Vapor-Liquid Equilibria of Cyclohexanone + Cyclohexanol and Cyclohexanone + 2-Methylcyclohexanone Systems at 4.00 and 26.66 kPa

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Vapor-liquid equilibrium data were measured for systems of cyclohexanone with cyclohexanol and 2-methylcyclohexanone at 4.00 and 26.66 kPa. The activity coefficients were found to be thermodynamically consistent. They can be equally well correlated with the Margules, Van Laar, Wilson, NRTL, and UNIQUAC equations.

Introduction

Caprolactam is an important raw material for manufacturing nylon-6 and other synthetic fibers. It is produced industrially by means of the Beckman transposition in an acid liquid phase. The optimum separation of cyclohexanone from cyclohexanol and the other byproducts is carried out by distillation and is very important, as the purity of the cyclohexanone directly affects the quality of the final product. Moreover, the recuperation of cyclohexanol in view of its dehydrogenation to cyclohexanone also affects the yield of the process. Equilibrium data of systems containing cyclohexanol, cyclohexanone, and their methyl derivatives 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 + cyclohexanol and cyclohexanone + 2-methylcyclohexanone. For the first system there are some experimental data published; however, a considerable difference exists between them (1), obliging us to include this system in the experimental determination. No literature data have been found for the second system up to 1991.

Experimental Section

Chemicals. Cyclohexanone was a high-purity-grade (>99.9%) product given by the Proquimed Co. The other two components were high-purity-grade (>99.0%) Merck reactives. 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 (3), equipped with a Cottrell pump. The still (Labodest model) manufactured by Fischer Labor und Verfahrenstechnik (Germany) is capable of handling pressures P from 0.25 to 400 kPa and temperatures T 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 was measured with a digital Fisher thermometer with an accuracy of 0.1 K, and the pressure with a digital manometer with an accuracy of 0.01 kPa. VLE data were obtained at two pressures (4.00 and 26.66 kPa) for both systems. The vapor pressures of 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

Table I. Densities d, Refractive Indexes n, and Boiling Points T_b of the Chemicals Used in This Study

compound	$d(293.15 \text{ K})/$ (g cm^{-3}) exptl	lit. (2)	$n(\text{D},293.15\text{K})$ exptl	lit. (2)	$T_b(26.66\text{kPa})/\text{K}$ exptl
cyclohexanone	0.948 51	0.9478	1.4506	1.4507	383.05
2-methylcyclo-hexanone	0.926 69	0.9250	1.4481	1.4483	391.65
cyclohexanol	0.949 84	0.9624	1.4654	1.4641	394.75

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

x_1	$n(\text{D},298.15\text{K})$	x_1	$n(\text{D},298.15\text{K})$
Cyclohexanol (2)		2-Methylcyclohexanone (2)	
0.0000	1.4633	0.0000	1.4456
0.1030	1.4616	0.1128	1.4458
0.1902	1.4601	0.2230	1.4461
0.3049	1.4583	0.3258	1.4462
0.4037	1.4566	0.4296	1.4465
0.5044	1.4552	0.5394	1.4468
0.5776	1.4540	0.6388	1.4470
0.7034	1.4521	0.7341	1.4474
0.7945	1.4508	0.8224	1.4478
0.8925	1.4496	0.9060	1.4479
1.0000	1.4481	1.0000	1.4481

out with special syringes which allowed us to take small volume samples in a system under partial vacuum.

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 gas chromatograph (GC) with a thermal-conductivity detector. The 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 cm³/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 of each liquid and each vapor composition.

