Ternary Liquid-Liquid Equilibrium by Infrared Spectrometry

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Ternary liquid-liquid equilibrium studies of acetonitrile-water-diammonium phosphate and acetonitrile-water-diammonium citrate at 25° C were made, using a modification of the cloud point technique. Binodal data were obtained without opening the sample vials once the salt had been added. Tie lines for both systems were obtained by analyzing the organic-rich phase by infrared spectrometry.

AN OUTGROWTH of Renard's work on ternary acetonitrile-water-salt (*5–8*) systems has been an interest in novel methods of equilibrium phase analysis as well as binodal curve determination. Various physical properties of conjugate solutions, both water-rich and organic-rich, have been studied, such as electrical conductivity (*3*) and surface tension (*4*). This paper describes a method of analyzing the organic-rich phase by infrared spectrometry, and a method of observing the cloud point, as an indication of the binodal curve, in which the sample under observation is contained in a vial kept completely closed, even during the addition of liquid increments.

MATERIALS

Double-distilled water was used in all samples. Matheson-Coleman and Bell spectroquality acetonitrile was used, 99 plus mole % acetonitrile.

Diammonium hydrogen phosphate 99.8% pure, lot 3484, by Mallinckrodt was used.

Diammonium citrate 99.8% pure, lot 0682, by Baker was used.

INFRARED ANALYSIS

The base line technique of Ewing (*1*) for quantitative determinations was modified for this investigation. The base line end points were chosen at 2230 and 2290 cm^{-1}, because they represent definite break points corresponding to the initiation and termination of the $C \equiv N$ stretch in the spectrum of interest. In each case, the net radiant power was measured at 2260 cm^{-1} for various acetonitrile-rich solutions saturated with salt. A calibration curve was then constructed by plotting the magnitude of the radiant power (often designated as peak height) against the weight per cent acetonitrile. This procedure is permissible because the radiant power is a measure of the absorbance of the $C \equiv N$ stretch and hence a measure of the quantity of acetonitrile present in the sample. This calibration, however, will not necessarily be a straight line, even for an ideal system obeying Beer's law, because of the very nature of the plot. Here, the radiant power *vs.* the weight per cent acetonitrile is plotted using Cartesian coordinates instead of the classical log per cent transmittance *vs.* concentration in parts per million.

BINODAL CURVE

So that liquid increments could be added without opening the sample container in observing the cloud point, sample containers were fashioned from 50-ml dropper bottles, modified by replacing the dropper with a self-sealing silicone rubber septum. Silicone rubber was chosen because of its negligible swelling in the presence of acetonitrile. After taring the sample container, 0.05 to 2.00 grams of salt were added and the sample container was immediately closed and weighed again. Five to 30 grams of acetonitrile were added by injection with a hypodermic syringe through the septum, followed by another weighing; then sufficient double-distilled water was injected through the septum to obtain two liquid phases. After a third weighing, the closed container was immersed in a water bath maintained at 25° ± 0.1° C. Double-distilled water was then injected in small amounts and the container was shaken and visually examined for cloudiness after each water addition. The final amount of water injected was 1 drop from the syringe (approximately 1.2 mg). Cloudiness was observed before the final drop, indicating two phases; the solution remained clear after the final drop, indicating a single phase. A final weighing gave a point on the binodal curve. Thirty-nine such observations were made for the system acetonitrile-water–diammonium phosphate and 21 for the diammonium citrate system.

TIE LINES

Samples of the organic-rich layers of both salt systems resulting from the binodal curve determinations were transferred by hypodermic syringe directly to an IRtran II cell (path length 0.015 mm) and analyzed with a Beckman IR-10 infrared spectrometer for the acetonitrile radiant power. The resulting peak heights were plotted against per cent acetonitrile for each salt to give calibration curves.

For each system, points in the two-phase region, near the salt-rich lines, were selected to give two mutually saturated phases. Samples having the desired over-all compositions were prepared by taring the sample container, adding the salt, weighing, closing the container, injecting acetonitrile, weighing, injecting water, and weighing. The containers were placed in the isothermal water bath for not less than one hour. During this time, the sample containers were manually shaken for 5 seconds every 5 minutes. Equilibrium was assumed after one hour of this treatment. Samples were taken from the acetonitrile-rich layer by syringe, injected into the IRtran II cell, and analyzed as before. Hence the point on the organic-rich portion at the binodal curve was determined. The composition of the salt-rich phase was computed from the known over-all composition of the sample, the organic-rich composition, and the salt-rich portion of the binodal curve.

