

Solubilities, Densities, and Vapor–Liquid Equilibria for the System EtOH + Cyclohexanone Oxime

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Vapor–liquid equilibrium data, solid–liquid solubilities, and densities for the system ethanol + cyclohexanone oxime were measured. The solubility was determined for temperatures between 263.15 K and 318.15 K, and density was determined at 293.15 K for ethanol concentrations from $w_{\text{EtOH}} = 0.55$ to 0.95. Vapor pressures of the mixture were measured in the concentration range of ethanol from $w_{\text{EtOH}} = 0.55$ to 0.95 and for temperatures between 303.15 K and 453.15 K. The experimental results were statistically analyzed and summarized with an empirical model. All necessary corrections of the VLE were performed with the help of the UNIFAC G^E-model, the Redlich–Kwong equation, and the Benedict–Webb–Rubin equation.

Introduction

In this work physical data for the mixture ethanol + cyclohexanone oxime, which is used in the Beckmann rearrangement (Figure 1) of the oxime to ϵ -caprolactam in a heterogeneous gas-phase reaction on a boron pentasil zeolite,^{1,2} are determined. The monomer for nylon-6 is ϵ -caprolactam. It is well-known for its application in high-quality fibers and engineering plastics. The classical liquid-phase Beckmann rearrangement, based on highly concentrated sulfuric acid, is ecologically and economically questionable because of the production of up to 2.7 tons of ammonium sulfate per ton of product in the rearrangement step and 4.5 tons of this salt per ton of product in the whole synthesis. Therefore, many efforts have been undertaken to find new routes to this important intermediate product. While a new industrial synthesis process starting from butadiene is planned by BASF in China,³ the heterogeneously catalyzed gas-phase Beckmann rearrangement still needs improvements. One is the reduction of byproducts formation, which occurs as a result of the technical infrastructure of the reaction system, especially in the evaporation of the liquid reactants. The objective of this work is to determine the solid–liquid solubilities, densities, and VLE for the reactant mixture of cyclohexanone oxime + ethanol, which are essential for the development and construction of new evaporators.

Experimental Section

Materials. Cyclohexanone oxime (purity > 97%, Fluka) was used without further purification. Verifying measurements yielded a purity of 99.5%. The ethanol (purity = 99.8%, Fluka) used was of technical grade and was also used without further purification.

Preparation of the Mixtures. The solutions used for the density and VLE experiments were prepared in glass flasks. The necessary amounts of the two substances were measured with the help of a laboratory scale (Sartorius BP 610, ± 0.01 g). The mixtures were stirred until complete dissolution was achieved.

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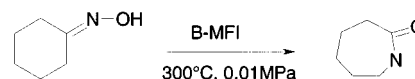


Figure 1. Beckmann rearrangement.

Solubility. The experiments determining the maximum solubilities of the oxime in ethanol were carried out by heating the solution to a temperature 5 K higher than the actual measuring point. The solution was then saturated with cyclohexanone oxime and subsequently cooled to the measuring point. To achieve a completely saturated solution, crystallization starters in the form of finely ground cyclohexanone oxime crystals were added. After the precipitation, a sample was taken from the clear liquid phase. To prevent unwanted crystallization, the sample was taken with a preheated metal pipet held at the same temperature as the mixture and put into a GC-glass, containing a defined amount of methyl undecanoate (purity > 99%, Lancaster Chemicals), which was used as external standard and additional solvent to keep the oxime dissolved. Subsequently, the samples were analyzed with gas chromatography (HP 6890 Series, 50 m FS-SE 54 column; 1.3% accuracy).

Density. The densities of the mixtures were determined at 293.15 K with a pycnometer (Schott, 20 cm³). The solution was prepared and injected into the pycnometer. The temperature of the pycnometer was adjusted to 293.15 K using a thermostat (Lauda, RML6, ± 0.1 K). Lack or surplus of solution was compensated, after which the weight of the pycnometer was determined.

Vapor Pressure. The experiments for the determination of the vapor pressure of the binary system were performed with a standard steel autoclave with a volume of 70 cm³ sealed with a special metallic seal (Figure 2). Attached to the cap of the autoclave was one main connector with a piping system connected to a vacuum pump (Edwards RV12, 0.1 Pa), an injection system, and an electronic pressure detector (Vacuubrand, DVR 1; Labom, E2314, 0.24% error referring to maximum readout). The pressure detector was connected to a multimeter (Keithley 2015 THD) with a five-digit readout. The complete pressure detection was calibrated with the vapor pressures of pure

