Phase Equilibria of Toluene in Mixtures with Helium or Nitrogen at High Temperatures

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Phase equilibria are measured for helium + toluene and nitrogen + toluene at temperatures from 423 to 545 K over the pressures of 50−150 bar. A flow apparatus was used for the measurement to reduce the possibility of thermal decomposition of toluene at high temperatures. The results are compared with the calculations from five cubic equations of state. All five equations appear to represent the phase behavior with reasonable accuracy for both mixtures. However, an anomalous value of the binary interaction parameter is required to fit the equilibrium data for helium + toluene.

Introduction

Vapor−liquid equilibria were measured for two binary asymmetric mixtures, helium + toluene and nitrogen + toluene, at high temperatures. While equilibrium data are vital to a diversity of industrial applications, data of asymmetric mixtures with significant dissimilarity in molecular sizes/shapes are of great value to the development of theoretical methods for the calculation of mixture properties and understanding of mixture behavior. Equilibrium data are plentiful at ambient temperatures. High-temperature measurements of importance to coal conversion and some other processes are relatively scarce.

Equilibrium compositions of vapor and liquid phases were determined at four temperatures from 423 to 545 K over the pressure range of 50−150 bar for both mixtures. The measurements were made in a flow apparatus to minimize thermal reaction of toluene at high temperatures. No data are available in the literature under similar conditions.

Various cubic equations of state were applied to correlate the experimental values. All the equations were found satisfactory, considering the simplicity of the equations. However, an exceptionally large value of k_{ij} (binary interaction parameter in mixing rule for "a") was obtained from each equation to the results of helium + toluene mixtures.

Experimental Method

A flow apparatus was used in this work for determination of equilibrium compositions. Its major advantage is to reduce the residence time of the chemicals in the high-temperature zone and, consequently, minimize possible thermal decomposition. A detailed description of the apparatus and the experimental procedure was presented by Lin and Lin (*1*).

The temperature was measured by a calibrated type K chromel−alumel thermocouple inserted into the thermowell in the equilibrium cell body to an accuracy of 0.05 °C. Two Hesie gauges of CMM model with maximum ranges of 1000 and 5000 psi were installed to read the pressure in the cell. The accuracy of the gauges is 0.1% of the maximum ranges. Equilibrium compositions of both vapor and liquid phases were determined by volumetrical methods (*1*). The cell effluent for each phase was diverted to a separator after its pressure and temperature were reduced. Toluene, which was a liquid at ambient conditions, was trapped in the separator and later weight to determine its mass by an analytical electronic balance with a precision of ±0.1 mg. The corresponding quantity of gas (helium or nitrogen) liberated from the sample was measured volumetrically: a precision wet test meter for the vapor stream of cell effluents and graduated cylinders of different sizes (250, 500, and 1000 mL) for the liquid stream. The accuracy of the wet test meter was claimed to be within ±0.5%, while the graduated cylinders are readable to 0.5% of their maximum capacities. The phase compositions of x and y (mole fractions of the liquid phase and vapor phase, respectively) are estimated to within 1.5% accuracy for most of the samples. The accuracy is nevertheless also susceptible to the size of the sample taken. The sampling system of this flow apparatus allows the samples of both phases to be taken to a desired quantity under normal operation by controlling the length of sampling time. This option is particularly important for the asymmetric mixtures of a light gas in a heavy compound of low volatility at some extreme conditions, for which a sufficiently large amount of the samples is needed for the compositions to be determined within reasonable accuracy. However, in many practical instances, the equilibrium conditions at constant temperature and pressure are rather difficult to maintain for long periods of sampling, and as a result, the experimental accuracy is often deteriorated for those samples.

Helium and nitrogen were supplied by Matheson with a minimum purity of 99.9 mass %. Toluene was purchased from Fisher Scientific Co. with a purity of 99+ mass %, which was confirmed by gas chromatographic analysis.

Samples of the condensates from the cell effluents were analyzed by gas chromatography for possible thermal decomposition at higher temperatures. No significant quantity of impurities was detected at all experimental conditions reported in Tables 1 and 2. Johns et al. (*2*) investigated the rate of thermal decomposition of toluene. Their results also indicated negligible decomposition under the conditions of this study.

