.3000	0.7000	1.03	4.67	76.0
0.5000	0.5000	5.52	8.54	53.8
0.6999	0.2999	18.7	14.3	41.3
0.8497	0.1499	40.8	15.8	29.9
		323.15 K		
0.1500	0.8500	0.369	4.91	155
0.3000	0.7000	1.77	10.5	147
0.5000	0.5000	8.68	21.3	114
0.6998	0.2999	28.7	28.4	75.3
0.8495	0.1499	55.1	38.6	64.3

Finally, the comparison with the sole literature solubility value (determined from the activity coefficient at infinite dilution) of 2,2,4-trimethylpentane in MEG at 298.15 K, measured by Arancibia and Catoggio,[4] is in quite good agreement with the experimental values (Figure 4).

Ternary Systems. In Tables 3 and 4 are reported experimental LLE data for the ternary systems MEG + water + *n*-hexane and MEG + water + 2,2,4-trimethylpentane at $T = 283.15$ K, $T = 303.15$ K, and $T = 323.15$ K. No literature data, for comparison, were found for these mixtures. The ternary systems studied by Folas et al.[2] were MEG + water + benzene/toluene, and the solubilities of MEG and water in the aromatic hydrocarbons are 100 times more important than in *n*-hexane for similar composition of MEG + water and similar temperature. The important solubilities of MEG and water are due to the interactions between MEG/water (polar compounds) and the delocalized electrons of the aromatic rings of benzene/toluene.

Conclusion

In this work, experimental liquid−liquid equilibrium data for binary and ternary mixtures containing monoethylene glycol, water, and alkane (*n*-hexane and 2,2,4-trimethylpentane) over the temperature range $T = 283.15$ K to $T = 323.15$ K have been presented. The solubilities of the binary mixtures are generally in a good agreement with the existing literature data. It can be observed that the solubility of monoethylene glycol in the organic phase is multiplied by a factor of 10 and 6, respectively, in *n*-hexane and 2,2,4-trimethylpentane, when the temperature varies from $T = 283.15$ K to $T = 323.15$ K. For the same interval of temperature, the solubility of *n*-hexane and 2,2,4-trimethylpentane in the monoethylene glycol-rich phase increases only by a factor of 2. For the binary systems water + *n*-hexane/2,2,4-trimethylpentane, the solubility of the two hydrocarbons is constant with the variation of temperature in the explored range. Concerning the ternary mixtures, no literature data were found for comparison. The solubility of *n*-hexane in the polar phase increases with temperature and with the quantity of monoethylene glycol.

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