Liquid−Liquid Equilibria for Glycols + Hydrocarbons: Data and Correlation

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Liquid−liquid equilibrium data for seven binary glycol−hydrocarbon systems have been measured in the temperature range 32 °C to 80 °C and at the pressure 1 bar. The measured systems are monoethylene glycol (MEG) + heptane, methylcyclohexane (MCH) + hexane, propylene glycol (PG) + heptane, diethylene glycol (DEG) + heptane, triethylene glycol (TEG) + heptane, and tetraethylene glycol (TETRA) + heptane. The data obtained were correlated with the NRTL model and two different versions of the UNIQUAC equation. The NRTL model and one of the UNIQUAC equations (UQ 4) have a linear temperature-dependent interaction parameter term, while the other UNIQUAC equation (UQ 2) has an interaction parameter that is independent of the temperature. There was a fairly good agreement between the experimental data and the models with an average deviation in the composition for both phases of 3% for both NRTL and UQ 4 and 15% for UQ 2. These results indicate the necessity of using the linearly dependent interaction parameters.

Introduction

In the oil industry, various chemicals are added to both production streams and processing streams in order to maintain optimal and safe running, for example, to inhibit gas hydrate formation. These chemicals may have a negative effect on the marine environment and might be found in the refined products going to the consumer, which is evidently not desired. In recent years, there has been an increasing demand from environmental agencies and the petrochemical industry to assess the risk of these hazardous chemicals on the marine environment and their potential threat to humans. Thus, it is important to know the partitioning of such chemicals between the gas, crude oil, and water phases either by experimental measurements or from thermodynamic models. Experimental measurements can be rather expensive and time-consuming.

The production chemicals considered in this work are the glycols such as monoethylene glycol and triethylene glycol. Monoethylene glycol has been used extensively in the petrochemical industry to prevent gas hydrate formation in transportation lines for gas and crude oil, and triethylene glycol is used in gas dehydration units.

Development of thermodynamic models requires experimental data to confirm their range of applicability and assess their validity. A few ternary LLE data are available in the literature for glycols, hydrocarbons, and water, while binary data between glycols and hydrocarbons are very scarce. Binary liquid−liquid equilibrium data for glycols and hydrocarbons are often reported only for the composition for the hydrocarbon phase.

In this work the solubility of each component in both phases is measured by gas chromatography. Earlier measurements of glycols and hydrocarbons have been carried out by the synthetic method for heptane and monoethylene glycol,[1] triethylene glycol,[2] tetraethylene glycol,[2] and diethylene glycol.[3] In the synthetic method, also known as the cloud point method, the solubility is measured for a mixture of known composition by determining the temperature where phase separation occurs.

The measured experimental data are correlated to local composition based activity coefficient models such as NRTL and UNIQUAC.

Experimental Section

Chemicals. The alkanes and the glycols were obtained from MERCK Eurolab AS (0945 Oslo). Table 1 summarizes both the specifications of the used chemicals obtained by MERCK and the measured water content. The water content was measured at 1 bar with a Karl Fischer apparatus of type Mitsubishi moisture meter model CA-06. The coulometric titration method was applied, since the water content in all the samples was below 1 mass %. The chemicals were used without any further purification.

Experimental Procedure. The liquid−liquid equilibrium measurements of glycols and hydrocarbons were carried out at 1 bar in two identical 550 cm^3 glass equilibrium cells. Sampling was possible from each phase, since the cells were equipped with several orifices sealed with Teflon-coated septa. The two cells were used to carry out two parallel measurements to check the reproducibility of the data. An illustration of the experimental setup, which consists of the sampling part and the analysis part, is shown in Figure 1.

The cells were vigorously shaken for approximately 18 h, which was sufficient to achieve equilibrium. The mixture was then transferred to the equilibrium cells to separate for 6 h. Both the mixing and the separation were preformed at the desired temperature in an air-heated oven, which

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Table 1. Specification of the Applied Chemicals

chemical	specified purity as mass %	specified water content as mass %	specified refractive index at 20 °C	measured water content as mass %
ethylene glycol	>99.5	max. 0.1	not specified	0.027
diethylene glycol	>99.0	<0.3	1.115−1.117	0.066
triethylene glycol	>99.0	<0.3	1.123−1.124	0.072
tetraethylene glycol	>97.0	not specified	1.123−1.124	0.116
1,2-propylene glycol	≥99.0	≤0.2	1.036−1.037	0.031
acetone	>99.8	max. 0.05	not specified	0.032
methylcyclohexane	>98.0	not specified	0.769−0.770	not measured
n-heptane	>99.0	max. 0.01	not specified	not measured
n-hexane	>99.0	max. 0.01	not specified	not measured

