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

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Both vapor-liquid equilibria and boiling temperatures have been measured for the ternary system acetonitrile-acrylonitrile-water under a constant total pressure of 760 mm. of Hg and for the corresponding binaries acrylonitrile-acetonitrile and acetonitrile-water. Experimental values are presented in tabular form and are shown graphically for convenience in interpolating. Of the three binaries, acrylonitrile and acetonitrile behave almost as ideal solutions, acetonitrile and water form a minimum boiling azeotrope, while acrylonitrile and water are partially miscible and form a heterogeneous azeotrope. The ternary mixture at its boiling point is immiscible at low acetonitrile concentration, but becomes miscible at higher acetonitrile concentrations. Activity coefficients were calculated from the experimental measurements and qualitatively checked for consistency according to suggestions in the literature. The equilibria presented are believed to be reliable and should be useful in the design of fractionation equipment for these mixtures.

FROM propylene, ammonia, and air the Sohio process (*4*) produces acrylonitrile, some acetonitrile, and relatively large quantities of water. Several other proposed processes for acrylonitrile produce acetonitrile and water, but in different amounts. Hence the recovery and purification of the desired acrylonitrile product require separation of acetonitrile-acrylonitrile-water mixtures. If this separation is carried out by fractionation, the optimum design and successful operation of the towers depend upon having reliable vapor-liquid equilibria for these mixtures.

Vapor compositions in equilibrium with the liquid at its boiling points under 760 mm. of Hg. pressure were measured for acetonitrile-acrylonitrile-water mixtures. The experimental measurements are recorded in Tables I, II, and III, and smoothed values for selected vapor compositions are presented as a triangular diagram in Figure 4.

Previous investigators report data for two of the three binary systems. Thus, for acetonitrile-water, both Othmer and Josefowitz (*8*) and Maslan and Stoddard (*6*) report phase equilibria over the complete composition range. Their measurements were obtained with conventional vapor recirculating stills operating under 760 mm. of Hg absolute pressure.

For acrylonitrile-water, Horsley (*2, 3*) lists an azeotropic composition of 88 wt. % water at 71.0° C., as unpublished data from the Dow Chemical Co.

No previous results are reported for the acrylonitrile-water binary or for the ternary.

Acetonitrile and water form a homogeneous azeotrope at 72.6 mole % acetonitrile (*6, 8*) and are completely miscible.

Between 25° C. and the normal boiling points, acrylonitrile and water are mutually soluble to less than 10 %. The heterogeneous azeotrope reported for acrylonitrile-water is actually the constant composition at the boiling point of an immiscible mixture.

APPARATUS

A Colburn equilibrium still (*5*) was modified by enlarging the reboiler to enable its operation for both miscible and immiscible liquid mixtures. It is constructed of borosilicate glass and shown diagramatically as Figure 1. The volume of the reboiler is about 1500 ml.; that of the condensate trap, about 50 ml.

The total pressure over the boiling mixtures was maintained at 760 mm. of Hg absolute by means of a Cartesian manostat.

Boiling points were measured by a mercury-in-glass thermometer calibrated and inserted in a Washburn ebulliometer.

PROCEDURE

When the condensate is miscible, the still is operated in precisely the same manner as a conventional Colburn still. About 800 ml. of liquid are charged to the reboiler; holdup in the condensate trap is maintained at about 30 ml.

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

			Activity Coefficients	
Boiling Temp., ° C.	Acrylonitrile in Liquid, Mole %	Acrylonitrile in Vapor, Mole %	Acrylonitrile	Acetonitrile
79.8	7.9	9.8	1.143	1.035
79.2	16.8	20.6	1.155	1.027
78.5	31.7	35.0	1.060	1.047
78.2	40.6	43.1	1.031	1.061
77.7	55.7	58.6	1.035	1.054
77.4	78.0	79.1	1.007	1.080
73.3	91.7	92.1	1.004	1.087

Table II. Vapor-Liquid Equilibria of Acetonitrile-Water System under 760 Mm. Total Pressure

			Activity Coefficients	
Boiling Temp., ° C.	Acetonitrile in Liquid, Mole %	Acetonitrile in Vapor, Mole %	Acetonitrile	Water
86.5	2.9	26.3	13.050	1.253
81.1	9.3	50.5	5.509	1.116
80.0	14.2	55.9	4.126	1.098
78.6	25.4	61.7	2.665	1.159
77.4	40.2	65.5	1.851	1.373
76.7	50.7	66.4	1.526	1.669
76.6	52.7	67.3	1.490	1.184
76.0	71.8	72.8	1.205	2.438
76.6	83.9	78.0	1.088	3.357
76.8	85.6	76.1	1.030	4.044
80.4	98.6	94.5	0.992	8.277