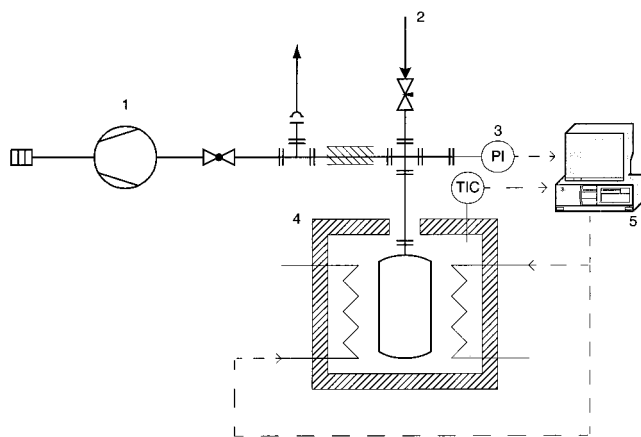


Figure 2. Scheme of the VLE apparatus: (1) vacuum pump; (2) injection system; (3) electronic pressure detector; (4) heated pressure detection device; (5) process control system.

Table 1. Solubilities of Cyclohexanone Oxime (2) in Ethanol (1) (263.15 K to 318.15 K)

T K	max. solubility $w_1 = w_{EtCH}$
318.15	0.166
313.15	0.199
303.15	0.308
293.15	0.401
283.15	0.523
273.15	0.632
263.15	0.693

Table 2. Densities of the Mixture Ethanol (1) and Cyclohexanone Oxime (2) at 293.15 K

composition $w_1 = w_{EtCH}$	density $g \cdot cm^{-3}$
0.55	0.889
0.65	0.865
0.75	0.843
0.85	0.821
0.95	0.800
1.00	0.789

ethanol at different temperatures with the necessary data from the literature.⁴ The complete volume of the measurement apparatus including the piping system and pressure detector was 75 cm³. The autoclave and its piping were heated in a temperature-controlled oven (Eurotherm 91e) and heating coils (Horst, HB, 1.5 m). The measurement procedure started with cleaning of the autoclave and the piping system. The equipment was dried, assembled, and thoroughly leak-tested under a pressure of 4 MPa and a vacuum of <0.1 kPa. Subsequently, the autoclave was evacuated, filled with 30 cm³ of the mixture using the injection system, and heated to the experimental temperature. An adequate time (>2 h) was allowed to reach equilibrium, after which the equilibrium pressure was recorded.

Results and Discussion

The experimental solubilities are shown in Table 1; the densities at 20 °C are shown in Table 2, and an extract of the experimental vapor pressures is presented in Figures 3 and 4. The equation used to calculate the model extracts can be found in the appendix.

Solubility. The maximum solubility at temperatures between 263.15 K and 373.15 K was measured at atmospheric pressure. The accuracy of the measurements is influenced by the exact adjustment of the temperature and

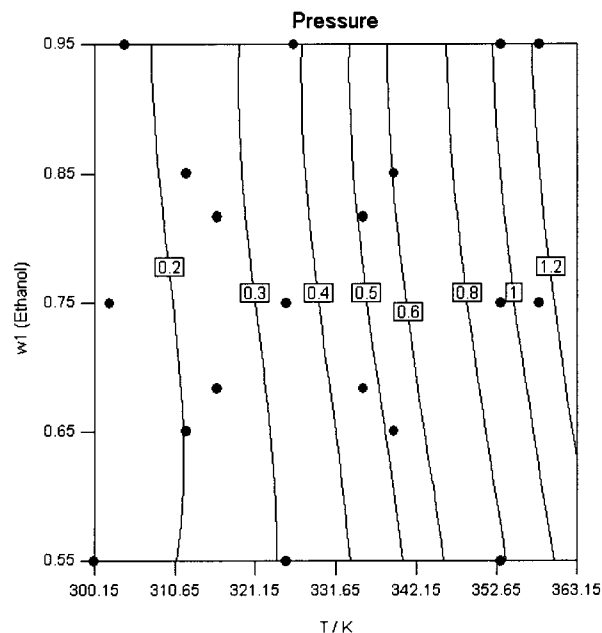


Figure 3. Vapor pressures ($\times 10^5$ Pa) at 300.15 K to 363.15 K and $w_{EtOH} = 0.55$ to 0.95.