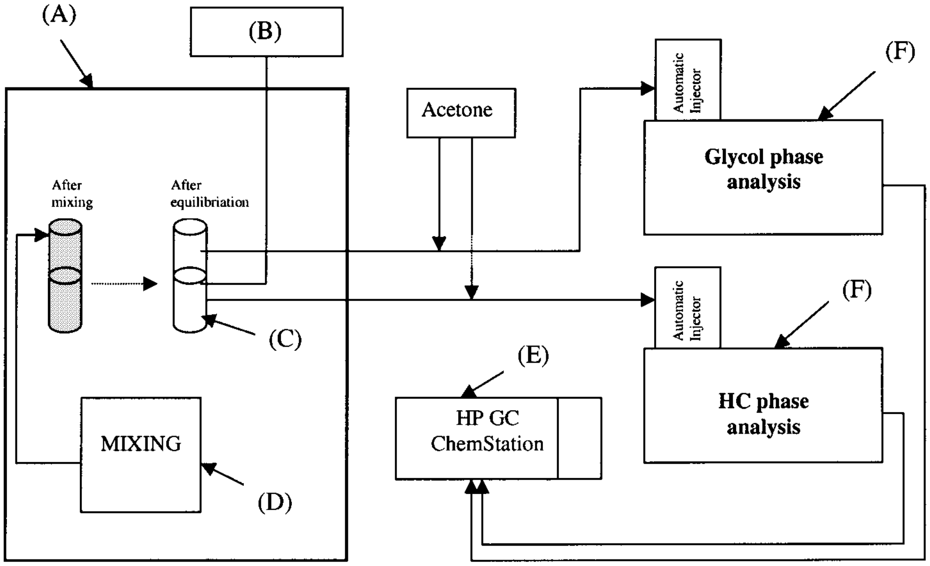

Figure 1. Sketch of the experimental apparatus: (A) air heated oven; (B) thermometer; (C) equilibrium cell; (D) shaker; (E) computer for data analysis; (F) gas chromatograph.

Table 2. Characteristics of the Two HP 5890, SERIES II Gas Chromatographs with an HP 6890 Injector

	GLC A	GLC B
column type	HP-PONA un-polar capillary column	CP-Wax 52 CB polar capillary column
column length	50 m	30 m
column i.d.	0.2 mm	0.53 mm
column film thickness	0.5 μm	1 μm
detector type	FID	FID
carrier gas	helium	helium
injection amount	0.2 μL	1.0 μL

can operate from −35 °C to 100 °C. When the mixture was transferred to the equilibrium cell for separation, both phases were cloudy and became transparent after ∼2 h, which indicated that the mixture reached the equilibrium state.

A FLUKE 52 K-type thermometer (precision ±0.1 °C) was used for the temperature measurements. The thermometer was calibrated with a PT-100 element (precision ±0.03 °C) from 0 °C to 100 °C.

Sampling and Analysis. Samples from the two phases were withdrawn and analyzed with gas−liquid chromatographs (GLCs). The hydrocarbon phase was analyzed for trace amounts of glycols using the column and conditions for GLC A, and the glycol phase was analyzed for trace amounts of hydrocarbons using GLC B. The characteristics of GLC A and B are found in Table 2.

The gas chromatographs are equipped with an enhanced integrator tool set for identification and quantification purposes.

The samples were withdrawn manually after equilibration with a preheated needle in order to avoid phase separation during sampling. Prior to analysis, acetone was added to the sample of both phases to ensure a homogeneous phase before injection into the GLC (Figure 1). For the glycol phase the mass of acetone added was equal to the mass of the sample, and acetone equal to one-third the mass of the sample was added to the hydrocarbon sample.

