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# Quaternary Liquid-Liquid Equilibrium of *n*-Heptane-Toluene-*o*-Xylene-Propylene Carbonate

Abu Bakr S. H. Salem,\* Esam Z. Hamad, and Muhammad A. Al-Naafa

Chemical Engineering Department, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

Liquid-liquid equilibrium data for the system *n*-heptane/toluene/*o*-xylene/propylene carbonate were obtained at 25 °C. Experimental tie line data were measured by gas chromatographic analysis. The UNIQUAC and NRTL models were used to predict the quaternary data from the corresponding ternary data. Agreement between the predictions and the experimental data was satisfactory.

## Introduction

Different solvents are commonly used for extracting aromatics from reformat. Among the solvents which have proved to be of commercial use are diethylene glycol (DEG), sulfolane, dimethyl sulfoxide, and morpholine (Yorulmaz and Karpuzcu, 1985). Work is still in progress for exploring other solvents with high selectivity and solvent capacity. Awwad et al. (1988) recommended  $\gamma$ -butyrolactone for aromatics extraction from paraffins. Salem (1993) reported the ternary data of systems containing aromatics, paraffins, and propylene carbonate solvent. Table 1 summarizes the capacities and selectivities of propylene carbonate and some other solvents. This table shows that propylene carbonate can be a competitor to sulfolane which is considered the most preferable solvent for such extractions. The table also shows some physical properties of these solvents. It is clear from Table 1 that propylene carbonate has a much lower viscosity than the other solvents. This is economically attractive since the power requirements for pumping and mixing will be lower. Its high density allows for easy separation during the settling of the phases. Although it is a nonvolatile liquid, its recovery will be easier than sulfolane due to the difference in boiling points as shown in the table. However, the low viscosity and high density of propylene carbonate can lead to difficulty in getting good contact of the phase, especially if the interfacial tension is particularly high. Besides, if the reformat under consideration contains a substantial amount of  $C_{9+}$  aromatics, their recovery from the solvent will be significantly more problematic than their separation from other solvents such as sulfolane or triethylene glycol (TEG). Such a problem results due to the higher boiling points of the  $C_{9+}$  aromatics compared to the propylene carbonate solvent.

Further investigation is still needed for the evaluation of the propylene carbonate capacities and selectivities for a number of aromatic components which are usually present in a multicomponent system as that actually represented by the naphtha reformat. The complete experimental determination of the liquid-liquid equilibrium (LLE) compositions in such systems may be tedious, and it is desirable to be able to predict such compositions with an available thermodynamic model such as the UNIQUAC or the NRTL equation.

In this paper, the experimental measurements of the quaternary system heptane/toluene/*o*-xylene/propylene carbonate at 25 °C are reported with the prediction results obtained by using the UNIQUAC and the NRTL models.

## Experimental Section

**Materials.** Toluene, *o*-xylene, and *n*-heptane were obtained from BDH Chemicals Ltd. Propylene carbonate was obtained from Surechem Products Ltd. The physical properties of these chemicals are given in Table 2.

**Data Collection.** The LLE data for the quaternary system investigated were obtained by using a Perkin Elmer 8500 gas chromatograph with a flame ionization detector. The separation column consists of a glass tube, 1/4-in.-diameter and 2 m long. The column is packed with Apiezon L on Chromosorb W-NAW 80-100 mesh.

The sample mixtures were diluted with acetone solvent. Helium flowing at 20 mL/min was used as the carrier gas. The gas chromatograph was calibrated by injecting standard solutions containing predetermined quantities of the mixture components, and their peaks were determined. For each sample, three analyses were performed to obtain an average response factor for each component from which its concentration was determined.

Sample mixtures for the LLE determination were prepared within the two-phase region using 200-mL flasks with Teflon-lined septum caps. The sample bottles were then placed in a shaker bath for 4 h at 25 °C. After agitation was stopped, the mixtures were transferred to jacketed separatory funnels similar to Smith-Bonner cells. The funnels were kept at 25 °C by using a thermostatically controlled water bath circulator. Proper phase separation in these funnels was allowed for 24 h. The phases were then separated and received in separate flasks. The phases were weighed for material balance checks. Table 3 shows the mass balance of the mixture before and after separation. The percentage error does not exceed 2%, which is satisfactory.