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

	Liquid Phase			Vapor Phase			Activity Coefficients		
Boiling Temp., ° C.	Acrylonitrile, mole %	Acetonitrile, mole %	Water, mole %	Acrylonitrile, mole %	Acetonitrile, mole %	Water, mole %	Acrylonitrile	Acetonitrile	Water
84.0	0.2	1.8	98.0	6.0	38.9	55.1	24.200	20.200	1.024
82.0	0.7	3.3	96.0	20.2	51.4	28.4	24.800	15.400	0.584
81.0	0.7	5.6	93.7	8.4	44.7	46.9	10.630	8.134	1.026
81.0	0.7	9.3	90.0	5.0	51.9	43.1	6.333	5.669	0.985
80.0	0.8	11.9	87.3	6.6	50.1	43.3	7.560	4.415	1.094
80.0	1.0	15.6	83.4	5.9	53.6	40.5	5.398	3.602	1.041
80.0	1.2	7.9	90.9	22.1	54.1	23.8	16.870	7.172	0.560
79.5	1.3	13.4	85.3	7.4	52.2	40.4	5.287	4.148	1.034
75.3	1.4	25.5	73.1	5.7	57.4	36.9	4.340	2.735	1.308
78.0	1.8	2.4	95.8	36.5	20.8	42.7	19.730	9.658	1.038
78.5	2.0	21.1	76.9	7.7	53.7	38.6	3.689	2.795	1.140
77.0	2.1	6.9	91.0	32.9	26.1	41.0	15.670	4.360	1.091
75.4	2.1	45.7	52.2	5.0	60.8	34.2	2.527	1.610	1.694
78.0	2.2	10.0	87.8	21.2	50.8	28.0	9.388	5.660	0.742
78.0	2.2	22.5	75.2	8.9	53.9	37.2	3.939	2.671	1.150
77.0	2.3	0.7	97.0	47.6	13.4	39.0	20.880	21.820	0.970
76.5	2.7	26.8	70.5	7.6	51.0	41.4	2.890	2.231	1.452
80.5	2.8	97.2	0.0	4.1	92.5	3.4	1.322	0.985	. . .
77.0	3.0	19.6	77.4	20.7	51.3	28.0	6.960	3.014	0.877
76.5	3.3	20.6	76.1	19.7	50.7	29.6	6.110	2.880	0.962
75.5	3.4	37.7	58.9	8.0	48.7	43.3	2.492	1.561	1.893
75.3	3.8	42.7	53.5	9.7	56.2	34.1	2.720	1.599	1.652
75.5	4.1	10.4	85.3	37.4	30.2	32.4	9.660	3.522	0.976
75.9	4.6	73.5	21.9	7.0	66.0	27.0	1.593	1.070	3.120
75.6	4.9	55.7	39.4	7.0	57.2	35.8	1.511	1.239	2.333
75.2	5.1	27.2	67.7	19.3	51.1	29.6	4.052	2.293	1.138
75.5	5.7	57.6	36.7	7.2	60.2	32.6	1.337	1.265	2.290
75.5	5.7	64.8	29.5	9.0	60.3	30.7	1.672	1.125	2.678
77.8	6.1	87.2	6.7	6.6	79.1	14.3	1.059	1.017	4.986
73.7	6.2	17.3	76.5	36.6	40.0	23.4	6.630	2.963	0.808
74.8	6.2	30.2	63.6	17.8	51.6	30.6	3.110	2.111	1.277
75.6	6.3	68.3	25.4	9.0	62.9	28.1	1.510	1.112	2.846
73.8	6.9	18.8	74.3	32.0	38.4	29.6	5.181	3.503	1.103
74.8	7.0	33.9	59.1	17.0	51.4	31.6	2.631	1.880	1.415
72.9	7.2	7.8	85.0	52.4	20.1	27.5	8.397	3.403	0.929
76.2	8.0	76.6	15.4	9.7	67.5	22.8	1.258	1.043	3.703