In principle, there should be no uncertainty connected with the concentration determination as a result of adding acetone, since the calculations should be normalized not to include acetone. Nevertheless, to eliminate that uncertainty, the mass of acetone added to the standard samples (for making the calibration curve) ought to be the same as that added to the withdrawn samples. Better analysis was obtained when the standard samples were analyzed at the same time as the actual samples. The standard samples were prepared by dissolving the analyte in acetone, after which the second component was added. All three chemicals that constitute the standard mixture were weighed, and the uncertainty of the weight was 3% for the utmost diluted standard sample.

The reproducibility of the gas chromatographs was in the worst case ±5% and in most cases 1 to 2%. That is considered to be very efficient. An enhanced integrator was used to optimize the area calculation, and the samples were injected into the gas chromatograph automatically, which meant that the amount of injected sample was approximately the same every time. As a result, an internal standard was unnecessary. The composition in each phase was calculated according to the normalization method, where acetone was excluded from the calculation. The composition was determined within an uncertainty of ±2%. The calibration curve (plot of peak area vs mass of analyte)

Table 3. Mutual Solubility Data of the Monoethylene Glycol (1) + Hydrocarbon (2) Systems Expressed in Mass Fraction (w) as a Function of Temperature for I = Glycol-rich Phase and II = Hydrocarbon-rich Phase

	t/°C	$100w_1^{\mathrm{II}}$	$100w_2^{\mathrm{I}}$
heptane	42.8	0.0198	0.1478
	49.6	0.0287	0.1532
	56.6	0.0399	0.1760
	63.4	0.0553	0.1903
	68.0	0.0677	0.2024
	73.8	0.0867	0.2119
	78.7	0.1066	0.2238
methylcyclohexane	39.5	0.0176	0.3591
	45.3	0.0238	0.3741
	51.3	0.0313	0.4085
	59.2	0.0446	0.4556
	68.9	0.0677	0.4937
	78.7	0.0971	0.5931
hexane	34.8	0.0153	0.1889
	39.6	0.0202	0.2085
	44.5	0.0250	0.2137
	49.3	0.0327	0.2239
	57.2	0.0472	0.2343

was linear for all the analysis. The equation used to calculate the mass fraction w of an analyte i is

$$w_i = \frac{A_i \cdot \mathrm{RF}_i}{\sum_{i=1}^{2}(A_i \cdot \mathrm{RF}_i)} \tag{1}$$

where A_i is the peak area of component i and RF_i is the response factor of component i.

Results and Data Correlation

Experimental Results. The mutual solubility data for monoethylene glycol and different hydrocarbons (heptane, methylcyclohexane, and hexane) as a function of temperature are given in Table 3.

The mutual solubility data for different glycols (propylene glycol, diethylene glycol, triethylene glycol, and tetraethylene glycol) and n-heptane as a function of temperature are given in Table 4.

Figure 2 shows a comparison of the solubility of MEG in n-heptane. It can be seen that the experimental results obtained in this work are in excellent agreement with the data from the literature.

Data Correlation. The experimental data were correlated using the NRTL[4] and UNIQUAC[5] models. Several versions of these models are found in the literature with different expressions for describing the temperature dependency of the binary interaction parameters. The ones used here are outlined below. The excess Gibbs energy for the NRTL model is given by

$$\frac{g^{\mathrm{E}}_{\mathrm{NRTL}}}{RT} = \sum_{i=1}^{m} x_i \frac{\sum_{j=1}^{m} \tau_{ji} G_{ji} x_j}{\sum_{l=1}^{m} G_{li} x_l} \tag{2}$$

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \quad (\alpha_{ij} = \alpha_{ji}) \tag{3}$$

$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T} \tag{4}$$

Table 4. Mutual Solubility Data of the Glycol (1) + Heptane (2) Systems Expressed in Mass Fraction (w) as a Function of Temperature for I = Glycol-rich Phase and II = Hydrocarbon-rich Phase

	t/°C	$100w_1^{\mathrm{II}}$	$100w_2^{\mathrm{I}}$
propylene glycol	34.9	0.0634	1.0948
	39.7	0.0806	1.2506
	44.5	0.1110	1.4807
	49.4	0.1247	1.5465
	59.2	0.1970	1.8377
	68.9	0.2849	2.0197
	78.7	0.4218	2.0662
diethylene glycol	39.6	0.0523	0.6699
	49.9	0.0785	0.7751
	59.9	0.1223	0.8356
	69.9	0.1779	0.8730
	79.9	0.2526	1.0227
triethylene glycol	36.2	0.0914	0.7478
	42.6	0.1150	0.8484
	48.9	0.1456	0.9460
	57.9	0.2073	1.0639
	68.0	0.2864	1.2095
	77.8	0.3928	1.3107
tetraethylene glycol	32.5	0.3043	1.0268
	38.0	0.3557	1.0783
	43.8	0.4217	1.1836
	48.8	0.4628	1.2123
	56.9	0.5599	1.3643
	65.4	0.6404	1.5079
	74.8	0.7699	1.6864
	80.4	0.8702	1.8350

