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Isobaric Vapor–Liquid Equilibria for Cyclopentane + Cyclohexene + 1,2-Dichloroethane and the Three Constituent Binary Systems

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Isobaric vapor–liquid equilibria at atmospheric pressure have been determined for the title ternary system and the three constituent binary systems 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 equilibria (VLE) are required for an engineering application such as in the design and operation of distillation equipment. Some sets of isobaric VLE have already been reported for the system cyclohexene + 1,2-dichloroethane (*1, 2*). However, to our knowledge, no VLE data for the ternary system cyclopentane + cyclohexene + 1,2-dichloroethane and for the two other binaries are available. In this paper, we present the VLE data for this ternary system and the three constituent binary systems at the pressure of 101.3 kPa. For each binary system the activity coefficients are evaluated and are correlated with three liquid models. The performance of various liquid models to predict the ternary VLE data from the constituent binary data has also been investigated.

Experimental Section

Vapor–liquid equilibrium measurements were carried out in a dynamic equilibrium still manufactured by Fischer Labor-und-Verfahrenstechnik (Germany). The still allows good mixing of the vapor and liquid phases and good separation of the phases once they reach equilibrium, and it prevents entrainment of liquid drops and partial condensation in the vapor phase. A detailed description of the apparatus and operating procedure has been reported elsewhere (*3, 4*).

The boiling temperature T in the equilibrium still was measured with a mercury-in-glass thermometer (0.1 K divisions), calibrated against a standard thermometer. The pressure P was maintained constant to within ±0.1 kPa by an electronic regulator.

The compositions of the liquid x_i and vapor y_i phases were determined by using a Shimadzu gas chromatograph, type GC-14A, equipped with a flame-ionization detector. The chromatographic column was 180 cm long, ready packed with 0.1% SP-1000 on 80/100 Carbopack, and operated isothermally at 413 K. Injection and detector temperatures were 413 and 473 K, respectively. Nitrogen gas was used as the carrier gas at a flow rate of 60 mL/min. The gas chromatograph was calibrated by using mixtures of known composition that were prepared gravimetrically. The uncertainty of composition measurements was estimated to be ±0.001 mole fraction.

The materials used for this experiment were purchased from Merck and had a minimum purity of 99%. No further purification of the chemicals was attempted since gas chromatographic analysis failed to show any significant impurities. Some physical properties determined for the chemicals were compared with values from the literature as shown in Table I.

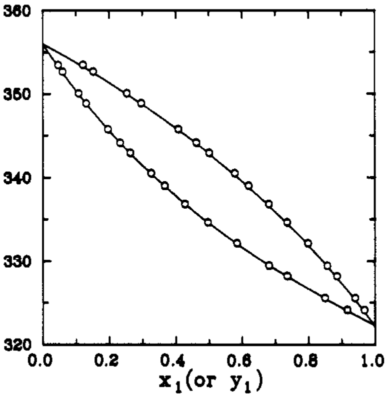

Figure 1. *T–x–y* diagram for the cyclopentane (1) + cyclohexene (2) system at 101.3 kPa: (○) experimental data; (—) NRTL equation.

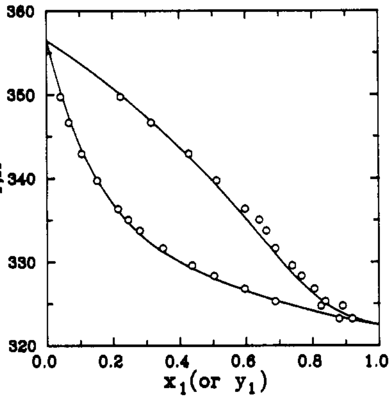

Figure 2. *T–x–y* diagram for the cyclopentane (1) + 1,2-dichloroethane (2) system at 101.3 kPa: (○) experimental data; (—) NRTL equation.

Results and Discussion

The VLE data of the three binaries are presented in Table II and are also plotted in Figures 1–3 together with literature data points (*1, 2*). The system cyclohexene + 1,2-dichloroethane forms an azeotrope, while the other systems do not.

The activity coefficients γ_i in the liquid phase were calculated as

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

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Table I. Physical Properties of Chemicals: Normal Boiling Points T_b, Densities ρ, and Refractive Indexes n_D

compound	T_b/K		ρ(293.15K)/(g cm^{-3})		n_D(293.15K)	
	exptl	lit.[a]	exptl	lit.[a]	exptl	lit.[a]
cyclopentane	322.43	322.412	0.7446	0.745 38	1.4060	1.406 45
cyclohexene	356.02	356.129	0.8105	0.810 96	1.4462	1.446 54
1,2-dichloroethane	356.54	356.633	1.2525	1.253 1	1.4443	1.444 8

[a] Reference 15.

