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Liquid–Liquid Equilibrium for the System Acrylonitrile–Styrene–Water at 338 K

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In this paper the liquid equilibrium for the ternary system of acrylonitrile–styrene–water at 338 K is characterized. Phase-boundary lines are correlated by regression lines and conjugate points on tie lines are correlated by the method of Othmer–Tobias. All components in the solvent and aqueous phases at equilibrium were determined by gas chromatography. Acrylonitrile is shown to distribute linearly between the two phases with a partition coefficient of 8.29 which is different from prior work.

Introduction

Styrene and acrylonitrile (ST and AN) are widely used as comonomers in the production of important engineering plastics like ABS and SAN resins. In some processes, ST and AN are copolymerized in heterogeneous systems containing water as in the case of emulsion and suspension polymerization methods. In these heterogeneous mixtures, AN distributes between the two immiscible phases because of its relatively high solubility in water. However, the composition of the copolymer depends mainly on the monomer composition prevailing in the solvent phase. This was clearly shown by Smith (*1*) who interpreted the composition data of emulsion copolymers of previous workers (*2*) on the basis of the liquid–liquid distribution of AN. Data from more recent studies (*3–5*) indicate that the equilibrium distribution of AN is most helpful in interpreting instantaneous copolymer compositions for a range of conversions wider than that studied by previous authors. Apparently (*1*), reported partition coefficients of AN change with the global AN fraction in the solvent mixture. This change may be due to the assumptions made in calculating the compositions of the equilibrium layers. A usual one is to assume that the solubility of water in the solvent phase as well as that of ST in the aqueous phase are both negligible (*1*).

The purpose of this work was to characterize the liquid ternary diagram of AN–ST–H_2O at 338 K by measuring the mass fractions of all components in the two layers and to obtain more reliable values of the distribution coefficients of AN.

Experimental Methods

A mixture of AN, ST, and water separates out into a heavier, water-rich phase and a lighter organic phase. The equilibrium phases were analyzed for the three components by gas chromatography (GC) and their mass fractions determined.

Chemicals. Technical grades (99.9% purity) of AN and ST, further purified by distillation, were used. ST was distilled under vacuum at 327 K and AN was distilled at ambient pressure under N_2 at 350 K. Prior to use, the solvents were dried with $CaCl_2$ at room temperature. Distilled water was used in all experiments.

Preparation and Analysis of Samples. To determine the ternary diagram, the global mixtures of Table I were directly weighed at room temperature into screw-capped Pyrex tubes, sealed, and placed in a thermostated shaking bath set at 338 ± 0.2 K, operated at 500 rpm (New Brunswick bath Model G-76). Each tube contained about 15 cm^3 liquid and 3 cm^3 gas phase (air and solution vapor). After 2 h, the shaker was stopped and the samples were allowed to separate at 338 K. Samples of the lower and upper layers were then taken with long-needled GC syringes and rapidly injected into a gas chromatograph. This was a DANI Model 6800 apparatus equipped with double-channel thermal conductivity detector (100 mA). The components separate well on a $^1/_8$-in., 50-cm-long Chromosorb 102 column with temperature programming (170 °C for 100 s, followed by a 10 °C/min ramp to 200 °C, and a final period of 500 s at 200 °C). GC-grade helium carrier was used at 40 mL/min.

Table I. Liquid–Liquid Equilibrium at 338 K[a]

	initial compn			solvent phase			aqueous phase		
mixt	AN	water	ST	AN	water	ST	AN	water	ST
1	0	35.5	64.5	0	0.29	99.7	0	99.0	0.91
2	5.8	35.7	58.5	8.4	0.8	90.8	0.7	98.5	0.85
3	11.6	36.0	52.4	17.0	1.0	82.0	1.9	97.3	0.75
4	17.5	36.3	46.2	25.7	1.9	72.4	3.3	96.1	0.64
5	23.5	36.6	39.9	34.2	2.2	63.6	4.6	94.9	0.55
6	29.7	36.9	33.4	44.7	2.3	53.0	5.4	94.1	0.47
7	35.8	37.2	27.0	53.4	3.0	43.6	6.9	92.7	0.38
8	42.2	37.5	20.3	62.9	3.9	33.2	8.0	91.7	0.28
9	48.5	37.8	13.7	72.8	4.5	22.7	8.5	91.3	0.19
10	55.0	38.1	6.9	82.3	6.5	11.2	9.8	90.1	0.09
11	61.6	38.4	0	90.6	9.4	0	10.3	89.7	0

[a] At variable pressure (140–210 kPa). Compositions in mass percent.

