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.

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

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

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

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

ACKNOWLEDGMENT

The authors are grateful to the authorities of the Indian Institute of Technology, Madras, India, for providing facilities to carry on this work.

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RECEIVED for review October 17, 1966. Accepted September 29, 1967.

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

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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.

EXPERIMENTAL

Vapor-liquid equilibrium data were obtained using modified Othmer and Rose-Williams stills. Essentially, modifications refer to the condensate line, which is suitably designed to avoid holdup. In addition, whenever fractioning of the condensed vapor into two liquid phases might occur because of cooling, this was prevented by moderately heating the line. When equilibrium was reached, turning a three-way stopcock allowed all condensate to be trapped and deviated into a collecting flask. The samples were 1 to 2 cc., approximately $1/1000$ to $1/500$ of the reboiler charge.

Liquid-liquid equilibrium data for the ternary system were determined by analysis and titration methods (*1*). At constant temperature, tie lines were obtained by using jacketed separators. At normal boiling point the Othmer still was used. At the beginning, intense bubbling was maintained in the reboiler. As equilibrium was approached, the boiling rate was reduced to a minimum, and then samples of the two liquid phases were taken. The boundary of the immiscibility field was also determined in a microboiler by adding water or acrylonitrile drop by drop to the homogeneous solution until clouding of the liquid was observed.

Specific gravity relative to water and refractive index were the best ways of measuring the composition of the binary solutions of acetonitrile and water, and of acetonitrile and acrylonitrile, respectively. Solutions containing water and acrylonitrile were analyzed by gas chromatography. In this case, the samples were directly collected in dry acetone, which acted as both solvent and reference component for quantitative measurements. Several known solutions, covering the whole miscible region of the two nitriles and water, were analyzed in order to check the accuracy of the measurements. The error might reach 0.5 mole %, but in only a very few cases was it greater.

Acetonitrile and acrylonitrile were bought from Carlo Erba (Milan, Italy). They were pure reagent products for analysis, used without further purification. Acrylonitrile was stabilized against polymerization with 30 p.p.m. of the monomethyl ether of hydroquinone. The normal boiling points of the acetonitrile and acrylonitrile were 81.3° and 76.5° C., respectively; the specific gravity relative to water at 25° C. was 0.7870 and 0.8000, and the refractive index, n_D^{25}, was 1.3412 and 1.3882. Ordinary laboratory-distilled water was used.

VAPOR-LIQUID EQUILIBRIA

Binary Systems. The acrylonitrile-acetonitrile system behaves almost ideally; the relative volatility of the two nitriles is nearly equal to the vapor pressure ratio. The acetonitrile-water binary shows a homogeneous low-boiling azeotrope with 68 to 69 mole % of nitrile. The acrylonitrile-

Table I. Vapor-Liquid Equilibria of the Acrylonitrile-Acetonitrile-Water System under 760 Mm. of Hg Total Pressure