75.0	8.1	40.7	51.2	16.5	52.6	30.9	2.196	1.587	1.588
74.4	8.5	37.2	54.3	18.2	51.4	30.4	2.478	1.738	1.509
75.0	9.3	47.3	43.4	15.7	52.1	32.2	1.819	1.356	1.954
75.2	10.3	62.6	27.1	15.5	64.6	19.9	1.611	1.262	1.912
75.5	10.7	55.7	33.6	14.9	53.3	31.8	1.476	1.157	2.442
74.2	10.9	25.3	63.8	34.9	39.0	26.1	3.543	1.946	1.111
75.2	11.1	64.4	24.5	14.0	58.4	27.6	1.185	1.107	2.937
74.8	12.0	53.5	34.5	17.0	51.4	31.6	1.536	1.188	2.424
75.3	12.1	56.9	31.0	16.9	53.4	29.7	1.698	1.140	2.498
75.1	12.6	62.7	24.7	9.3	58.6	32.1	0.793	1.144	3.408
74.5	13.7	51.6	34.7	18.5	48.8	32.7	1.690	1.185	2.536
72.6	14.0	13.5	72.5	53.6	25.1	21.3	4.468	2.478	0.856
75.7	14.3	70.5	15.2	10.0	65.8	24.2	0.738	1.113	4.060
75.5	14.9	68.7	16.4	17.2	58.5	24.3	1.214	1.034	3.816
73.5	15.5	33.5	51.0	32.5	41.9	25.6	2.370	1.614	1.408
73.5	20.3	42.1	37.6	30.5	43.6	25.9	1.701	1.335	1.931
73.8	22.1	50.3	27.6	27.5	45.6	26.9	1.457	1.161	2.688
74.9	24.2	59.5	16.3	25.7	49.7	24.6	1.149	1.027	3.987
73.6	26.0	48.5	25.5	42.2	36.7	21.1	1.834	0.976	2.305
72.3	26.3	22.1	51.6	45.8	25.8	28.4	2.052	1.570	1.623
73.2	28.2	43.9	27.9	35.5	40.7	23.8	1.440	1.212	2.432
74.6	29.3	55.0	15.7	31.8	47.3	20.9	1.186	1.075	3.561
74.4	29.8	53.4	16.8	35.5	40.7	23.8	1.311	0.954	3.816
71.3	36.2	10.5	53.3	63.1	12.4	24.5	2.124	1.644	1.414
72.9	38.1	39.3	22.6	44.0	35.2	20.8	1.331	1.186	2.639
72.3	39.1	31.9	29.0	51.5	30.1	18.4	1.552	1.265	1.869
74.0	40.0	45.0	15.0	41.0	37.2	21.8	1.139	1.052	3.983
73.9	42.2	43.5	14.3	41.9	36.7	21.4	1.108	1.077	4.116
72.7	44.1	35.4	20.5	50.7	30.9	18.4	1.337	1.158	2.603
72.7	47.8	32.5	19.7	53.0	29.0	18.0	1.292	1.182	2.651
72.9	47.8	39.1	13.1	48.9	32.3	18.8	1.181	1.089	4.118
72.9	58.6	26.1	15.3	60.9	23.0	16.1	1.199	1.163	3.022
71.4	59.3	15.9	24.8	66.9	13.3	19.8	1.369	1.161	1.369
73.3	59.4	27.4	13.2	60.0	24.0	16.0	1.152	1.140	3.425
74.7	65.9	26.7	7.4	64.7	23.3	12.0	1.069	1.086	4.302
72.8	67.1	17.4	15.5	71.3	15.6	13.1	1.229	1.186	2.441
73.4	70.5	17.6	11.9	71.4	15.6	13.0	1.150	1.150	3.078
73.8	72.3	17.7	10.0	72.2	14.8	13.0	1.116	1.068	3.593
73.5	76.7	12.0	11.3	80.9	7.9	11.2	1.194	0.849	2.781
74.1	83.2	8.1	8.7	81.8	7.2	11.0	1.069	1.121	3.455