Sample volumes of 0.5  $\mu$ L from each phase were injected into the gas chromatograph for composition measurements. The quaternary LLE data are presented in Table 4. The distribution coefficients  $K$  are calculated by  $K_i = y_i/x_i$ ; the selectivities  $S$  of the solvent are calculated by dividing the distribution coefficient for the aromatic component by that of heptane.  $K_A$  and  $S_A$  are, respectively, the distribution coefficients and selectivity of the solvent toward the total aromatic content relative to heptane in the system.

This table shows that the capacity of the solvent toward toluene at 25 °C ranges from 0.31 to 0.46, which is slightly higher than that obtained when toluene was the sole aromatic present in the system as shown in Table 1. The capacity of propylene carbonate toward *o*-xylene ranges from 0.25 to 0.34. Comparison with the ternary data containing *o*-xylene only as shown in Table 1 indicates that the presence of toluene in this system has also

\* Author to whom correspondence is to be addressed.

Table 1. Characteristics of Some Solvents Used for Aromatics Extraction from Paraffins

no.	system			temp, °C	reference	solvent				
	solvent used	aromatic	paraffin			capacity range	selectivity range	density, kg/L	viscosity, <sup>a</sup> cP	boiling point, °C
1	TEG + 7.7% water	benzene	heptane	121	Graham (1962)	0.2–0.4	17–2	1.125	41.90	285
2	DEG + 7.7% water	benzene	heptane	121	Graham (1962)	0.1–0.2	21–12	1.118	31.23	245
3	sulfolane	toluene	heptane	30	Aschcroft et al. (1982)	0.3–0.8	38–1.7	1.261	11.87	285
4	sulfolane	toluene	heptane	30	Hassan et al. (1988)	0.3–0.5	23–19			
5	sulfolane	toluene	pentane	25	Cassel et al. (1989)	0.25–0.58	16.9–2.5			
6	sulfolane	benzene	pentane	25	Cassel et al. (1989)	0.52–0.69	42–5			
7	diethylene glycol methyl ether	toluene	isooctane	25	Bottini (1986)	0.7–0.8	6–3	1.02		
8	N-methylpyrrolidone	aromatics	paraffins		Bailes et al. (1976)	0.8	8	1.033		
9	propylene carbonate	toluene	heptane	25	Salem (1993)	0.3–0.4	14–6	1.189	2.59	240
10	propylene carbonate	o-xylene	heptane	25	Salem (1993)	0.2–0.3	13–7			

<sup>a</sup> Measured values for the pure solvent.

Table 2. Physical Properties of the Liquids Used

chemical	formula	molecular wt, kg/kmol	density, kg/L	boiling point, °C	RI
n-heptane	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> CH <sub>3</sub>	100.40	0.883	98	1.387
propylene carbonate	C <sub>3</sub> H <sub>6</sub> CO <sub>3</sub>	102.09	1.189	240	1.421
toluene	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	92.14	0.867	111	1.496
o-xylene	C <sub>6</sub> H <sub>4</sub> (CH <sub>3</sub> ) <sub>2</sub>	106.17	0.879	142	1.502

Table 3. Mass Balance of the Extract and Raffinate Phases<sup>a</sup>

PC, g	T, g	o-X, g	n-Hep, g	M, g	E, g	R, g	E + R, g	% error <sup>b</sup>
50	2	3	50	105	51.16	52.15	103.31	1.600
50	4	3	50	110	52.26	55.47	107.73	2.000
50	6	9	50	115	53.57	59.94	113.51	1.300
50	8	12	50	120	54.58	63.14	117.72	1.900
50	12	18	50	130	56.63	72.01	128.64	1.046
50	14.6	21.4	50	136	56.79	77.74	134.53	1.080
50	16	24	50	140	57.74	81.08	138.75	0.890

<sup>a</sup> PC = propylene carbonate; T = toluene; o-X = o-xylene; n-Hep = n-heptane; M = mixture; E = extract; R = raffinate. <sup>b</sup> % error = [M - (E + R)/(M)] × 100.

improved the capacity of the solvent toward o-xylene. The same trend is indicated also in the selectivities toward both aromatics. However, the solvent capacity toward the total aromatic content ranges from 0.274 to 0.387 and the selectivity ranges from 15.6 to 7.5 as shown in the same table. The effect of the presence of other paraffins, cycloparaffins, and other types of aromatics on the capacity and selectivity of such solvents needs also to be investigated.