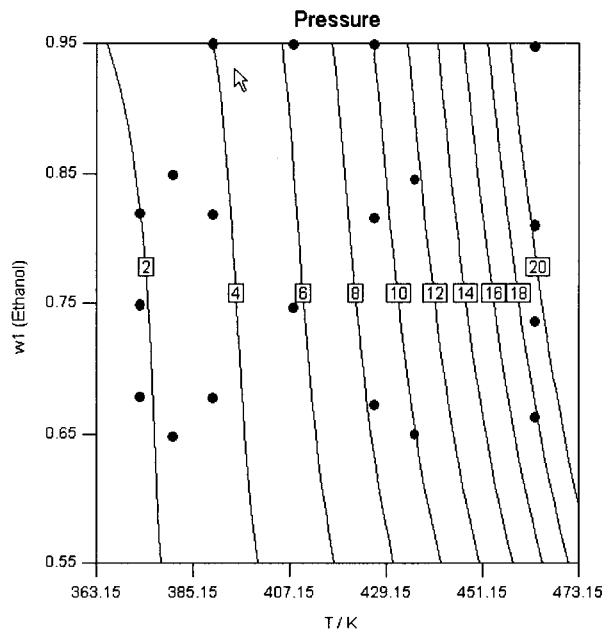


Figure 4. Vapor pressures ($\times 10^5$ Pa) at 363.15 K to 473.15 K and $w_{EtOH} = 0.55$ to 0.95.

the GC-analysis. The values shown in Table 1 have a maximum uncertainty of 1.3%.

Density. The density at 293.15 K was determined for mixtures of cyclohexanone oxime and ethanol with contents of ethanol from 55% by mass to 100% by mass. The accuracy was influenced by the exact adjustment of the temperature. The values shown in Table 2 have a maximum uncertainty of 0.1%.

Analysis of the Vapor Pressure Data. To allow for the calculation of an empirical model for the vapor pressure, the experiments were performed according to an experimental design which was set up with DesignExpert 5.0 (StatEase). This program allows for a good statistical analysis of experimental data and prevents the occurrence of outliers influencing the empirical model.

A complete filling of the autoclave had to be avoided because of the thermal expansion of the injected mixture

Table 3. Vapor Pressures at 300.15 K to 353.15 K and $w_{\text{EtOH}} = 0.55$ to 0.95 (Selected Measurements)

wt fraction ethanol	T	pressure(model)	pressure(meas)
kg/kg	K	bar	bar
0.55	300.15	0.12	0.113
0.55	325.15	0.31	0.321
0.55	353.15	0.78	0.775
0.65	312.15	0.20	0.190
0.66	339.15	0.52	0.506
0.75	302.15	0.13	0.140
0.75	325.15	0.35	0.354
0.75	353.15	0.94	0.922
0.85	312.15	0.24	0.223
0.85	339.15	0.60	0.602
0.95	304.15	0.17	0.173
0.95	326.15	0.39	0.387
0.95	353.15	1.04	1.056

had to be taken into account. Therefore, only 30 cm³ was injected into the autoclave, making a correction of the VLE data necessary. These corrections were done according to eq 1.

$$y_i P \Phi_i = x_i \gamma_i \Phi_i^S P_i^S \exp((P - P_i^S) v_i^L / RT) \quad (1)$$

Activities were estimated with the UNIFAC equation according to eqs 2–4:

$$G^E = G_{\text{comb}}^E + G_{\text{res}}^E \quad (2)$$

$$\ln \gamma_i^C = \ln \frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \sum_j x_j l_j \quad (3)$$

$$\ln \gamma_i^R = \sum_k V_k^{(i)} (\ln \Gamma_k - \ln \Gamma_k^{(i)}) \quad (4)$$

The complete model, the group specification matrix, and other necessary data can be taken from refs 5–7. The fugacities of the pure substances and mixtures were calculated using the Redlich–Kwong equation (eqs 5 and 6) and checked with the Benedict–Webb–Rubin⁵ equation.

$$\ln \varphi = Z - 1 - \ln \left[Z \left(1 - \frac{b}{V} \right) \right] - \frac{a}{RT^{1.5}} \ln \left(1 + \frac{b}{V} \right) \quad (5)$$

$$a = 0.42748 \frac{R^2 T_c^{2.5}}{P_c} \quad b = 0.08664 \frac{RT_c}{P_c}$$

$$\ln \varphi_i = \frac{b_i}{b} (z - 1) - \ln \left[Z \left(1 - \frac{b}{V} \right) \right] + \frac{1}{bRT^{1.5}} \left[\frac{a^* b_i}{b} - 2\sqrt{a^* a_i} \right] \ln \left(1 + \frac{b}{V} \right) \quad (6)$$

The exact calculation of the gas-phase composition was compared to the estimation of the gas phase containing pure ethanol. With nearly no cyclohexanone oxime in the gas phase (maximum 2% calculated by the exact method) the differences between the two methods are smaller than the random error of the experiments. Because of this, no gas-phase composition is given.

The quality of the experimentally determined vapor pressures is influenced by uncertainties in the pressure detection and in the exact temperature control. The combination of these errors results in a 0.6% deviation, referring to the maximum system pressure 2.2 MPa.