	Liquid Phase Concentration, Mole %			Vapor Phase Concentration, Mole %			
Run	Acrylonitrile	Acetonitrile	Water	Acrylonitrile	Acetonitrile	Water	Boiling Temp., *t*, ° C.
1	1.2	3.6	95.2	28.5	24.9	46.6	81.3
2	1.2	3.4	95.4	29.7	22.1	48.2	81.6
3	1.5	6.8	91.7	22.9	34.4	42.7	76.9
4	1.5	7.2	91.3	25.9	38.3	35.8	77.2
5	2.0	20.0	78.0	14.2	53.9	31.9	79.4
6	3.0	7.0	90.0	38.7	28.2	33.1	76.9
7	3.8	9.8	86.4	34.4	32.0	33.6	75.5
8	3.9	9.9	86.2	34.6	33.0	32.4	75.5
9	4.0	9.8	86.2	36.5	32.0	31.5	75.3
10	4.3	6.0	89.7	46.5	20.7	32.8	72.3
11	5.4	74.3	20.3	7.0	68.8	24.2	76.3
12	5.8	72.6	21.6	6.3	69.0	24.7	76.2
13	6.2	13.8	80.0	34.5	31.9	33.6	73.5
14	6.2	85.2	8.6	7.1	75.4	17.5	77.1
15	6.3	72.6	21.1	7.7	65.4	26.9	76.5
16	6.5	84.2	9.3	7.6	74.2	18.2	77.1
17	6.6	83.7	9.7	7.7	74.0	18.3	76.7
18	7.7	42.0	50.3	15.7	52.1	32.2	75.8
19	7.9	40.9	51.2	15.2	51.8	33.0	75.8
20	8.0	42.2	49.8	15.4	53.0	31.6	76.0
21	8.1	40.5	51.4	15.5	51.7	32.8	75.7
22	9.3	53.3	37.4	15.7	52.4	31.9	75.3
23	9.5	52.0	38.5	13.6	56.0	30.4	75.3
24	9.5	53.7	36.8	15.0	55.7	29.3	75.3
25	9.5	52.4	38.1	15.5	56.0	28.5	75.3
26	9.9	32.0	58.1	23.0	44.6	32.4	75.9
27	10.0	30.0	60.0	23.5	44.2	32.3	76.0
28	10.0	50.0	40.0	15.0	52.4	32.6	74.8
29	10.0	50.4	39.6	14.1	51.8	34.1	74.7
30	12.0	27.9	60.1	28.2	41.0	30.8	75.2
31	13.0	20.9	66.1	36.7	32.2	31.1	73.2
32	13.4	21.0	65.6	39.2	31.3	29.5	73.1
33	13.5	62.6	23.9	18.0	55.0	27.0	75.2
34	13.8	82.1	4.1	14.7	74.1	11.2	78.2
35	14.2	81.8	4.0	15.1	74.7	10.2	78.2
36	14.4	20.9	64.7	37.1	32.1	30.8	73.2
37	14.7	62.9	22.4	17.2	54.2	28.6	75.2
38	15.5	61.9	22.6	19.5	55.0	25.5	75.3
39	15.5	61.7	22.8	17.4	56.0	26.6	75.4
40	15.8	62.1	22.1	19.0	56.2	24.8	76.2
41	15.9	80.0	4.1	17.1	72.2	10.7	78.0
42	16.2	23.8	60.0	37.1	32.9	30.0	73.0
43	17.9	72.1	10.0	22.2	62.8	15.0	76.2
44	17.9	71.7	10.4	19.6	62.9	17.5	76.1
45	17.9	74.1	7.8	22.4	63.6	14.0	76.2
46	17.9	65.0	17.1	21.9	54.3	23.8	75.1
47	18.2	63.7	18.1	19.5	56.3	24.2	75.0
48	18.3	63.0	18.7	22.1	52.3	25.6	75.3
49	18.4	30.4	51.2	35.6	33.8	30.6	73.4
50	18.5	63.9	17.6	18.7	57.4	23.9	75.0
51	18.6	71.9	9.5	20.7	62.5	16.8	76.3
52	19.0	41.2	39.8	25.3	42.3	32.4	74.0
53	19.2	40.5	40.3	27.7	40.0	32.3	73.8
54	19.5	40.0	40.5	26.9	41.0	32.1	74.1
55	19.6	31.6	48.8	36.3	32.5	31.2	73.0
56	20.1	40.5	39.4	27.0	40.9	32.1	73.9
57	20.4	30.7	48.8	34.0	34.5	31.5	73.0
58	21.2	29.6	49.2	37.1	33.8	29.1	73.4
59	28.3	41.2	30.5	34.8	36.3	28.9	73.5
60	30.1	42.5	27.4	34.7	36.8	28.5	73.5
61	30.2	41.3	28.5	36.2	35.8	28.0	73.3
62	31.6	42.6	25.8	34.8	38.8	26.4	73.4
63	32.0	48.0	20.0	34.4	38.9	26.7	74.0
64	32.3	47.7	20.0	34.9	40.2	24.9	73.5
65	32.9	47.1	20.0	35.3	40.2	24.5	74.0
66	32.9	48.4	18.7	33.9	40.2	25.9	73.7
67	33.1	48.1	18.8	33.8	41.4	24.8	74.0
68	35.1	53.6	11.3	38.1	42.2	19.7	74.4
69	36.7	51.4	11.9	38.5	41.9	19.6	74.4
70	40.0	30.0	30.0	45.2	24.2	70.6	72.5
71	43.2	35.6	21.2	46.1	26.8	27.1	72.9
72	44.2	23.9	31.9	49.4	18.6	32.0	72.4
73	44.5	24.1	31.4	49.0	18.6	32.4	72.4
74	46.0	24.0	30.0	50.2	18.6	31.2	72.6
75	46.2	33.6	20.2	45.9	27.9	26.2	72.5
76	53.0	38.5	8.5	51.3	31.0	17.7	73.9
77	53.0	39.0	8.0	52.3	30.5	17.2	74.1
78	53.0	38.9	8.0	51.3	30.3	18.4	74.0
79	53.3	38.9	7.8	51.0	32.1	16.9	74.1
80	60.3	16.8	22.9	60.9	12.3	26.8	71.1
81	63.0	16.0	21.0	56.2	11.1	32.7	71.4
82	63.0	16.7	20.3	60.5	10.7	28.9	71.2
83	63.4	15.6	21.0	57.2	11.6	31.2	71.2
84	76.5	14.3	9.2	69.6	8.0	22.4	72.3
85	81.8	10.1	8.1	75.9	6.7	17.4	73.3
86	82.0	11.2	6.8	76.2	7.5	16.3	73.3
87	82.7	13.2	4.1	81.4	9.8	9.8	74.1

