JOURNAL OF
CHEMICAL &
ENGINEERING
DATA

ARTICLE

pubs.acs.org/jced

Ternary Liquid−Liquid Equilibria for the (Methanol + Methylbenzene + Decane) System at Different Temperatures

F. S. Mohammad Doulabi,[†] M. Mohsen-Nia,[*,†,‡] and H. Rasa[†]

[†]Thermodynamic Research Laboratory, University of Kashan, Kashan, Iran

[‡]Department of Chemical Engineering, Amirkabir University of Technology, Tehran, Iran

ABSTRACT: Liquid−liquid equilibrium (LLE) results for ternary mixtures of {methanol (1) + methylbenzene (2) + decane (3)} at different temperatures from (298.15 to 313.15) K are reported. The compositions of the liquid phases at equilibrium were determined by gas−liquid chromatography. The data were correlated with the NRTL and UNIQUAC equations. Also, the selectivity and distribution coefficient of methanol for the extraction of methylbenzene from decane at different temperatures are compared. The phase diagrams for the ternary mixtures are presented, and the correlated tie line results are compared with the experimental data. The comparison indicates the applicability of the NRTL and UNIQUAC activity coefficient models for LLE calculations on the studied mixtures.

INTRODUCTION

Although ternary mixtures are frequently encountered in (liquid + liquid) extraction processes, there is considerable current interest in using suitable solvents for extraction of aromatic hydrocarbons from alkane mixtures in different practical fields.[1−3]

Liquid−liquid equilibria (LLE) of ternary systems have been the subject of interest of many researchers from various fields. The design of industrial units for separation processes requires reliable phase equilibrium data for the different systems involved in a given process. Ternary LLE data are essential for a proper understanding of solvent extraction process.[4] Therefore, measurements of the phase equilibrium properties of ternary liquid systems are common.

The key to an effective (liquid + liquid) extraction process is the discovery of a suitable solvent. In addition to being nontoxic, inexpensive, and easily recoverable, a good solvent should be relatively immiscible with feed components other than the solute and have a different density from the feed to facilitate phase separation. Also, it must have a very high affinity for the solute, from which it should be easily separated by distillation or other simple separation processes.

Correlation of the experimental LLE data has been achieved by minimizing the Gibbs free energy of the system. From the theoretical viewpoint for LLE systems at constant temperature and pressure, the equality of the chemical potential of each component in the two phases is the necessary requirement for thermodynamic equilibrium. Therefore, considering the relation between the chemical potential and the activity coefficient of each component, the theoretical-based activity coefficient models provide a useful tool for correlating LLE data.[5,6]

In this work, we report LLE data for the system {methanol (1) + methylbenzene (2) + decane (3)} at T = (298.15, 303.15, and 315.15) K. In the theoretical study of the results obtained, two activity coefficient models, the nonrandom two-liquid (NRTL) model[5] and the universal quasichemical (UNIQUAC) model,[6] were applied to correlate the LLE data, and the values of the model parameters were evaluated and are reported. The obtained results show that the UNIQUAC and NRTL activity coefficient models are applicable for LLE calculations on the studied systems. The selectivity factors and distribution coefficients of methanol were calculated and are reported. The calculated selectivity factors and distribution coefficients indicate that methanol may be used as a potential solvent for extraction of methylbenzene from (methylbenzene + decane) mixtures.

EXPERIMENTAL SECTION

Pure-grade compounds methylbenzene, decane, and methanol were supplied by Merck (Germany). However, the purity of each compound was checked using gas chromatography, and the results confirmed that the mass fraction purity was higher than 0.99.

The experimental points defining the tie line in the phase diagram were measured using a glass cell with a water jacket in order to maintain a constant temperature. A schematic diagram of the apparatus is presented in Figure 1. The cell temperature was regulated by a thermostatic bath with an uncertainty of ± 0.1 K. The solutions were made by mass using a Sartorius analytical balance (Model A200S) with an uncertainty of ± 0.0001 g. The mixtures were prepared inside the cell and vigorously agitated with a magnetic stirrer for 2 h in order to allow intimate contact between the phases. The mixtures were then set to rest for 24 h to split into two liquid phases and achieve equilibrium. The split liquid phases were transparent with a well-defined interface. Samples of both phases were collected and analyzed to determine their compositions. The sample analysis was performed using a PerkinElmer model 8500 gas chromatograph (GC) equipped with a flame ionization detector. The operating conditions for the