### Models and Predictions

Liquid–liquid equilibrium can be predicted from appropriate models for the excess Gibbs free energy in the liquid state. However, not all models are capable of predicting liquid-phase separation. For example, the Wilson model (Wilson et al., 1964) is successful in predicting vapor–liquid equilibrium, but cannot predict liquid–liquid equilibrium. In this work the UNIQUAC (Abrams and Prausnitz, 1975) and the NRTL (Renon and Prausnitz, 1968) models will be used due to their success in predicting similar systems. The UNIQUAC model has pure species parameters  $r_i$  and  $q_i$  as well as binary interaction parameters  $A_{ij}$ . This model is given by

$$g^E/RT = \sum_i x_i \ln(\phi_i/x_i) + (\omega/2) \sum_i x_i q_i \ln(\theta_i/\phi_i) - \sum_i q_i x_i \ln(\sum_j \theta_j \tau_{ji}) \quad (1)$$

where

$$\tau_{ji} = \exp(-A_{ij}/T) \quad (2)$$

$$\theta_i = x_i q_i / \sum_j x_j q_j \quad (3)$$

and

$$\phi_i = x_i r_i / \sum_j x_j r_j \quad (4)$$

The NRTL model, on the other hand, has binary parameters only. This model is written as follows:

$$g^E/RT = \sum_i x_i (\sum_j \tau_{ji} x_j G_{ji}) / (\sum_k x_k G_{ki}) \quad (5)$$

where

$$\tau_{ji} = A_{ji}/T \quad (6)$$

and

$$G_{ji} = \exp(-\alpha_{ji} \tau_{ji}) \quad (7)$$

The pure species parameters of the UNIQUAC model,  $r$  and  $q$ , are usually available in the literature (Gmehling et al., 1977; Sorensen and Arlt, 1980). These parameters can be also estimated using a group contribution method (Fredenslund et al., 1977). The binary interaction parameters for the two models are obtained by fitting the model to experimental LLE or VLE (vapor–liquid equilibrium) data. The estimated parameters are not unique, and one must be careful not to mix parameters from different literature sources. For the NRTL model the value of the parameter  $\alpha$  was set to 0.2 throughout this work (Renon and Prausnitz, 1968).

To predict the liquid–liquid equilibrium behavior for the quaternary system of heptane/toluene/o-xylene/propylene carbonate, the binary interaction parameters were estimated from previously reported LLE for the ternary systems heptane/toluene/propylene carbonate and heptane/o-xylene/propylene carbonate (Salem, 1993). The estimation of the six interaction parameters for each of the UNIQUAC and NRTL models was carried out by minimizing the following composition objective function.

$$F = \sum_k \sum_j \sum_i (x_{ijk}(\text{exptl}) - x_{ijk}(\text{pred}))^2 \quad (8)$$

where  $x(\text{exptl})$  and  $x(\text{pred})$  are the experimental and predicted mole fractions,  $i = \text{I, II}$  is the phase index,  $j = 1, 2, 3$  is the component index, and  $k = 1, 2, \dots, M$  is the tie line index. The predicted mole fractions were calculated using a method similar to that of Sorensen and Arlt

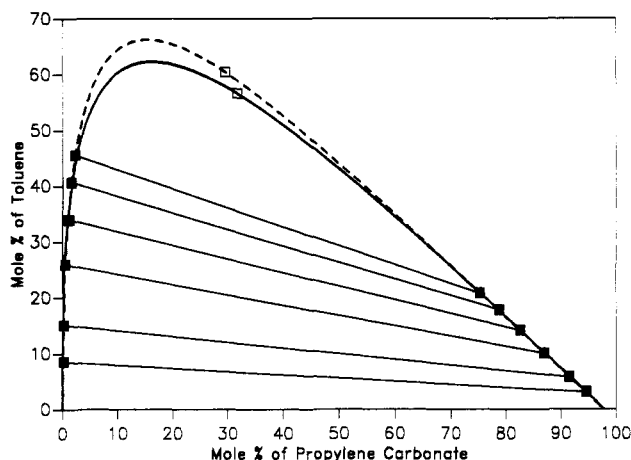
**Table 4. Equilibrium Data of the Quaternary System *n*-Heptane (1), Toluene (2), *o*-Xylene (3), Propylene Carbonate (4) at 25 °C**

