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Isobaric Vapor–Liquid Equilibria for Cyclohexanone + 3-Methylcyclohexanone or 4-Methylcyclohexanone Systems at 4.00 and 26.66 kPa

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Isobaric vapor–liquid equilibrium data were measured for cyclohexanone + 3-methylcyclohexanone or + 4-methylcyclohexanone at 4.00 and 26.66 kPa. The data are thermodynamically consistent and can be well correlated with the Margules, Van Laar, Wilson, NRTL, and UNIQUAC equations.

Introduction

Caprolactam is an important raw material for the manufacturing of nylon-6 and other synthetic fibers. It is produced industrially by Beckman transposition in an acid liquid medium. Since the purity of cyclohexanone affects directly the quality of the final product, its separation from the byproducts is very important. The separation is carried out by distillation, and equilibrium data of systems containing cyclohexanone and its methyl derivates are needed for the correct design of the distillation columns.

In this work, we report vapor–liquid equilibrium (VLE) data for two of these systems, cyclohexanone + 3-methylcyclohexanone and cyclohexanone + 4-methylcyclohexanone. No literature references have been found for these systems up to 1991.

Experimental Section

Chemicals. Cyclohexanone was a high-purity-grade (>99.9%) product given by the Proquimed Co. 3-Methylcyclohexanone and 4-methylcyclohexanone were high-purity-grade (>99.0%) Merck reactives. The purity of all chemicals was checked by gas chromatography (GC). The physical properties of these components are listed in Table I together with literature values.

Apparatus and Procedure. The apparatus used in this work was an all-glass, dynamic recirculating still described by Walas (*2*), equipped with a Cottrell pump. The still (Labodest model) manufactured by Fischer Labor und Verfahrenstechnik (Germany) is capable of handling pressures from 0.25 to 400 kPa, and temperatures up to 523.15 K. The Cottrell pump ensures that both liquid and vapor phases are in intimate contact and also in contact with the temperature-sensing element. The equilibrium temperature T was measured with a digital Fisher thermometer with an accuracy of 0.1 K, and the pressure P with a digital manometer with an accuracy of 0.01 kPa. The vapor pressures of the pure components were measured with the same recirculating still.

In each experiment the work pressure was fixed and the heating and shaking system of the liquid mixture was connected. This was kept at the boiling point for 15 min to ensure the stationary state. Once it was sure that the stationary state was reached, a sample of liquid and vapor of the Cottrell pump was taken. The extractions were carried out with special syringes which allowed us to take reduced volume samples in a system in partial vacuum.

Table I. Densities *d*, Refractive Indexes *n*, and Boiling Points T_b of the Chemicals

	d(293.15K)/(g cm^{-3})		n(D,293.15K)		T_b(26.66 kPa)/K
compound	exptl	lit. (*1*)	exptl	lit. (*1*)	exptl
cyclohexanone	0.948 51	0.9478	1.4506	1.4507	383.05
3-methylcyclohexanone	0.916 34	0.9136	1.4456	1.4456	395.65
4-methylcyclohexanone	0.916 41	0.9138	1.4450	1.4451	396.95

Samples of 3 μL were withdrawn from the condensed vapor and liquid streams of the still, and were analyzed with a Hewlett-Packard 5710 A GC with a thermal-conductivity detector. GC response peaks were integrated by using a Hewlett-Packard 3394 A integrator. The GC column used was packed with 25% de UCON LB 550X upon Chrom W (80/100), of 2-m length and 1/8-in. diameter. Chromatographic analyses were carried out at the following conditions: temperature, 120 °C; gas carrier, helium, 20 cm^3/min.

The GC was calibrated with gravimetrically prepared standard solutions. A single analysis of the vapor or liquid composition by gas chromatography is frequently imprecise. However, with repeated measurements, the standard deviation of a composition analysis was usually less than 0.001 mole fraction. At least two analyses were made for each liquid and each vapor composition.

Results and Discussion

Refractive indexes, n, at 298.15 K, for the systems cyclohexanone (1) + 3-methylcyclohexanone (2) or + 4-methylcyclohexanone (2) are presented in Table II.