Results and Discussion

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

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		cyclohexanol		2-methylcyclo-hexanone	
	T/K	$P_i°$/kPa	T/K	$P_i°$/kPa	T/K	$P_i°$/kPa
	318.15	1.69	343.45	2.27	331.35	2.23
	330.25	3.11	349.85	3.24	356.55	7.16
	341.95	5.35	354.65	4.20	378.95	17.05
	349.95	7.61	364.75	7.08	392.35	27.03
	355.85	9.69	369.85	9.09	402.05	37.02
	370.35	16.92	379.25	13.96	409.85	46.93
	382.25	25.90	386.35	18.92	421.25	65.28
	392.35	36.02	396.55	28.50	431.45	86.05
	402.25	48.95	405.35	39.72	433.55	91.32
	410.55	62.41	411.55	49.80	437.45	100.18
	419.85	81.01	416.95	59.39		
	424.05	90.43	421.55	69.38		
	425.35	94.04	425.45	78.30		
	428.25	101.37	430.25	91.00		
			433.55	100.69		
A	14.00725		13.94898		13.98513	
B	3402.602		2905.618		3443.763	
C	−65.8948		−122.3649		−70.0874	
MAD($P_i°$)	0.066		0.070		0.096	

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

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

and the mean absolute deviation 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:

$$F = \sum [\ln(P_{\text{exptl}}°/\text{kPa}) - \ln(P_{\text{calcd}}°/\text{kPa})]^2 \qquad (2)$$

The VLE data for both binary systems have been obtained at 4.00 and 26.66 kPa and are presented in Tables IV and V. The T-x-y diagram for the cyclohexanone (1) + 2-methylcyclohexanone (2) is shown in Figure 1.

The activity coefficients γ_i of the components were calculated from

$$\gamma_i = y_iP/x_iP_i° \qquad (3)$$

The γ_i values are listed in Tables IV and V.

The Poynting factor was considered as unity at the experimental conditions of this work (4), 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 (5), with the modification introduced by Soave (6) are nearly unity. The critical properties of 2-methylcyclohexanone were estimated by the Ambrose method (7, 8).

The thermodynamic consistency of the experimental data was checked by means of the point-to-point test of Van Ness et al. (9), modified by Fredenslund et al. (10), 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 obtained for the cyclohexanone + cyclohexanol system were 0.0092 for P = 4.00 kPa and 0.0048 for P = 26.66 kPa, and for the cyclohexanone + 2-methylcyclohexanone system the MAD(y) values were 0.0053 for P = 4.00 kPa and 0.0036 for P = 26.66 kPa, thereby showing them to be thermodynamically consistent.

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) + Cyclohexanol (2) System at Constant Pressure P

