Vapor-Liquid Equilibria of n-Hexane + Cyclohexane + n-Heptane and the Three Constituent Binary Systems at 101.0 kPa

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Vapor-liquid equilibrium data for the title ternary system and the three constituent binary systems have been measured at 101.0 kPa by using a dynamic equilibrium still. The binary data were tested for thermodynamic consistency and were correlated by the Wilson, NRTL, and UNIQUAC equations. Predictions for the ternary system by these equations have been compared with the experimental data.

Introduction

Vapor-liquid equilibrium (VLE) data are of great importance in designing and operating distillation equipment. Some sets of isobaric VLE data have already been reported for the systems n-hexane + cyclohexane (1, 2) and cyclohexane + n-heptane (1, 3). However, to our knowledge, the isobaric VLE data for the ternary system n-hexane + cyclohexane + n-heptane and the other binary are not found in the available literature, although the isothermal VLE data for the binary system n-hexane + n-heptane have been reported (4-6). The ternary system is required for an engineering application because it is a representative petroleum system, containing a cycloparaffin and two straight-chain aliphatic hydrocarbons. Furthermore, the three components are close-boiling, so that the isobaric vapor-liquid equilibria are not very different. In this paper, we present the VLE data for this ternary system and the three constituent binary systems at the pressure of 101.0 kPa. For each binary system the activity coefficients are evaluated and are correlated with three liquid models. The performance of various liquid models for predicting the ternary VLE from the constituent binary data has also been investigated.

Experimental Section

Chemicals. The n-hexane, cyclohexane, and n-heptane were high-purity-grade (>99.5%) products supplied by Fluka. The purity was verified using a gas chromatograph (Hewlett-Packard 5880A). All chemicals were used without further purification.

Apparatus and Procedure. A dynamic equilibrium still manufactured by Fischer Labor-und-Verfahrenstechnik (Germany) was used for measuring the VLE data. A detailed description of the apparatus and operation procedure has been reported (7,8). About 120 mL of liquid mixture is heated in the heating section of the still. The boiling liquid rises through a Cottrell pump and jets out of the nozzle onto the thermometer wall in the equilibrium chamber, where the liquid and vapor are separated into different paths out of the chamber. The vapor is totally condensed, allowing sampling as a liquid. Condensed vapor and liquid are mixed and sent to the heating section to be boiled again. The pressure in the system was maintained constant to within ±0.1 kPa by an electronic regulator. The attainment of a constant temperature for about 1 h was the sign that equilibrium had been reached. Once equilibrium was achieved, the temperature value was recorded and samples of both phases were withdrawn for analysis.

Temperature in the equilibrium chamber was measured with a standard mercury-in-glass thermometer, having an accuracy of ±0.1 K. The liquid and vapor samples were analyzed by using a Hewlett-Packard 5880A gas chromatograph equipped with a flame-ionization detector. The chromatographic column was 6 ft long, ready packed with 15% Thermol-3 on 60/80 Sbimalite, and operated isothermally at 313 K. Both injection and detector temperatures were 443 K. Nitrogen gas was used as the carrier gas at a flow rate of 30 mL/min. The gas chromatograph was calibrated with gravimetrically prepared standard mixtures. For each binary system 10 calibration mixtures were prepared, covering the entire composition range of interest. At least four injections were made for both standard as well as unknown mixtures. An injection volume of 0.4 μL was used. The uncertainty of the composition measurements was estimated to be ±0.001 mole fraction.

Results and Discussion

The VLE data of the three binaries are summarized in Table 1 and are also compared with the previous data (1-3), as shown in Figures 1-3. For the n-hexane + cyclohexane system, the present experimental data lie below the literature values due chiefly to the system pressure being controlled under 101.3 kPa.

The activity coefficients γ_i in the liquid phase were calculated as

$$\ln \gamma_i = \ln\left(\frac{y_i P}{x_i P_i^s}\right) + \frac{(B_{ii} + V_i^L)(P - P_i^s)}{RT} + \frac{P}{2RT}\sum_{j=1}^{n}\sum_{k=1}^{n} y_j y_k (2\delta_{ji} - \delta_{jk}) \quad (1)$$

where

$$\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj} \quad (2)$$

The second virial coefficients B_{ij} for both the pure components and the mixtures were determined according to Tsonopoulos's empirical correlations (9). The molar volumes V_i^L of the saturated pure liquid were estimated by the modified Rackett equation (10). The Antoine equation with the constants obtained from Reid et al. (11) was used to represent the vapor pressures of the pure components P_i^s.