Special Issue: John M. Prausnitz Festschrift

Received: October 30, 2010
Accepted: February 24, 2011
Published: March 31, 2011

Table 1. Operating Conditions for the Gas Chromatography Instrument

	this work	previous work[4]
column	6% Silar 10C sorb WHP 100−200 mesh	OV- 17 Csorb WHP 100−200 mesh
detector temp	548.15 K	523.15 K
injector temp	548.15 K	523.15 K
oven temp	348.15 K (isotime = 0.5 min) $\xrightarrow{298.15\ \mathrm{K \cdot min^{-1}}}$ 498.15 K	333.15 K (isotime = 1 min) $\xrightarrow{298.15\ \mathrm{K \cdot min^{-1}}}$ 463.15 K
carrier gas	nitrogen	nitrogen
flow rate	50 $\mathrm{cm^3 \cdot min^{-1}}$	25 $\mathrm{cm^3 \cdot min^{-1}}$

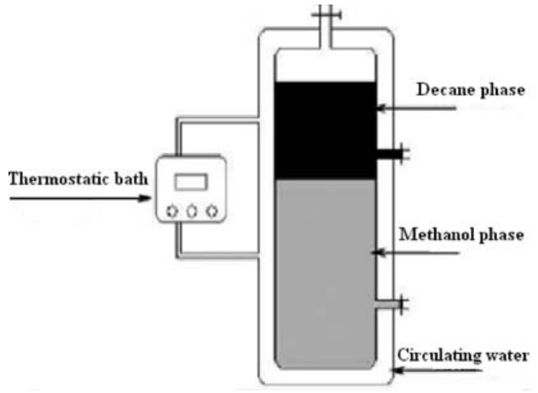

Figure 1. Schematic diagram of the equilibrium apparatus.

GC measurements were different from those in the previous work;[4] a comparison is shown in Table 1. The measured LLE concentrations had an uncertainty of less than 0.5 % for each mole fraction.

RESULTS AND DISCUSSION

The mole fractions x_i^{m} and x_i^{d} of constituent i in the methanol-rich (m) and decane-rich (d) phases, respectively, for the studied ternary mixtures are reported in Table 2. The effectiveness of the extraction of methylbenzene (2) by the solvent, methanol (1), is given by the selectivity (S), a measure of the ability of the solvent to separate methylbenzene from decane that is defined by the following equation:[7]

$$S = \frac{(x_2/x_3)^{\mathrm{m}}}{(x_2/x_3)^{\mathrm{d}}} \tag{1}$$

where $(x_2/x_3)^{\mathrm{m}}$ is the ratio of the methylbenzene mole fraction to the decane mole fraction in the methanol-rich phase and $(x_2/x_3)^{\mathrm{d}}$ is the ratio of the methylbenzene mole fraction to the decane mole fraction in the decane-rich phase. The experimental values of S are listed in Table 2. As the results in this table show, the selectivity in all cases is greater than 1, which means that the extraction of methylbenzene by methanol is possible. The distribution coefficient (K), also called the dissolving capacity of the solvent, is defined as follows:

$$K = \frac{x_2^{\mathrm{m}}}{x_2^{\mathrm{d}}} \tag{2}$$

where x_2^{m} and x_2^{d} are the mole fractions of methylbenzene (2) in methanol-rich and decane-rich phases, respectively. The experimental values of K obtained in this study are presented in Table 2.

Table 2. Experimental LLE Data for Ternary Mixtures {Methanol (1) + Methylbenzene (2) + Decane (3)}