Chromatographic analyses were performed by injecting 1-μL samples. The area normalization technique was used to obtain the concentrations. From previous calibrations, the relative peak areas, measured with a Shimadzu CR-1A integrator, could be converted to mass fractions.

As is seen, a small gas phase (air and vapors of solutions) was present in the equilibration tubes, with a negligible effect on liquid equilibria. Since air is sparingly soluble, its only effect is to compress the liquid samples above their vapor pressures. Under these conditions, the influence of pressure on liquid–liquid distribution is insignificant (*6*, *7*).

Correlation of Data and Discussion

Values of the experimentally determined equilibrium concentrations are given in Table I. The phase diagram for the system is presented in Figure 1, in which phase-boundary lines and experimentally determined tie lines correspond to the values of Table I. As can be seen in Figure 1, no plait point is observed at this temperature, as expected from the fact that two of the three possible binary solutions, AN–H_2O and ST–H_2O, exhibit limited miscibilities (*6*).

It was observed that the phase-boundary lines of Figure 1 could be correlated by the following regression equations. For the solvent-rich line

$$\%\ \mathrm{AN} = 91.4 - 0.836(\%\ \mathrm{ST}) - 8.55 \times 10^{-4}(\%\ \mathrm{ST})^2 \qquad (1)$$

with a correlation index of 0.999. The quadratic term of eq 1 accounts for the slight curvature of the line (see Figure 1). For the water-rich equilibrium line, a linear regression is sufficient. This is

$$\%\ \mathrm{AN} = 10.8 - 11.26(\%\ \mathrm{ST}) \qquad (2)$$

with a correlation coefficient of 0.993.

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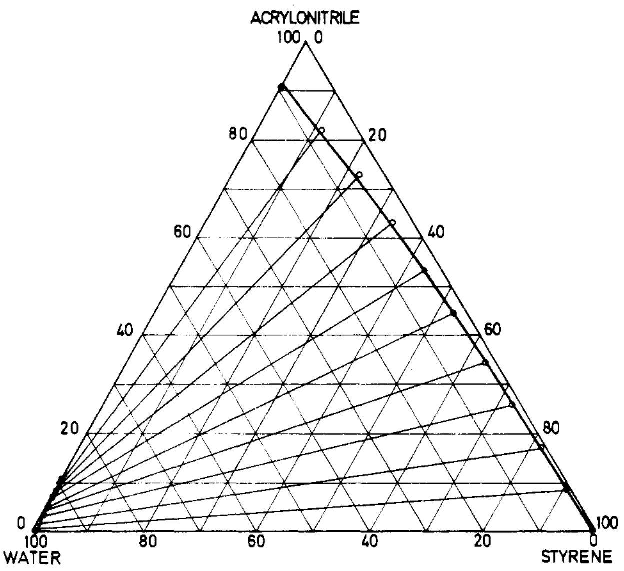

Figure 1. Equilibrium diagram for the system acrylonitrile-styrene-water at 338 K (variable pressure, 140-210 kPa).