The experimental vapor pressure data of the three pure components, $P_i°$, in the range of work temperatures, together with the parameters of the Antoine equation

$$\ln(P_i°/\mathrm{kPa}) = A_i - \frac{B_i}{(T/\mathrm{K}) + C_i} \tag{1}$$

and the mean absolute deviations between experimental and calculated vapor pressures, MAD($P_i°$), are shown in Table III.

In order to fit the Antoine constants, the following objective function F was minimized by using a linear regression method:

$$F = \sum[\ln(P°_{\mathrm{exptl}}/\mathrm{kPa}) - \ln(P°_{\mathrm{calcd}}/\mathrm{kPa})]^2 \tag{2}$$

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Table II. Refractive Indexes at 298.15 K of Cyclohexanone (1) + 3-Methylcyclohexanone (2) or 4-Methylcyclohexanone (2) Systems as a Function of the Mole Fraction

x_1	n(D,298.15K)	x_1	n(D,298.15K)
3-methylcyclohexanone (2)		4-methylcyclohexanone (2)	
0.0000	1.4434	0.0000	1.4452
0.1184	1.4440	0.1219	1.4455
0.2204	1.4445	0.2254	1.4456
0.3286	1.4449	0.3327	1.4459
0.4366	1.4454	0.4337	1.4465
0.5334	1.4459	0.5303	1.4466
0.6346	1.4464	0.6293	1.4470
0.7256	1.4469	0.7259	1.4473
0.8236	1.4473	0.8167	1.4475
0.9109	1.4477	0.9097	1.4478
1.0000	1.4481	1.0000	1.4481

Table III. Vapor Pressure P_i°, Fitted Antoine Constants *A*, *B*, and *C* (Equation 1), and Mean Absolute Deviation MAD(P_i°) of Pure Components

cyclohexanone		3-methylcyclohexanone		4-methylcyclohexanone	
T/K	P_i°/kPa	T/K	P_i°/kPa	T/K	P_i°/kPa
318.15	1.69	334.15	2.23	339.15	2.72
330.25	3.11	341.65	3.19	350.45	4.69
345.95	5.35	349.85	4.64	356.85	6.17
349.95	7.61	361.55	7.65	360.65	7.22
355.85	9.69	366.05	9.13	366.55	9.16
370.35	16.92	370.15	10.77	371.45	11.02
382.25	25.90	374.85	12.86	381.55	15.98
392.35	36.02	380.85	15.98	393.85	24.15
402.25	48.95	389.05	21.33	405.65	35.10
410.55	62.41	395.25	26.23	412.05	42.75
419.85	81.01	403.15	33.79	418.95	52.08
424.05	90.43	410.25	41.82	423.95	59.76
425.35	94.04	415.15	48.45	430.65	71.96
428.25	101.37	421.55	58.37	434.55	79.42
		427.85	69.04	439.05	89.35
		432.75	79.17	444.55	102.39
		434.65	82.90		
		439.45	94.15		
		441.85	99.92		
A	14.00725		14.18426		13.14045
B	3402.602		3630.724		3014.145
C	−65.8948		−62.7765		−90.7545
MAD(P_i°)	0.066		0.082		0.201

The vapor–liquid equilibrium data are presented in Tables IV and V. They have been obtained at two pressures (4.00 and 26.66 kPa) to observe the influence of this variable upon the equilibrium. Both pressures are small, so that the boiling temperatures are not very high, which could result in undesirable reactions. The T–x–y diagram for cyclohexanone (1) + 4-methylcyclohexanone (2) is shown in Figure 1.

The activity coefficients γ_i of the components were calculated from

$$\gamma_i = y_i P / x_i P_i^\circ \qquad (3)$$

The Poynting factor was considered as unity at the experimental conditions of this work (*3*), and the vapor pressures P_i° were calculated with the Antoine equation (Table III). The fugacity coefficients, calculated on the basis of the Redlich–Kwong equation of state (*4*) with the modification introduced by Soave (*5*), are nearly unity. The critical properties of 3-methylcyclohexanone and 4-methylcyclohexanone were estimated by the Ambrose method (*6*, *7*).