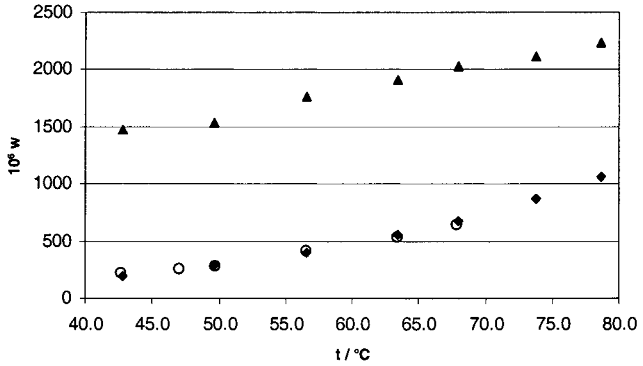

Figure 2. Mutual solubility of the monoethylene glycol (1) + heptane (2) system: ◆, w_1^{II}, this work; ▲, w_2^{I}, this work; ○, w_1^{II}, Staveley and Milward.[1]

where x_i is the mole fraction of component i, α_{ij} is the nonrandomness parameter, and τ_{ij} is the interaction parameter. For a binary mixture, the NRTL model contains five parameters, two binary interaction parameters for each component and the nonrandomness parameter for the binary mixture. The nonrandomness parameter is between 0 and 1, and a recommended value by Renon and Prausnitz[4] is 0.2 for LLE. However, in this work this parameter is optimized along with the other binary interaction parameters.

The excess Gibbs energy for the UNIQUAC model is given by

$$\frac{g^{\mathrm{E}}_{\mathrm{UNIQUAC}}}{RT} = \frac{g^{\mathrm{E}}(\mathrm{c})}{RT} + \frac{g^{\mathrm{E}}(\mathrm{r})}{RT} \tag{5}$$

$$\frac{g^{\mathrm{E}}(\mathrm{c})}{RT} = \sum_{i=1}^{m} x_i \ln\frac{\Phi_i}{x_i} + \frac{Z}{2}\sum_{i=1}^{m} q_i x_i \ln\frac{\theta_i}{\Phi_i} \tag{6}$$

$$\frac{g^{\mathrm{E}}(\mathrm{r})}{RT} = -\sum_{i=1}^{m} q_i x_i \ln\left(\sum_{j=1}^{m}\theta_j \tau_{ji}\right) \tag{7}$$

Table 5. Interaction Parameters for the Temperature-Independent UNIQUAC Model (UQ 2) and the Temperature-Dependent Model (UQ 4) for the Glycol (*i*) + Hydrocarbon (*j*) Systems

		binary interaction parameters			
system	model type	a_{ij}/K	a_{ji}/K	b_{ij}	b_{ji}
monoethylene glycol (*i*) + heptane (*j*)	UQ 2	226.63	909.07		
	UQ 4	162.12	2116.6	0.191 39	−3.557
monoethylene glycol (*i*) + methylcyclohexane (*j*)	UQ 2	215.42	916.96		
	UQ 4	171.9	2090.7	0.120 97	−3.4972
monoethylene glycol (*i*) + hexane (*j*)	UQ 2	248.19	916.77		
	UQ 4	139.50	2232.0	0.344 45	−3.9751
propylene glycol (*i*) + heptane (*j*)	UQ 2	63.55	667.37		
	UQ 4	186.51	1309.9	−0.389 02	−1.9005
diethylene glycol (*i*) + heptane (*j*)	UQ 2	97.42	543.25		
	UQ 4	33.014	1150.1	0.189 88	−1.7972
triethylene glycol (*i*) + heptane (*j*)	UQ 2	102.09	359.05		
	UQ 4	56.79	725.57	0.135 87	−1.1052
tetraethylene glycol (*i*) + heptane (*j*)	UQ 2	132.22	208.10		
	UQ 4	74.2	348.57	0.1765	−0.428 84

