Vapor–Liquid Equilibria of the Cyclohexane–Cyclohexanone System at 323.15 and 348.15 K

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Isothermal vapor–liquid equilibrium data were determined by means of a recirculating still for the cyclohexane–cyclohexanone system at 323.15 and 348.15 K. The results obtained were correlated in terms of the liquid activity coefficients of the two components by a two-suffix Margules equation.

It is well known that cyclohexane is an excellent solvent, and is of great importance as a chemical intermediate in the preparation of cyclohexanone, cyclohexanol, and adipic acid used in the manufacture of nylon (*5*). A mixture of cyclohexane, cyclohexanone, and cyclohexanol is produced by the catalytic air oxidation of cyclohexane and is separated by distillation.

Vapor–liquid equilibrium data in the cyclohexane-cyclohexanone–cyclohexanol system were reported by Susarev and Lyzlova (*6*) at atmospheric pressure. However, an examination of their isobaric data for the binary system cyclohexane-cyclohexanone revealed that the thermodynamic consistency of the data was doubtful, because their reported vapor composition values could not be approximated from the T–x curve by means of the Gibbs–Duhem equation with the known techniques compiled by Hala et al. (*4*). Furthermore, it appears that this set of data is the only known reference available in the literature (*8*) inspite of the industrial importance of the system.

It was, therefore, decided to determine in this work vapor-liquid equilibrium data for the cyclohexane–cyclohexanone mixtures at two isothermal conditions, 323.15 and 348.15 K.

Experimental Section

The design and operation of the recirculating still used for studying the vapor–liquid equilibria have been described previously (*2, 3*). A calibrated mercury thermometer enabling the determination of the temperature with an accuracy of ±0.005 K was used. Values of the equilibrium pressure were obtained from measurements of the boiling temperature of water in an ebulliometer connected to the same pressure reservoir as the equilibrium still. The error in the values of the pressure is estimated to be about 0.05 Torr.

The analytical grade cyclohexane (Reanal) was treated with H_2SO_4 and HNO_3, dried, and rectified and the pure grade cyclohexanone (Lachema) was dried and rectified. Values of their refractive indices and densities measured at 20 °C and of their boiling points determined at 760 Torr for cyclohexane and at 100 Torr for cyclohexanone are compared with known values from the literature (*6, 7*) in Table I.

Compositions of the equilibrium liquid and condensed vapor phases were obtained from measurements of their refraction indices at 20 °C using the following relationship

$$n_D^{20}(x_1) = 1.42623x_1 + 1.45060(1 - x_1) + x_1(1 - x_1)[-0.004322 - 0.001919(2x_1 - 1) - 0.002173(2x_1 - 1)^2] \quad (1)$$

where x_1 is the mole fraction of cyclohexane. This equation correlates the results of a series of known composition mixtures of the two components. An Abbe-type refractometer (Zeiss Jena Model G) capable of precision to ±0.000 03 RI units was used for the refractive-index determinations, and the standard error in the determination of x_1 totaled 0.001.

Results

The experimentally determined equilibrium values of T, p, x, and y for the cyclohexane-cyclohexanone system are listed in Table II.

The ratio of the liquid activity coefficients of the two components, γ_1/γ_2, was calculated in terms of the relative volatility, α,

$$\frac{\gamma_1}{\gamma_2} = \frac{y_1x_2p_2^0}{y_2x_1p_1^0} = \alpha\frac{p_2^0}{p_1^0} \quad (2)$$

and correlated by means of eq 3

$$\log(\gamma_1/\gamma_2) = A_{12}(1 - x_1)^2 - A_{21}x_1^2 - 2(A_{12} - A_{21})x_1(1 - x_1) \quad (3)$$

The nonideality of the vapor phase was not taken into account in the calculation. Equation 3 is equivalent to the following two-suffix Margules equation:

$$\begin{aligned}\log\gamma_1 &= (1 - x_1)^2[A_{12} + 2x_1(A_{21} - A_{12})]\\ \log\gamma_2 &= x_1^2[A_{21} + 2(1 - x_1)(A_{12} - A_{21})]\end{aligned} \quad (4)$$

The vapor pressure values of the two components were obtained from the Antoine equation.

$$\log P = A - B/(t + C) \quad (5)$$

with the values of A, B, and C as listed below (*1*)

	A	B	C
Cyclohexane	6.849 41	1206.001	223.148
Cyclohexanone	7.315 28	1745.140	237.416

Hence, at 323.15 K, p_1^0 = 272.22 Torr, p_2^0 = 17.52 Torr and at 348.15 K, p_1^0 = 637.43 Torr, p_2^0 = 53.62 Torr. The values obtained for the coefficients A_{12} and A_{21} of eq 3 are as follows:

