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Vapor−Liquid Equilibrium for Binary Systems of Cyclohexane + Cyclohexanone and + Cyclohexanol at Temperatures from (414.0 to 433.7) K

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In this work, the vapor−liquid equilibrium (VLE) data for binary systems of cyclohexane + cyclohexanone and cyclohexane + cyclohexanol were measured using a static-analytical apparatus at temperatures from (414.0 to 433.7) K. To avoid the disturbance of pressure drop during the sampling process, a stopcock was designed inside the autoclave to block out a part of vapor-phase space quickly before sampling. The measured VLE data were correlated by the Soave−Redlich−Kwong state equation (SRK) and Wilson activity coefficient models. The Redlich−Kwong (RK) and Hayden−O'Connell (HOC) equations were used to modify the vapor ideality in the Wilson models. The fitted Wilson model with the HOC equation (Wilson-HOC) was also compared against predictive universal functional activity coefficient (UNIFAC) models (standard UNIFAC and Dortmund modified UNIFAC). By error analysis, the Wilson-HOC model gave the best fit.

Introduction

Cyclohexanol and cyclohexanone are used as raw materials for adipic acid synthesis, as well as precursors of nylon 6-polymers.[1] They are usually obtained by the liquid oxidation of cyclohexane with air or oxygen at (413 to 443) K and about 1 MPa. The oxidation reaction is a strong exothermal reaction, and the removal of reaction heat from the reactor is a normal challenge during an industrial operation. Because the deep oxidation of cyclohexanone and cyclohexanol at high temperatures leads to lower yield and selectivity,[2] commercial devices often use the recycle cooling system to control the temperature of reactors.

A new idea for the removal of reaction heat is proposed, in which the reactant cyclohexane is partially evaporated and a large amount of the reaction heat is removed by vaporization. It can also partially separate the unreacted reactant cyclohexane from the product stream and hereby reduce the energy consumption in the following product separation. For the view of the design of the new reaction system, the vapor−liquid equilibrium (VLE) data of the reactants system at reaction conditions are needed.

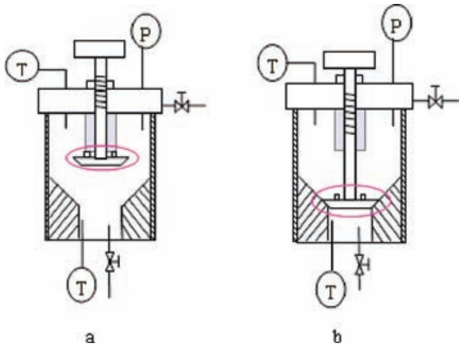

Figure 1. Diagram of the equilibrium autoclave (a, heating state; b, sampling state).

Table 1. Component, Supplier, and Component Purity (Mass Fraction)

component	supplier	purity
pentane	Kelong Chemical Co.	0.9997
ethanol	Kelong Chemical Co.	0.9995
cyclohexane	Kelong Chemical Co.	0.9997
cyclohexanone	Kelong Chemical Co.	0.9997
cyclohexanol	Jingchun Chemical Co.	0.9923

However, the VLE data available this moment are those almost at low temperature (isothermal data) or ambient pressure (isobaric data) for these binary mixtures. Susarev and Lyzlova[3] determined the VLE data for the systems of cyclohexane + cyclohexanol + cyclohexanone at 101.00 kPa. Steyer and Sundmacher[4] measured the VLE data for the system cyclohexane + cyclohexanol at pressures from (100.4 to 101.60) kPa, and the temperature range was from (354.20 to 433.20) K. Jones et al.[5] determined the thermodynamic properties of cyclohexane−cyclohexanol system at 298.15 K. For the system of cyclohexane and cyclohexanone, Boublik and Lu[6] measured the VLE data at (323.15 and 348.15) K. Prasad et al.[7] measured the data at 94.70 kPa, and the temperature changed from (351.85 to 426.35) K. Matteoli and Lepori[8] measured the data at 298.15 K. In the present work, we experimentally measured the VLE data for the mixtures of the reactants at temperatures and pressures near the real reaction conditions (*T* varies from (414.0 to 433.7) K). The data were also correlated with the thermodynamic models, and the results provided a method to calculate the VLE data in the operation situation.

