J. Chem. Eng. Data **1982**, *27*, 306-308

nonidealities were computed by using Chueh's modification of the Redlich–Kwong equation of state (*2*), and Table VI lists the parameters used in the equation. The binary interaction parameter, k_{12}, was set to zero for all mixtures. Table VII gives the average error between the experimental vapor-phase compositions and the thermodynamically consistent compositions. Based on these results, the data look reasonably consistent.

Figures 3 and 4 show the excess Gibbs energy calculated from the consistency test as a function of liquid composition for the systems studied. The liquid-phase nonidealities are comparable for the isopropyl fluoride + alkane systems with G^E decreasing slightly with increasing temperature. However, the isopropyl fluoride/propylene system is much more ideal and G^E slightly increases with increasing temperature. The difference in the liquid-phase behavior between the propane and propylene systems is in the affinity of the fluorine atom for the π electrons in the double bond of propylene.

Acknowledgment

We acknowledge the outstanding technical support in the work of J. L. Durm, who took all of the data reported here.

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Received for review July 6, 1981. Accepted February 5, 1982.

Low-Temperature Solubility of Caprolactam in Water

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The low-temperature (0 to −20 °C) solubility and a phase diagram for caprolactam (CAP) (=nylon 6 monomer) have been determined in pure water. Results show a stable eutectic with ice at −13.7 °C and 52.4 mass % CAP in the aqueous solution. Also they show a metastable eutectic at −19.3 °C with 60.3% CAP in the solution. The solid phase for the metastable eutectic is anhydrous CAP, called phase a, while that for the stable eutectic is of unknown composition, called phase b. There is also an incongruent melting point (a + b + solution) at −7 °C and 67.5 mass % CAP. The low-temperature data presented here line up well with the higher-temperature data of Puffr (*1*), although no data exist in the range 11–20 °C.

Introduction

Caprolactam (CAP) is a monomer which, when polymerized, yields nylon 6, and as such it is an important industrial chemical. The 1980 production of CAP was 9.05 × 10^8 lb (4.1 × 10^5 metric ton) in the USA. Caprolactam is made from cyclohexane and NH_3 or NO_x, but one can also start with benzene or toluene. Waste products are usually aqueous solutions containing 20 ppm to 2% CAP by mass, with several other organic and inorganic substances present in small amounts. The main inorganic salt present in these waste streams is ammonium sulfate.

It would be useful to have a process to clean up these waste streams and also to recover the CAP. Such a process would be eutectic freezing (*2*, *3*), but to design such a process requires low-temperature solubility data and a phase diagram for CAP in water. We have determined these data and report on them here. For process design one really needs the low-temperature solubilities of the complex collection of materials in a specific waste stream, but the data on CAP alone in water make a necessary starting point with which to do further work.

Seidel (*4*) gives data on the binary system $(NH_4)_2SO_4$ + water and on the ternary CAP + $(NH_4)_2SO_4$ + H_2O, but the latter are very few and limited to only two temperatures, 30 and 50 °C.

Table I. Refractive Indices for CAP Solutions in Water at about 25 °C

C, mass % CAP	n_D	$\Delta C/\Delta n$	C, mass % CAP	n_D	$\Delta C/\Delta n$
0	1.3327		45.84	1.4095	568
9.86	1.3484	628	85.47	1.4752	603
20.67	1.3652	643			

Experimental Methods

The melting point of pure ϵ-caprolactam is at least 69 °C, so it can be dried at 60 °C. Samples manufactured by Aldrich Chemical Co. were dried for 24 h and assumed to be anhydrous. Aldrich's stated purity is 99+%.

Dried samples were weighed, partially dissolved in distilled water with warming, and placed in a cell of about 1500-cm^3 volume, and the cell was put in a refrigerated bath, the temperature of which could be set between +10 and −30 °C, and regulated to ±0.2 °C. The cell was rocked by a mechanical rocker in the bath, and samples taken at successive intervals indicated that equilibrium was easily reached in 24 h since the liquid composition remained fixed.