The γ_i values are listed in Tables IV and V.

Table IV. Vapor–Liquid Equilibrium Data, Liquid-Phase Mole Fraction x_1, Vapor-Phase Mole Fraction y_1, Temperature *T*, and Activity Coefficients γ_i for the Cyclohexanone (1) + 3-Methylcyclohexanone (2) System at Constant Pressure *P*

P/kPa	x_1	y_1	T/K	γ_1	γ_2
4.00	0.000	0.000	346.45		
	0.045	0.075	345.55	1.053	1.009
	0.108	0.167	344.65	1.017	1.014
	0.186	0.271	343.55	1.008	1.023
	0.286	0.397	342.45	1.008	1.015
	0.348	0.465	341.85	0.996	1.015
	0.397	0.520	341.15	1.008	1.017
	0.468	0.592	340.35	1.008	1.018
	0.537	0.657	339.65	1.006	1.017
	0.588	0.699	339.35	0.991	1.018
	0.668	0.766	338.55	0.991	1.020
	0.749	0.830	337.75	0.994	1.017
	0.812	0.876	337.15	0.994	1.024
	0.862	0.910	336.75	0.991	1.030
	0.940	0.963	335.95	0.998	1.031
	1.000	1.000	335.35		
26.66	0.000	0.000	395.75		
	0.051	0.078	394.85	1.045	0.998
	0.121	0.178	393.75	1.041	0.996
	0.202	0.281	392.55	1.021	0.999
	0.251	0.343	391.95	1.022	0.993
	0.323	0.422	390.95	1.012	0.997
	0.378	0.483	390.25	1.010	0.996
	0.456	0.564	389.35	1.007	0.990
	0.536	0.642	388.35	1.007	0.986
	0.610	0.708	387.45	1.006	0.987
	0.699	0.781	386.45	1.001	0.993
	0.788	0.851	385.45	1.000	0.994
	0.864	0.905	384.65	0.996	1.020
	0.914	0.941	384.15	0.996	1.010
	1.000	1.000	383.05		

Table V. Vapor–Liquid Equilibrium Data, Liquid-Phase Mole Fraction x_1, Vapor-Phase Mole Fraction y_1, Temperature *T*, and Activity Coefficients γ_i for the Cyclohexanone (1) + 4-Methylcyclohexanone (2) System at Constant Pressure *P*

P/kPa	x_1	y_1	T/K	γ_1	γ_2
4.00	0.000	0.000	347.05		
	0.048	0.079	346.25	1.022	0.999
	0.104	0.165	345.35	1.011	1.004
	0.176	0.267	344.25	1.018	1.007
	0.216	0.319	343.75	1.010	1.007
	0.319	0.444	342.35	1.015	1.010
	0.397	0.540	341.15	1.045	1.000
	0.488	0.626	340.05	1.039	1.005
	0.559	0.690	339.25	1.033	1.010
	0.667	0.774	338.25	1.018	1.018
	0.738	0.829	337.45	1.021	1.021
	0.817	0.883	336.75	1.014	1.039
	0.885	0.927	336.15	1.012	1.048
	0.948	0.967	335.65	1.009	1.068
	1.000	1.000	335.35		
26.66	0.000	0.000	396.65		
	0.065	0.100	395.65	1.022	0.993
	0.123	0.183	394.65	1.020	0.993
	0.181	0.258	393.75	1.009	0.995
	0.238	0.333	392.75	1.024	0.992
	0.292	0.388	391.95	0.994	1.008
	0.330	0.438	391.45	1.010	0.994
	0.417	0.542	390.15	1.033	0.971
	0.523	0.644	388.65	1.026	0.971
	0.624	0.731	387.45	1.015	0.972
	0.682	0.776	386.75	1.009	0.980
	0.753	0.830	385.95	1.004	0.982
	0.823	0.881	385.05	1.005	0.989
	0.901	0.934	384.25	1.000	1.008
	0.952	0.968	383.65	1.000	1.045
	1.000	1.000	383.05		