Experimental Section

Apparatus. The VLE data at high temperatures were measured with a static-analytical method. An autoclave used for the VLE measurement was particularly designed with a stopcock inside (see Figure 1), which allowed the separation of gas and liquid phases during the sampling process. The total internal volume of the autoclave was 380 cm^3. The volume of the upper cell separated by the stopcock for the vapor phase was 318.2 cm^3, and the lower cell for the liquid phase was 61.8 cm^3.

The autoclave was connected with a pressure gauge (CYB13, (0 to 4) MPa, accuracy < 0.3 %) and also a vacuum pump (SHZ-

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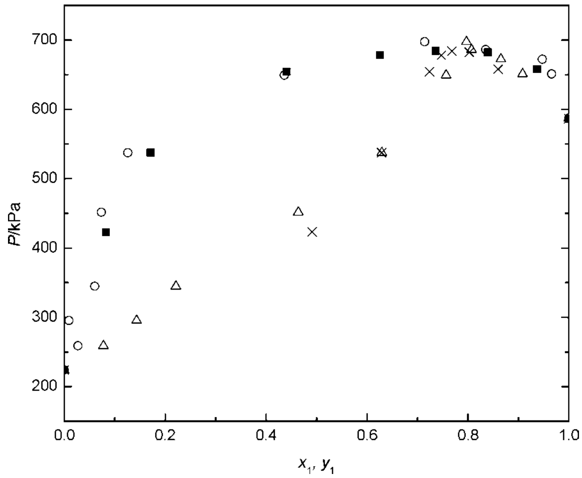

Figure 2. Comparison of the experimental $P-x-y$ data with the literature data for the pentane (1) + ethanol (2) system at 372.7 K. This work: ○, △; ref 9: ■, ×.

D(III)). K-type thermocouple thermometers were used to measure the temperatures of both the gas and the liquid phases (uncertainty ± 0.1 K), and the whole autoclave was put into an air bath that was controlled with an intelligent temperature controller to maintain a stable circumstance temperature.

Compositions were analyzed by gas chromatography (GC112A) equipped with a 30 m × 0.25 mm × 0.33 μm AT FFAP column and an flame ionization (FID) detector. Its reproducibility was evaluated by repetitive measurements. The standard deviation measured was below 5 %.

Procedure. The liquid mixture with a given composition was degassed and filled into the evacuated autoclave. Then, the autoclave was sealed, and the whole setup was put into the thermostatic air bath. The system was heated to the given temperature and maintained in this temperature for about 5 h, until the temperature difference between gas and liquid phases was kept below 0.3 K for at least half of an hour. Meanwhile, the system was considered to be in equilibrium.

Table 4. Physical Properties of the Pure Components[a]

	cyclohexane	cyclohexanone	cyclohexanol	ethanol	pentane
M/g·mol^{-1}	84.162	98.145	100.161	46.069	72.151
T_b/K	353.9	428.8	434.3	351.5	309.2
T_c/K	553.4	664.3	650.0	516.2	469.6
P_c/MPa	4.073	4.600	4.260	6.383	3.374
V_c/cm^3·mol^{-1}	308.0	312.0	327.0	167.0	304.0
Z_c	0.273	0.230	0.240	0.248	0.262
ρ/g·cm^{-3}	0.779^{20}	0.951^{15}	0.942^{30}	0.789^{20}	0.626^{20}
ω	0.213	0.443	0.550	0.635	0.251
η	0	0.9	1.55		

[a] Literature data sourced from ref 19.