P/kPa	x_1	y_1	T/K	γ_1	γ_2
4.00	0.000	0.000	353.75		
	0.054	0.149	351.25	1.361	1.022
	0.092	0.247	349.85	1.413	1.017
	0.138	0.333	348.45	1.351	1.026
	0.187	0.410	347.25	1.294	1.030
	0.193	0.427	346.35	1.355	1.061
	0.308	0.567	344.15	1.238	1.063
	0.412	0.660	342.25	1.173	1.098
	0.503	0.728	341.25	1.107	1.106
	0.602	0.793	339.55	1.089	1.164
	0.684	0.837	338.75	1.048	1.211
	0.781	0.889	337.85	1.015	1.264
	0.892	0.944	336.25	1.017	1.424
	0.942	0.969	335.65	1.016	1.545
	1.000	1.000	335.35		
26.66	0.000	0.000	394.75		
	0.046	0.082	393.85	1.252	0.999
	0.096	0.157	392.85	1.198	1.006
	0.143	0.216	392.15	1.128	1.015
	0.183	0.280	391.45	1.166	1.006
	0.241	0.347	390.85	1.117	1.007
	0.269	0.383	390.35	1.123	1.007
	0.309	0.415	389.95	1.075	1.026
	0.368	0.487	388.95	1.094	1.024
	0.396	0.511	388.75	1.072	1.031
	0.494	0.606	387.45	1.062	1.048
	0.542	0.647	386.85	1.057	1.060
	0.648	0.733	385.85	1.033	1.091
	0.753	0.817	384.85	1.024	1.114
	0.802	0.854	384.55	1.017	1.118
	0.852	0.893	384.15	1.013	1.123
	0.919	0.940	383.65	1.006	1.167
	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) + 2-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	343.35		
	0.075	0.125	341.95	1.235	1.008
	0.121	0.185	341.45	1.165	1.010
	0.185	0.274	340.65	1.162	1.009
	0.252	0.339	340.15	1.082	1.024
	0.335	0.423	339.45	1.050	1.038
	0.450	0.539	338.75	1.026	1.038
	0.544	0.631	337.95	1.029	1.043
	0.649	0.723	337.35	1.018	1.045
	0.741	0.801	336.75	1.015	1.047
	0.768	0.823	336.55	1.015	1.052
	0.838	0.878	336.15	1.012	1.051
	0.906	0.930	335.85	1.005	1.060
	0.957	0.968	335.55	1.005	1.066
	1.000	1.000	335.35		
26.66	0.000	0.000	391.85		
	0.068	0.090	390.75	1.025	1.011
	0.118	0.154	390.25	1.036	1.009
	0.177	0.221	389.65	1.008	1.016
	0.219	0.281	389.15	1.052	1.005
	0.272	0.341	388.65	1.043	1.006
	0.332	0.405	388.15	1.035	1.006
	0.404	0.484	387.45	1.039	1.002
	0.414	0.489	387.35	1.025	1.014
	0.435	0.512	386.95	1.037	1.017
	0.519	0.594	386.35	1.028	1.015
	0.644	0.710	385.15	1.031	1.021
	0.737	0.791	384.45	1.027	1.022
	0.822	0.860	383.75	1.026	1.034
	0.871	0.899	383.45	1.023	1.038
	0.909	0.930	383.25	1.020	1.034
	1.000	1.000	383.05		

Table VI. Correlation Parameters for Activity Coefficients

P/kPa		A_{12}	A_{21}	α_{12}	γ_1^∞	γ_2^∞	MAD(y)	MAD(T)
			Cyclohexanone (1) + Cyclohexanol (2) System					
4.00	Margules	0.4901[a]	0.4561[a]		1.64	1.58	0.0080	0.18
	Van Laar	0.4930[a]	0.4568[a]		1.64	1.58	0.0080	0.19
	Wilson	258.7656[b]	92.2759[b]		1.63	1.59	0.0079	0.19
	NRTL	31.9781[b]	312.9485[b]	0.3527[a]	1.63	1.56	0.0078	0.18
	UNIQUAC	-56.3245[b]	161.5277[b]		1.63	1.58	0.0079	0.18
26.66	Margules	0.2036	0.2187		1.23	1.24	0.0033	0.11
	Van Laar	0.2019	0.2216		1.22	1.25	0.0033	0.10
	Wilson	179.4421	393.1439		1.18	1.28	0.0034	0.10
	NRTL	166.1245	2.3189	0.3207	1.22	1.25	0.0033	0.10
	UNIQUAC	255.5272	-175.1559		1.20	1.31	0.0033	0.10
			Cyclohexanone (1) + 2-Methylcyclohexanone (2) System					
4.00	Margules	0.2198	0.1015		1.25	1.11	0.0049	0.08
	Van Laar	0.2218	0.1189		1.25	1.13	0.0046	0.08
	Wilson	932.4478	-527.9610		1.42	1.08	0.0052	0.08
	NRTL	-486.6275	794.2797	0.3079	1.32	1.10	0.0050	0.07
	UNIQUAC	-302.0224	439.3650		1.32	1.11	0.0052	0.08
26.66	Margules	0.0519	0.1118		1.05	1.12	0.0037	0.18
	Van Laar	0.0522	0.1412		1.05	1.15	0.0032	0.17
	Wilson	-321.1104	610.1084		1.04	1.19	0.0036	0.15
	NRTL	750.7168	-525.8032	0.2985	1.05	1.15	0.0037	0.16
	UNIQUAC	421.8886	-312.8719		1.05	1.18	0.0036	0.15