	A_{12}	A_{21}
323.15 K	0.4297	0.5653
348.15 K	0.3669	0.4610

The values of P and y_1 were computed using eq 4 and the expressions

$$P_{calcd} = x_1\gamma_1p_1^0 + x_2\gamma_2p_2^0$$

and

$$y_{1(calcd)} = x_1\gamma_1p_1^0/P_{calcd}$$

over the complete concentration range. The calculated results are compared with the experimental values in Figures 1 and 2 with the differences between the experimental and the calculated

Table I. Physical Properties of Chemicals Used

	Normal bp (P = 760 Torr)		n_D^{20}		d_4^{20}	
	Exptl	Lit.	Exptl	Lit.	Exptl	Lit.
Cyclohexane	80.69	80.738 (7)	1.42623	1.42623 (7)	0.7785	0.77853 (7)
Cyclohexanone	90.48[a]	155.65 (7)	1.45060	1.4507 (6)	0.9465	0.9464 (6)

[a] P = 100 Torr.

Table II. Experimental and Calculated Isothermal Vapor-Liquid Equilibrium Results for Cyclohexane (1)-Cyclohexanone (2)

Exptl x_1	Exptl y_1	P, Torr	$P_{\text{exptl}} - P_{\text{calcd}}$ (Torr)	$y_{\text{exptl}} - y_{\text{calcd}}$
		T = 323.15 K		
0.9470	0.9905	263.37	1.95	0.0016
0.8920	0.9810	254.55	2.66	0.0010
0.8655	0.9750	250.45	2.76	−0.0013
0.7910	0.9690	240.43	3.45	0.0011
0.6975	0.9615	228.79	3.72	0.0020
0.5656	0.9530	208.81	0.20	0.0037
0.5365	0.9510	205.06	0.40	0.0041
0.4320	0.9400	185.42	−2.69	0.0031
0.3346	0.9270	160.96	−6.49	0.0039
0.2755	0.9225	149.66	−1.62	0.0120
0.1640	0.8695	107.82	−2.73	0.0048
0.1185	0.8255	86.01	−3.18	−0.0025
0.0963	0.8120	77.24	−0.37	0.0174
		T = 348.15 K		
0.9600	0.9905	620.60	1.82	−0.0004
0.9470	0.9890	617.85	4.86	0.0008
0.8935	0.9830	596.91	6.51	0.0048
0.7925	0.9650	564.38	12.22	0.0021
0.6723	0.9580	526.70	15.92	0.0101
0.5796	0.9430	490.02	12.39	0.0063
0.4525	0.9240	436.00	7.19	0.0050
0.4426	0.9240	433.28	8.86	0.0067
0.3790	0.9105	385.82	−8.00	0.0052
0.2493	0.8790	329.09	15.23	0.0132
0.1745	0.8325	261.04	7.90	0.0109
0.1416	0.8045	225.43	2.77	0.0141
0.1325	0.7920	221.82	8.20	0.0124
0.0650	0.6620	139.45	0.30	0.0233

values at the experimental values of x_1 reported in Table II. The average absolute deviations of P and y_1 are summarized as follows

	$\lvert \Delta P/P \rvert / N$, %	$\lvert \Delta y_1 \rvert / N$
323.15 K	1.50	0.0045
348.15 K	2.03	0.0082

The still and the equipment used in this work are capable of accuracy much better than those indicated by the deviations. No significant improvement of the calculated results was obtained if a three-suffix Margules equation was used for correlating the γ values.

It seems that the discrepancy is due to a possible reaction undergoing in cyclohexanone, especially at the higher temperature. This suspicion was manifested by the change of color from the originally colorless liquid solution to a yellowish one. This phenomenon may have caused some errors in the determination of the equilibrium phase compositions and/or prevented the reaching of true equilibrium.

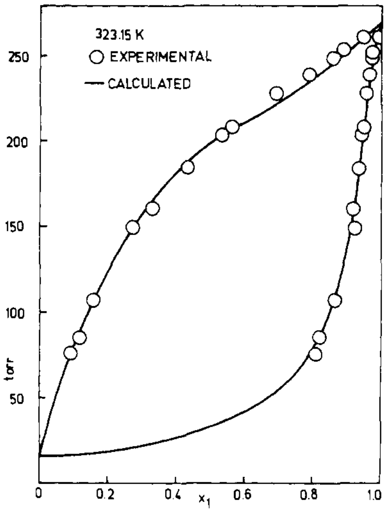

Figure 1. Comparison of experimental and calculated P-x-y values for the cyclohexane-cyclohexanone system at 323.15 K.

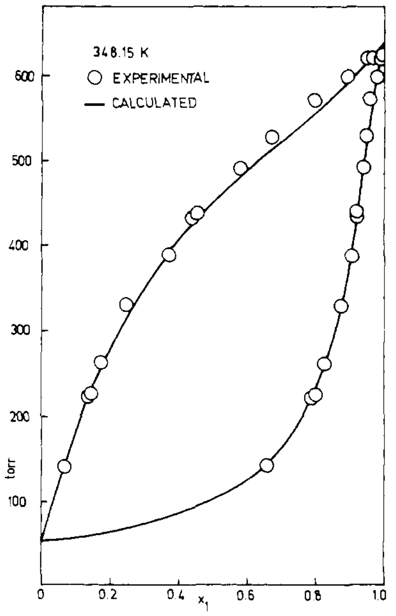

Figure 2. Comparison of experimental and calculated P-x-y values for the cyclohexane-cyclohexanone system at 348.15 K.