Analysis for CAP was made by refractive index measurements with frequent recalibration of the curves of refractive index vs. mass % CAP in solution, particularly in the composition range to be used immediately. Checks on different samples showed the repeatability to be ±0.2% CAP.

The refractometer was an Abbé type made by Bausch and Lomb. The temperature for this determination was usually about 26 °C, and the refractive indices are temperature sensitive. To determine whether this method was suitable, we first made a curve of mass % CAP vs. n_D at about 25 °C with the results as shown in Table I.

The precision was not great, but the results above plus many others showed that this method was adequate to analyze CAP in water to ±0.19% CAP (with 90% confidence) and to ±0.26% CAP (with 95% confidence).

Each time a sample of solution from the equilibrium cell was to be analyzed, a short new calibration curve spanning the expected composition range was made with three to five standard solutions at the same temperature in the refractometer

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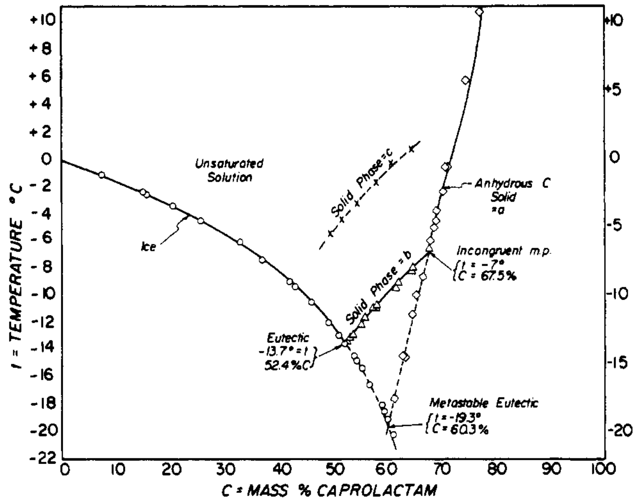

Figure 1. Condensed phase diagram for caprolactam + water.

to be used with the unknown sample.

All thermometers used were calibrated against US NBS standard thermometers with certified calibration curves, except the thermometer in the refractometer.

Experimental Results

The results are given in Table II and plotted in Figure 1. The only solid phases whose compositions we feel certain about are the ice and the anhydrous CAP. There are 21 points on the ice part of the curve, 16 on the anhydrous CAP line, 13 on the b-phase line, and 6 points on the c-phase line for a total of 56 points presented.

We could find no suitable method of determining the composition of solid phases b and c. Solid phase a is the anhydrous CAP. We determined this by noting that addition of well-dried samples of CAP to distilled water gave a consistent set of data on Figure 1, and adding dried CAP to an equilibrium mixture on the a-phase line did not affect the equilibrium. The data of Puffr (*1*) on the melting point of CAP vs. percent water, which extend from 19.65 to 68.62 °C, make a very smooth and credible extension to our line, or our data make a smooth extension to his line.

Solid phase c was inadvertently formed once only, and we could never form it again, in spite of diligent efforts to do so.

Solid phase b also appeared occasionally, but we found that it could be formed when needed, by cooling a solution containing 52–67 mass % CAP to a temperature below −19 °C in a test tube or in the cell.

One experiment was performed to demonstrate conclusively the enhanced stability of phase b over that of phase a in its temperature and concentration range. A solution containing about 66 mass % CAP was charged to the cell and rocked at −12.46 °C. Analysis of the mother liquor gave 64.5% CAP, which placed it definitely on the equilibrium curve for solid phase a (anhydrous CAP). To this equilibrium mixture was added some slurry made in a test tube as described above and containing phase-b solid. The temperature was maintained at −12.5 °C and then allowed to equilibrate. The resulting slurry was almost all solid; therefore, to form more liquid for analysis, we raised the temperature to −9.2 °C and equilibrated again. Analysis of the mother liquor gave 61.6% CAP, which puts it squarely on the b leg of the phase diagram. This proves that the b phase is more stable than the a phase at these temperatures.