water binary has a limited region of miscibility at the normal boiling point, up to 2.5 and above 78 mole % of acrylonitrile.

Vapor-liquid equilibria for the first two systems, as determined by the author, agree satisfactorily with those of Blackford and York. As these investigators do not supply data for the acrylonitrile-water binary, comparison has not been possible for such a system.

Ternary System. The vapor-liquid equilibrium results for the acrylonitrile-acetonitrile-water ternary are given in Table I. The runs covered the whole range of homogeneous liquid solutions, and care was taken not to operate with any vapor phase whose composition falls inside the heterogeneous field of the system. The degree of uncertainty of chromatographic measurements prevented investigation with liquid solutions containing less than 1 to 2 mole % of each component. In this case, the material balance of the low concentration component was a supplementary aid for checking the reliability of analysis.

The results in Table I differ notably from those of Blackford and York, as far as may be assessed from a general estimation and from the few directly comparable data. Although the stills used in the present study were of different design from the Colburn type used by Blackford and York, their performance was essentially the same.

ACTIVITY COEFFICIENTS AND PREDICTION OF VAPOR-LIQUID EQUILIBRIUM

The activity coefficients, γ, of the binary and ternary components were calculated from the experimental data by means of the equation:

$$\gamma = \frac{y\pi}{xP} \qquad (1)$$

assuming ideal behavior of the vapor phase, which is likely to occur under the working pressure.

For the binary systems, the activity coefficients are well correlated by both the Van Laar and Redlich-Kister well-known equations for two components.

For the ternary system, the activity coefficients closely follow the Redlich-Kister equations (*3*):

$$\log \frac{\gamma_1}{\gamma_2} = x_3[B_{13} + C_{13}(2x_1 - x_3) + D_{13}(x_1 - x_3)(3x_1 - x_3) - B_{23} - C_{23}(2x_2 - x_3) - D_{23}(x_2 - x_3)(3x_2 - x_3) + C(x_2 - x_1) + Dx_1(2x_2 - x_3) + Ex_2(x_2 - 2x_1)] \qquad (2)$$

$$\log \frac{\gamma_l}{\gamma_3} = B_{13}(x_3 - x_1) - C_{13}[(x_1 - x_3)^2 - 2x_1x_3] + D_{13}(x_3 - x_1)[(x_1 - x_3)^2 - 4x_1x_3] + x_2[- B_{23} - C_{23}(x_2 - 2x_3) - D_{23}(x_2 - x_3)(x_2 - 3x_3) + C(x_3 - x_1) + Dx_1(2x_3 - x_1) + Ex_2(x_3 - x_1)] \qquad (3)$$