Table 6. Interaction Parameters for the Temperature-Dependent NRTL Model for the Glycol (*i*) + Hydrocarbon (*j*) Systems

	binary interaction parameters				nonrandomness parameter
system	a_{ij}	a_{ji}	b_{ij}/K	b_{ji}/K	α_{ij}
monoethylene glycol (*i*) + heptane (*j*)	0.76226	−7.9586	1924.3	4938.4	0.398 67
monoethylene glycol (*i*) + methylcyclohexane (*j*)	0.040125	−8.1325	1281.9	4487.9	0.182 64
monoethylene glycol (*i*) + hexane (*j*)	0.84609	−7.7434	1716.7	4823.1	0.380 69
propylene glycol (*i*) + heptane (*j*)	−1.9112	−6.4613	2055.9	3954.8	0.40
diethylene glycol (*i*) + heptane (*j*)	−1.6333	−7.6360	1790.7	4378.1	0.279 06
triethylene glycol (*i*) + heptane (*j*)	−2.4885	−5.441	1853.7	3557.9	0.269 1
tetraethylene glycol (*i*) + heptane (*j*)	−1.3819	−2.0214	1310.9	2201.6	0.267 7

Table 7. AAD (%) for the Seven Binary Systems Considered with the Three Activity Coefficient Models[a]

	UQ 2		UQ 4		NRTL	
system	I	II	I	II	I	II
monoethylene glycol (*i*) + heptane (*j*)	1.2	31.5	1.6	1.5	1.6	1.0
monoethylene glycol (*i*) + methylcyclohexane (*j*)	3.4	32.7	2.8	2.2	1.6	1.1
monoethylene glycol (*i*) + hexane (*j*)	2.0	19.0	2.0	1.5	2.4	2.3
propylene glycol (*i*) + heptane (*j*)	12.0	40.3	6.1	6.0	4.8	7.6
diethylene glycol (*i*) + heptane (*j*)	2.7	28.0	2.4	1.5	4.3	2.0
triethylene glycol (*i*) + heptane (*j*)	4.8	21.6	2.5	1.3	2.3	1.0
tetraethylene glycol (*i*) + heptane (*j*)	1.7	5.4	1.3	3.7	1.1	3.2

[a] I = glycol-rich phase, and II = hydrocarbon-rich phase.

where $g^E(c)$ and $g^E(r)$ are the combinatorial and the residual contributions. The segment fraction Φ and the area fraction θ are given by

$$\Phi_i = \frac{r_i x_i}{\sum_{j=1}^{m} r_j x_j}, \quad \theta_i = \frac{q_i x_i}{\sum_{j=1}^{m} q_j x_j} \tag{8}$$

$$\tau_{ij} = \exp\left[-\frac{U_{ij}}{T}\right] \tag{9}$$

$$U_{ij} = a_{ij} \quad (\text{UQ 2}) \tag{10}$$

$$U_{ij} = a_{ij} + b_{ij}T \quad (\text{UQ 4}) \tag{11}$$

where r_i and q_i are pure-component relative volume and surface area parameters, respectively, and τ_{ij} is the interaction parameter. The coordination number Z was set to 10. Two parameters, U_{ij} and U_{ji}, are required for each binary mixture. These parameters are temperature dependent, as described above.

The parameters in both models were found by minimizing the objective function

$$F = \sum_{i=1}^{N}\sum_{j=1}^{\text{NOC}}\left(1 - \frac{K_{D_{ij}}(\text{calc})}{K_{D_{ij}}(\text{exp})}\right)^2 \tag{12}$$

where N is the number of experimental points, NOC is the number of components, and K_D is the distribution coefficient defined as the ratio between mole fraction i in phase I and mole fraction j in phase II.

Minimization of the objective function was implemented with the commercial software PRO/II[6] of SimSci. The optimization of the five-parameter NRTL equation and the four-parameter UNIQUAC model (UQ 4) has led to multiple sets of parameters when different initial estimates of the parameters are used. The parameters which were selected were those which yielded the best fit and the lowest relative deviation. Nevertheless, the parameters obtained from the two-parameter UNIQUAC model (UQ 2) were unique even with different initial estimates. In Tables 5 and 6, the optimized values of the interaction parameters for the UNIQUAC and NRTL models are given.