The thermodynamic consistency of the data was tested by using the method described by Fredenslund et al. (12). This test uses a Legendre polynomial for the excess Gibbs free energy and applies the method of Barker (13) to get the best fit of the polynomial to the data. The P-T-x-y data are

Table 1. Isobaric VLE Data: Temperature T, Liquid-Phase x_1 and Vapor-Phase y_1 Mole Fractions, and Activity Coefficients γ_i for Binary Systems at 101.0 kPa

T/K	x_1	y_1	γ_1	γ_2
n-Hexane (1) + Cyclohexane (2)
353.75	0.0000	0.0000		
352.02	0.0796	0.1212	1.1351	1.0045
351.30	0.1250	0.1830	1.1134	1.0032
350.51	0.1806	0.2519	1.0844	1.0040
350.00	0.2165	0.2930	1.0673	1.0074
349.44	0.2592	0.3413	1.0549	1.0093
349.00	0.2939	0.3792	1.0465	1.0111
348.44	0.3352	0.4238	1.0419	1.0135
347.86	0.3786	0.4693	1.0385	1.0162
347.38	0.4163	0.5071	1.0346	1.0194
346.73	0.4672	0.5563	1.0303	1.0252
346.26	0.5066	0.5921	1.0251	1.0324
345.41	0.5926	0.6728	1.0206	1.0293
344.26	0.6943	0.7607	1.0184	1.0392
343.60	0.7618	0.8140	1.0126	1.0580
342.21	0.9070	0.9313	1.0139	1.0451
341.79	1.0000	1.0000		
n-Hexane (1) + n-Heptane (2)
371.47	0.0000	0.0000		
369.45	0.0383	0.0852	1.0568	1.0063
367.18	0.0964	0.1986	1.0345	1.0007
365.50	0.1363	0.2731	1.0489	0.9967
363.52	0.1904	0.3600	1.0402	0.9919
361.41	0.2459	0.4407	1.0405	0.9906
359.11	0.3146	0.5258	1.0300	0.9903
356.37	0.3953	0.6236	1.0452	0.9690
355.56	0.4321	0.6534	1.0239	0.9743
353.95	0.4853	0.7030	1.0245	0.9688
352.93	0.5123	0.7270	1.0320	0.9706
351.94	0.5571	0.7622	1.0224	0.9608
350.27	0.6187	0.8074	1.0215	0.9538
348.72	0.6824	0.8495	1.0178	0.9411
348.13	0.7012	0.8615	1.0215	0.9385
346.66	0.7679	0.8993	1.0154	0.9221
345.55	0.8160	0.9240	1.0138	0.9110
343.74	0.8991	0.9637	1.0116	0.8434
341.81	1.0000	1.0000		
Cyclohexane (1) + n-Heptane (2)
371.45	0.0000	0.0000		
369.45	0.0795	0.1275	1.0477	1.0028
368.40	0.1312	0.2040	1.0435	0.9985
365.95	0.2511	0.3670	1.0454	0.9882
364.34	0.3379	0.4669	1.0313	0.9866
362.77	0.4258	0.5601	1.0239	0.9832
362.06	0.4664	0.6010	1.0224	0.9801
360.15	0.5685	0.6936	1.0198	0.9856
359.95	0.5848	0.7076	1.0169	0.9835
358.60	0.6613	0.7697	1.0154	0.9893
357.74	0.7160	0.8111	1.0122	0.9937
357.05	0.7641	0.8475	1.0104	0.9865
356.18	0.8180	0.8843	1.0093	0.9967
354.85	0.9109	0.9445	1.0053	1.0181
354.15	0.9634	0.9775	1.0037	1.0272
353.79	1.0000	1.0000		

considered to be consistent if the average absolute deviation in the vapor-phase mole fraction is less than 0.01. Table 2 lists the results of the thermodynamic consistency test using a three-parameter Legendre polynomial for the excess Gibbs free energy. It can be seen that the three binary systems studied here satisfy the Fredenslund test.

The experimental data were correlated by the Wilson (14), NRTL (15), and UNIQUAC (16) equations. The definitions of the equations and the pure component parameters are given in the literature (17). As recommended by Renon and Prausnitz (15), the mixture nonrandomness parameter α_{12} in the NRTL equation was set as 0.3.