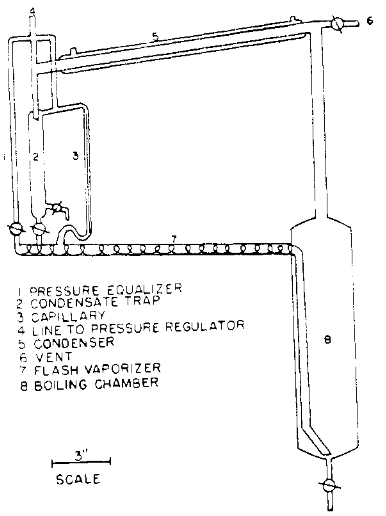

Figure 1. Equilibrium still

When the condensate is immiscible, no holdup is maintained in the trap and all condensate is returned to the reboiler. The large volume of the reboiler permits withdrawal of a small vapor sample without appreciably altering equilibrium conditions. After equilibrium is reached, the stopcock at the bottom of the condensate trap is closed and a 10-ml. sample is collected.

Runs were at least 5 hours in duration. Several different investigators have estimated that equilibrium is reached between 20 and 40 minutes.

The solubility curve at the normal boiling point was determined graphically by the departure from linearity of the equilibrium composition line from the straight tie line of both constant temperature and constant composition. (An auxiliary plot was sometimes necessary to establish such a departure in vapor composition.)

Visual observation of the cloud point in the region of high water composition is not satisfactory under constant boiling conditions, because of only a slight change in refractive index with composition along the solubility curve for the water-rich phase. The liquid solubility curve at 25° C., shown on Figure 2, could not be used to establish the end of the tie line because of the large change in solubility with temperature.

For reasons of *safety*, equilibrium measurements were carried out with the apparatus under a hood. Nitriles are absorbed and ingested through the skin and hence were handled with great care to prevent contact. Rubber gloves, first used, were discarded as they are not impervious to nitriles and only helped to retain the liquid near the skin surface. First aid equipment was provided for emergencies.

MATERIALS

Commercial acrylonitrile was donated by the Monsanto Chemical Co. and purified by fractional distillation. The purified material has a boiling point of 77.1° C. and a refractive index of 1.3888 at 25.0° C., as compared with literature values of 77.1° to 77.3° C. and 1.3887. The purity is estimated to be greater than 99.9%.

The acetonitrile was obtained from the Union Carbide Chemicals Co. and purified by drying and fractional distillation. The purified material had a boiling point of 81.5° C., a specific gravity of 0.7776 at 25° C., and a refractive index of 1.3422 at 25.0° C. Maslan and Stoddard (*6*) report a boiling point of 82.0° C., a refractive index at 25.0° C. of 1.3416, and a specific gravity of 0.7756 at 25.0° C.

Ordinary laboratory distilled water was used in the experimental determinations.

When the actual runs were made, the monomethyl ether of hydroquinone was added to inhibit polymerization during prolonged heating. It was added at a level of 35 p.p.m. based on acrylonitrile and assumed to have a negligible effect on the equilibrium measurements.