propylene carbonate-rich phase, wt %			heptane-rich phase, wt %			capacities and selectivities						
$y_1$	$y_2$	$y_3$	$x_1$	$x_2$	$x_3$	$K_1$	$K_2$	$S_2$	$K_3$	$S_3$	$K_A$	$S_A$
1.611	0.910	1.1236	92.302	2.925	4.493	0.01750	0.3110	17.770	0.250	14.286	0.274	15.664
1.805	1.734	2.1555	86.086	5.318	8.331	0.02097	0.3260	15.550	0.260	12.40	0.285	13.591
1.908	2.526	3.1707	80.627	7.486	11.869	0.02367	0.3374	14.253	0.267	11.280	0.294	12.430
1.975	3.253	3.7480	75.389	9.438	14.769	0.02620	0.3447	13.160	0.254	9.690	0.273	10.410
1.982	4.358	5.2247	67.244	12.543	19.121	0.02948	0.3475	11.789	0.273	9.270	0.303	9.614
2.800	6.387	7.6455	63.350	14.293	22.279	0.04420	0.4469	10.110	0.343	7.765	0.384	8.681
3.075	6.837	8.1267	59.458	14.865	23.813	0.05172	0.4600	8.890	0.341	6.60	0.387	7.482

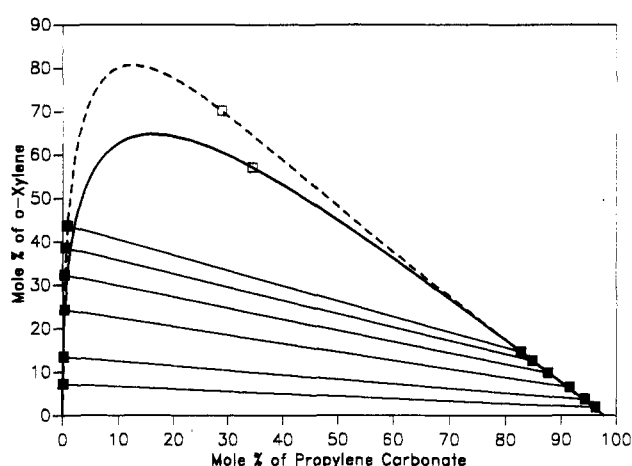
**Table 5. Parameters of the UNIQUAC and NRTL Models at 25 °C**

			UNIQUAC					NRTL ( $\alpha = 0.2$ )		
$i$	$j$	$k$	$A_{ij}$	$A_{ji}$	$r_k$	$q_k$	$s^a$	$A_{ij}$	$A_{ji}$	$s^a$
<i>n</i> -Heptane/Toluene/Propylene Carbonate										
1	2	1	347.16	-218.52	5.1742	4.396	$0.44 \times 10^{-3}$	224.08	-197.49	$0.37 \times 10^{-2}$
1	3	2	1266.60	-15.667	3.9228	2.968		1836.00	646.69	
2	3	3	190.06	-22.650	3.2815	2.736		577.17	-36.53	
<i>n</i> -Heptane/ <i>o</i> -Xylene/Propylene Carbonate										
1	2	1	-11.240	-13.184	5.1742	4.396	$0.78 \times 10^{-3}$	102.63	-170.04	$0.41 \times 10^{-3}$
1	3	2	1266.60	-15.667	4.6578	3.536		1836.00	646.69	
2	3	3	190.310	-22.100	3.2815	2.736		814.86	-83.07	

$$s^a = F^{1/2}/6M.$$

**Figure 1.** LLE data for the system heptane/toluene/propylene carbonate. The solid curve represents the UNIQUAC model, and the dashed curve represents the NRTL model. The solid squares are the experimental measurements, and the open squares are the calculated Plait points.

(1980) in which the criterion of equality of the activities of component  $j$  in both phases is used to solve for the unknown mole fractions. The binodal curve was then constructed by establishing a series of tie lines. The minimization procedure to obtain the model parameters was carried out using a nonlinear least squares subroutine from the IMSL library. Generally the minimization procedure does not give a unique set of parameters. The values reported in Table 5 were chosen to give common binary parameters in different ternary systems; for example the binary parameter for heptane/propylene carbonate has the same value in the two ternary systems heptane/toluene/propylene carbonate and heptane/*o*-xylene/propylene carbonate. The fitted UNIQUAC and NRTL models are shown in Figures 1 and 2. These figures as well as the values of the objective function at the minimum,  $s = F^{1/2}/6M$ , indicate that the UNIQUAC model predicts the behavior of the heptane/toluene/propylene carbonate slightly better than the NRTL model, and vice versa for the heptane/*o*-xylene/propylene carbonate system. The ternary system toluene/*o*-xylene/propylene carbonate will not phase separate in the liquid phase, and