Table II. Constants in Van Laar and Redlich-Kister Equations

System	Van Laar	Redlich-Kister Equations 2 and 3
Acrylonitrile-water	$M_{13} = 1.554$	B_{13} = 1.105
	$M_{31} = 0.860$	C_{13} = −0.319
		D_{13} = 0.096
Acetonitrile-water	$M_{23} = 0.927$	B_{23} = 0.844
	$M_{32} = 0.765$	C_{23} = −0.08
		D_{23} = 0.02
Acrylonitrile-acetonitrile-water		C = −1.0
		D = 1.1
		E = 0.9

where subscripts 1, 2, and 3 refer to the acrylonitrile, acetonitrile, and water, respectively. The values of the constants relating to the binary systems (with subscripts) and the ternary system (without subscripts) are grouped in Table II.

Average deviation, δ, between experimental and calculated vapor mole fractions is about 1.5 mole %—that is,

$$\delta = \frac{\sum_{k=1}^{n} |y_{1,k} - y''_{1,k}| + |y_{2,k} - y''_{2,k}| + |y_{3,k} - y''_{3,k}|}{3n} \cong 1.5\,\%$$

where $''$ indicates calculated values and n is the number of runs. Maximum differences up to 4 mole % are observed for water concentration in the liquid greater than 90 mole %. Differences are not balanced, being the arithmetic mean

$$\left[\sum_{k=1}^{n} (y_{i,k} - y''_{i,k})\right] / n$$

less than 0.004 for nitriles (i = 1,2) and about − 0.008 for water (i = 3). Application of the Redlich-Kister equations, which assume constancy of temperature, could be partly responsible for the greatest differences at high water concentration, where the boiling point approaches 100° C. as compared with 75° to 80° C. measured in the remaining field of liquid solutions.

Figures 1 to 4 show boiling temperatures and equilibrium vapor compositions for the ternary system. Concentrations are expressed as mole fractions. The curves were obtained by using balance, equilibrium, and thermodynamic correlations. Details on the calculations are reported by Volpicelli (5).

LIQUID-LIQUID EQUILIBRIA

Ternary System. Figure 5 shows the heterogeneous regions at 25°, 40°, 60° C. and at the normal boiling point as experimentally determined in this investigation. Tables III and IV list the composition of coexisting phases at different work temperature. Other experimental points of the binodal curves at 25° C. and at the boiling point are also reported in Table V.

Measured tie lines satisfy the empirical equation stated by Othmer and Tobias (*4*):

$$\log \frac{1 - W_3}{W_3} - \log \frac{1 - W_{3\,\text{ref.}}}{W_{3\,\text{ref.}}} = a\left(\log \frac{1 - W'_1}{W'_1} - \log \frac{1 - W'_{1\,\text{ref.}}}{W'_{1\,\text{ref.}}}\right) \qquad (4)$$