Table II. 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 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2	T/K	x_1	y_1	γ_1	γ_2
Cyclopentane (1) + Cyclohexene (2)									
353.50	0.0467	0.1216	1.086	0.994	339.05	0.3672	0.6206	1.032	1.011
352.70	0.0602	0.1523	1.077	0.996	336.85	0.4280	0.6807	1.033	1.012
350.10	0.1082	0.2537	1.066	0.998	334.65	0.4974	0.7353	1.023	1.027
348.90	0.1310	0.2968	1.063	1.001	332.15	0.5851	0.7983	1.015	1.032
345.80	0.1968	0.4084	1.055	1.002	329.50	0.6809	0.8566	1.012	1.046
344.20	0.2336	0.4625	1.051	1.003	328.25	0.7362	0.8859	1.005	1.052
343.00	0.2641	0.5016	1.041	1.006	325.60	0.8498	0.9401	1.002	1.066
340.55	0.3263	0.5790	1.040	1.004	324.15	0.9171	0.9679	1.000	1.090
Cyclopentane (1) + 1,2-Dichloroethane (2)									
349.75	0.0416	0.2234	2.464	1.011	331.65	0.3493	0.6882	1.487	1.101
346.65	0.0664	0.3147	2.357	1.011	329.60	0.4366	0.7387	1.357	1.147
342.95	0.1050	0.4278	2.236	0.994	328.35	0.5034	0.7661	1.267	1.220
339.75	0.1514	0.5120	2.026	0.995	326.80	0.5960	0.8050	1.179	1.324
336.35	0.2141	0.5976	1.839	0.996	325.30	0.6872	0.8384	1.115	1.499
335.05	0.2450	0.6401	1.787	0.970	324.75	0.8251	0.8908	1.004	1.850
333.75	0.2799	0.6606	1.676	1.004	323.20	0.8797	0.9192	1.019	2.111
Cyclohexene (1) + 1,2-Dichloroethane (2)									
355.55	0.0537	0.0891	1.687	1.004	351.85	0.5361	0.5257	1.111	1.195
354.50	0.1152	0.1695	1.542	1.011	351.95	0.5853	0.5642	1.088	1.225
353.70	0.1715	0.2367	1.480	1.017	352.15	0.6359	0.6060	1.070	1.253
353.05	0.2308	0.2918	1.382	1.037	352.25	0.6410	0.6123	1.069	1.247
352.70	0.2772	0.3349	1.334	1.047	353.05	0.7795	0.7261	1.018	1.399
352.20	0.3705	0.4076	1.233	1.088	354.00	0.8736	0.8242	1.003	1.522
351.90	0.4606	0.4733	1.162	1.140	354.95	0.9355	0.9041	0.999	1.580

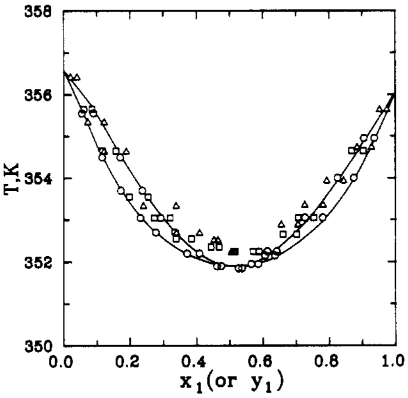

Figure 3. *T–x–y* diagram for the cyclohexene (1) + 1,2-dichloroethane (2) system at 101.3 kPa: (○) this work; (△) Mesnage and Marsan (1); (□) Mato et al. (2); (—) NRTL equation.

Table III. Correlation Parameters A_{12}, A_{21}, and α_{12} 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})	ΔT/K	Δy_1	Δy_2	Δy_3
Cyclopentane (1) + Cyclohexene (2)						
Wilson	45.26	15.64	0.07	0.0007		
NRTL (α_{12} = 0.3)	82.86	−21.86	0.07	0.0007		
UNIQUAC	−55.40	81.21	0.07	0.0006		
Cyclopentane (1) + 1,2-Dichloroethane (2)						
Wilson	259.47	477.92	0.35	0.0109		
NRTL (α_{12} = 0.3)	300.07	391.51	0.37	0.0111		
UNIQUAC	144.37	104.54	0.37	0.0111		
Cyclohexene (1) + 1,2-Dichloroethane (2)						
Wilson	131.18	294.86	0.05	0.0017		
NRTL (α_{12} = 0.3)	55.26	360.64	0.05	0.0017		
UNIQUAC	112.28	29.44	0.05	0.0017		
Cyclopentane (1) + Cyclohexene (2) + 1,2-Dichloroethane (3)						
Wilson			0.90	0.0268	0.0134	0.0214
NRTL			0.78	0.0120	0.0104	0.0116
UNIQUAC			0.79	0.0121	0.0104	0.0116

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

where

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

The second virial coefficients B_{ij} for both the pure components and the mixtures were determined according to Tsonopoulos's empirical correlations (*5*). The molar volumes V_i^L of the saturated liquid were estimated by the modified Rackett equation (*6, 7*). The vapor pressures of the pure components P_i^s were obtained by use of the Antoine equation with the constants from Reid et al. (*8*).

The thermodynamic consistency of the data was tested by using the Herington integral method (*9*) and the point-to-point method as described by Fredenslund et al. (*10*). The three binary systems studied here proved to be consistent in both methods, presenting deviations below the limits established for each test.