**Figure 2.** LLE data for the system heptane/*o*-xylene/propylene carbonate. Curves and symbols are the same as in Figure 1.

therefore it is not included in Table 5. The toluene/*o*-xylene binary parameters are therefore not obtainable from LLE data with propylene carbonate. However, these two species are very similar in structure, size, and nature of their interaction forces and, as a result, their VLE behavior conforms closely to Raoult's law. For solutions of such species the interaction parameters for UNIQUAC and NRTL can be set equal to zero. Hence, a complete set of parameters is available for predicting the quaternary system phase behavior.

Predicting the phase behavior of this quaternary system was carried out by minimizing the Gibbs energy of mixing  $n^I \Delta G^I + n^{II} \Delta G^{II}$  subject to the usual materials balance constraints  $n_j^I + n_j^{II} = n_j$ , where

$$\Delta G = \sum_j x_j \ln(x_j \gamma_j) \quad (9)$$

The percentage relative errors in predicting the mole fractions using the UNIQUAC and NRTL models are shown in Table 6. The predictions of the two models are reasonably accurate with an error of about 1% when the mole fractions were in the range between 0.5 and 0.9. However, as the mole fractions decrease the relative errors

**Table 6. Percentage Relative Errors in Predicting the Quaternary LLE Behavior of the System *n*-Heptane/Toluene/*o*-Xylene/Propylene Carbonate<sup>a</sup>**

<i>n</i> -heptane <sup>b</sup>	PRE		toluene <sup>b</sup>	PRE		<i>o</i> -xylene <sup>b</sup>	PRE	
	U	N		U	N		U	N
Phase I								
0.9230	-0.4	-0.2	0.0293	-0.8	-4.5	0.0449	2.0	3.4
0.8610	0.1	0.1	0.0532	-6.4	-7.6	0.0833	1.3	3.1
0.8060	0.6	0.3	0.0749	-8.0	-7.7	0.1190	2.9	4.9
0.7540	0.6	0.1	0.0944	-8.6	-7.3	0.1480	2.4	4.3
0.6720	1.7	0.6	0.1250	-10.9	-9.0	0.1910	-0.6	0.9
0.6330	3.0	1.6	0.1430	-10.7	-8.9	0.2230	3.6	4.7
0.5959	1.1	-0.5	0.1490	-12.2	-10.5	0.2380	3.7	4.6
Phase II								
0.0161	-37.7	-46.0	0.0091	-32.2	-19.8	0.0112	11.2	5.6
0.0180	-27.8	-36.1	0.0173	-25.7	-22.1	0.0225	15.3	7.5
0.0191	-24.0	-33.1	0.0253	-19.1	-21.3	0.0317	12.9	3.2
0.0197	-23.2	-33.4	0.0325	-16.1	-22.1	0.0378	4.4	-7.0
0.0198	-27.9	-40.5	0.4360	-17.9	-28.4	0.0522	1.3	-10.7
0.0280	7.2	-2.4	0.0639	6.5	-2.8	0.0765	21.0	11.7
0.0307	14.3	5.2	0.0684	6.7	-3.0	0.0813	18.4	9.1

<sup>a</sup> PRE = percentage relative error; U = UNIQUAC; N = NRTL.<sup>b</sup> Weight fraction.

increase due to division by small values of the mole fractions to get the relative error. The increase in relative errors points out the approximate nature of the two models and their lack of predictive power in the very dilute region.

## Conclusion

Liquid-liquid equilibrium data for the *n*-heptane/toluene/*o*-xylene/propylene carbonate system at 25 °C are presented. The UNIQUAC and NRTL models were used to correlate the experimental tie line data obtained for the ternary systems *n*-heptane/toluene/propylene carbonate and *n*-heptane/*o*-xylene/propylene carbonate and for the quaternary system presented in this work. It was found that the UNIQUAC model represents the behavior of the first ternary system in a better way than that produced by the NRTL model. On the other hand, the NRTL model better fits the second ternary system. The two models used were found to successfully predict the LLE behavior of the quaternary system in concentrated solutions. However, in dilute solutions the models are not accurate in predicting the mole fraction of the components having the lower concentrations in these solutions.