Experimental Results

Vapor−liquid equilibrium compositions are presented in Table 1 for helium + toluene and Table 2 for nitrogen + toluene. Four temperatures from 423 to 545 K and five pressures from 50 to 150 bar at each temperature were measured. At least two samples were taken from each phase under a fixed condition of temperature and pressure. The values as reported in the tables are the averages of

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Table 1. Experimental Vapor–Liquid Equilibrium Data for Helium (1) + Toluene (2)

P/bar	x_1	y_1	K_1	K_2
		T = 423.5 K		
51.04	0.0152	0.9401	61.9	0.0608
75.72	0.0226	0.9569	42.3	0.0441
101.1	0.0296	0.9659	32.6	0.0351
126.6	0.0365	0.9717	26.6	0.0294
151.6	0.0433	0.9756	22.5	0.0255
		T = 464.4 K		
50.91	0.0194	0.8570	44.2	0.146
75.79	0.0294	0.9017	30.7	0.101
101.3	0.0393	0.9224	23.5	0.0808
126.5	0.0489	0.9366	19.2	0.0667
152.0	0.0585	0.9450	16.2	0.0584
		T = 505.2 K		
51.45	0.0242	0.7040	29.1	0.303
76.06	0.0386	0.7964	20.6	0.212
101.3	0.0527	0.8422	16.0	0.167
127.3	0.0662	0.8719	13.2	0.137
152.3	0.0777	0.8910	11.5	0.118
		T = 545.6 K		
50.63	0.0257	0.4606	17.9	0.554
76.79	0.0467	0.6049	13.0	0.415
101.4	0.0662	0.6912	10.4	0.331
126.8	0.0850	0.7447	8.77	0.279
151.7	0.1022	0.7795	7.63	0.246

Table 2. Experimental Vapor–Liquid Equilibrium Data for Nitrogen (1) + Toluene (2)

P/bar	x_1	y_1	K_1	K_2
		T = 423.5 K		
50.83	0.0385	0.9175	23.9	0.0858
76.20	0.0604	0.9304	15.4	0.0741
101.7	0.0809	0.9363	11.6	0.0693
126.9	0.1015	0.9378	9.24	0.0692
151.7	0.1195	0.9419	7.88	0.0660
		T = 464.5 K		
51.91	0.0432	0.8225	19.0	0.186
75.99	0.0683	0.8611	12.6	0.149
101.4	0.0919	0.8761	9.54	0.136
126.5	0.1163	0.8862	7.62	0.129
152.2	0.1407	0.8897	6.32	0.128
		T = 505.5 K		
50.83	0.0467	0.6647	14.2	0.352
75.79	0.0785	0.7305	9.31	0.293
101.3	0.1099	0.7642	6.95	0.265
126.8	0.1393	0.7857	5.64	0.249
152.3	0.1716	0.7972	4.65	0.245
		T = 545.2 K		
51.11	0.0428	0.4273	9.98	0.598
75.65	0.0821	0.5361	6.53	0.505
101.2	0.1233	0.5913	4.80	0.466
126.1	0.1682	0.6163	3.66	0.461
151.6	0.2170	0.6281	2.89	0.475

multiple samples which were reproducible to within 1% under any condition. Included in the tables are also the K values (equilibrium ratios) of helium (or nitrogen) and toluene. The results are shown in Figures 1 and 2 as a function of pressure for each isotherm. Under the experimental conditions, solubilities of helium and nitrogen in toluene increase with pressure and also with temperature at a constant pressure. Nitrogen is more soluble in toluene than helium.

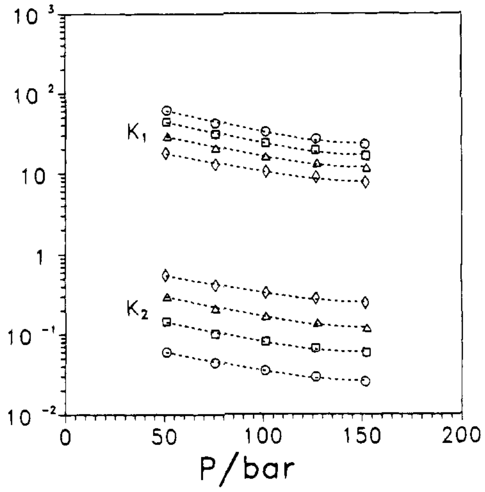

Figure 1. K values of helium (1) + toluene (2) mixtures (○, 423.5 K; □, 464.4 K; △, 505.2 K; ◇, 545.6 K).