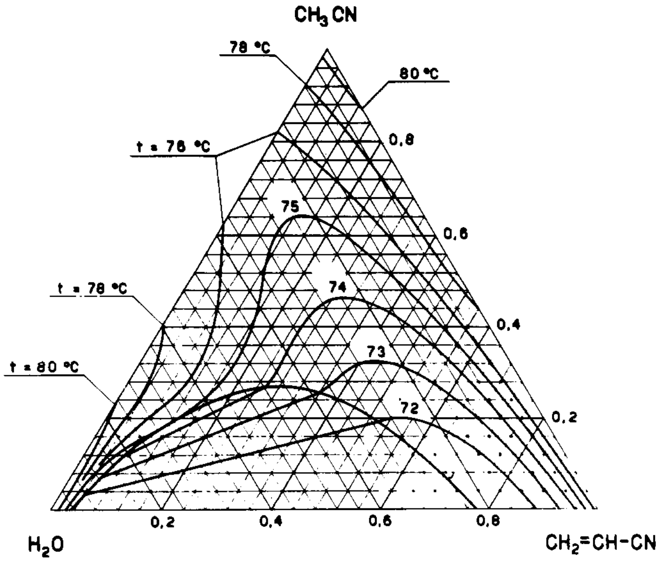

Figure 1. Vapor-liquid equilibria at boiling temperatures

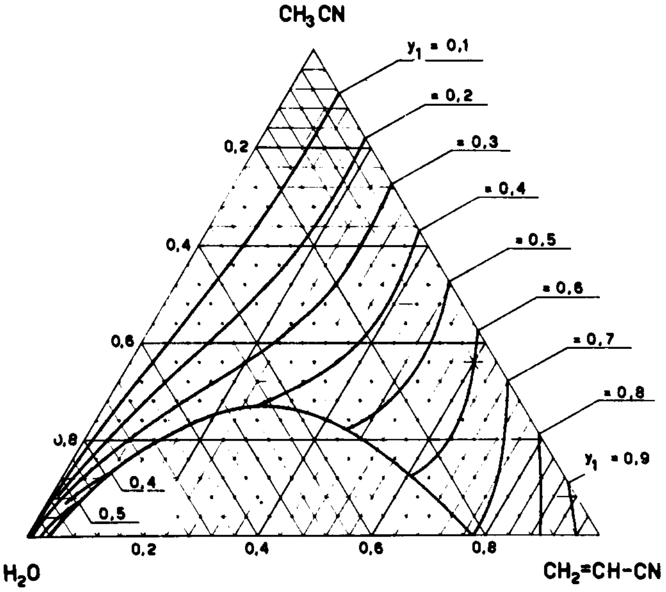

Figure 2. Vapor-liquid equilibria

Constant concentration of acrylonitrile in the vapor phase

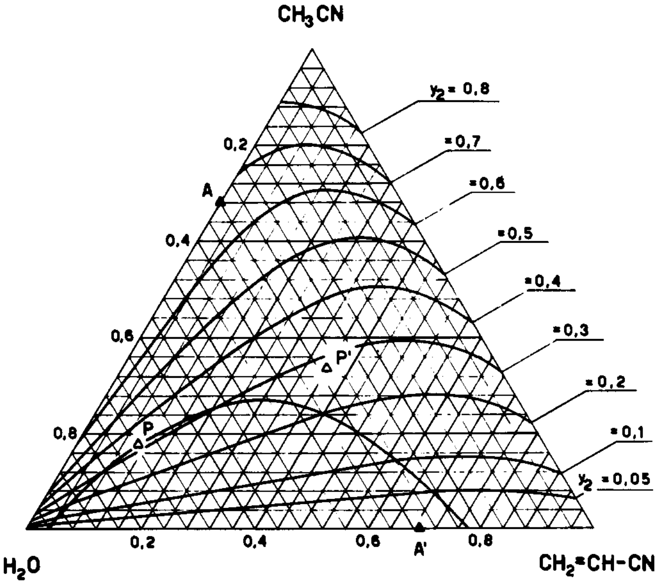

Figure 3. Vapor-liquid equilibria

Constant concentration of acetonitrile in the vapor phase

△ Plait point *P* and vapor phase *P'* in equilibrium

▲ Acetonitrile-water homogeneous azeotrope *A* and acrylonitrile-water heterogeneous azeotrope *A'*