x_1^{d}	x_2^{d}	x_3^{d}	x_1^{m}	x_2^{m}	x_3^{m}	S	K
			T = 298.15 K				
0.1633	0.2855	0.5512	0.7540	0.1459	0.1001	2.81	0.51
0.1499	0.2739	0.5762	0.7850	0.1301	0.0849	3.22	0.47
0.1369	0.2377	0.6254	0.8321	0.1062	0.0617	4.52	0.44
0.1336	0.1861	0.6803	0.8812	0.0759	0.0429	6.52	0.41
0.1332	0.1627	0.7041	0.9056	0.0602	0.0342	7.61	0.37
			T = 303.15 K				
0.2468	0.2675	0.4857	0.715	0.1548	0.1302	2.15	0.58
0.2283	0.2583	0.5134	0.7321	0.1485	0.1194	2.47	0.57
0.2184	0.2314	0.5502	0.7675	0.1302	0.1023	3.02	0.56
0.1913	0.2175	0.5912	0.7898	0.1181	0.0921	3.48	0.54
0.2089	0.1493	0.6418	0.8618	0.0762	0.062	5.28	0.51
			T = 313.15 K				
0.3188	0.2483	0.4329	0.6667	0.1725	0.1608	1.86	0.69
0.3125	0.2156	0.4719	0.7005	0.1462	0.1533	2.08	0.67
0.2818	0.1922	0.526	0.7356	0.1274	0.137	2.53	0.66
0.2305	0.1805	0.589	0.7743	0.1148	0.1109	3.34	0.63
0.2344	0.1553	0.6103	0.8138	0.0952	0.091	4.15	0.61

Table 3. UNIQUAC Structural Parameters

component	r	q
decane	7.1974	6.0160
methylbenzene	3.9228	2.9680
methanol	1.4311	1.4320

The NRTL and UNIQUAC models were used to correlate the experimental data. For the UNIQUAC correlation, the pure-component structural parameters (r and q) were calculated by the method outlined elsewhere[5] and are listed in Table 3.

The phase diagrams for the studied ternary mixtures at three temperatures, (298.15, 303.15, and 313.15) K, are presented in Figures 2 to 4). The experimental selectivities and distribution coefficients for the {methanol (1) + methylbenzene (2) + decane (3)} system at these same temperatures are presented in Figures 5 and 6, respectively. According to these figures, increasing the temperature decreases the selectivity, and therefore, it is better to perform the extraction at lower temperatures. However, for an efficient extraction, an optimum temperature may be found by considering safety and technoeconomic factors.

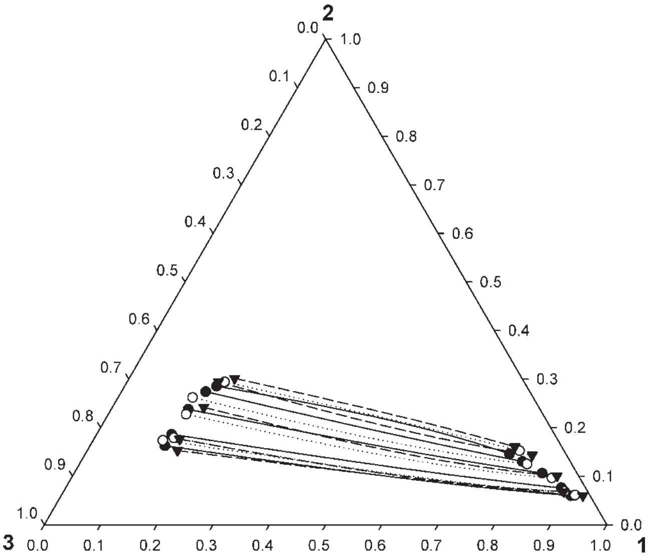

Figure 2. LLE data for the {methanol (1) + methylbenzene (2) + decane (3)} system at 298.15 K: ●, experimental tie line data; ○, NRTL model; ▼, UNIQUAC model.

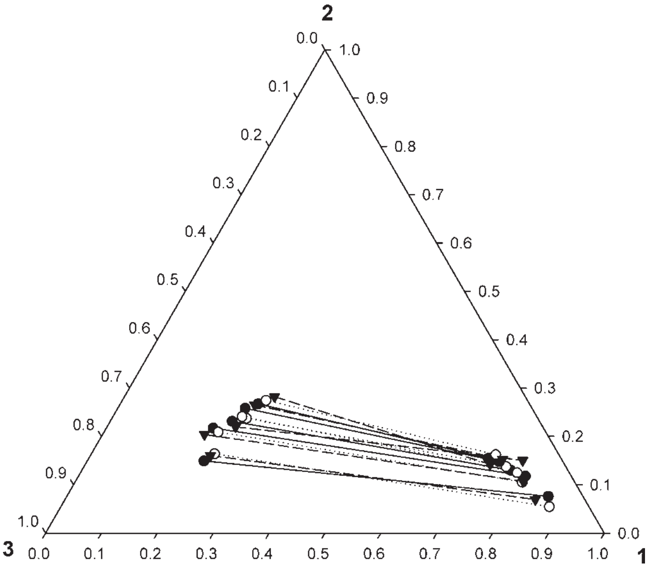

Figure 3. LLE data for the {methanol (1) + methylbenzene (2) + decane (3)} system at 303.15 K: ●, experimental tie line data; ○, NRTL model; ▼, UNIQUAC model.