The values of binary parameters for each equation were determined with the simplex search method. The calculation procedure was based on the minimization of the objective function
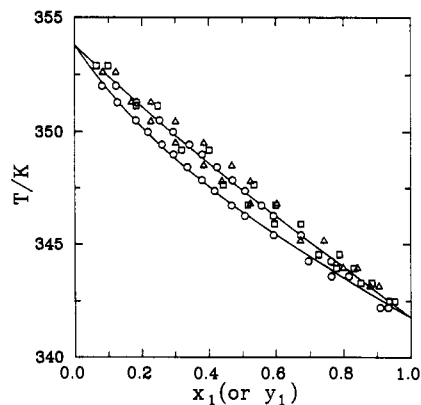

Figure 1. T-x-y diagram for the n-hexane (1) + cyclohexane (2) system at 101.0 kPa: (O) this work; (△) Butler and Ridgway (2); (□) Myers (1); (—) NRTL equation.
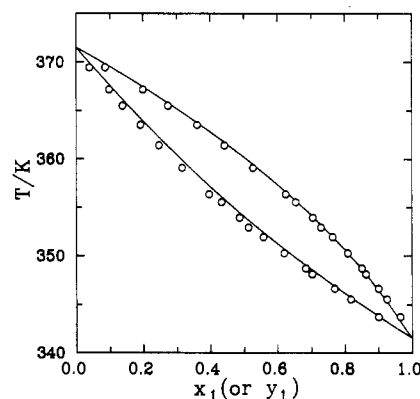

Figure 2. T-x-y diagram for the n-hexane (1) + n-heptane (2) system at 101.0 kPa: (O) experimental data; (—) NRTL equation.
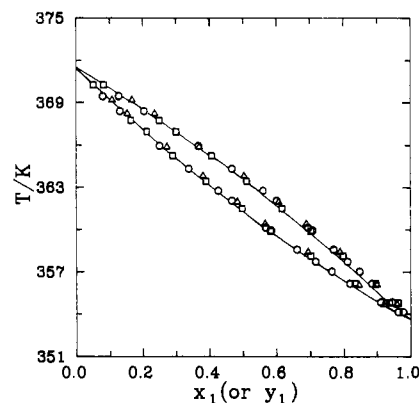

Figure 3. T-x-y diagram for the cyclohexane (1) + n-heptane (2) system at 101.0 kPa: (O) this work; (△) Sieg (3); (□) Myers (1); (—) NRTL equation.

$$OF = \sum_{i=1}^{N}\left[\left(\frac{\gamma_{1,\text{calcd}} - \gamma_{1,\text{exptl}}}{\gamma_{1,\text{exptl}}}\right)_i^2 + \left(\frac{\gamma_{2,\text{calcd}} - \gamma_{2,\text{exptl}}}{\gamma_{2,\text{exptl}}}\right)_i^2\right]$$

(3)

where N is the number of measurements.

The binary parameters for the correlation equations are shown in Table 3, along with the average deviations between the calculated and experimental boiling temperatures ΔT and vapor-phase mole fractions Δy_i where

$$\Delta T = (1/N)\sum_{i=1}^{N}|T_{\text{calcd}} - T_{\text{exptl}}|_i$$

(4)

Table 2. Coefficients of the Legendre Polynomial and Average Deviations between Calculated and Experimental Total Pressures $\Delta P/P$ and Vapor-Phase Mole Fractions Δy

system	coefficients of Legendre polynomial			$(\Delta P/P)/\%$	Δy
	a_0	a_1	a_2		
n-hexane + cyclohexane	0.133 434	0.006 444	0.069 005	0.16	0.0025
n-hexane + n-heptane	0.023 745	−0.007 552	0.015 475	0.22	0.0039
cyclohexane + n-heptane	0.046 651	0.000 059	0.048 531	0.10	0.0027

Table 3. Correlation Parameters and Average Deviations between Calculated and Experimental Boiling Temperatures ΔT and Vapor-Phase Mole Fractions Δy_i for the Binary Systems and Ternary System

equation[a]	A_{12}/(cal mol^{-1})	A_{21}/(cal mol^{-1})	$\Delta T/K$	Δy_1	Δy_2	Δy_3
		n-Hexane (1) + Cyclohexane (2)				
Wilson	326.82	−152.13	0.12	0.0027		
NRTL (α_{12} = 0.3)	−400.83	579.39	0.12	0.0025		
UNIQUAC	−205.26	258.49	0.11	0.0022		
		n-Hexane (1) + *n*-Heptane (2)				
Wilson	−388.06	584.47	0.56	0.0108		
NRTL (α_{12} = 0.3)	566.00	−479.25	0.57	0.0112		
UNIQUAC	436.46	−335.77	0.51	0.0096		
		Cyclohexane (1) + *n*-Heptane (2)				
Wilson	−132.46	271.02	0.10	0.0050		
NRTL (α_{12} = 0.3)	601.98	−466.15	0.10	0.0048		
UNIQUAC	228.43	−193.09	0.10	0.0050		
		n-Hexane (1) + Cyclohexane (2) + *n*-Heptane (3)				
Wilson			0.56	0.0097	0.0039	0.0084
NRTL			0.46	0.0087	0.0031	0.0076
UNIQUAC			0.82	0.0125	0.0065	0.0103