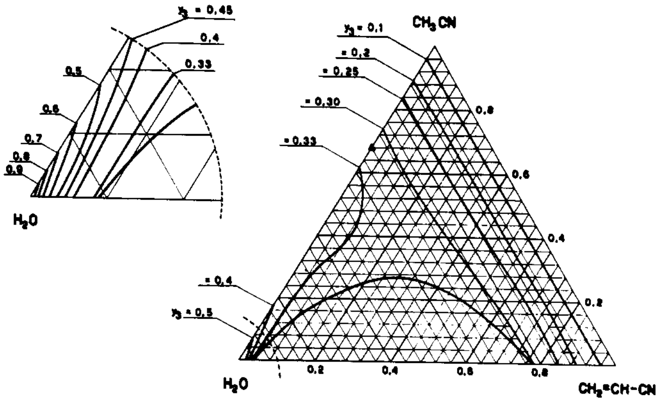

Figure 4. Vapor-liquid equilibria

Constant concentration of water phase

▲ Acetonitrile-water homogeneous azeotrope

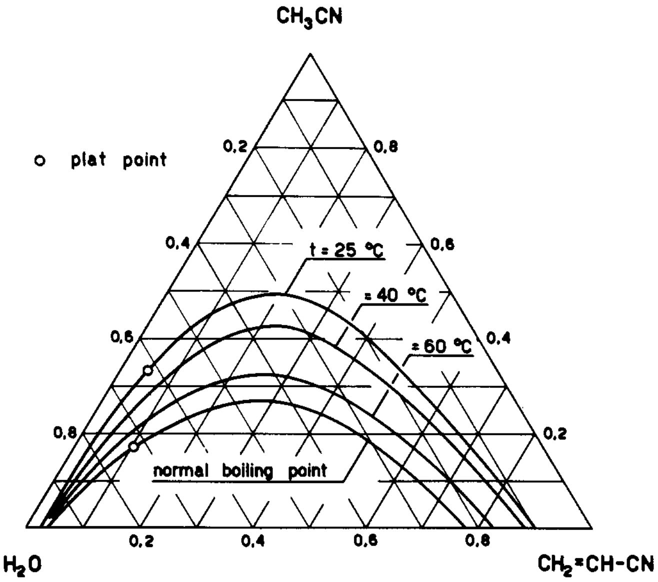

Figure 5. Liquid-liquid equilibria

Phase boundaries for two-phase liquid mixture

Table III. Liquid-Liquid Equilibria of the Acrylonitrile-Acetonitrile-Water System at 25°, 40°, and 60° C.

		Heavy Phase Concentration, Mole %		Light Phase Concentration, Mole %	
Run	Temp., *t*, ° C.	Acrylonitrile	Acetonitrile	Acrylonitrile	Acetonitrile
1	25	2.6	14.5	14.4	48.0
2	25	2.5	8.5	30.6	48.0
3	25	2.7	1.2	81.6	6.9
4	25	2.3	5.4	42.8	36.9
5	25	2.7	3.3	57.8	26.9
6	25	2.8	2.6	67.7	20.1
7	25	2.5	5.6	40.6	39.9
8	25	2.3	4.4	49.9	33.4
9	25	2.5	3.5	58.4	27.4
10	25	2.5	13.5	19.3	49.4
11	25	2.6	0.0	90.0	0.0
12	40	2.6	4.6	47.5	31.2
13	40	2.6	9.6	22.2	43.2
14	40	2.5	1.1	76.3	9.8
15	40	3.4	9.6	24.6	42.7
16	40	2.8	5.6	42.7	34.5
17	40	2.7	1.7	70.5	14.2
18	40	2.5	3.2	60.0	21.9
19	40	3.0	5.1	47.2	30.3
20	40	3.4	11.7	21.8	41.5
21	40	2.8	1.2	78.0	10.3
22	40	3.0	8.7	28.0	40.4
23	40	3.2	9.2	27.3	41.4
24	40	3.0	1.0	75.0	10.0
25	40	2.9	4.1	49.7	29.6
26	40	3.3	2.4	62.3	21.0
27	40	2.8	0.0	88.5	0.0
28	60	3.3	1.8	64.8	13.3
29	60	3.8	4.6	43.7	25.9
30	60	3.3	2.3	57.8	17.2
31	60	3.6	1.4	68.8	11.6
32	60	5.3	11.6	21.0	30.8
33	60	3.3	0.0	82.7	0.0

Table IV. Liquid-Liquid Equilibria of the Acrylonitrile-Acetonitrile-Water System at Boiling Point under 760Mm. of Hg Total Pressure