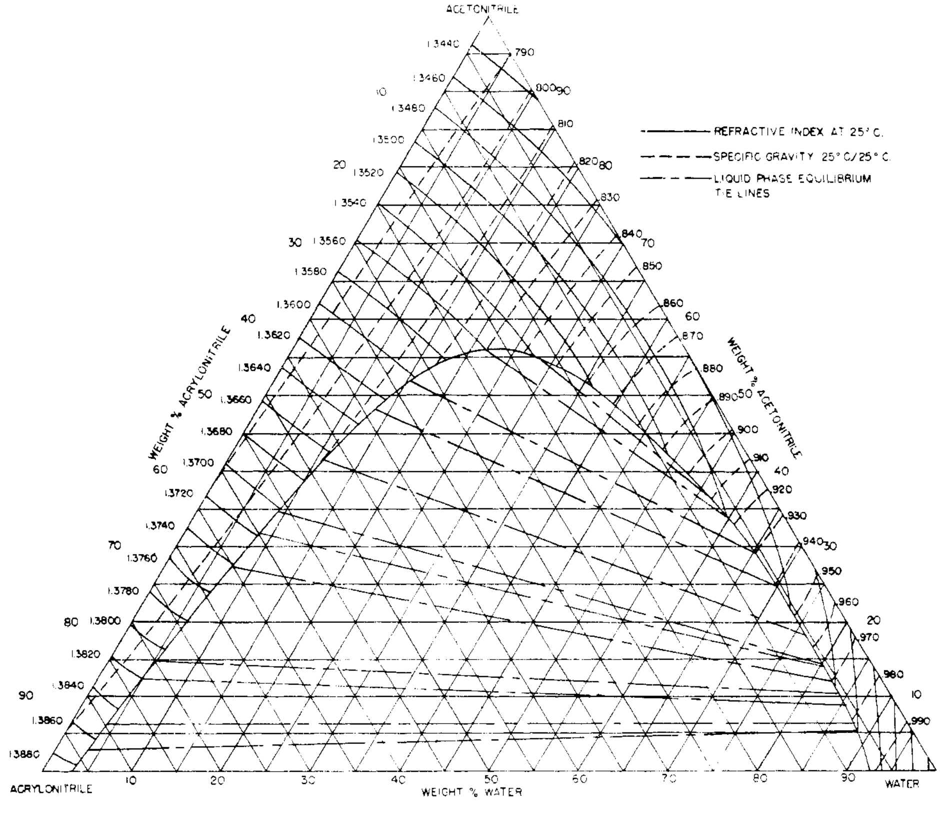

Figure 2. Analytical diagram—specific gravity and refractive index of acetonitrile-acrylonitrile-water solutions at 25° C.

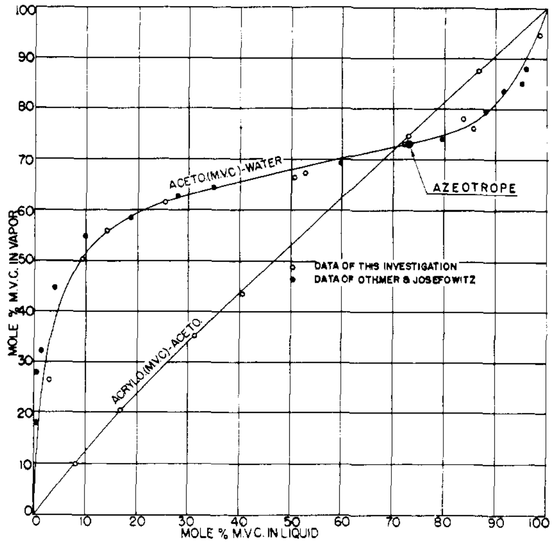

Figure 3. Equilibrium diagrams for binaries under 760 mm.

ANALYSIS

For the acrylonitrile-acetonitrile binary and for miscible regions of the acrylonitrile-water binary, refractive index at 25° C. was selected as the best means for analysis. For the acetonitrile-water binary, specific gravity relative to water at 25° C. was selected.

For the ternary system both refractive index and specific gravity were necessary to determine the composition of mixtures in the miscible region. In the immiscible region, refractive index and the solubility curve were used to determine the composition of the separate liquid phases. From these compositions and the weight ratios of the two liquid phases, the over-all composition in the immiscible region was calculated.

The solubility curve was determined from the end points of the tie lines. These end points were obtained directly, by titrating with water to the cloud point, known mixtures of acetonitrile and acrylonitrile. The construction of a conjugate line gave a smooth curve for these end points and, in this sense, may be regarded as a check on the experimental data.

As described above, the several mixtures were analyzed by means of specific gravity, refractive index, and solubility. Data for such analyses are plotted on triangular coordinates and shown as Figure 2, where compositions are in weight per cent.

Uncertainties or errors in the measurements of the several quantities and the resulting uncertainty arising therefrom are estimated as follows: refractive index, ±0.0002, corresponding to 0.4 wt. %; specific gravity, ±0.001, corresponding to 0.5 wt. %; separating and weighing immiscible phases, ±1% maximum; reading of composition from intersection of constant refractive index line and constant specific gravity line at small angles, ±1 wt. %. In the miscible region, the left side of Figure 2, the maximum uncertainty in composition would be between 1.0 and 1.9 wt. %; in the immiscible region, 3.0 wt. %. When these uncertainties in composition are converted to mole %, they become 1.0 mole % in the miscible region approaching either pure acetonitrile or pure acrylonitrile and 3.0 mole % for both the miscible and immiscible regions from about 80 to 100 mole % water.

Uncertainties for measurements other than composition were estimated to be ±1.5 mm. of Hg out of 760 mm. of Hg total pressure and ±0.1° C. Both of these are negligible compared to the uncertainties of analysis.

RESULTS

Experimental results consist of liquid phase equilibria at 25° C., as shown by Figure 2; of normal boiling points and of the corresponding liquid phase equilibria, as shown by Figure 5; and of the vapor-liquid equilibria, as shown by Figure 4. These results are presented in both tabular and graphical form for convenience and are discussed in more detail in the sections that follow.

ACETONITRILE-ACRYLONITRILE BINARY

Vapor-liquid equilibria and boiling points for this binary are presented in Table I and in Figure 3.