[a] The definitions of the Wilson, NRTL, and UNIQUAC equations are given in ref 14.

Table 4. Isobaric VLE Data: Temperature T, Liquid-Phase x_i and Vapor-Phase y_i Mole Fractions, and Activity Coefficients γ_i for the *n*-Hexane (1) + Cyclohexane (2) + *n*-Heptane (3) System at 101.0 kPa

T/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
363.16	0.0731	0.2390	0.1409	0.3260	1.0698	1.0508	0.9829
363.06	0.0917	0.2076	0.1760	0.2829	1.0680	1.0527	0.9823
362.49	0.1013	0.2183	0.1916	0.2924	1.0679	1.0507	0.9811
362.00	0.0649	0.3174	0.1214	0.4155	1.0693	1.0405	0.9842
360.20	0.1338	0.2857	0.2365	0.3550	1.0585	1.0374	0.9749
359.50	0.1888	0.2152	0.3235	0.2648	1.0450	1.0473	0.9774
359.45	0.1691	0.2614	0.2881	0.3180	1.0404	1.0368	0.9802
357.80	0.1078	0.4639	0.1855	0.5370	1.0973	1.0327	0.9657
357.04	0.1153	0.4946	0.1940	0.5584	1.0948	1.0289	0.9685
356.95	0.1637	0.4075	0.2689	0.4608	1.0714	1.0332	0.9644
356.92	0.2825	0.1900	0.4461	0.2183	1.0309	1.0508	0.9740
355.90	0.1272	0.5442	0.2066	0.5922	1.0895	1.0241	0.9679
355.01	0.2732	0.3215	0.4128	0.3480	1.0382	1.0449	0.9589
355.00	0.1376	0.5846	0.2162	0.6191	1.0798	1.0225	0.9639
354.19	0.2352	0.4520	0.3513	0.4686	1.0493	1.0245	0.9600
354.09	0.1479	0.6264	0.2269	0.6422	1.0806	1.0160	0.9703
353.66	0.0944	0.7710	0.1476	0.7753	1.1143	1.0089	0.9716
353.49	0.0738	0.8253	0.1173	0.8252	1.1380	1.0081	0.9720
353.27	0.0390	0.9188	0.0636	0.9120	1.1746	1.0071	0.9932
352.34	0.2687	0.5129	0.3784	0.5019	1.0406	1.0200	0.9690
352.26	0.3948	0.2777	0.5455	0.2771	1.0233	1.0426	0.9598
352.20	0.3294	0.4012	0.4578	0.3957	1.0310	1.0323	0.9656
352.20	0.4308	0.2128	0.5942	0.2129	1.0233	1.0472	0.9608
352.13	0.2259	0.6043	0.3234	0.5853	1.0640	1.0158	0.9572
351.93	0.2905	0.4936	0.4041	0.4788	1.0396	1.0233	0.9716
349.74	0.4862	0.2822	0.6241	0.2619	1.0197	1.0441	0.9459
349.24	0.5893	0.1269	0.7446	0.1169	1.0180	1.0519	0.9530
346.61	0.6813	0.1480	0.7964	0.1260	1.0150	1.0520	0.9680
345.08	0.7353	0.1616	0.8206	0.1339	1.0129	1.0727	0.9890

$$\Delta y_1 = (1/N) \sum_{i=1}^{N} |y_{1,\text{calcd}} - y_{1,\text{exptl}}|_i \quad (5)$$

It indicates that all equations give a good fit of the data. This result is expected since the systems studied are only slightly nonideal.

Table 4 presents the VLE data for the ternary system *n*-hexane + cyclohexane + *n*-heptane. Table 3 lists the

average deviations in calculated boiling temperatures and vapor-phase mole fractions by using various liquid models coupled with the corresponding binary parameters. As observed, the predicted results by the NRTL equation are superior to those of the other two equations.

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