The binary interaction parameters a_{ij} in the NRTL and UNIQUAC models for the studied systems are presented in Tables 4 and 5, respectively. All of the nonrandomness factors α_{ij} in the NRTL model were fixed at a value of 0.2 and not adjusted during the correlation.

The root-mean-square deviation (RMSD) is a measure of the agreement between the experimental data and the calculated values. It is defined as follows:[8]

$$\text{RMSD} = \left\{ \sum_i \sum_j \sum_k \frac{[x_{ijk}(\text{exptl}) - x_{ijk}(\text{calcd})]^2}{6M} \right\}^{1/2} \qquad (3)$$

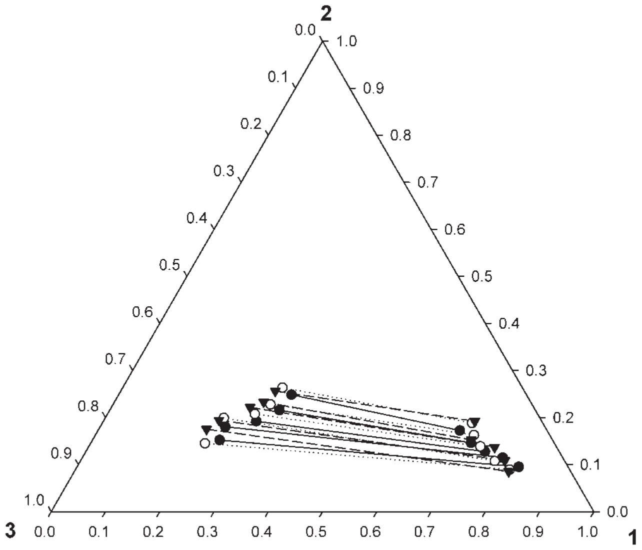

Figure 4. LLE data for {methanol (1) + methylbenzene (2) + decane (3)} system at 313.15 K: ●, experimental tie line data; ○, NRTL model; ▼, UNIQUAC model.

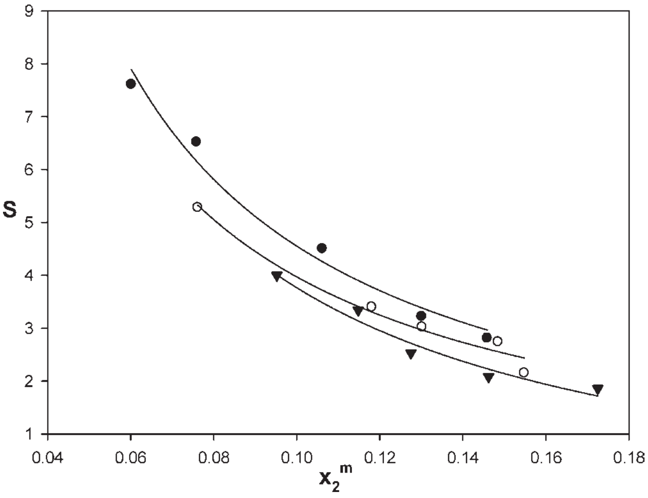

Figure 5. Experimental selectivity data for the {methanol (1) + methylbenzene (2) + decane (3)} system at various temperatures: ●, 298.15 K; ○, 303.15 K; ▼, 313.15 K.

where M is the total number of tie lines, x(exptl) and x(calcd) are the experimental and calculated mole fractions, and the subscripts i, j, and k designate the component, phase, and tie line, respectively. The RMSD values are listed in Table 6. According to this table, the UNIQUAC and NRTL activity coefficient models satisfactorily predicted the equilibrium compositions.