Table 5. Parameters of the Wilson-RK, Wilson-HOC, and SRK Models for the Binary Systems Cyclohexane (1) + Cyclohexanone (2) and Cyclohexane (1) + Cyclohexanol (3)

model	system $i + j$	a_{ij}	a_{ji}	b_{ij}	b_{ji}
Wilson[a]-RK	1 + 2	−25.447	8.073	9793.101	−3472.521
	1 + 3	−1.300	4.875	140.020	−2309.286
Wilson[a]-HOC	1 + 2	−24.637	7.826	9475.976	−3383.759
	1 + 3	−1.953	4.937	421.021	−2342.643
		$k_{ij}(1)$	$k_{ij}(2)$	l_{ij}	l_{ji}
SRK[b]	1 + 2	−0.430	0.001	−5.977	−2.440
	1 + 3	−0.205	0.001	−6.182	−2.132

[a] $\ln A_{ij} = a_{ij} + b_{ij}/(T/\text{K})$, where $a_{ij} \neq a_{ji}$ and $b_{ij} \neq b_{ji}$.

[b]

$$P = \frac{RT}{V_m + c - b} - \frac{a}{(V_m + c)(V_m + c + b)}$$

where $a = a_0 + a_1$, $b = \sum_i x_i b_i$, and $c = \sum_i x_i c_i$.

$$a_0 = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \sqrt{a_i a_j}(1 - k_{ij})$$

$$a_1 = \sum_{i=1}^{n} x_i (\sum_{j=1}^{n} x_j ((a_i a_j)^{1/2} l_{j,i})^{1/3})^3$$

where $k_{ij} = k_{ij}(1) + k_{ij}(2)(T/\text{K})$, $k_{ij} = k_{ji}$, and $l_{ij} \neq l_{ji}$.

After the equilibrium was reached, both gas and liquid phases were separated by closing the inner stopcock of the autoclave

Table 2. VLE Measurements for the Cyclohexane (1) + Cyclohexanone (2) System at (414.0 to 433.7) K

P/kPa	x_2	y_2	P/kPa	x_2	y_2	P/kPa	x_2	y_2
T/K = 414.0 ± 0.3			T/K = 423.4 ± 0.3			T/K = 433.7 ± 0.3		
457.667	0.0000	0.0000	555.246	0.0000	0.0000	677.813	0.0000	0.0000
456.050	0.0211	0.0107	555.185	0.0259	0.0129	674.445	0.0052	0.0022
455.039	0.0302	0.0138	539.009	0.0632	0.0301	672.117	0.0194	0.0083
453.482	0.0418	0.0232	534.454	0.0715	0.0341	657.795	0.0482	0.0231
448.588	0.0684	0.0324	531.759	0.0826	0.0392	646.325	0.0770	0.0383
440.481	0.0949	0.0433	528.450	0.1040	0.0480	634.757	0.0947	0.0448
434.153	0.1167	0.0552	513.243	0.1485	0.0660	631.494	0.1185	0.0557
427.621	0.1345	0.0670	510.110	0.1562	0.0700	623.838	0.1373	0.0676
420.828	0.1660	0.0747	497.955	0.1948	0.0826	610.784	0.1737	0.0820
413.604	0.1991	0.0760	491.440	0.2458	0.1021	595.647	0.2105	0.0903

Table 3. VLE Measurements for the Cyclohexane (1) + Cyclohexanol (3) System at (414.0 to 433.7) K

P/kPa	x_3	y_3	P/kPa	x_3	y_3	P/kPa	x_3	y_3
T/K = 414.0 ± 0.3			T/K = 423.4 ± 0.3			T/K = 433.7 ± 0.3		
457.667	0.0000	0.0000	555.246	0.0000	0.0000	677.813	0.0000	0.0000
457.085	0.0324	0.0136	554.538	0.0205	0.0102	670.112	0.0183	0.0089
454.123	0.0414	0.0186	549.610	0.0443	0.0206	661.574	0.0356	0.0177
451.423	0.0460	0.0233	536.895	0.0661	0.0307	658.508	0.0609	0.0272
440.254	0.0860	0.0327	531.718	0.0881	0.0355	637.392	0.0987	0.0434
434.413	0.1117	0.0399	517.629	0.1247	0.0504	629.176	0.1263	0.0522
429.593	0.1201	0.0450	515.255	0.1456	0.0574	610.125	0.1613	0.0671
426.325	0.1338	0.0492	509.592	0.1705	0.0633	607.643	0.1795	0.0757
416.235	0.1844	0.0685	499.500	0.2048	0.0698	592.967	0.2413	0.0916
402.831	0.2478	0.0792	493.942	0.2384	0.0860			