The thermodynamic consistency of the experimental data was checked by means of the point-to-point test of Van Ness et al. (*8*), modified by Fredenslund et al. (*9*), using a fifth-order Legendre polynomial. According to this test, the data are considered consistent if the mean absolute deviation in y, MAD(y), is less than 0.01. In our case, MAD(y) values

Table VI. Correlation Parameters for Activity Coefficient Equations, Activity Coefficients at Infinite Dilution γ_i^∞, and Mean Absolute Deviations MAD(y) and MAD(T)

P/kPa		A_{12}	A_{21}	α_{12}	γ_1^∞	γ_2^∞	MAD(y)	MAD(T)
		Cyclohexanone (1) + 3-Methylcyclohexanone (2) System						
4.00	Margules	0.1109[a]	0.0357[a]		1.12	1.04	0.0038	0.16
	Van Laar	0.1115[a]	0.0401[a]		1.12	1.04	0.0028	0.13
	Wilson	961.2351[b]	−567.7678[b]		1.34	1.03	0.0061	0.26
	NRTL	−627.0267[b]	971.3537[b]	0.2758[a]	1.27	1.03	0.0070	0.28
	UNIQUAC	−352.5297[b]	518.7269[b]		1.32	1.03	0.0080	0.33
26.66	Margules	0.0512	0.0205		1.05	1.02	0.0029	0.17
	Van Laar	0.0509	0.0219		1.05	1.02	0.0030	0.14
	Wilson	132.7213	−98.7242		1.04	1.05	0.0024	0.21
	NRTL	−420.4275	525.9380	0.2752	1.05	1.02	0.0029	0.15
	UNIQUAC	−123.3522	147.2349		1.05	1.04	0.0024	0.22
		Cyclohexanone (1) + 4-Methylcyclohexanone (2) System						
4.00	Margules	0.0501	0.1525		1.05	1.16	0.0051	0.11
	Van Laar	0.0497	0.1759		1.05	1.19	0.0038	0.08
	Wilson	−303.5325	619.7056		1.05	1.27	0.0046	0.10
	NRTL	805.4383	−535.6425	0.2966	1.05	1.21	0.0044	0.09
	UNIQUAC	431.1855	−308.3318		1.05	1.24	0.0046	0.09
26.66	Margules	0.0385	0.0521		1.04	1.05	0.0050	0.20
	Van Laar	0.0392	0.0513		1.04	1.05	0.0050	0.20
	Wilson	97.0180	−55.4883		1.05	1.06	0.0054	0.23
	NRTL	−16.9128	55.5101	0.3089	1.05	1.05	0.0054	0.22
	UNIQUAC	25.2781	−12.8235		1.04	1.05	0.0051	0.20

[a] Dimensionless. [b] Calories per mole.

Table VII. Relative Volatilities α of Cyclohexanone + 3-Methylcyclohexanone and Cyclohexanone + 4-Methylcyclohexanone Systems and Standard Deviations $\sigma(\alpha)$

system	P/kPa	α	$\sigma(\alpha)$
cyclohexanone + 3-methylcyclohexanone	4.00	1.640	0.014
	26.66	1.549	0.014
cyclohexanone + 4-methylcyclohexanone	4.00	1.653	0.020
	26.66	1.525	0.033