		Heavy Liquid Phase Concentration, Mole %		Light Liquid Phase Concentration, Mole %		Heavy Liquid Phase, Mole %			Light Liquid Phase, Mole %		
Run	Boiling Temp., *t*, °C.	Acrylonitrile	Acetonitrile	Acrylonitrile	Acetonitrile	*t*, °C.	Acrylonitrile	Acetonitrile	*t*, °C.	Acrylonitrile	Acetonitrile
		Experimental				Redlich-Kister Equations 2 and 3					
1	70.9	3.7	1.5	64.4	9.5	71.4	62.0	6.2	71.2	61.8	6.0
2	70.7	4.0	1.5	62.5	10.9	70.9	63.0	6.5	71.2	60.8	7.6
3	71.4	4.2	3.0	55.4	16.9	71.7	57.5	12.2	71.8	56.3	11.8
4	71.3	4.1	2.9	54.6	16.2	71.9	57.4	12.0	71.8	56.2	11.3
5	71.4	4.4	3.1	50.9	18.6	71.4	57.9	12.3	71.9	53.9	13.2
6	71.5	4.3	3.2	52.9	16.9	71.7	57.1	12.8	71.8	55.3	12.1
7	71.5	4.0	3.0	54.1	17.6	72.1	56.6	12.5	71.9	55.5	12.4
8	71.7	4.7	3.9	48.2	20.0	71.6	56.0	14.5	72.1	52.3	14.9
9	71.5	4.3	3.9	46.3	19.8	72.2	54.5	15.2	72.2	51.7	15.1
10	72.0	5.4	5.9	37.2	24.5	72.1	51.7	19.3	72.9	45.9	21.0
11	72.6	5.8	8.4	29.8	26.5	73.2	45.9	24.7	73.5	41.5	25.4
12	74.8	10.0	17.8	10.0	17.8	75.0	36.3	33.0	75.0	36.3	33.0

Table V. Concentration of Liquid Phases[a]

Run	*t*, °C.	Acrylonitrile, Mole %	Acetonitrile, Mole %	Run	*t*, °C.	Acrylonitrile, Mole %	Acetonitrile, Mole %
1	25	2.5	1.6	17	25	51.0	31.4
2	25	2.5	1.0	18	25	46.1	36.5
3	25	2.6	3.9	19	25	14.1	48.2
4	25	2.6	6.5	20	25	45.3	37.3
5	25	2.9	9.1	21	25	71.5	15.9
6	25	2.7	8.4	22	25	29.5	47.3
7	25	2.7	13.5	23	74.8	11.9	19.0
8	25	3.3	15.8	24	74.7	14.8	21.5
9	25	2.8	19.0	25	74.5	17.7	23.4
10	25	4.8	34.0	26	74.2	20.0	24.2
11	25	6.8	40.0	27	71.8	50.8	18.1
12	25	6.5	38.2	28	71.5	53.0	16.6
13	25	3.9	26.2	29	74.6	9.9	15.7
14	25	9.7	44.9	30	70.2	3.6	0.0
15	25	5.8	35.5	31	70.1	77.8	0.0
16	25	12.0	47.6				

[a] On boundary of heterogeneous field of ternary system at 25° C. and normal boiling point.

in which W and W' are weight fractions of the heavy and light liquid phases, and ref. relates to a reference couple of liquid phases coexisting at equilibrium. For practical purposes, the data in Tables III and IV are well correlated by Equation 4 with values of $a = 0.3$ and 0.7 at 25° C. and at the normal boiling point, respectively. The extension of the equation to normal boiling points is justified by the fact that the temperature varies only a few degrees throughout the heterogeneous region.

The gradual and congruent narrowing of the immiscibility field from 25° C. to the normal boiling point (Figure 5) and the agreement in results obtained by analysis (Tables III and IV) and titration (Table V) show the reliability of the experimental data. A further proof is afforded by comparing columns 7, 8, and 9 with 10, 11, and 12 in Table IV. The boiling temperatures and vapor-phase compositions, calculated for the heavy and light liquid phases in equilibrium, show good agreement.

Comparison with Blackford and York's data, at the two temperature levels they investigated, shows satisfactory agreement at t = 25° C., but complete disagreement at the normal boiling point. Broadly, according to Blackford and York, the immiscibility region is extended up to 44 mole % of acetonitrile at the normal boiling point, against 27 mole % found in this research.

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RECEIVED for review February 13, 1967. Accepted August 4, 1967.