END POINTS

The salt-rich end point of the binodal curve was taken as that point lying on the extrapolation of the experimental curve having the same ratio of salt to water as a saturated aqueous solution of the salt. The solubility data of Seidell and Linke (*9*) were used for the diammonium phosphate system.

For the organic-rich end point of the binodal curve, a point was selected that lies in the three-phase region. A sample having this over-all composition was then made up as previously described and placed in the bath for not less than 2 hours. During this time, the sample was manually shaken for 5 seconds every 5 minutes for the first hour, with a final 5-second agitation after 1.5 hours. After at least 2 hours of bath residence, a sample was taken from the acetonitrile-rich layer by syringe, injected into the same IRtran II cell, and analyzed for acetonitrile.

Table I. Binodal Data at 25° C

(Weight per cent)

System			System		
CH_3CN	$(NH_4)_2HPO_4$	H_2O	CH_3CH	$(NH_4)_2HC_6H_5O_7$	H_2O
73.77	0.09	26.14	77.01	0.17	22.81
65.03	0.21	34.76	77.01	0.18	22.76
65.09	0.22	34.69	76.22	0.18	23.60
62.62	0.27	37.11	76.05	0.19	23.76
63.08	0.28	36.64	74.36	0.24	25.40
62.19	0.30	37.51	72.61	0.29	27.10
59.99	0.37	39.64	70.32	0.39	29.29
58.03	0.46	41.51	68.40	0.49	31.11
58.00	0.46	41.54	66.94	0.60	32.46
57.51	0.50	41.99	64.00	0.80	35.20
51.12	0.90	47.98	61.30	1.00	37.70
50.32	0.94	48.74	54.36	1.86	43.78
50.43	0.97	48.60	48.71	2.58	48.71
45.84	1.43	52.73	35.58	5.39	59.03
45.64	1.43	52.93	30.16	7.29	62.55
45.70	1.44	52.86	22.32	11.86	65.82
41.91	1.82	56.17	17.16	17.04	65.80
41.78	1.85	56.37	10.96	27.10	61.94
42.11	1.90	55.99	10.46	28.26	61.28
41.96	1.90	56.14	7.17	37.75	55.08
38.83	2.38	58.79	5.95	42.97	51.08
38.84	2.38	58.78			
38.73	2.39	58.88			
35.95	2.80	61.25			
35.86	2.87	61.27			
33.63	3.25	63.12			
31.41	3.52	66.07			
31.39	3.67	64.94			
31.36	3.70	64.94			
28.04	4.51	67.45			
27.77	4.59	67.64			
27.59	4.62	67.79			
22.45	6.46	71.09			
22.05	6.55	71.40			
17.09	9.18	73.73			
11.69	13.55	74.76			
11.57	13.55	74.88			
7.92	18.06	74.02			
5.31	23.64	71.05			

Table II. Tie Line Data at 25° C

(Weight per cent)

Salt-Rich Phase			Acetonitrile-Rich Phase		
$(NH_4)_2HPO_4$	H_2O	CH_3CN	CH_3CN	H_2O	$(NH_4)_2HPO_4$
41.8	56.1	2.1	87.7	12.3	0.0
26.2	69.3	4.5	77.5	22.4	0.1
21.0	72.6	6.4	75.0	24.8	0.2
16.4	74.4	9.2	60.9	38.8	0.3
13.5	74.8	11.7	54.4	45.0	0.6
10.7	74.2	15.1	48.3	50.4	1.3
6.9	71.6	21.5	44.2	44.1	1.7
4.9	68.2	26.9	42.2	55.9	1.9
		P.P.[a]	35.5	61.5	3.0
$(NH_4)_2HC_6H_5O_7$	H_2O	CH_3CN	CH_3CN	H_2O	$(NH_4)_2HC_6H_5O_7$
43.0	51.1	5.9	78.9	21.0	0.1
36.5	56.0	7.5	78.1	21.7	0.2
31.3	59.6	9.1	77.8	22.0	0.2
27.5	61.9	10.6	77.0	22.8	0.2
22.2	64.2	13.6	76.9	22.9	0.2
17.3	65.8	16.9	76.4	23.4	0.2
13.7	66.0	20.3	76.1	23.7	0.2
11.8	65.8	22.4	74.2	25.5	0.3
9.5	64.5	26.0	72.4	27.3	0.3
5.8	59.3	34.9	67.3	32.1	0.6
4.7	56.4	38.9	64.2	34.0	0.8
		P.P.[a]	52.2	47.8	2.0

[a] Plait point by method of rectilinear diameters (*6*).