While we were unable to find the composition of solid phases b and c, we did inspect them (and phase a) under a microscope. All three appeared superficially to have different crystal structures.

Table II. Low-Temperature Phase Data for the System Caprolactam + Water[a]

our sample no.	C, wt %	t, °C
Solid Phase = Ice[b]		
H	7.8	−1.21
G	15.4	−2.43
A	16.0	−2.55
F	20.5	−3.43
E	25.8	−4.53
D	32.7	−6.15
C	37.0	−7.50
B	42.0	−9.12
N	43.1	−9.45
M	46.2	−10.66
O	49.2	−12.11
ii	51.3	−13.13
P	52.3	−13.67
Q	53.8	−14.55
r	54.4	−14.87
R	55.3	−15.42
t	56.7	−16.64
s	58.7	−18.06
jj	59.2	−18.49
kk	60.0	−19.10
ll	61.5	−20.23
Solid Phase = Anhydrous Caprolactam (Phase a)[b]		
ww	77.2	+10.3
xx	74.6	+5.7
h	71.2	−0.64
j	71.1	−0.72
i	71.0	−0.72
k	70.4	−2.53
ss	69.2	−3.95
l	69.3	−4.70
rr	68.5	−5.06
m	68.1	−6.07
n	66.7	−8.75
uu	65.4	−10.06
o	64.9	−11.48
tt	62.9	−14.48
p	63.1	−14.66
q	61.3	−17.68
Solid Phase = Unknown Solid (Phase b, Stable)		
qq	67.7	−6.74
ff	64.7	−8.15
hh	64.7	−8.21
oo	62.1	−9.19
gg	61.6	−9.56
y	58.1	−10.83
pp	58.1	−10.89
nn	57.3	−11.04
x	55.9	−11.71
w	55.2	−12.33
mm	53.7	−13.02
v	53.3	−13.19
u	52.6	−13.44
Solid Phase = Unknown Solid (Phase c, Probably Metastable)		
ee	64.7	+0.72
dd	61.8	−0.30
cc	58.1	−1.81
bb	54.6	−3.21
aa	51.8	−4.43
z	49.6	−5.47

[a] Caprolactam = $C_6H_{11}NO$, mol wt = 113.16; experimental data points (see Figure 1). [b] The data above the dashed line represent the stable region, and the data below the dashed line represent the metastable region.

From the data we have estimated the several invariant points in the system caprolactam + water at 1 atm to be as shown in Table III.

The invariant points with phase c have not been estimated, but this could be done approximately by extending the c curve to both the ice line and the anhydrous CAP line (phase a). Until

Table III. Invariant Points in the System Caprolactam + H_2O at 1 atm

	wt % CAP	t, °C
stable eutectic (ice + phase b + solution)	52.4	−13.7
metastable eutectic (ice + phase a + solution)	60.3	−19.3
incongruent melting point (phase a + phase b + solution)	67.5	−7

we know the composition and nature of solid phase c, and are able to form it at will, this extension does not seem useful. We presume c to be a metastable phase since it proved to be so elusive and impossible to form again.

The presence of two eutectics, one stable and one metastable, would give no problems in a continuous eutectic freezing process in a stirred vessel as long as some phase b were introduced to the crystallizer during start-up. It should then produce ice and phase b continuously with no trouble by operating at a temperature somewhat below −13.7 °C (e.g., −16 °C) to give a driving force of 2.3 °C for crystallization. In a batch process, however, this might not be true and either eutectic might first form, in which case the temperature might have to be either −16 or −22 °C to get reasonable rates depending on which eutectic first formed on cooling the feed. In this (batch) case, one might have to introduce some crystals of phase b at the beginning of each batch. A temperature of −16 °C would, of course, be more economical for operation than would −22 °C.

