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Vapor−Liquid Equilibria of Binary Mixtures Cyclopentane + Isopropyl Acetate, Isopropyl Acetate + Hexane, and Cyclopentane + Methyl Methacrylate at 101.3 kPa

Kong-Wei Cheng, Jia-Yuh Chen, Muoi Tang, and Yan-Ping Chen*

Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan, Republic of China

Vapor−liquid equilibria were measured at 101.3 kPa for three binary mixtures of cyclopentane + isopropyl acetate, isopropyl acetate + hexane, and cyclopentane + methyl methacrylate. The isobaric $T-x-y$ data were reported, including an azeotropic point for the binary mixture of isopropyl acetate + hexane. Calculations of the nonideality of the vapor phase were made with the second virial coefficients determined by the Tsonopoulos correlation equation. Various activity coefficient models were used to correlate the experimental data. Satisfactory results were obtained, and optimally fitted binary parameters are presented.

Introduction

Vapor−liquid equilibria (VLE) are important in chemical process design and development. The VLE data of three binary mixtures of cyclopentane + isopropyl acetate, isopropyl acetate + hexane, and cyclopentane + methyl methacrylate were measured at 101.3 kPa. An all-glass recirculating still was employed, and the equilibrium temperatures and compositions of the coexisting vapor and liquid phases were measured. Thermodynamic consistency tests were examined on these systems. The experimental data were then correlated by various activity coefficient models.

Experimental Section

Chemicals. All the chemicals were high-purity grade purchased from Merck Co. Cyclopentane was purified in a distillation column at a reduced pressure. The other three chemicals were used without further purification. No detectable impurities were found on the gas chromatography (GC) analyses. The purities of all chemicals were better than 99.6 mass %. The pure compound properties were measured in this study, and the comparisons with literature data are shown in Table 1. The refractive indices of the pure compounds were measured at (293.15 ± 0.1) K by an Abbe refractometer, Atago 3T, with the accuracy of ±0.0001. The densities of pure chemicals were measured at (293.15 ± 0.01) K using the Anton Paar DMA 60/602 density meter with an accuracy of $\pm 1.0 \times 10^{-5}$ $g\cdot cm^{-3}$.

Apparatus and Procedures. The apparatus used was an all-glass recirculating still described by Paul (1976). This equipment has a side-heating unit which ensures complete mixing of the liquid mixtures. This design also prevented liquid drop entrainment and partial condensation of the vapor phase. A digital quartz thermometer (DMT-610, Tokyo Electrical, Japan), with an accuracy of ±0.01 K, was used to measure the equilibrium temperatures. The pressure was maintained at 101.3 kPa through a dibutyl phthalate manometer. The accuracy of the pressure control was within ±0.05%.

In each experiment, the liquid mixture was heated in the recirculating still at a fixed pressure of 101.3 kPa. Equilibrium was usually reached after 1 h, where the temperatures of the liquid and vapor phases were constant and their difference was within 0.02 K. Samples of the equilibrium phases were then taken at small volumes and were analyzed in a gas chromatograph.

A Shimadzu GC, type 8A, equipped with a thermal conductivity detector, was used to determine the equilibrium compositions. The GC column was made of a 3 m length stainless steel tube with 3 mm diameter and was packed with Porapak Q. The GC response peaks were integrated by using a Shimadzu C-R3A integrator. The temperature of the injection port of the GC was maintained at 503.15 K. The oven temperature of the GC was at 483.15 K. Helium gas with a purity of 99.9% was used as the carrier gas at a flow rate of 30 cm^3/min. The GC was calibrated using mixtures of known compositions which were prepared gravimetrically. More than two analyses were made for each liquid and vapor composition, respectively. With these repeated procedures, the accuracy of the equilibrium composition measurements was within ±0.001 mole fraction.

Results and Discussion

VLE had been measured at 101.3 kPa for cyclopentane + isopropyl acetate, isopropyl acetate + hexane, and cyclopentane + methyl methacrylate. The results are shown in Tables 2−4, respectively. The liquid phase activity coefficients γ_i were calculated by the classical equation

$$\gamma_i = (\hat{\phi}_i y_i P)/\{x_i P_i^{\rm sat} \phi_i^{\rm sat} \exp[V_i^{\rm L}(P - P_i^{\rm sat})/RT]\} \qquad (1)$$

where ϕ is the fugacity coefficient and x and y are the equilibrium mole fractions in the liquid and vapor phases, respectively. $P^{\rm sat}$ is the saturated vapor pressure, and $V^{\rm L}$ is the saturated liquid molar volume.