The accuracy of the empirical model, as shown in Figures 3 and 4 and Tables 3 and 4, is dependent on the density of measurements in the area of interest. In both parts of the

Table 4. Vapor Pressures at 380.15 K to 463.15 K and $w_{\text{EtOH}} = 0.55$ to 0.95 (Selected Measurements)

wt fraction ethanol	T	pressure(model)	pressure(meas)
kg/kg	K	bar	bar
0.55	389.82	3.07	2.95
0.65	380.65	2.39	2.29
0.65	435.65	9.99	9.69
0.65	463.15	17.86	18.02
0.74	463.15	19.30	18.79
0.75	373.15	1.84	1.84
0.75	408.15	5.67	5.52
0.85	380.65	2.07	2.09
0.85	435.65	11.64	11.75
0.95	389.82	4.00	3.70
0.95	463.15	22.55	22.36

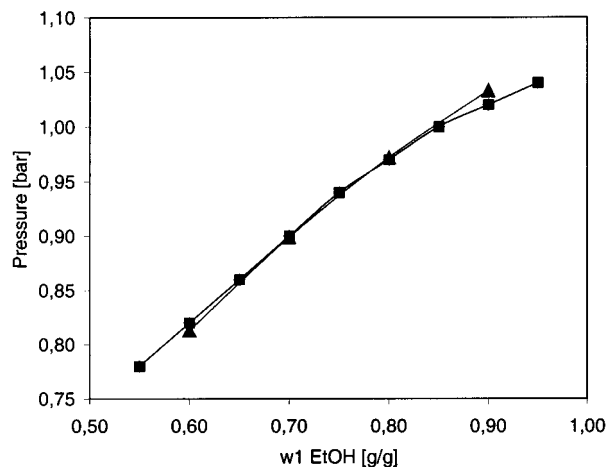
Table 5. Physical Data of Pure Compounds

property	unit	ethanol	cyclohexanone oxime
mol wt	kg/kmol	46.07	113.159
crit temp	K	513.92	715.00
crit pressure	Pa	6.1480 × 10 ⁶	4.6900 × 10 ⁶
melting point	K	159.05	363.15
normal boiling point	K	351.44	481.15

$$\text{Equation Form for Vapor Pressure (Pa)} \\ Y = \exp[A + B/T + C \ln(T) + DT^E]$$

Equation Coefficients for Vapor Pressure

	ethanol	cyclohexanone oxime
A	74.475	75.453
B	-7.1643 × 10 ³	-9.3635 × 10 ³
C	-7.3270	-7.2066
D	3.1340 × 10 ⁶	2.7505 × 10 ⁻¹⁸
E	2.0000	6.0000

**Figure 5.** Vapor pressure at 353.15 K: (▲) UNIFAC model; (■) empirical model.

model—for the lower and the higher pressures—the center area of the cube described by the model shows the lowest deviation between experimental data and calculation (<0.6%). In the outer part of the cube the approximation loses accuracy and errors of up to 1.5% of the maximum pressure can occur.

The comparison of the model data with the calculation of the vapor pressure based on the equations given above (Figure 5) shows good agreement.

Conclusion

The measured data were used to develop a new evaporation method for the binary system ethanol and cyclohexanone oxime.

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Appendix

The physical properties of the pure compounds are presented in Table 5.

The equations for the empirical model are based on a simple interaction polynomial. To suit the needs the DOE (Design of Experiments), the models were calculated on a transformed scale with an upper value of 1 and a lower value of -1.

The general equation for the calculation of the transformed values is

$$\text{transformed value} = 2 \times \frac{\text{actual value} - C_1}{C_2 - C_1} - 1$$

Formula for Determination of Vapor Pressures (0.02 to 0.12 MPa). The constants for the calculation of the transformed temperatures and compositions are ($C_{Ti} = A$ $C_{Wi} = B$)

$$C_{T1} = 298.15 \text{ K}; \quad C_{T2} = 353.15 \text{ K}; \quad C_{W1} = 0.55; \\ C_{W2} = 0.95$$

$$P = 0.35 + 0.34A + 0.05B + 0.16A^2 - 4.401E^{-03}B^2 + \\ 0.057AB + 0.087A^3 - 0.019B^3 + 0.04A^2B - 0.024AB^2$$

Formula for Determination of Vapor Pressures (0.2 to 2 MPa). The constants for the calculation of the transformed temperatures and compositions are ($C_{Ti} = A$ $C_{Wi} = B$)

$$C_{T1} = 353.15 \text{ K}; \quad C_{T2} = 436.15 \text{ K}; \quad C_{W1} = 0.55; \\ C_{W2} = 0.95$$

$$P = 5.67 + 7.91A + 0.64B + 4.08A^2 - 0.017B^2 + \\ 1.37AB + 1.74A^3 + 0.14B^3 + 1.39A^2B - 0.36AB^2$$

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