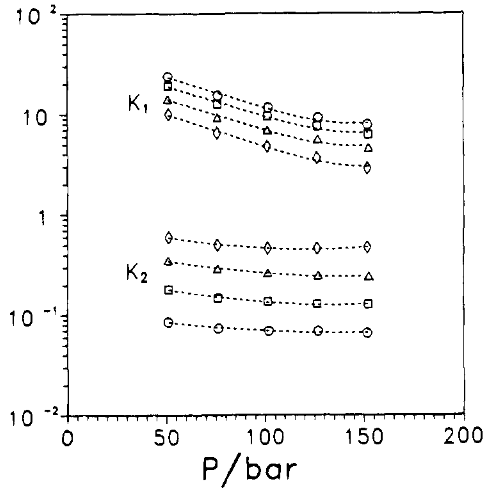

Figure 2. K values of nitrogen (1) + toluene (2) mixtures (○, 423.5 K; □, 464.5 K; △, 505.5 K; ◇, 545.2 K).

Comparison with Equations of State

Five cubic equations of state were applied to represent the phase behavior for both mixtures: the Soave (SRK) (*3*), the Peng–Robinson (PR) (*4*), the Patel–Teja (PT) (*5*), the Iwai–Margerum–Lu (IML) (*6*), and the Jan–Tsai (JT) (*7*). All these equations adopted the traditional van der Waals one-fluid mixing rules for prediction of mixture equation constants a_m and b_m from the properties of constituent components:

$$a_m = \sum_{i=1}^{c} \sum_{j=1}^{c} z_i z_j a_{ij} \tag{1}$$

with

$$a_{ij} = (1 - k_{ij})(a_i a_j)^{0.5}$$

and

$$b_m = \sum_{i=1}^{c} z_i b_i \tag{2}$$

where z_i and z_j are the mole fractions of the vapor or liquid phase for components i and j, respectively. Subscript m in eqs 1 and 2 indicates mixture. The mixing rules for other equation constants (e.g., c in the PT equation, u in the IML equation, and u and w in the JT equation) are given in the cited references. The values of critical temperature, critical pressure, and acentric factor used in the calculations were taken from Reid et al. (*8*).

Table 3 summarizes the calculated results in comparison with experimental data. The calculations were based on the minimization of the AAD (absolute average deviation,

Table 3. Comparison of Vapor–Liquid Equilibrium Data with Calculated Results from Equations of State (EOS)

	helium (1) + toluene (2)			nitrogen (1) + toluene (2)		
		AAD[a] (%)			AAD[a] (%)	
EOS	k_{ij}	K_1	K_2	k_{ij}	K_1	K_2
SRK[b]	1.821	7.3	11.1	0.217	5.0	9.6
	(2.612)[c]	(8.3)	(11.5)	(0.564)	(9.1)	(10.6)
PR[d]	1.337	5.8	9.9	0.207	4.2	7.5
	(1.973)[c]	(6.6)	(8.7)	(0.485)	(7.8)	(8.5)
PT[e]	1.432	6.1	10.0	0.196	4.1	7.6
IML[f]	0.952	4.1	4.5	0.271	4.4	4.5
JT[g]	1.618	5.9	6.2	0.253	4.2	4.7

[a] $\mathrm{AAD}(K_i) = (100/n)\sum_{k=1}^{n}(|K_{i,k}^{\mathrm{cal}} - K_{i,k}^{\mathrm{exp}}|/K_{i,k}^{\mathrm{exp}})$. [b] Soave (*3*). [c] Set $\alpha = 1$ at supercritical temperatures. [d] Peng and Robinson (*4*). [e] Patel and Teja (*5*). The needed values for equation parameters ζ_c and F are $\zeta_c = 0.329$, $F = 0.450\,751$ for nitrogen (*17*); $\zeta_c = 0.306$, $F = 0.753\,893$ for toluene (*17*); and $\zeta_c = 0.338$, $F = -0.180$ for helium as determined by this work. [f] Iwai et al. (*6*). The equation constant $u = 1.181$ for helium as determined by this work, while u values for nitrogen and toluene were estimated from generalized correlation (*6*). [g] Jan and Tsai (*7*).

%) in K values of both helium (or nitrogen) and toluene

$$\pi = (100/2n)\sum_{k=1}^{n}\left(\frac{|K_{1,k}^{\mathrm{cal}} - K_{1,k}^{\mathrm{exp}}|}{K_{1,k}^{\mathrm{exp}}} + \frac{|K_{2,k}^{\mathrm{cal}} - K_{2,k}^{\mathrm{exp}}|}{K_{2,k}^{\mathrm{exp}}}\right) \qquad (3)$$

while the adjustable interaction constant k_{ij} was determined for each equation. π in eq 3 is the objective function used in the optimization for K values of component 1 (helium or nitrogen), $K_{1,k}$, and component 2 (toluene), $K_{2,k}$, where the second subscript k corresponds to the number of the data point. The superscripts exp and cal represent the experimental and the calculated values, respectively.