The obtained selectivity and distribution coefficient for the extraction of methylbenzene from (methylbenzene + decane) mixtures by methanol at 313.15 K were compared with those for the extraction of methylbenzene from (methylbenzene + octane) mixtures by ethylene glycol and sulfolane at 307.15 and 313.15 K respectively.[1,2] The comparisons of the S and K

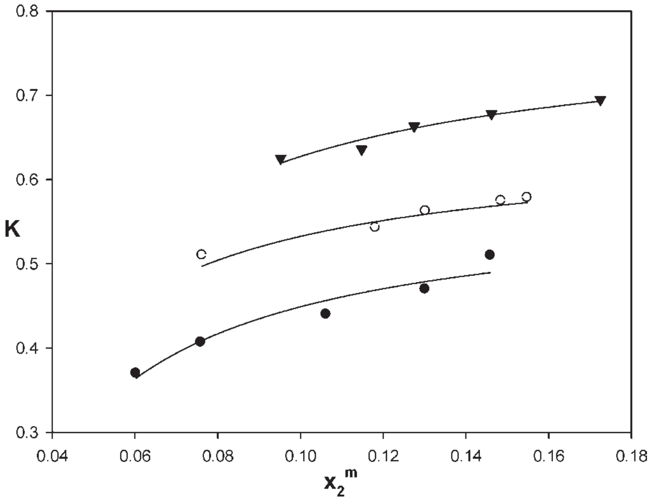

Figure 6. Experimental distribution coefficient data for {methanol (1) + methylbenzene (2) + decane (3) } system at various temperatures: ●, 298.15 K; ○, 303.15 K; ▼, 313.15 K.

Table 4. Values of the Binary Interaction Parameters in the NRTL Model for the {Methanol (1) + Methylbenzene (2) + Decane (3)} System at Different Temperatures

i	*j*	a_{ij}	a_{ji}
1	2	1232.4	991.1
1	3	550.2	1579
2	3	1280.8	100.5

Table 5. Values of the Binary Interaction Parameters in the UNIQUAC Model for the {Methanol (1) + Methylbenzene (2) + Decane (3)} System at Different Temperatures

i	*j*	a_{ij}	a_{ji}
1	2	1119.161	−999.29
1	3	699.676	2.194462
2	3	−499.635	140.898

Table 6. Root-Mean-Square Deviation (RMSD) Values for the Studied Ternary Mixtures at Different Temperatures

298.15 K		303.15 K		313.15 K	
NRTL	UNIQUAC	NRTL	UNIQUAC	NRTL	UNIQUAC
0.0253	0.257	0.0233	0.0307	0.0315	0.0219

values, which are shown in Figures 7 and 8, respectively, indicate that the selectivity of the methanol system is lower than those of the two other systems while the distribution coefficient is higher.

■ CONCLUSIONS

Liquid−liquid equilibrium data for the ternary mixtures {methanol (1) + methylbenzene (2) + decane (3)} at different temperatures have been presented. The NRTL and UNIQUAC models were used to correlate the experimental LLE results. The estimated interaction parameters were successfully used to predict the equilibrium compositions by the two models. The comparisons indicate the applicability of the NRTL and UNIQUAC activity coefficient models for LLE calculations on the studied mixtures. The effect of temperature on the extraction of methylbenzene from (methylbenzene + decane) mixtures by methanol (Table 2) indicates that at lower temperatures, *S* is higher but *K* is lower. Therefore, in practical extractions, the optimum temperature should be considered. The selectivity and distribution coefficient of methanol at different temperatures were calculated. The calculated selectivity and distribution coefficient for the extraction of methylbenzene from (methylbenzene + decane) mixtures by methanol have been compared with those for the extraction of methylbenzene from (methylbenzene + octane) mixtures by ethylene glycol and sulfolane.