The pure component with the lower boiling point, and hence the greater volatility, is termed the more volatile component and labelled M.V.C. As might be expected from the similar nature of the molecules, the equilibrium compositions do not deviate greatly from those predicted by Raoult's Law. These deviations from ideality are calculated in terms of the activity coefficients and are discussed in a later section of this paper.

ACETONITRILE-WATER BINARY

Vapor-liquid equilibria and boiling points for this binary are presented in Table II and in Figure 3. Also shown on Figure 3 for comparison are the experimental results of Othmer and Josefowitz (*8*).

Since equilibrium data from two independent sources were available, this binary provided a check of the accuracy of the equilibrium still used in this investigation. The data for both the other investigations were obtained with a conventional vapor recirculation still. The homogeneous binary azeotrope is 72.6 mole % acetonitrile at 76.0° C.

The authors' data agree well with those of Othmer and Josefowitz (*8*). The root-mean-square deviation of vapor composition from the upper curve of Figure 3 is 2.3 mole % for this investigation and 5.0 mole % for the results of Othmer and Josefowitz. The large deviations are for higher vapor concentration of acetonitrile in the region of low liquid acetonitrile concentration. Disagreement in this region may be attributed to an inherent difference in the operation of the two equilibrium stills. The still used by Othmer and Josefowitz may have operated with some reflux, which would be expected to be greater at higher boiling temperatures (low acetonitrile cencentrations) because of heat loss by radiation. Such operation could explain the higher concentration of acetonitrile in the vapor phase. The pycnometer used to determine the authors' specific gravities should be more precise for analysis than the Westphal balance used by Othmer and Josefowitz.

Our data agree fairly well with those of Maslan and Stoddard (*6*). Maslan and Stoddard admit a total pressure variation of 15 mm. of Hg out of 760 mm. which may explain deviations of some of their values.

ACRYLONITRILE-WATER BINARY

No experimental runs were made for this binary, as the vapor composition is constant over the entire region of liquid immiscibility. The miscible region is relatively small.

Horsley (*2, 3*) has recorded the composition and temperature of the heterogeneous azeotrope, while a Monsanto Data Sheet (*7*) has recorded the mutual liquid solubility at the normal boiling point.

By extrapolating values from the ternary measurements, the immiscible region of this binary at its normal boiling point was estimated to lie between 3.8 and 76.7 mole % liquid acrylonitrile. This agrees with the Monsanto values.