The fugacity coefficient was calculated by using the virial equation of state truncated at the second virial term. The second virial coefficient was determined from the correlation equation according to Tsonopoulos (1974). The critical constants were taken from literature (TRC Data Bases, 1993; Daubert and Danner, 1989). The vapor pressures of the pure compounds were expressed by

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* Corresponding author.

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Table 1. Comparison of the Measured Normal Boiling Temperatures, Refractive Indices, and Densities of Pure Fluids in This Work with Literature Data

component	T_b/K exptl	lit.	n^D(293.15 K) exptl	lit.	ρ(293.15K) exptl	lit.	purity (mass %)
cyclopentane	322.35	322.41[a]	1.4065	1.4064[a]	0.7451	0.7457[a]	>99.6
hexane	341.84	341.88[a]	1.3754	1.3749[a]	0.6594	0.6594[a]	>99.9
isopropyl acetate	361.54	361.65[b]	1.3772	1.3773[c]	0.8721	0.8718[c]	>99.9
methyl methacrylate	373.49	373.45[b]	1.4148	1.4142[c]	0.9432	0.9440[c]	>99.9

[a] TRC Data Base (1993). [b] Daubert and Danner (1989). [c] Lide and Frederikes (1994).

Table 2. Experimental VLE Data for Cyclopentane (1) + Isopropyl Acetate (2) at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2
322.35	1.000	1.000	1.000	
322.45	0.989	0.994	1.001	2.229
322.99	0.950	0.976	1.006	1.931
323.36	0.923	0.963	1.011	1.840
323.73	0.902	0.954	1.013	1.804
324.36	0.858	0.937	1.026	1.642
342.81	0.823	0.927	1.044	1.500
325.41	0.787	0.915	1.059	1.416
326.02	0.756	0.903	1.068	1.376
326.80	0.713	0.889	1.089	1.300
327.61	0.675	0.874	1.105	1.260
328.54	0.629	0.858	1.132	1.201
330.20	0.554	0.821	1.172	1.175
331.75	0.509	0.798	1.187	1.134
332.42	0.478	0.784	1.215	1.118
333.47	0.441	0.769	1.255	1.069
334.53	0.412	0.750	1.271	1.059
337.16	0.349	0.709	1.321	1.008
340.12	0.281	0.643	1.371	1.006
343.54	0.220	0.571	1.427	0.986
350.78	0.112	0.376	1.539	0.986
355.98	0.052	0.213	1.683	0.984
357.63	0.036	0.159	1.721	0.983
361.54	0.000	0.000		1.000

Table 3. Experimental VLE Data for Isopropyl Acetate (1) + Hexane (2) at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2
341.84	0.000	0.000		1.000
341.68	0.013	0.015	2.163	1.003
341.61	0.027	0.028	2.108	1.004
341.58	0.049	0.050	2.001	1.007
341.59	0.079	0.074	1.843	1.013
341.61	0.100	0.093	1.828	1.015
341.65	0.114	0.103	1.778	1.018
341.70	0.137	0.118	1.681	1.027
341.99	0.203	0.165	1.565	1.044
342.09	0.226	0.179	1.518	1.055
342.21	0.249	0.190	1.457	1.068
342.46	0.282	0.213	1.426	1.079
342.67	0.304	0.227	1.400	1.086
343.17	0.368	0.260	1.299	1.130
344.04	0.448	0.302	1.196	1.193
345.09	0.528	0.353	1.144	1.255
346.91	0.633	0.424	1.074	1.369
349.49	0.757	0.526	1.019	1.589
350.85	0.792	0.571	1.011	1.623
352.66	0.837	0.639	1.008	1.665
357.04	0.933	0.804	0.989	1.956
361.54	1.000	1.000	1.000	

Table 4. Experimental VLE Data for Cyclopentane (1) + Methyl Methacrylate (2) at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2
322.35	1.000	1.000	1.000	
322.72	0.982	0.994	1.001	2.042
323.63	0.936	0.979	1.004	1.957
324.03	0.914	0.971	1.009	1.913
324.75	0.876	0.961	1.019	1.756
325.51	0.840	0.952	1.029	1.606
326.16	0.803	0.944	1.046	1.501
326.92	0.762	0.935	1.067	1.395
327.79	0.728	0.925	1.077	1.357
328.82	0.681	0.913	1.102	1.285
329.74	0.639	0.901	1.129	1.238
330.74	0.597	0.889	1.158	1.195
332.03	0.545	0.873	1.200	1.153
333.40	0.506	0.857	1.219	1.134
334.97	0.467	0.843	1.245	1.084
336.45	0.426	0.821	1.275	1.084
338.61	0.375	0.796	1.325	1.045
340.70	0.334	0.768	1.357	1.029
343.43	0.290	0.736	1.393	0.994
349.96	0.195	0.630	1.499	0.975
357.65	0.115	0.471	1.584	0.976
366.99	0.041	0.230	1.756	0.975
373.49	0.000	0.000		1.000

