remains the stable hydrate. Of the systems studied, only $K_5P_3O_{10}$ increased the solubility of sodium tripolyphosphate in water.

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Vapor-Liquid Equilibria of the Benzene–Cyclohexane–Acetic Acid System at Atmospheric Pressure

A. BARADARAJAN and M. SATYANARAYANA
Department of Chemical Engineering, Indian Institute of Technology, Madras 36, India

Vapor-liquid equilibrium data of benzene–cyclohexane–acetic acid system are determined experimentally at atmospheric pressure. The ternary system is azeotropic. The activity coefficients are correlated by Van Laar equations involving the three relevant binary constants.

THE separation of the azeotropic mixture of benzene and cyclohexane has been studied by previous workers using various third components including *n*-propanol (*5*), methyl ethyl ketone (*7*), diethyl ether (*9*), and ethyl acetate (*1*). In the present work, acetic acid is chosen as the third component. A comparative study can be made regarding the suitability of the chosen third component.

APPARATUS

The vapor-liquid equilibrium data were determined in a Fowler-Norris still (*2*) with a special heating system for better agitation. To have a decreased total capacity for each run, an equilibrium still with reduced dimensions was used. The still was standardized with the benzene-acetic acid system for which equilibrium data have been reported (*3, 6*). The temperature was measured by a set of short range thermometers (0.2° C. accuracy). Radiation correction for the exposed thread as well as the boiling point correction to 760 mm. of mercury were applied as described by Hala *et al.* (*4*). The pressure variation from 760 mm. of mercury was ± 5 mm. of mercury.

ANALYSIS

Refractive index and specific gravity at 30° C. were chosen for analysis. The measurements were made with the aid of an ultra thermostat maintained at 30° ± 0.05° C., a semimicro Mettler balance, and an Abbé refractometer provided with a source for monochromatic light. A 20-ml. pycnometer was used for specific gravity determination.

Nine binary mixtures of benzene and cyclohexane with various concentrations were prepared. Then each one was subdivided into a number of fractions when various quantities of acetic acid were added to each of these fractions. Specific gravity and refractive index were determined for each of the ternary mixtures thus prepared. The data were first plotted on linear coordinates. Then, from these graphs, constant property compositions were read, and constant specific gravity and refractive index lines were constructed (Figure 1). This was used as a standard graph for analysis.

EQUILIBRIUM DATA AND CORRELATION

The properties of the pure components are given in Table I. The equilibrium data are presented in Table II and in

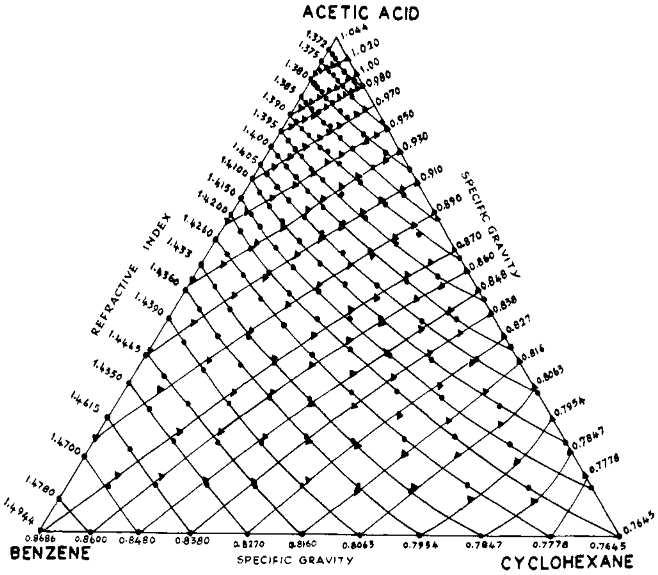

Figure 1. Standard data for analysis
▲ Constant specific gravity lines
● Constant refractive index lines

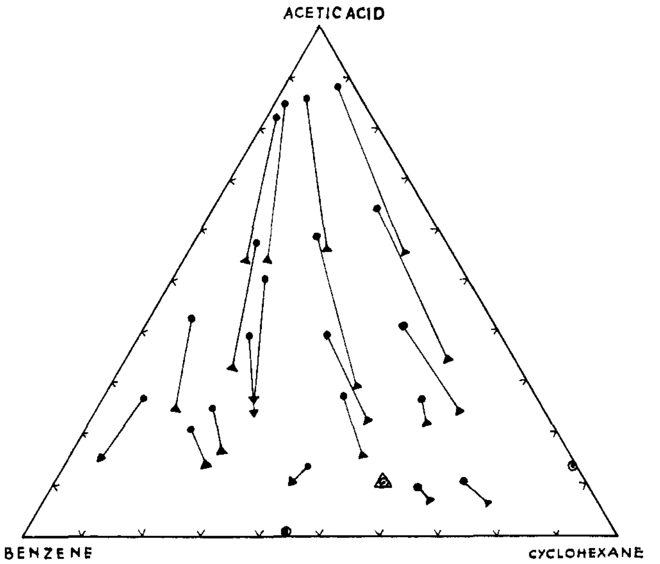

Figure 2. Vapor-liquid equilibrium data

● Liquid composition
▲ Vapor composition in equilibrium with liquid
⊙ Binary azeotropic composition
△ Ternary azeotropic composition