The experimental data were correlated by the Wilson (*11*), NRTL (*12*), and UNIQUAC (*13*) equations. The definitions of the equations and the pure component parameters are given in ref 14. As recommended by Renon and Prausnitz (*12*), the mixture nonrandomness parameter α_{12} in the NRTL equation was set as 0.3.

Table IV. Isobaric VLE Data: Temperature T, Liquid-Phase x_i and Vapor-Phase y_i Mole Fractions, and Activity Coefficients γ_i for the Cyclopentane (1) + Cyclohexene (2) + 1,2-Dichloroethane (3) System at 101.3 kPa

T/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
353.35	0.0130	0.9354	0.0350	0.8857	1.128	1.026	1.715
351.55	0.0340	0.9059	0.0926	0.8148	1.194	1.028	1.818
350.95	0.0245	0.0561	0.1268	0.0945	2.303	1.960	1.018
349.10	0.0664	0.8556	0.1812	0.7069	1.273	1.016	1.828
347.50	0.0574	0.1058	0.2300	0.1397	1.949	1.705	1.010
343.55	0.0979	0.1398	0.3659	0.1421	2.019	1.484	0.984
343.05	0.1137	0.3344	0.3268	0.2831	1.574	1.255	1.096
342.15	0.1317	0.3918	0.3517	0.3004	1.498	1.170	1.166
342.05	0.1267	0.1837	0.3936	0.1622	1.747	1.352	1.032
341.45	0.1542	0.4477	0.3674	0.3234	1.362	1.127	1.270
340.95	0.1811	0.5177	0.3907	0.3505	1.251	1.073	1.428
340.05	0.1798	0.3698	0.4231	0.2597	1.398	1.146	1.207
339.50	0.2184	0.4464	0.4453	0.3079	1.230	1.146	1.286
339.45	0.2130	0.4440	0.4406	0.2890	1.250	1.083	1.379
339.45	0.1847	0.2972	0.4463	0.2070	1.460	1.159	1.170
339.05	0.2190	0.4507	0.4585	0.2704	1.279	1.011	1.455
338.70	0.2138	0.4329	0.4624	0.2295	1.334	0.904	1.565
336.95	0.2980	0.3847	0.5273	0.2200	1.146	1.033	1.517
336.15	0.3097	0.4090	0.5628	0.2223	1.204	1.008	1.497
334.35	0.3488	0.3341	0.6205	0.1622	1.241	0.956	1.430
332.75	0.3882	0.2547	0.6655	0.1144	1.253	0.934	1.361
331.30	0.4545	0.2256	0.7038	0.0975	1.181	0.945	1.445
329.70	0.5610	0.2299	0.7664	0.0930	1.092	0.935	1.658
328.80	0.5626	0.1718	0.7687	0.0684	1.123	0.949	1.563
328.10	0.6165	0.1948	0.8028	0.0722	1.093	0.906	1.732
327.25	0.6483	0.1452	0.8096	0.0551	1.075	0.956	1.768
326.15	0.7114	0.1107	0.8451	0.0392	1.058	0.927	1.828
324.85	0.8103	0.0853	0.8978	0.0292	1.027	0.940	2.064
323.80	0.8840	0.0490	0.9331	0.0167	1.011	0.972	2.302

The values of binary parameters for each equation were determined with the simplex search procedure. The following objective function was minimized:

$$\mathrm{OF} = \sum_{i=1}^{N}\left[\left(\frac{\gamma_{1,\mathrm{calcd}} - \gamma_{1,\mathrm{exptl}}}{\gamma_{1,\mathrm{exptl}}}\right)_i^2 + \left(\frac{\gamma_{2,\mathrm{calcd}} - \gamma_{2,\mathrm{exptl}}}{\gamma_{2,\mathrm{exptl}}}\right)_i^2\right] \tag{3}$$

where N is the number of measurements.

The binary parameters for the correlation equations are shown in Table III, along with the average deviations between the calculated and experimental boiling temperatures ΔT and vapor-phase mole fractions Δy_1 where

$$\Delta T = (1/N)\sum_{i=1}^{N}|T_{\mathrm{calcd}} - T_{\mathrm{exptl}}|_i \tag{4}$$

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

The results indicate that all equations are equally suitable to represent the data. Also, for the cyclohexene (1) + 1,2-dichloroethane (2) system the azeotropic temperature T_{AZ} and composition $x_{1,\mathrm{AZ}}$ predicted by the NRTL equation (351.9 K, 0.513) compare fairly well with those of Mesnage and Marsan (*1*) (352.3 K, 0.505) and Mato et al. (*2*) (352.3 K, 0.528).

Table IV presents the VLE data for the ternary system cyclopentane + cyclohexene + 1,2-dichloroethane. The average deviations in the calculated boiling temperatures and vapor-phase mole fractions by using various liquid models coupled with the corresponding binary parameters are listed in Table III. As observed, the results predicted by the NRTL and UNIQUAC equations are superior to those of the Wilson equation.

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