All five equations were found satisfactory to represent the phase equilibria of both helium + toluene and nitrogen + toluene mixtures, particularly considering the simplicity of the equations. However, helium + toluene mixtures require an exceptionally large value of k_{ij}, ranging from 1 to 1.8, to best fit the experimental data. The primary reason is likely attributable to the erroneous repulsive term of the equations. All equations of Table 3 express the repulsive contribution to pressure by the same form, $RT/(V-b)$, which is known to be theoretically incorrect (*9*). This term overestimates the repulsive pressures that are compensated by an attractive term in a sense of mutual cancellation of errors. The experimental conditions of this work are in the region of high reduced temperatures (T_r = 82–105) and pressures (P_r = 22–67) for helium, at which the repulsive contribution comes to dominate. The parameter k_{ij} plays an important part in adjusting the attractive contribution to correct the total pressure. Other factors that are also related to the optimization of k_{ij} include the expression of $\alpha(T_r)$ for the temperature-dependent (equation constant) a and the mixing rules for the calculation of mixture equation constants.

Each of the equations incorporated an $\alpha(T_r)$ or similar function to account for its energy constant a's dependence on temperature, $a = a_c\alpha(T_r)$, where a_c is a under critical conditions. The applicability of this $\alpha(T_r)$ function is much in doubt, as it is extrapolated to extremely high reduced temperatures. Soave (*3*), for example, has found the need for a refined expression of $\alpha(T_r)$ in the Soave equation to improve its accuracy for mixtures containing light compounds. An alternative is to set $\alpha(T_r) = 1$ at all supercritical temperatures. However, Han et al. (*10*) obtained results in favor of extrapolated $\alpha(T_r)$ under supercritical conditions for a variety of mixtures. Table 3 compares the calculations for the Soave and the Peng–Robinson equations using both methods. Extrapolation of $\alpha(T_r)$ is apparently the better of the two.

Other modifications to the original $\alpha(T_r)$ function of the Soave equation have also been suggested by various studies (*11–13*) specifically for such light gases as hydrogen. A comparison of these variations of $\alpha(T_r)$ for nitrogen, hydrogen, and helium is presented elsewhere (*14*). The expression of $\alpha(T_r)$ was often determined in conjugation with the mixing rules used in the calculations.

Another explanation for the large values of k_{ij} is probably the inadequacy of the van der Waals mixing rules. A variety of new rules have been developed (*11–13*, *15*, *16*), in place of the traditional rules, for representation of phase equilibria in mixtures of hydrogen and heavy hydrocarbons. Lin and co-workers (*14*) recently examined some of these rules with equilibrium data of helium + *m*-xylene. Similar results are obtained for helium + toluene. The calculations with two versions of mixing rules that are conceptually different from the van der Waals rules are presented next.

El-Twaty and Prausnitz (*12*) introduced a quadratic rule for the covolume parameter b_m in the Soave equation for hydrogen containing mixtures:

$$b_m = \sum_{i=1}^{c} z_i b_i + z_H \sum_{j \neq H} z_j E_{Hj} \qquad (4)$$

subscript H stands for hydrogen. The binary interaction parameter E_{Hj} that has the dimensions of volume is adjusted directly to the equilibrium data at each temperature. However, for the simplification of calculations, E_{Hj} is treated as independent of temperature. The mixing rule for a_m is the same as eq 1.

Radosz et al. (*15*) applied a different approach to propose a set of conformal solution mixing rules for the Soave equation constant a_m:

$$a_m b_m^{-0.25} = \sum_{i=1}^{c}\sum_{j=1}^{c} z_i z_j a_{ij} b_{ij}^{-0.25} \qquad (5)$$

with

$$a_{ij} b_{ij}^{-0.25} = (1 - k_{ij})[a_i a_j (b_i b_j)^{-0.25}]^{0.5} \qquad (6)$$

b_m was defined in eq 2.

The calculated results with the mixing rules of El-Twaty and Prausnitz for helium + toluene (AAD in K values of helium and toluene, 10.7% and 6.1%, respectively, with k_{ij} = 1.154 and E_{Hj} = 11.98 cm^3 mol^{-1}), like helium + *m*-xylene, show no advantage over the van der Waals rules even with the addition of an adjustable interaction parameter E_{Hj}. The conformal solution mixing rules of Radosz et al. (*15*) were again found to improve significantly the AAD for both helium and toluene (3.6% and 5.2% with k_{ij} = 1.295). The problem of the peculiar value in k_{ij} remains unsolved, however.

The calculations for nitrogen + toluene are reasonable for engineering applications. The values of k_{ij} (0.2–0.27) are also within the acceptable range.

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