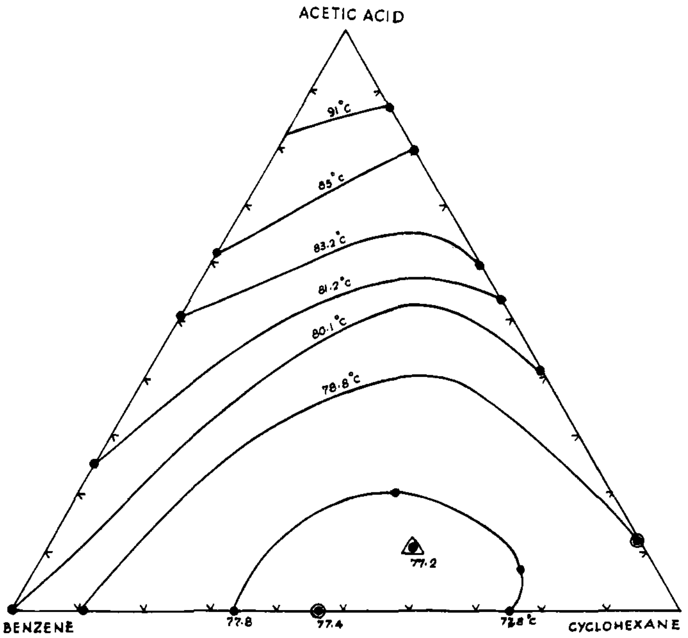

Figure 3. Temperature-liquid composition data

● Constant temperature lines
⊙ Binary azeotropic temperature
△ Ternary azeotropic temperature

Figure 2. Constant temperature lines are shown in Figure 3.

The activity coefficients are calculated using the equation

$$\gamma = \frac{\pi Y}{p X} \tag{1}$$

These activity coefficients are correlated by Van Laar equations as presented by Robinson and Gilliland (*8*). For a binary system,

$$T \ln \gamma_1 = \frac{B_{12} X_2^2}{\left(1 + A_{12} \frac{X_1}{X_2}\right)^2} \tag{2}$$

$$T \ln \gamma_2 = \frac{A_{12} B_{12} X_1^2}{\left(A_{12} + \frac{X_2}{X_1}\right)^2} \tag{3}$$

The constants A_{12} and B_{12} are evaluated from the plots of;

$$\frac{1}{(T \ln \gamma_1)^{1/2}} \ vs. \ \frac{X_1}{X_2} \text{ and } \frac{1}{(T \ln \gamma_2)^{1/2}} \ vs. \ \frac{X_2}{X_1} \tag{4}$$

Table I. Properties of Pure Components

Component	B.P., °C.	Sp. Gr. at 30° C.	n_D^{30}
Benzene	80.1	0.8686	1.4944
Cyclohexane	80.8	0.7647	1.4201
Acetic acid	118.1	1.0440	1.3691