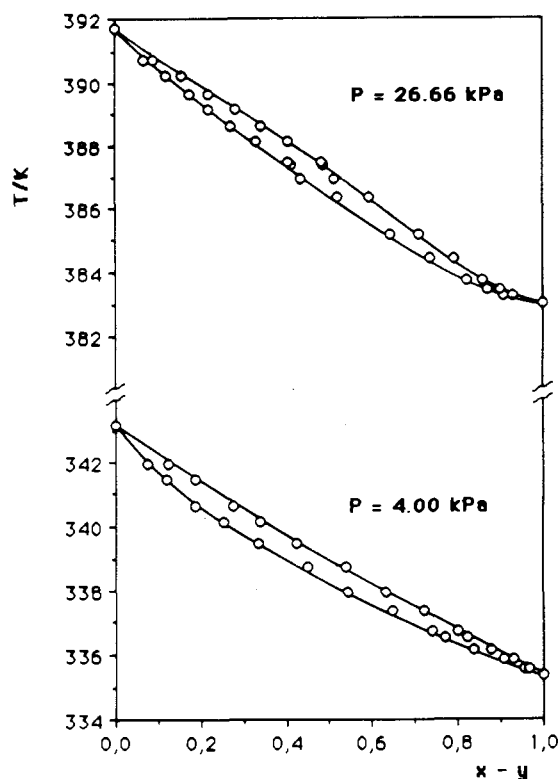[a] Dimensionless. [b] Calories per mole.

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

The activity coefficients were correlated with the Margules, Van Laar, Wilson, NRTL, and UNIQUAC equations (*11*). The adjustable parameters A_{12}, A_{21}, and α_{12} for the correlation data, mean absolute deviations, and activity coefficients at infinite dilution γ_i^∞ for the two systems are listed in Table VI. Mean absolute deviations between experimental and calculated temperatures, MAD(T), and vapor compositions, MAD(y), are of the order of estimated experimental uncertainties.

For fitting the binary parameters the Rosenbrok method (*12*) was used to minimize the following objective function, using the activity coefficients obtained from the consistency

Table VII. Relative Volatilties α of Cyclohexanone + Cyclohexanol and Cyclohexanone + 2-Methylcyclohexanone Systems and Standard Deviations $\sigma(\alpha)$

system	P/kPa	α	$\sigma(\alpha)$
cyclohexanone + cyclohexanol	4.00	3.142	0.040
	26.66	1.761	0.031
cyclohexanone + 2-methylcyclohexanone	4.00	1.742	0.037
	26.66	1.358	0.021

test as experimental values:

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

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, especially the cyclohexanone + 2-methylcyclohexanone system. This behavior can be qualitatively explained in terms of molecular interactions. In the cyclohexanone + 2-methylcyclohexanone system there is almost complete compensation between the like and unlike polar interactions of the carbonyl groups. In the other system, cyclohexanol forms hydrogen bonds with itself which are in part compensated by hydrogen bonding with cyclohexanone. Therefore, the deviations from ideality are small but relatively stronger than in the first system.

(2) In both systems, the separation is more favorable at reduced pressures as can be seen from the relative volatilities α calculated by means of the following equation (Table VII):

$$\alpha = \left[\frac{dy_{exptl}}{dx_{exptl}} \right]_{x_{exptl} \to 0} \tag{5}$$

(3) The VLE data for the cyclohexanone + cyclohexanol system reported in this work define an equilibrium curve similar to those found in the literature (*1*), but in our case the dispersion is smaller and the correlation is better. Only two works (*13, 14*) present experimental data at the pressures used in this paper. The first (*13*) reports many data, but they have a high dispersion, showing, in some cases, an azeotropic point. The second (*14*), reports very few experimental data, and the dispersion is also high.

We can conclude that the experimental data for the cyclohexanone + cyclohexanol system reported in this paper present, in principle, a higher degree of trust than the previously mentioned.

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