It should be indicated that industrial practice with sulfolane or TEG is usually to run the process at high temperatures, with the consequence that the vapor pressure of the overall mixture is much greater than 1 atm. Therefore, further experimental data using the propylene carbonate solvent may be tried at 200 °F or more.

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## Nomenclature

$A_{ij}$  = binary interaction parameters  
 $g^E$  = molar excess Gibbs energy  
 $F$  = objective function

$G$  = total Gibbs energy  
 $G_{ij}$  = NRTL model constant  
 $M$  = number of tie lines  
 $m$  = number of components  
 $n$  = number of moles  
 $q$  = pure component area parameter  
 $r$  = pure component volume parameter  
 $R$  = gas constant  
 $S$  = selectivity  
 $s$  = standard deviation  
 $T$  = temperature  
 $x$  = solute concentration in the raffinate phase, mole fraction  
 $y$  = solute concentration in the extract phase, mole fraction

## Greek Letters

$\alpha$  = NRTL model parameter  
 $\gamma$  = activity coefficient  
 $\phi$  = segment fraction  
 $\theta$  = area fraction  
 $\tau$  = NRTL and UNIQUAC constant  
 $\omega$  = coordination number

## Literature Cited

- Abrams, D. S.; Prausnitz, J. M. Statistical Thermodynamics of Liquid Mixtures: A New Expression for the Excess Gibbs Energy of Partly or Completely Miscible Systems. *AIChE J.* **1975**, *21*, 116-128.
- Aschcroft, S. J.; Clayton, A. D.; Shearn, R. B. Liquid-Liquid Equilibria for Three Ternary and Six Quaternary Systems Containing sulfolane, *n*-Heptane, Toluene, 2-Propanol, and Water at 303.15 K. *J. Chem. Eng. Data* **1982**, *27*, 148-151.
- Awad, A. M.; Salman, M. A.; Hassan, F. A. Liquid-Liquid Equilibria for the Ternary Systems:  $\gamma$ -Butyrolactone-*n*-Heptane-Benzene,  $\gamma$ -Butyrolactone-*n*-Heptane-Toluene, and  $\gamma$ -Butyrolactone-*n*-Heptane-*p*-Xylene. *J. Chem. Eng. Data* **1988**, *33*, 262-265.
- Bailes, P. J.; Hanson, C.; Hughes, M. A. Extraction of Aromatics. *Chem. Eng.* **1976**, *5*, 115-120.
- Bottini, S. B. Liquid-Liquid Equilibria for the System Toluene-Isooctane-Diethylene Glycol Methyl Ether. *J. Chem. Eng. Data* **1986**, *31*, 84-86.
- Cassel, G. W.; Dural, N.; Hines, A. L. Liquid-Liquid Equilibrium of Sulfolane-Benzene-Pentane and Sulfolane-Toluene-Pentane. *Ind. Eng. Chem. Res.* **1989**, *28*, 1369-1374.
- Fredenslund, A.; Gmehling, J.; Rasmussen, P. *Vapor-liquid equilibrium using UNIFAC*; Elsevier: Amsterdam, 1977.
- Gmehling, J.; Onken, U.; Arlt, W. *Vapor-liquid equilibrium data collection*; DECHEMA: Frankfurt, 1977.
- Graham, H. L. Extraction of Benzene with Di- and Triethylene Glycols. *J. Chem. Eng. Data* **1962**, *7*, 214-217.
- Hassan, M. S.; Fahim, M. A.; Mumford, C. J. Correlation of Phase Equilibria of Naphtha Reformate with Sulfolane. *J. Chem. Eng. Data* **1988**, *33*, 162-165.
- Renon, H.; Prausnitz, J. M. Local Composition in thermodynamic excess functions for liquid mixtures. *AIChE J.* **1968**, *14*, 135-144.
- Salem, A. S. H. Liquid-Liquid Equilibria for the Systems Triethylene Glycol-Toluene-Heptane, Propylene Carbonate-Toluene-Heptane and Propylene Carbonate-*o*-Xylene-Heptane. *Fluid Phase Equilib.* **1993**, *86*, 351-361.
- Sorensen, J. M.; Arlt, W. *Liquid-liquid equilibrium data collection*; DECHEMA: Frankfurt, 1980.
- Yorulmaz, Y.; Karpuzcu, F. Sulpholane Versus Diethylene Glycol In Recovery of Aromatics. *Chem. Eng. Res. Des.* **1985**, *63*, 184-190.

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