Table 5. Pure Component Properties Used in This Work[a]

component	T_c/K	P_c/bar	ω	a	b	c
isopropyl acetae	538.0	35.8	0.355	6.46612	1436.53	−39.485
cyclopentane	511.7	45.1	0.196	6.0087	1122.21	−42.011
methyl methacrylate	564.0	36.8	0.317	6.64083	1597.9	−28.76
hexane	507.5	30.1	0.299	6.00448	1172.04	−48.747

[a] The critical constants and acentric factors were taken from TRC Data Bases (1993). Those for methyl methacrylate and isopropyl acetate were taken from Daubert and Danner (1989). The parameters in the vapor pressure equation (log P_i^{sat} (kPa) = $a_i - b_i/(T(\mathrm{K}) + c_i)$) were taken from Richard and Stanislaw (1987), where parameters a_i were adjusted using experimental normal boiling temperatures listed in Table 1.

the Antoine equation:

$$\log P_i^{\mathrm{sat}}/\mathrm{kPa} = a_i - b_i/[T/\mathrm{K} + c_i] \tag{2}$$

The constants *a*, *b*, and *c* in eq 2 were taken from literature (Richard and Stainslaw, 1987), and values for parameter *a* were adjusted using measured normal boiling temperatures of pure fluids shown in Table 1. The pure fluid properties are listed in Table 5. The liquid molar volumes were calculated by the Rackett equation (Spencer and Danner, 1972). The calculated activity coefficients for each binary mixture are also listed in Tables 2−4. All binary mixtures show positive deviations. The activity coefficients were used in a thermodynamic consistency test where Herington's method was employed (Gmehling et al., 1980). In this integral test, the activity coefficient ratios of each binary system were plotted against the mole fraction and the following two terms were determined:

$$D = \frac{|K_1 - K_2|}{|K_1 + K_2|} \times 100 \tag{3}$$

$$J = \frac{T_{\max} - T_{\min}}{T_{\min}} \times 150 \tag{4}$$

K_1 and K_2 are the areas lying above and below the axis where the logarithm of the activity coefficient ratio is zero. $T_{\max}$ and $T_{\min}$ are the maximum and minimum temperatures measured in this study. According to Herington's

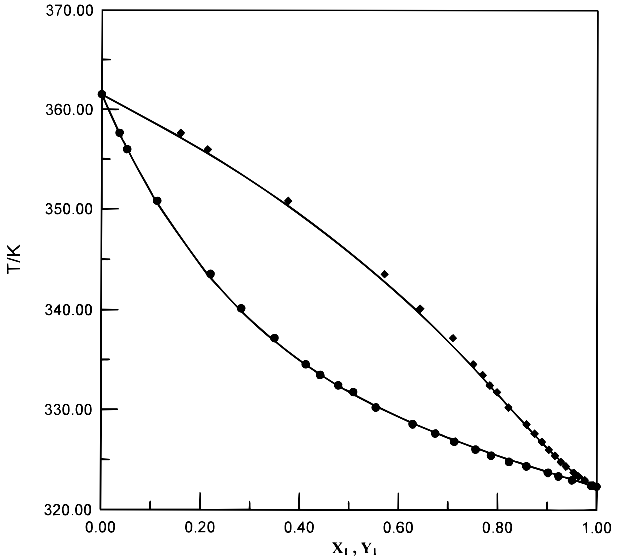

Figure 1. *T*−*x*−*y* curve for cyclopentane (1) + isopropyl acetate (2) at 101.3 kPa. (—) Wilson model. experimental data: (●) liquid phase; (◆) vapor phase.

Table 6. Consistency Test Results of the Binary VLE Experimental Data of This Work

binary systems	D	J	$D-J$
cyclopentane (1) + isopropyl acetate (2)	7.89	18.24	−10.35
isopropyl acetate (1) + hexane (2)	9.94	8.76	1.18
cyclopentane (1) + methyl methacrylate (2)	9.08	23.80	−14.72

Table 7. Correlation Parameter and Absolute Average Deviation in Boiling Temperature (Δ*T*) and Vapor-Phase Mole Fraction (Δ*y*) for the Binary Mixtures

equations	A_{12}/J mol^{-1}	A_{21}/J mol^{-1}	α_{12}	Δy_1	ΔT/K
Cyclopentane (1) + Isopropyl Acetate (2)					
Wilson	72.21	443.22		0.005	0.14
NRTL	926.57	−373.32	0.2	0.005	0.15
UNIQUAC	62.96	44.51		0.005	0.29
Isopropyl Acetate (1) + Hexane (2)					
Wilson	406.76	157.09		0.005	0.24
NRTL	217.91	308.11	0.2	0.005	0.25
UNIQUAC	49.86	70.53		0.006	0.25
Cyclopentane (1) + Methyl Methacrylate (2)					
Wilson	127.21	392.22		0.006	0.20
NRTL	872.23	−322.00	0.2	0.006	0.17
UNIQUAC	60.47	42.77		0.006	0.26

test, the experimental data are considered to be thermodynamically consistent if ($D - J$) is less than 10. The thermodynamic consistency test results of this study are listed in Table 6. It is observed that all three binary isobaric data sets satisfied the thermodynamic consistency requirement.