Table II. Equilibrium Data

		Experimental							Calculated	
No.	T, °C.	X_1	X_2	Y_1	Y_2	γ_1	γ_2	γ_3	Y_{1c}	Y_{2c}
1	89.5	0.0250	0.0900	0.2200	0.4200	3.290	3.784	1.405	0.080	0.445
2	80.6	0.0750	0.2800	0.1750	0.4700	2.290	1.936	1.990	0.124	0.600
3	78.6	0.1500	0.4400	0.1950	0.5850	1.319	1.410	2.090	0.179	0.659
4	78.6	0.1900	0.5400	0.2150	0.5800	1.113	1.160	3.040	0.203	0.632
5	77.8	0.3250	0.4100	0.3550	0.4700	1.170	1.240	2.67	0.346	0.540
6	78.8	0.5500	0.1920	0.5950	0.2500	1.081	1.368	2.335	0.605	0.283
7	79.1	0.2900	0.3120	0.3600	0.4675	1.074	1.565	1.665	0.351	0.490
8	77.2	0.2950	0.6100	0.3000	0.6200	1.055	1.156	3.243	0.303	0.642
9	80.0	0.4200	0.1850	0.5150	0.2800	1.661	1.479	1.928	0.526	0.315
10	80.8	0.2100	0.2030	0.2900	0.4200	1.326	2.016	1.788	0.332	0.431
11	91.0	0.0930	0.0520	0.2200	0.2300	1.577	3.283	1.620	0.270	0.195
12	81.6	0.3400	0.1570	0.4800	0.2600	1.333	1.603	1.853	0.489	0.308
13	80.2	0.6600	0.0700	0.7900	0.1000	1.188	1.440	1.500	0.766	0.110
14	81.2	0.5000	0.0730	0.6150	0.1350	1.182	1.068	2.088	0.685	0.140
15	83.2	0.3140	0.1060	0.4800	0.2000	1.371	1.651	1.880	0.519	0.237
16	91.8	0.1550	0.0200	0.3500	0.1100	1.579	3.962	1.594	0.435	0.072
17	93.8	0.1300	0.0200	0.3300	0.1400	1.625	4.750	1.442	0.380	0.093
18	77.8	0.1900	0.7400	0.2050	0.7100	1.153	1.051	4.900	0.210	0.740
19	77.2	0.3500	0.5500	0.3500	0.5500	2.857	1.102	4.108	0.352	0.591
20	77.4	0.4500	0.4150	0.4600	0.3950	1.182	1.045	4.352	0.448	0.401
21	78.4	0.6100	0.1800	0.6250	0.2200	1.073	1.377	2.560	0.707	0.208

Table III. Binary Van Laar Constants

System	A	B
Benzene–cyclohexane	1.15	135.5
Cyclohexane–acetic acid	1.7631	419.881
Benzene–acetic acid	2.1992	330.5488

A_{23}, A_{13}, and B_{13} are also evaluated by the same method. The constants are given in Table III.

The following equations involving the binary constants are used for correlating the experimental equilibrium data for the ternary system.

$$T \ln \gamma_1 = (X_2[B_{12}]^{1/2} + X_3A_{32}[B_{13}]^{1/2})^2/(X_1A_{12} + X_2 + X_3A_{32})^2 \quad (5)$$

$$T \ln \gamma_2 = (X_1A_{12}[B_{21}]^{1/2} + X_3A_{32}[B_{23}]^{1/2})^2/(X_1A_{12} + X_2 + X_3A_{32})^2 \quad (6)$$

$$T \ln \gamma_3 = (X_1A_{12}[B_{31}]^{1/2} + X_2[B_{32}]^{1/2})^2/(X_1A_{12} + X_2 + X_3A_{32})^2 \quad (7)$$

CONCLUSION

The experimental and calculated values of vapor compositions corresponding to the same liquid compositions varied to within 3 to 4%. The ternary system exhibited an azeotrope at 77.2° C. at atmospheric pressure. The composition of the azeotrope in mole fractions is: acetic acid = 0.10; benzene = 0.35; and cyclohexane = 0.55. Hence, acetic acid is unsuitable as a third component for the separation of the benzene-cyclohexane azeotrope, since a ternary azeotrope occurs.

NOMENCLATURE

A = binary Van Laar constant
B = binary Van Laar constant
p = vapor pressure
T = temperature (absolute)
X = mole fraction in liquid phase
Y = mole fraction in vapor phase
γ = activity coefficient
π = total pressure of the system

Subscripts

1 = acetic acid
2 = benzene
3 = cyclohexane

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Vapor-Liquid and Liquid-Liquid Equilibria of the System Acrylonitrile-Acetonitrile-Water

GENNARO VOLPICELLI
Istituti di Chimica Industriale e Impianti Chimici, Università di Napoli, Napoli, Italia

Vapor-liquid equilibria of the ternary system acrylonitrile-acetonitrile-water have been measured under 760 mm. of Hg total pressure. Acrylonitrile and water are only partially miscible, and the ternary system presents an immiscibility field. Liquid-liquid equilibria for the ternary at 25°, 40°, and 60° C. and at normal boiling points have also been determined. Experimental vapor-liquid equilibrium data are well correlated by Redlich-Kister equations for three-component systems.

RECENTLY vapor-liquid and liquid-liquid equilibrium data for binary and ternary systems with acrylonitrile, acetonitrile, and water were published by Blackford and York (2). Independently, similar research was carried out by the author at the University of Naples. The results of the two investigations show some discrepancies. Whereas Blackford and York have not attempted an analytical correlation of their results, the author was able to correlate the activity coefficients for the binaries with both the Van Laar and Redlich-Kister equations for two component systems and the activity coefficients for the ternary with the appropriate forms of the Redlich-Kister equations.

This paper gives equilibrium data for the ternary system and briefly summarizes the results for the binary systems. A detailed description of the apparatus and operating procedure is given by Volpicelli (5). Equipment and techniques used are mentioned here only in so far as discrepancies between Blackford and York's results and the author's may be attributable to differences in experimental conditions.