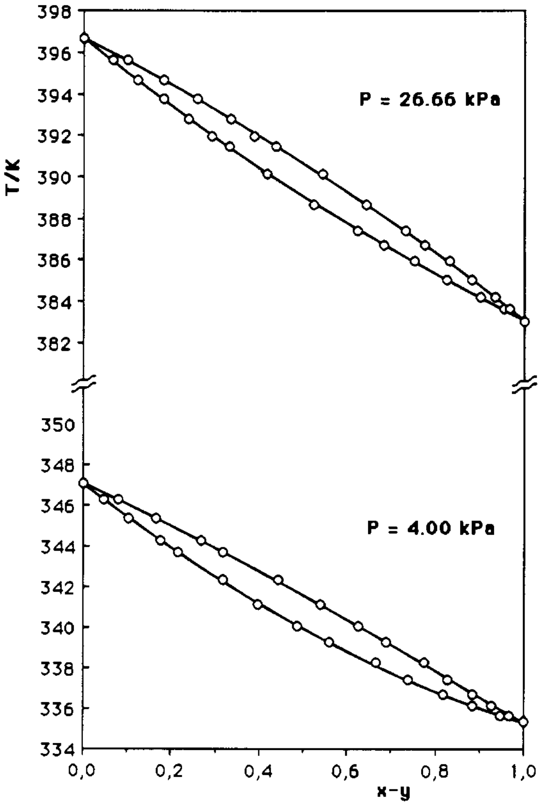

Figure 1. Vapor–liquid equilibrium temperature T of the system cyclohexanone (1) + 4-methylcyclohexanone (2) at P = 4.00 and 26.66 kPa as a function of the mole fraction of component 1.

obtained for the cyclohexanone + 3-methylcyclohexanone system were 0.0038 for P = 4.00 kPa and 0.0038 for P = 26.66 kPa, and for the cyclohexanone + 4-methylcyclohexanone system they were 0.0042 for P = 4.00 kPa and 0.0047 for P = 26.66 kPa, thereby showing them to be thermodynamically consistent.

The activity coefficients were correlated with the Margules, Van Laar, Wilson, NRTL, and UNIQUAC equations (*10*). The parameters A_{12}, A_{21}, and α_{12} of the equations (see definitions in ref 10), mean absolute deviations, and activity coefficients at infinite dilution, γ_i^∞, for the two systems are listed in Table VI. The mean absolute deviations between experimental and calculated temperatures, MAD(T), and vapor compositions, MAD(y), are of the order of the estimated experimental uncertainties.

For fitting the binary parameters the Rosenbrok method (*11*) was used to minimize the following objective function, using the activity coefficients obtained from the consistency test as experimental values:

$$F = \sum\left(\frac{\gamma_{\text{exptl}} - \gamma_{\text{calcd}}}{\gamma_{\text{exptl}}}\right)^2 \qquad (4)$$

Conclusions

The examination of the activity coefficients reported in Tables IV and V reveals the following: (1) Both systems present small positive deviations from ideality at 4.00 and 26.66 kPa; since the three compounds have practically the same polarity, the interactions cancel. The negative deviations observed for some concentrations are due to the dispersion of the experimental data. (2) In both systems, the separation is slightly more favorable at reduced pressures as can be seen from the relative volatilities α calculated by means of the following equation (Table VII):

$$\alpha = [\mathrm{d}y_{\text{exptl}}/\mathrm{d}x_{\text{exptl}}]_{x_{\text{exptl}}\to 0} \qquad (5)$$

Within the limits of $\sigma(\alpha)$ these systems have nearly the same relative volatility at two pressures. This indicates that the influence of the pressure on the equilibrium is small.

Literature Cited

(1) Lide, D. R., Ed. *CRC Handbook of Chemistry and Physics*, 71st ed.; CRC Press: Boca Raton, FL, 1990.

(2) Walas, S. M. *Phase Equilibria in Chemical Engineering*; Butterworth: London, 1985.

(3) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill: New York, 1987.

(4) Redlich, O.; Kwong, J. N. S. *Chem. Rev.* **1949**, *44*, 233.

(5) Soave, G. *Chem. Eng. Sci.* 1971, *27* (6), 1197.

(6) Ambrose, D. *Natl. Phys. Lab. Rep. Chem.* **1978**, 92.

(7) Ambrose, D. *Natl. Phys. Lab. Rep. Chem.* **1979**, 92.

(8) Van Ness, H. C.; Byer, S. M.; Gibbs, R. E. *AIChE J.* **1973**, *19*, 238.

(9) Fredenslund, A.; Gmehling, J.; Rasmussen, P. *Vapor-Liquid Equilibria Using UNIFAC*; Elsevier: Amsterdam, 1977.

(10) Gmehling, J., Onken, U., Eds. *Vapor-Liquid Equilibrium Data Collection*; Chemistry Data Series; DECHEMA: Frankfurt/Main, 1977; Vol. 1, Part 1.

(11) Rosenbrok, H. H. *Comput J.* **1960**, *3*, 175.

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