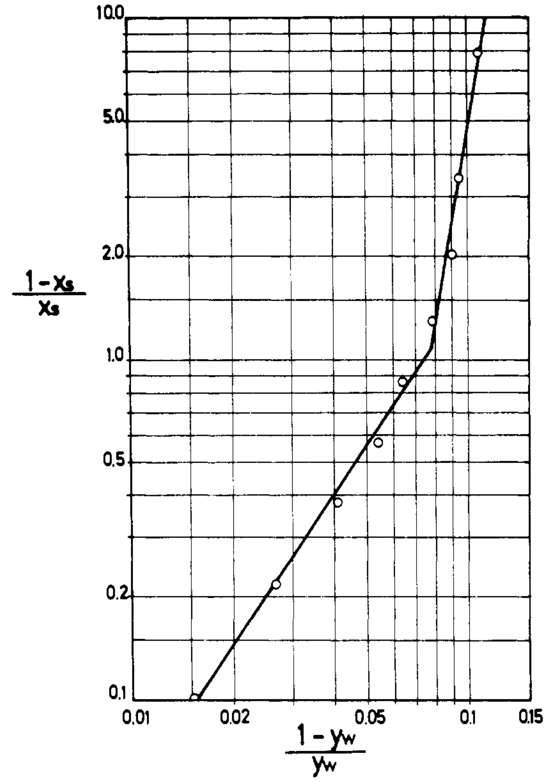

Figure 2. Othmer-Tobias plot for correlating tie lines. See eq 3. Upper line: $m = 5.571$, $n = 6.21$ ($R^2 = 0.981$). Lower line: $m = 1.477$, $n = 1.664$ ($R^2 = 0.993$).

The tie lines of Figure 1 can be correlated through the use of a standard method (*8*). We used the Othmer-Tobias method (*7*) which involves a graphical representation of the conjugate curve (not shown in Figure 1 for clarity) for plotting conjugate points of a tie line according to the empirical equation

$$\log (1 - x_S)/x_S = m \log (1 - y_W)/y_W + n \tag{3}$$

The data points of eq 3 obtained from this study are presented in Figure 2, where two regression lines can represent all the data with adequate precision. Even though all ternary liquid systems originally examined by Othmer and Tobias (*8*) could be correlated with single straight lines, Treybal gives a few exceptions where two tie-line correlations are needed (*7*), as in Figure 2. In our case the best values of the parameters of eq 3, m and n, together with the corresponding correlation coefficients, are given in Figure 2.

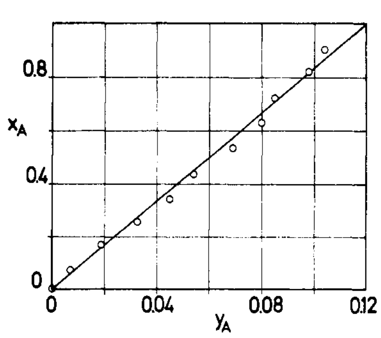

Figure 3. AN mass fraction in solvent vs. AN mass fraction in water. Slope is $\alpha = 8.29$.

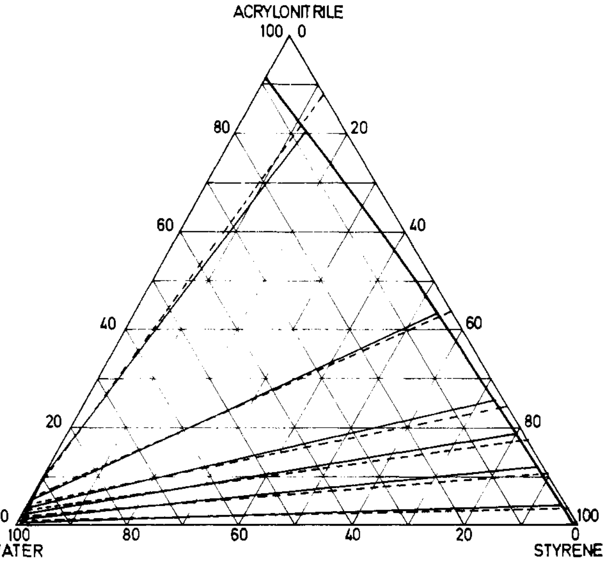

Figure 4. Equilibrium diagram with continuous tie lines from this study and dotted ones from Smith (*1*).

In most polymerization applications a distribution coefficient of AN will be needed. The observed distribution coefficient for AN, defined as

$$\alpha = x_A/y_A \tag{4}$$

was obtained from Figure 3, where equilibrium pairs $x_A - y_A$ are represented. As is seen, AN distributes linearly between the organic and aqueous phases, and thus a single value of α can account for all data points. Least-squares linear regression gives $\alpha = 8.29$, with a correlation coefficient of 0.995. x_A can be calculated from y_A with an average relative deviation of less than ±5.6%.