Table 6. Results of Correlation for All of the Systems Investigated

		Equation					
		Wilson-HOC		Wilson-RK		SRK	
systems	T/K	$D(P)^a$/%	$D(y_1)^a$/%	$D(P)$/%	$D(y_1)$/%	$D(P)$/%	$D(y_1)$/%
cyclohexane (1) + cyclohexanol (3)	414.0	0.51	0.27	0.53	0.32	1.18	0.26
	423.4	0.79	0.21	0.60	0.23	1.21	0.19
	433.7	0.55	0.16	0.59	0.19	0.57	0.15
cyclohexane (1) + cyclohexanone (2)	414.0	0.47	0.37	0.46	0.37	1.22	0.31
	423.4	0.74	0.14	0.76	0.14	1.09	0.24
	433.7	0.39	0.28	0.40	0.28	0.41	0.14

[a] $D(P)$/% and $D(y)$/% mean the relative root-mean-square deviations of total pressure and vapor composition.

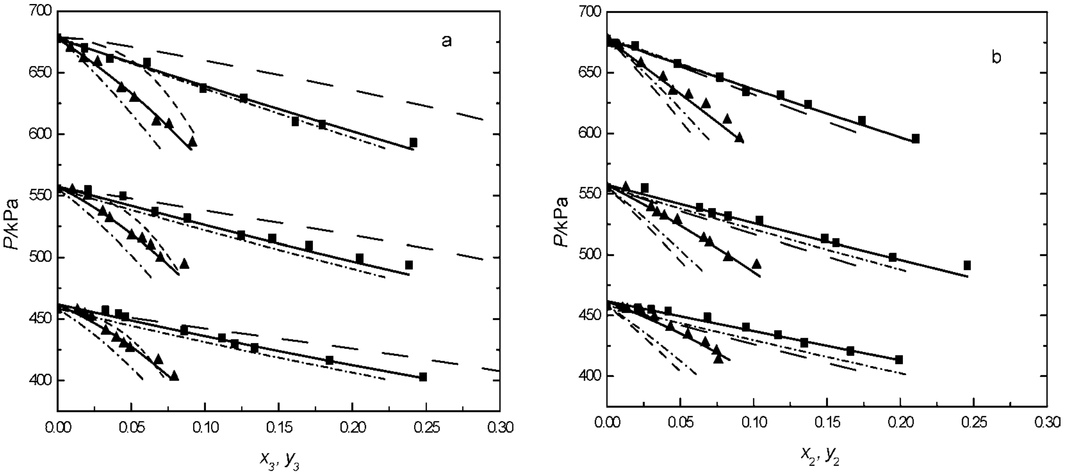

Figure 3. Comparison of the measured $P-x-y$ data with the correlation results at (414.0 to 433.7) K. (a) Cyclohexane (1) + cyclohexanol (3) system. Experimental data: ■, x; ▲, y; —, Wilson-HOC; —•—, UNIFAC-DMD; — —, UNIFAC. (b) Cyclohexane (1) + cyclohexanone (2) system. Experimental data: ■, x; ▲, y; —, Wilson-HOC; —•—, UNIFAC-DMD; — —, UNIFAC.

and then sampled from each phase for chromatography measurements.

Materials. Table 1 lists the reagents we used in the experiments. The purities of components were determined by gas chromatography (GC112A). The reagents were used without any further purification.