The experimental results were then used to obtain the binary parameters in various activity coefficient models. The Wilson, NRTL, and UNIQUAC models were used in the regressions. The expressions of the activity coefficients for each model were listed in literature (Gmehling et al., 1980). The following objective function was minimized in the regressions:

$$Q = \sum_N \sum_i \left(\frac{\gamma_i^{\text{exp}} - \gamma_i^{\text{cal}}}{\gamma_i^{\text{exp}}} \right)^2 \tag{5}$$

The regression results are shown in Table 7. The deviations in vapor phase compositions and equilibrium temperatures are reasonably small, and it is indicated that all three activity coefficient models are suitable to represent the binary experimental data. The *T*−*x*−*y* diagrams of these binary systems are shown in Figures 1−3, respectively. The binary mixture of isopropyl acetate (1) + hexane (2) has an azeotrope. The azeotropic temperature at 101.3 kPa is 341.58 K with $x_1 = 0.053$. No azeotrope was found for the other two binary systems.

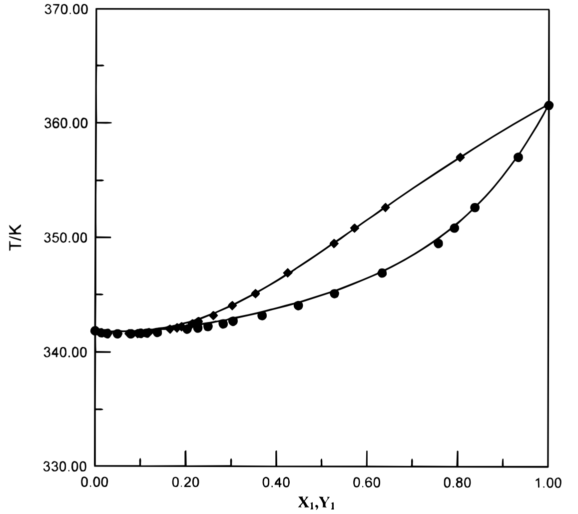

Figure 2. *T*−*x*−*y* curve for isopropyl acetate (1) + hexane (2) at 101.3 kPa. (—) Wilson model. experimental data: (●) liquid phase; (◆) vapor phase.

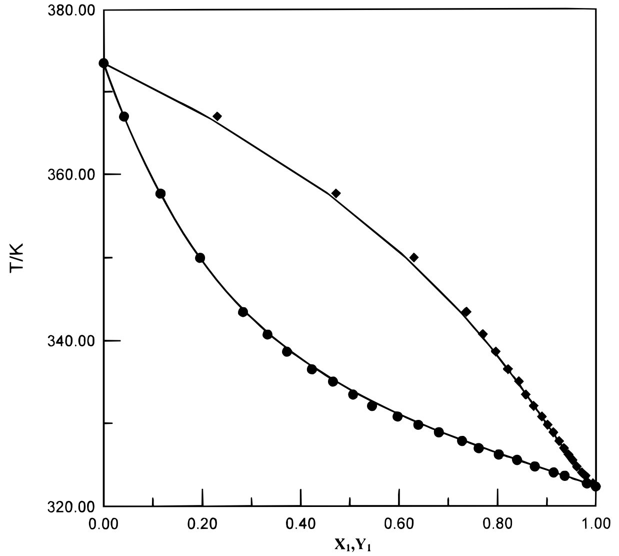

Figure 3. *T*−*x*−*y* curve for cyclopentane (1) + Methyl methacrylate (2) at 101.3 kPa. (—) Wilson model. experimental data: (●) liquid phase; (◆) vapor phase.

Conclusion

Vapor−liquid equilibria of three binary mixtures of cyclopentane + isopropyl acetate, isopropyl acetate + hexane, and cyclopentane + methyl methacrylate were measured at 101.3 kPa. The results of all binary mixtures satisfied the thermodynamic consistency test. Various activity coefficient models are suitable to correlate the experimental data where the deviations in vapor phase compositions and equilibrium temperatures are reasonably small.

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