Table 7 gives the percentage average absolute deviation, AAD (%), of the composition in both phases over the considered temperature range with the three models.

Both the NRTL model and the UQ 4 model predict the experimental data for both phases with an AAD of 3%,

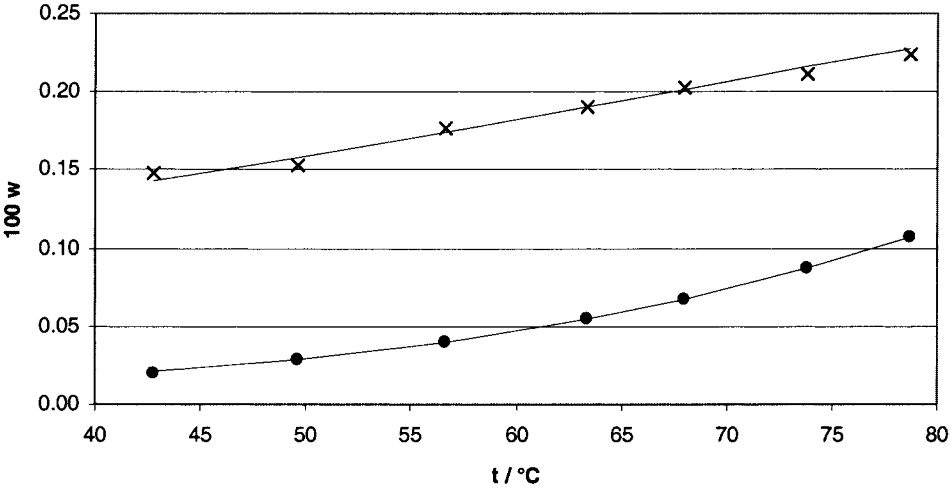

Figure 3. Modeling of the LLE split for the monoethylene glycol (1) + heptane (2) system: ●, w_1^{II}, experimental; ×, w_2^{I}, experimental; solid lines, NRTL model.

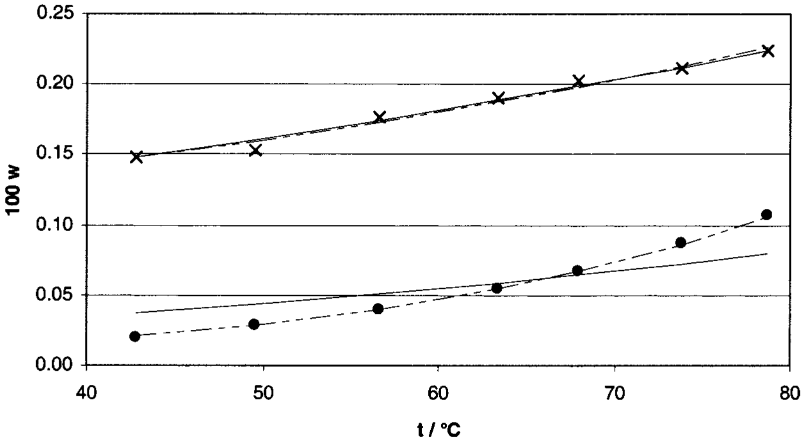

Figure 4. Modeling of the LLE split for the monoethylene glycol (1) + heptane system (2): ●, w_1^{II}, experimental; ×, w_2^{I}, experimental; solid lines, UNIQUAC 2 model; dashed lines, UNIQUAC 4 model.

while the deviation is 15% for the UQ 2 model. However, the deviation is only 4% for the glycol-rich phase for the UQ 2 model. In Figure 3, the NRTL model is compared to the experimental data for the monoethylene glycol + heptane system. The two UNIQUAC models are compared with the experimental data for the same system in Figure 4. Both the NRTL and the UNIQUAC 4 models give an excellent correlation of the experimental solubility data for both the liquid phases. UNIQUAC 2, however, has some difficulty in predicting correctly the solubility of monoethylene glycol in *n*-heptane.

Conclusion

Liquid−liquid equilibrium data for seven binary glycol + hydrocarbon systems were measured in the temperature range 32 °C to 80 °C using GLCs for the analysis. The measured data were successfully correlated with the temperature-dependent UNIQUAC and NRTL models. The temperature-independent UNIQUAC model was not as successful.

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