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(4) Seidell, A.; Linke, W. F. "Solubilities"; American Chemical Society: Washington, DC, 1965; Vol. II, p 755 for $(NH_4)_2SO_4$ in water and pp 773–4 for CAP + $(NH_4)_2SO_4$ + water (at 30 and 50 °C only).

Received for review August 21, 1981. Accepted February 8, 1982. This work was supported in part by NSF Grant ENG 77-14894.

Binary Systems of Tetrachloroethylene with Benzene, Toluene, *p*-Xylene, Carbon Tetrachloride, and Cyclohexane. 1. Ultrasonic Velocities and Adiabatic Compressibilities at 293.15 and 303.15 K, Dielectric Constants at 298.15 and 308.15 K, and Refractive Indexes at 298.15 K

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Measurements of ultrasonic velocities and adiabatic compressibilities at 293.15 and 303.15 K, dielectric constants at 298.15 and 308.15 K, and refractive indexes at 298.15 K have been made for binary liquid mixtures of tetrachloroethylene (C_2Cl_4) with benzene, toluene, *p*-xylene, carbon tetrachloride, and cyclohexane. The values of the quantity k_s^E, which refers to the deviations of the adiabatic compressibilities of the mixtures from the ideal mole fraction mixture law values, have been calculated and have been fitted by the method of least squares to the equation $k_s^E = x_1x_2[A + B(x_1 - x_2) + C(x_1 - x_2)^2]$ where x_1 refers to the mole fraction of C_2Cl_4, x_2 refers to the mole fraction of aromatic hydrocarbon, CCl_4, or c-C_6H_{12}, and *A*, *B*, and *C* are constants which are characteristic of a system. For the systems C_2Cl_4–aromatics at 293.15 and 303.15 K, the values of k_s^E at $x_1 = 0.5$ have the sequence benzene > toluene > *p*-xylene. The values of the quantity $\Delta\epsilon$, which refers to the deviations of the dielectric constants of the mixtures from the ideal volume fraction mixture law values, have also been calculated. The values of $\Delta\epsilon$ at 298.15 K are found to be slightly negative or zero for all of the systems, and, at 308.15 K, the values are less negative or slightly positive. The values of the dipole moments of cyclohexane, carbon tetrachloride, and *p*-xylene, as determined from the dielectric constant and refractive index data for their dilute solutions in C_2Cl_4, have been found to be 0.04, 0.26, and 0.12 D, respectively.

Introduction

The binary systems of tetrachloroethylene (C_2Cl_4) with aromatic hydrocarbons, carbon tetrachloride (CCl_4), and cyclohexane are of considerable interest from the viewpoint of the existence of specific interaction between the components in the liquid state. The specific interaction of C_2Cl_4 with aromatics and CCl_4 can be visualized to be due to the presence of four Cl atoms and an olefinic π-electron system in C_2Cl_4, on account of which it can act both as a σ- and π-type sacrificial electron acceptor toward aromatics and as a π-type electron donor toward CCl_4. The system of cyclohexane with C_2Cl_4, in which case only the dispersion forces are believed to be present between the components, is of interest as it will act as a reference system. Extensive studies concerning the properties of these systems have not been made. The measurements of excess volumes (V^E) for binary mixtures of C_2Cl_4 with benzene, toluene, *p*-xylene, CCl_4, and cyclohexane at 293.15 and 303.15 K have, however, been reported (*1*, *2*). But these do not provide useful information concerning the existence of specific interaction between the components of the various systems. Hence, in the present program, the measurements of ultrasonic velocities in, and adiabatic compressibilities, dielectric constants, and refractive indexes of, binary liquid mixtures of C_2Cl_4 with benzene, toluene, *p*-xylene, CCl_4, and cyclohexane have been undertaken, and the results obtained have been interpreted in this paper.

Experimental Section

Materials. Benzene and toluene which were of AR or GR

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