Glossary

A_{12}, A_{21}	coefficients of eq 3
A, B, C	coefficients of the Antoine equation
d	density, g mL^{-1}
N	number of observations
n_D	refractive index (sodium D line)
P	total pressure
P^0	vapor pressure
t	temperature, °C
x	mole fraction in the liquid phase
y	mole fraction in the vapor phase
α	relative volatility
γ	liquid activity coefficient

Subscript

1	cyclohexane
2	cyclohexanone

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Some Physicochemical Properties of the Binary Mixtures Heptane–Propanone and Heptane–Ethyl Acetate

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The density, viscosity, dielectric constant, and electric conductivity of binary mixtures of propanone or ethyl acetate with heptane were measured at 22.5 °C. The experimental results are expressed as functions of the mole fractions. The excess volumes are given. The equations of Mc Allister and Heric for the viscosity of binary systems are applied. Different relationships, expressing the dielectric constants of mixtures, are tested. A new equation is proposed to calculate the electric conductivity from the conductivities of both components. The results agree with the results for mixtures containing ethyl acetate. There are deviations for the system propanone–heptane.

In the framework of a systematic study on the electrokinetic behavior of liquids and liquid mixtures of very low conductivity, it was necessary to know the values of certain physicochemical properties of binary mixtures of heptane with propanone (system A) or with ethyl acetate (system B), i.e., the density, viscosity, static dielectric constant, and electric conductivity.

In this paper, experimental results are presented concerning these properties, on which hitherto no literature data were available.

In view of their application in the electrokinetic study, the properties are correlated by simple power series of the molar fraction of the polar component. The validity of existing equations for the viscosity and the dielectric properties is tested.

In order to explain the electric conductivity of these mixtures a new relation is proposed and checked.

Experimental Section

Materials. All liquids were GR products (Merck). Before use they were distilled in an all-glass multiple-plate still. The purity of the constant boiling point fraction was checked by gas chromatography. All mixtures were prepared by weighing.

Density Measurements. The density ρ was determined by means of a pycnometer of about 10 cm^3 volume. Each reported density is the mean value of three sample weighings. No correction to vacuum was applied. The solutions were not degassed. To prevent loss of weight by evaporation, the pycnometer and the mixture were thermostated separately at 22.5 °C. The pycnometer was weighed immediately after filling.

Viscosity Measurements. The viscosity η was determined by means of an Ostwald viscometer, placed in a thermostat at 22.5 °C. The time of effluence of the apparatus always exceeded 100 s. The measurement was repeated until three equal time values were obtained.

Measurement of the Static Dielectric Constant. The dielectric constant ϵ of the liquids was determined by means of a WTW-Dekameter DK03. The value of ϵ is deduced from the measurement of the cell capacitance at 1.8 MHz. The cell was thermostated at 22.5 °C by a circulating water jacket.

Measurement of Electric Conductivity. The resistance of all mixtures was measured in a stainless steel cell, described by Klinkenberg (*7*). The cell constant (7.19 × 10^{-3} cm^{-1}) was determined by means of a 10^{-3} M KCl solution. Because of the wide range of conductivities (from 10^{-7} to 10^{-17} Ω^{-1} cm^{-1}), different measuring devices were used.

Resistances less than 10^6 Ω were determined with a Philips Measuring Bridge GM 4249. For higher resistances (up to 10^{10} Ω) a Keithley Electrometer 610 A was used. To determine resistances above 10^{10} Ω, five external dc voltages (100, 200, 300, 400, and 500 V) were subsequently applied to the cell and the resulting currents were measured. From the slope of the resulting linear current–voltage plot, the resistance was deduced. As the conductivity cell could not be placed in a thermostated water bath, the mixture was placed preliminarily in the bath and then poured into the cell, while keeping the room temperature as near to 22.5 °C as possible.

Results

Density. The density data are listed in Table I, which also contains the values of the molar volume (V_m) of each sample:

$$V_m = \frac{x_1M_1 + x_2M_2}{\rho} \qquad (1)$$

The excess volume V_E is the difference between the actual molar volume and the molar volume of an ideal mixture:

$$V_E = V_m - (x_1V_1 + x_2V_2) \qquad (2)$$

The excess volumes of both systems are plotted in Figure 1 as a function of x_1. They can be fitted to

$$V_E = kx_1x_2 \qquad (3)$$

This equation is represented by the full line in Figure 1, calculated with a value of k = 4.4.