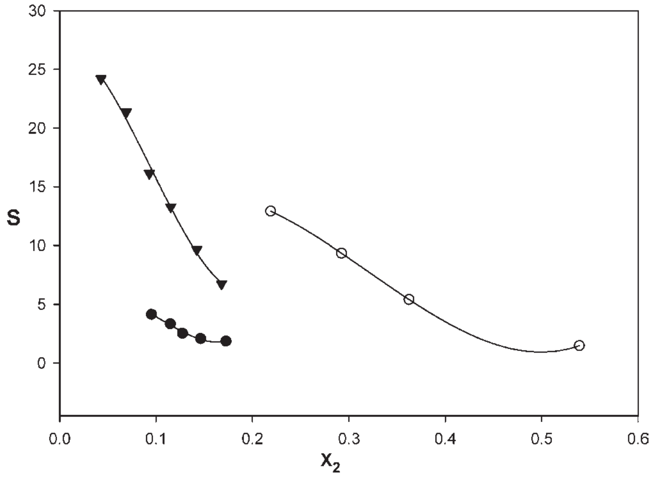

Figure 7. Experimental selectivity data for various systems: ●, {methanol (1) + methylbenzene (2) + decane (3)}; ▼, {ethylene glycol (1) + methylbenzene (2) + octane (3)}; ○, {sulfolane (1) + methylbenzene (2) + octane (3)}.

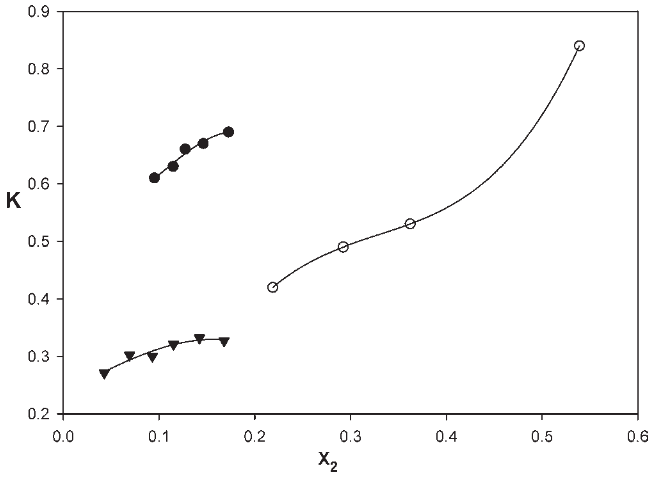

Figure 8. Experimental distribution coefficient data for various systems: ●, {methanol (1) + methylbenzene (2) + decane (3)}; ▲, {ethylene glycol (1) + methylbenzene (2) + octane (3)}; ○, {sulfolane (1) + methylbenzene (2) + octane (3)}.

AUTHOR INFORMATION

Corresponding Author

*Tel.: +983615555333. Fax: +983615552930. E-mail: m.mohsennia@kashanu.ac.ir.

REFERENCES

(1) Mohsen-Nia, M.; Mohammad Doulabi, F. S.; Manousiouthakis, V. I. Liquid + liquid equilibria for ternary mixtures of (ethylene glycol + methylbenzene + *n*-octane). *J. Chem. Thermodyn.* **2008**, *40*, 1269–1273.

(2) Mohammad Doulabi, F. S.; Mohsen-Nia, M.; Modarress, H. Ternary Liquid−Liquid Equilibria for Systems of (sulfolane + methylbenzene or chloronaphthalene + *n*-octane). *J. Chem. Eng. Data* **2006**, *51*, 1431–1435.

(3) Mohsen-Nia, M.; Mohammad Doulabi, F. S. Separation of aromatic hydrocarbons (methylbenzene or benzene) from aliphatic hydrocarbon (heptane) by extraction with ethylene carbonate. *J. Chem. Thermodyn.* **2010**, *42*, 1281–1285.

(4) Mohsen-Nia, M.; Modarress, H.; Doulabi, F.; Bagheri, H. Liquid−liquid equilibria for ternary mixtures of (solvent + aromatic hydrocarbon + alkane). *J. Chem. Thermodyn.* **2005**, *37*, 1111–1118.

(5) 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.

(6) Renone, H.; Prausnitz, J. M. Local composition in thermodynamic excess functions for liquid mixtures. *AIChE J.* **1968**, *14*, 135–144.

(7) Letcher, T. M.; Redhi, G. G.; Radloff, S. E.; Domanksa, U. Liquid−liquid equilibria of the ternary mixtures with sulfolane at 303.15 K. *J. Chem. Eng. Data* **1996**, *41*, 634–638.

(8) Rappel, R.; de Gois, L. M. N.; Mattedi, S. Liquid−liquid equilibria data for systems containing aromatic + nonaromatic + sulfolane at 308.15 and 323.15 K. *Fluid Phase Equilib.* **2002**, *202*, 263–276.