Final Remarks

In Figure 4 a ternary diagram with special tie lines is presented. The continuous ones are those obtained in the present study at 338 K, while the dotted tie lines join data points calculated from data of previous workers (*1*, *2*) at 233-348 K. The latter were calculated by neglecting the solubility of ST in the aqueous phase and the solubility of water in the solvent phase. Under these assumptions, the observed partition coefficient of AN would vary from 4.0 to about 11.7. In mixtures with low concentrations of AN, the above hypothesis is reasonable as seen in the lower part of the diagram. In high AN mixtures however, significant water extraction into the solvent takes place. If we neglect this effect, the calculated values of α are seen to change. In our study, where analysis of all components in both phases was performed, we find a rather constant $\alpha = 8.29$, in the midrange of Smith's values.

Glossary

AN	acrylonitrile
m, n	slope and intercept, respectively, in the Othmer–Tobias plot, eq 3
R^2	correlation coefficient in linear regressions
ST	styrene
x	mass fraction of the component in solvent-rich phase in equilibrium with y, kg/kg of organic phase
y	as above, in the water-rich phase, kg/kg of aqueous phase
α	distribution coefficient of AN defined by eq 4

Subscripts

A	acrylonitrile
S	styrene
W	water

Registry No. ST, 100-42-5; AN, 107-13-1.

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Vapor–Liquid Critical Curve of the System Ethane + 2-Methylpropane

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The vapor–liquid critical curve of the binary system ethane + 2-methylpropane was determined from the critical temperature of ethane up to the critical temperature of 2-methylpropane. The results are compared with vapor–liquid equilibrium data reported earlier on this system and with the critical curve that is predicted for this system from the Peng–Robinson equation of state.

Introduction

Vapor–liquid equilibria in the binary system ethane + 2-methylpropane are of interest to the petroleum and natural gas processing industry since both components are present in the multicomponent systems that are handled by these industries. Experimental data at temperatures below the critical temperatures of ethane are reported by Skripa et al. (*1*). Besserer and Robinson (*2*) reported four isotherms in the temperature region 310–395 K, at temperatures above the critical temperature of ethane. These authors have used the analytical method for the measurements of the vapor–liquid equilibria in this system and therefore they were not able to measure critical points. In this paper experimentally determined critical points are presented and the Peng–Robinson equation of state (*3*) is used to describe the critical curve.

Experimental Section

The measurements were carried out in an apparatus for use with pressures up to 20 MPa and temperature up to 473 K described earlier by de Loos et al. (*4*). With this so-called Cailletet apparatus, which is shown in Figure 1, dew points and bubble points of mixtures of known composition can be determined visually. The sample of the mixture M is confined over mercury in the sealed end of a thick-walled, capillary Pyrex glass tube C, 4 × 12 mm and 50 cm long. At about $^2/_3$ of its length this tube has a conical thickening which fits in the closing plug P of the stainless-steel autoclave A. Glass to metal and metal to metal sealing is achieved by using Viton O-rings R. The autoclave is filled with mercury up to the line to the pressure generating system. The open end of the tube is immersed in the mercury; thus the mercury in the tube and of the autoclave serves as a pressure intermediate between the sample and the hydraulic oil. The sample can be agitated by a small stirrer which consists of a soft-iron rod, sealed in with glass, with a slightly smaller diameter than the bore of the glass capillary tube. This stirrer is activated by two button magnets B which move up and down.

The glass capillary tube is kept at the desired temperature by a thermostat with circulating oil. The temperature was measured to an accuracy within ±0.01 K by using a platinum resistance thermometer; it was maintained constant to better than ±0.02 K. The pressure is generated hydraulically with screw pump H and is measured with a dead-weight pressure gauge to accuracy within 0.001 MPa.

During an experiment the mixture is first brought to the temperature and pressure conditions corresponding to the two-phase fluid region. Then the pressure is changed slowly until one of the phases just disappears. By observing the descent or ascent of the meniscus at constant temperature as function of pressure it can be ascertained whether the observed phase behavior is characteristic of a dew point or of a bubble point. The same procedure is followed at other temperatures. The critical point can be located in that temperature interval in which the observed phase behavior changes from bubble-point to dew-point behavior. For a given composition the accuracy in the measured critical temperature is 0.1 K and in the critical pressure 0.02 MPa. The mixture can be prepared with an accuracy in the mole fraction of 0.002.

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