Uncertainty. The uncertainty in the temperature measurements was < 0.3 K for the air bath, and the uncertainty of the pressure measurement was < 20 kPa. Parallel experiments show that the uncertainties of GC were as follows:

$$\sigma(x_i) = 0.05$$

$$\sigma(y_i) = 0.05$$

To check the accuracy of our experiments, the VLE data of pentane (1) + ethanol (2) at 372.7 K were measured and compared with the literature data.[9] The results are presented in Figure 2. The maximal relative errors were 0.9 % for pressure, 5 % for x_1, and 7 % for y_1.

Results and Discussion

The isotherm VLE data of the binary systems cyclohexane (1) + cyclohexanone (2) and cyclohexane (1) + cyclohexanol (3) at 414.0 ± 0.3 K, 423.4 ± 0.3 K and 433.7 ± 0.3 K were measured and are listed in Tables 2 and 3. The parameters detected include the temperature, pressure, and the compositions of both liquid and vapor phases.

The Wilson[10] and Soave−Redlich−Kwong (SRK)[11] models were used to correlate the binary VLE data. In the SRK model, l_{ij} parameters were used concerning the existence of polar components in the systems. In the Wilson model, the Redlich−Kwong (RK)[12] and Hayden−O'Connell (HOC) equations[13] were used to modify the nonideality of the vapor phase, and the results were compared. The RK equations are applicable for nonpolar or mildly polar mixtures[14] at low-to-moderate pressures. The HOC equations are recommended for a more nonideal vapor phase, such as in systems containing organic acids.[15] The necessary auxiliary data were given in Table 4. The universal functional activity coefficient (UNIFAC) model[16] has predictive capability. Here, the Dortmund modified UNIFAC (UNIFAC-DMD) model and standard UNIFAC were used for comparison.

The regression was carried out using the Aspen Plus v 7.1 chemical process simulator.[17] The ordinary least-squares method and Britt-Luecke algorithm[18] were used. The minimization objective functions (OFs) were defined as eq 1:

$$\mathrm{OF} = \sum_i^n \frac{|P_i^{\mathrm{cal}} - P_i|/P_i}{n} + \sum_i^n \frac{|y_i^{\mathrm{cal}} - y_i|/y_i}{n} \qquad (1)$$

The binary interaction parameters evaluated from the regression for the Wilson model with the RK equation (Wilson-RK), the Wilson model with the HOC equation (Wilson-HOC), and the SRK model are presented in Table 5. The relative root-mean-square deviations (rmsd's) of vapor composition (in Table 6) showed that SRK gave poorer fits than Wilson-RK and Wilson-HOC. In the correlated results of the Wilson model, as the composition range of cyclohexanone or cyclohexanol is low, there does not seem to be much difference between results given by RK equations and HOC equations. Their $D(P)$ varies between (0.5 to 0.8) %, and their $D(y_1)$ varies between (0.2 to 0.3) %.

The predictive UNIFAC models were compared against the fitted Wilson-HOC model in Figure 3. The Wilson-HOC gave the best fit again. The error is an order of magnitude smaller than with UNIFAC models. The UNIFAC-DMD performs better than the standard UNIFAC with all of the binary pairs. For the cyclohexane−cyclohexanol system, the standard UNIFAC results are much higher than experimental data and the results of UNIFAC-DMD. However, for the cyclohexane−cyclohexanone system, the error between UNIFAC and UNIFAC-DMD is smaller than with the cyclohexanol-contained system.

Conclusion

In this study, the thermodynamic behavior of cyclohexane and its main oxidation product systems at temperatures from (414.0 to 433.7) K were carried out with a static-analytical method. We used the Wilson and SRK models to correlate the experimental data. For comparison, the predictive UNIFAC models (standard UNIFAC and UNIFAC-DMD) were also used. As our system is moderately polar, at low composition ranges of cyclohexanol (cyclohexanone), using the Wilson equations with the RK or HOC equations to modify the nonideality of the vapor phase obtained a promising accuracy. The results of using UNIFAC-DMD are better than using the standard UNIFAC model. However, the error of the UNIFAC-DMD model is an order of magnitude bigger than with the Wilson model.

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