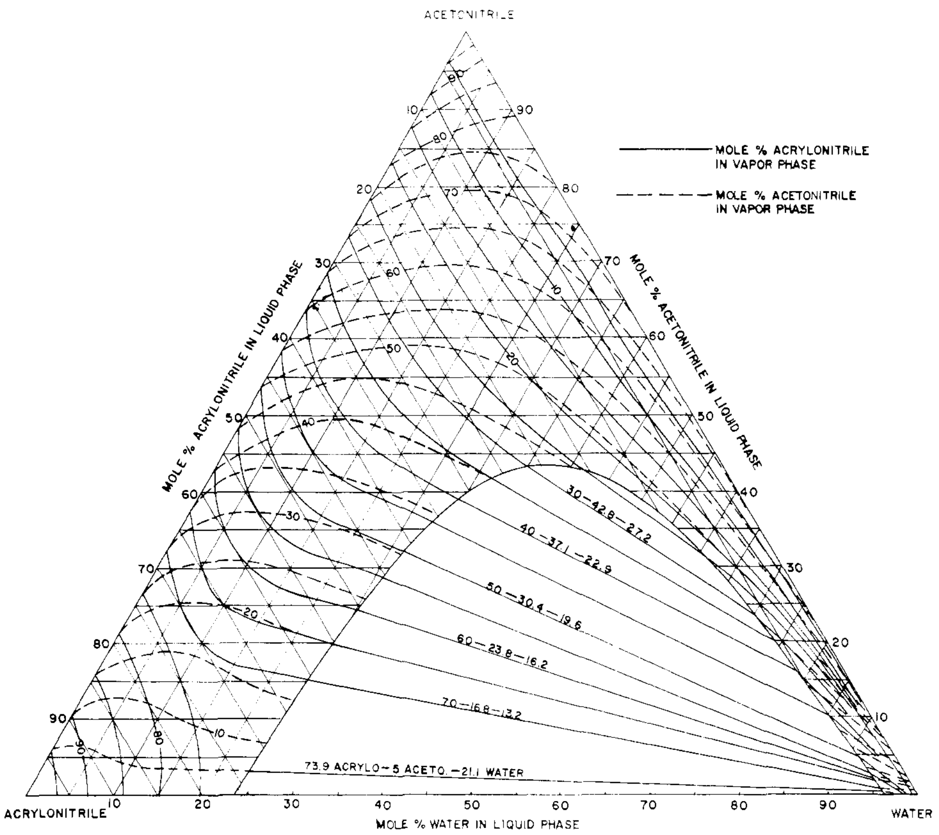

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Figure 4. Vapor-liquid equilibria for acetonitrile-acrylonitrile-water ternary under 760 mm. total pressure

ACRYLONITRILE-ACETONITRILE-WATER TERNARY

Vapor-liquid equilibria for this ternary, as measured, are presented in Table III and are represented as a conventional triangular diagram by Figure 4. Normal boiling points are presented in Table III and are shown graphically on triangular coordinates as Figure 5.

The phase boundary for the two-phase liquid mixtures was determined by a combination of measurements from both the vapor-liquid still and the boiling-point apparatus. The vapor composition lines in the immiscible region on Figure 4 should be straight as required by equilibria and material balances. These lines have been drawn straight in this region, although the vapor-liquid equilibria alone indicated a slight curvature in the high water range. Such a curvature may be explained by several factors, but is believed to be caused by error in analysis in this high water region. Reference to the analytical diagram (Figure 2) will show the difficulty of analyzing such a mixture because of the small angle between the lines of constant refractive index and the phase boundary.

ACTIVITY COEFFICIENTS

The activity coefficients reported for the components of the binary and ternary systems have been calculated from the relationship:

$$\pi\, y_i = \gamma_i P_i^0\, x_i$$

where

π = total pressure of the system = 760 mm.
y_i = mole fraction of component i in the vapor phase
x_i = mole fraction of component i in the liquid phase
P_i^0 = vapor pressure of pure component i at the boiling point of the mixture
γ_i = the idealized activity coefficient for component i

This relationship assumes that the vapor phase obeys Dalton's Law of partial pressures, that the equation of state for the vapor phase is that for a perfect gas, and that the volume of the liquid phase may be neglected. These assumptions are believed to be valid under the pressure at which this investigation was conducted.

For the acrylonitrile-acetonitrile binary, the activity coefficients were calculated and are presented in Table I. As might be expected from the similar nature of the molecules, the equilibrium compositions do not deviate much from those predicted by Raoult's Law, the maximum activity coefficient being 1.155.

When the activity coefficients of acetonitrile are plotted on a large scale against liquid composition, the curve is concave downward; a similar plot for acrylonitrile gives a curve that is concave upward. Such curvatures are contrary to those required by the Gibbs-Duhem relation. Of several explanations that are possible, the authors' believe that the analysis is not sufficiently accurate to plot activity coefficients on such a large scale.

For the acetonitrile-water binary, the activity coefficients were calculated and are presented in Table II. When the activity coefficients for each component in this binary were plotted against liquid composition, the curves were both concave upward and showed marked deviation from ideality. These deviations may be attributed to polarity, association, or hydrogen bonding.

For the acrylonitrile-water binary, the activity coefficients were not calculated because no actual experimental values were measured or published over the miscible range. However, these coefficients may be calculated for the two-phase region from the limits of the mutual solubility at the normal boiling point. Outside the two-phase region (the miscible region), these coefficients may be estimated from the familiar van Laar, Margules, or Scatchard-Hamer equations.

CONSISTENCY OF MEASUREMENTS FOR TERNARY SYSTEM

Several forms of the Gibbs-Duhem equation may be applied to ternary systems to check measurements for thermodynamic consistency. Unfortunately, such checks are limited to systems measured at constant temperature and not under constant pressure.