RESULTS

Binodal data and tie lines for both systems are given in Tables I and II. Work on the diammonium phosphate system indicated that a salt composition greater than 5% masked the acetonitrile peak to the extent that it was unusable for quantitative analysis. For this reason, samples of the salt-rich layers were not analyzed in the tie line determinations.

Calibration data of peak height *vs.* weight per cent acetonitrile for both systems were treated by regression analysis. A linear analysis of the diammonium phosphate system data gave a correlation coefficient of 0.92. Maximum relative error resulting from use of the calibration data was 2.0% of the true acetonitrile composition. A quadratic analysis of the diammonium citrate system data gave a correlation coefficient of 0.994 with a maximum relative error of 1.74% of the true acetonitrile composition.

A typical measure of the reproducibility obtained using the infrared analysis technique was exemplified by the determination of the acetonitrile-rich end points for the diammonium citrate system in which seven individual determinations were made. The mean peak height was 107.9 units and the standard error, $s(\bar{x})$, was 2.461 units. At the 95% confidence level, the peak height is 107.9 ± 6.0 units, which corresponds to a 0.7 weight % deviation in the true composition of acetonitrile.

DISCUSSION

The determination of the acetonitrile-rich end point of the binodal curve in previous work has been particularly troublesome, because it has been determined by an extrapolation technique. One of the outstanding features of this infrared analysis technique is that it has facilitated the actual experimental determination of the end point.

The upper limit of 5 weight % salt could be extended by aliquot dilution with pure acetonitrile. Extension beyond the plait point by this method is not recommended.

The plait points for the two systems were determined by the novel technique of rectilinear diameters proposed by Renard and Heichelheim (*6*). These values differed from values determined by the conventional Coolidge (*2*) technique of extrapolation of the conjugation curve to the binodal curve by 5.1 and 4.7% for the diammonium citrate and diammonium phosphate systems, respectively.

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Isothermal Vapor-Liquid Equilibrium Data by Total Pressure Method

Systems Acetaldehyde-Ethanol, Acetaldehyde-Water, and Ethanol-Water

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Isothermal vapor-liquid equilibrium data were obtained by the total pressure method for the binary systems acetaldehyde-ethanol, acetaldehyde-water, and ethanol-water at 10°, 15°, 20°, 25°, and 30° C, using a modified Menzies and Smith's isoteniscope. Barker's method was employed for the numerical calculations.

AT A STAGE of the catalytic process for the manufacture of acetaldehyde from ethanol, the separation of components of the acetaldehyde-ethanol-water mixture is necessary. Vapor-liquid equilibrium data were nonexistent in the literature for the working range of interest in this process.

This paper presents the vapor-liquid equilibrium data for the binary systems acetaldehyde-ethanol, acetaldehyde-water, and ethanol-water at 10°, 15°, 20°, 25°, and 30° C, obtained through the method of total pressure.

The total pressure method for obtaining vapor-liquid equilibrium data consists of the determination of the total pressure above a liquid solution of known composition in equilibrium at a fixed temperature. Analyses of the liquid and vapor phases are not necessary.

The binary data have been extended to the ternary system acetaldehyde-ethanol-water by means of the Redlich-Kister equation, assuming ideal behavior of the vapor phase within the temperature interval under consideration (*11*).

APPARATUS

The experimental apparatus (Figure 1) is a modification of Menzies and Smith's isoteniscope (*3*). Serrano (*10*) tested it with the system chloroform-ethanol, in the range 30° to 50° C and his equilibrium data agreed with those of the literature (*9*).

The apparatus consists of a cylindrical bulb, *A*, of approximately 25 ml, containing the liquid mixture; a capillary mercury manometer, *B*, to establish the equilibrium; a mercury reservoir, *C*; and the open-tube mercury manometer, *F*, which was designed to measure pressures up to 1480 mm of Hg.

The liquid mixtures were prepared from the pure components using a microburet (precision, ±0.02 ml). The maximum error involved in this operation was estimated as 0.25% (*13*).

After degassing the sample, sections *A* and *B* were placed in a thermostatic bath, controlled by a mercury thermostat (accuracy, ±0.1° C). The equilibrium is established when the heights of mercury in both branches of the manometer

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