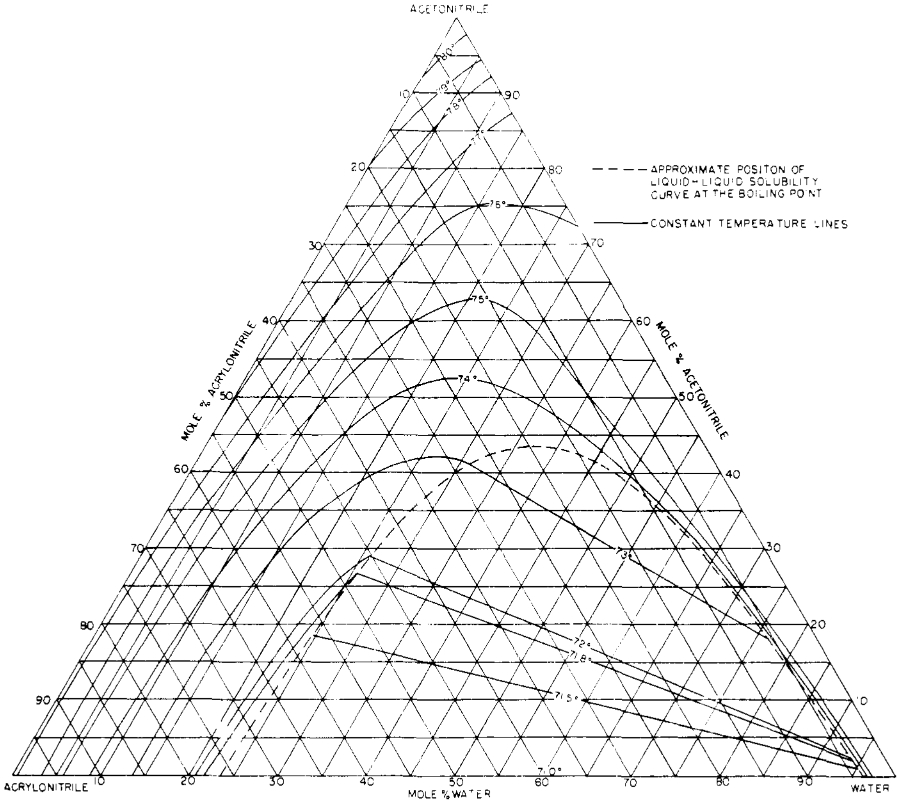

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Figure 5. Boiling point diagram for acetonitrile-acrylonitrile-water ternary under 760 mm. total pressure

The activity coefficients for all three components in the ternary system are given in Table III.

Methods have been proposed for correlating and testing the consistency of ternary equilibrium data. Carlson and Colburn (*1*) propose that the calculated activity coefficients for each of the three components be plotted on separate graphs *vs.* the mole fractions of the respective components. Their assumption for such a test is that activity coefficients are equal to or greater than unity. On these same plots, the calculated values for the limiting binary systems are also plotted. If the values for the ternary activity coefficients fall between the two limiting binary curves, then the data are probably consistent. These authors also state that a family of curves may be drawn between the limiting binary curves on each graph, each curve representing the mole ratio of one of the components not used as the abscissa to the sum of both of the components not used as the abscissa—in other words, the mole fraction on an abscissa-component-free basis.

When plotted in this manner, the data for the acetonitrile and acrylonitrile activity coefficients fell generally within the limiting binary curves except for a few isolated points. The coefficients for the acrylonitrile-water binary were calculated and not determined from experimental data. The data for the water activity coefficients fell between their two binary curves in the intermediate concentration range, but deviate fairly substantially in the areas of high and low water concentrations.

An alternative method of correlation of the ternary activity coefficients involves plotting the logarithm of the ratio of the activity coefficients of acetonitrile and that of water *vs.* the acetonitrile concentration; likewise, the logarithm of the ratio of the coefficients for water and acrylonitrile *vs.* the water composition.

These plots gave fairly good correlations, but the theoretical justification for using this method of plotting is not readily evident.

Redlich and Kister (*9*) and Wohl (*10*) have developed equations based on the concept of excess free energy which correlate the ratios of the logarithms of ternary activity coefficients and equilibrium compositions. Such equations indicate that this type of plot is a valid and effective way of testing the consistency of ternary experimental data.

No attempt was made to correlate analytically the activity coefficient and vapor-liquid equilibria for either the binaries or the ternary with one of the theoretical equations such as the van Laar or Margules solutions of the Gibbs-Duhem equation for binaries or the more complicated Wohl, Scatchard-Hamer, or the van Laar and Margules-type solutions of the Wohl equation for ternaries.

DISCUSSION OF RESULTS

Based upon the experimental techniques and the checks for consistency through activity coefficients, the vapor-liquid equilibria presented are believed to be reliable and useful in the design of fractionating equipment for separating acrylonitrile, acetonitrile, and water.

Modifications made to the Colburn-type still for use with immiscible liquids have been successful in this application.

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