Vapor-Liquid Equilibrium Data for the Ternary System Acetone–2-Propanol–Water and Corresponding Binaries from Total Pressure Measurements

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Isothermal vapor-liquid equilibrium data were obtained by the total pressure method for the binaries acetone–2-propanol, acetone–water, and 2-propanol–water at 75° C. Ternary data were obtained, also at 75° C, for the system acetone–2-propanol–water. A numerical method was employed in all binary and ternary calculations.

The total pressure method for obtaining vapor-liquid equilibrium data consists in the determination of bubble point temperatures of mixtures of known compositions as functions of pressure. The main advantages of the method are elimination of the analysis of vapor and liquid phases at equilibrium, which usually introduces appreciable error in the results, and a considerable reduction of the time required to obtain the data.

In a previous paper (*5*), a numerical method for calculating vapor-liquid equilibrium data for binary and ternary systems, from total pressure measurements, was presented. This method has been used in performing the calculations needed in this investigation. This paper presents isothermal data at 75° C for the binary systems acetone–2-propanol, acetone–water, and 2-propanol–water, as well as ternary data, also at 75° C, for the system acetone–2-propanol–water.

EXPERIMENTAL

The experimental apparatus was, with some minor modifications, that employed by Prengle and Palm (*4*). Three ebulliometers were operated concurrently at the same pressure, to speed up the collection of data. Detailed drawings of the equipment and operating procedure are available from the authors (*1, 2*). The probable uncertainties in each of the primary variables for this type of experimental determination are discussed by Prengle and Palm (*4*).

The temperatures were measured by platinum resistance thermometers, calibrated by the National Research Council of Canada. These thermometers are accurate to ±0.001° C. However, because of small temperature fluctuations, the accuracy of the temperature measurements is estimated to be ±0.05° C.

The pressures were measured by a mercury manometer. A cathetometer was employed for reading the height of the mercury column. Although a reading accurate to 0.1 mm is theoretically possible, small pressure fluctuations limit the accuracy of the measurement to ±1 mm Hg.

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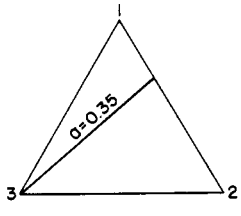

Figure 1. Typical path for obtaining ternary data

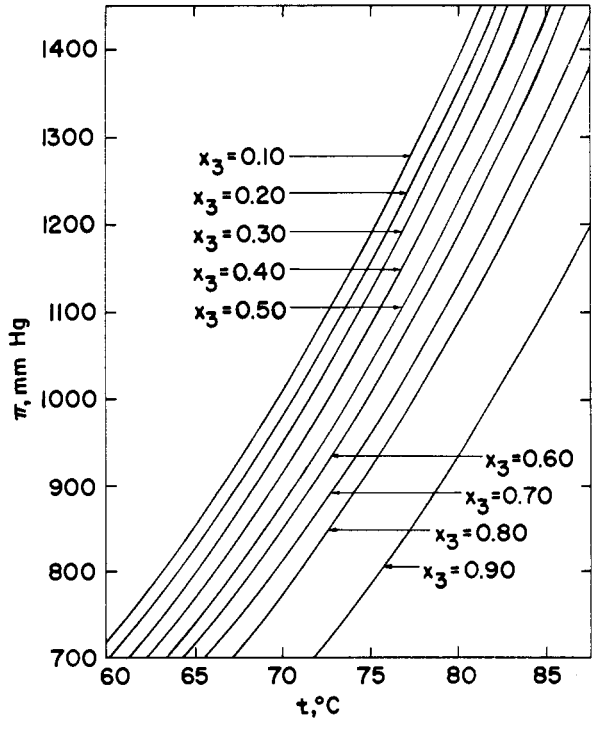

Figure 2. Total pressure for system acetone–2-propanol–water
α = 0.35

Table I. Experimental Measurements for System Acetone–2-Propanol

x_1'	π, Mm Hg	t, °C	x_1'	π, Mm Hg	t, °C
0.1	524.1	66.92	0.6	759.1	62.11
	750.2	76.38	0.6	898.4	66.97
	889.8	81.01	0.6	1099.7	73.21
	1086.7	86.55	0.6	1293.0	78.48
	1286.3	91.58	0.6	1502.1	83.34
0.2	524.1	62.41	0.7	757.4	60.21
	750.2	72.15	0.7	894.2	65.14
	889.0	77.08	0.7	1096.8	71.39
	1086.7	82.93	0.7	1288.5	76.57
	1286.3	88.22	0.7	1489.7	81.87
0.3	524.1	58.69	0.8	757.4	58.68
	750.2	68.61	0.8	894.8	63.59
	888.8	73.60	0.8	1096.8	69.91
	1086.7	79.50	0.8	1288.5	75.12
	1286.3	85.00	0.8	1489.7	80.21
0.4	759.1	66.23	0.9	757.4	57.21
	898.4	71.02	0.9	894.8	62.09
	1099.7	77.14	0.9	1096.8	68.38
	1293.0	82.48	0.9	1288.5	73.54
	1502.1	87.18	0.9	1489.7	78.38
0.5	759.1	64.15			
	898.4	69.15			
	1099.7	75.69			
	1293.0	80.74			
	1502.1	85.69			

Table II. Experimental Measurements for System Acetone–Water

x_1'	π, Mm Hg	t, °C	x_1'	χ, Mm Hg	t, °C
0.9	751.5	56.24	0.4	762.3	60.91
	889.6	61.11	0.4	904.1	66.06
	1089.5	67.31	0.4	1102.6	72.19
	1283.0	72.47	0.4	1294.8	77.33
	1486.5	77.24	0.4	1493.4	81.97
0.8	763.1	57.63	0.3	761.2	61.60
	892.5	62.28	0.3	902.8	66.66
	1077.6	67.93	0.3	1101.5	72.66
	1290.0	73.34	0.3	1294.0	77.91
	1492.9	78.34	0.3	1490.0	82.73
0.7	751.0	58.02	0.2	766.0	63.46
	890.1	62.90	0.2	913.3	68.57
	1089.5	69.08	0.2	1109.8	74.41
	1283.4	74.16	0.2	1296.9	79.25
	1485.1	78.81			
0.6	751.5	58.71	0.1	750.2	69.74
	889.4	63.69	0.1	887.8	74.91
	1088.5	69.99	0.1	1080.6	81.55
	1283.4	75.13	0.1	1275.5	87.58
	1488.9	79.78			
0.5	762.1	60.14			
	904.8	65.16			
	1102.3	71.21			
	1294.5	76.34			
	1493.6	80.98			

The errors in the mole fractions were estimated as being at most 1%. Details of this estimate are presented by Drolet (2).

BINARIES ACETONE–2-PROPANOL, ACETONE–WATER, AND 2-PROPANOL–WATER

The experimental measurements are presented in Tables I through III. Total pressure curves and the vapor-liquid composition curves at 75°C are available from the authors (2). Table IV presents the vapor-liquid equilibrium data

Table III. Experimental Measurements for System 2-Propanol–Water

x_2'	π, Mm Hg	t, °C	x_2'	π, Mm Hg	t, °C
0.02	334.8	72.26	0.6	489.1	69.50
	519.8	81.73	0.6	749.3	79.81
	739.9	90.48	0.6	884.6	84.03
	880.5	95.02	0.6	1089.2	89.47
	1082.4	100.70	0.6	1283.0	93.91
0.06	400.0	69.67	0.7	489.1	69.39
	584.6	77.68	0.7	749.3	79.72
	755.3	83.58	0.7	884.6	84.01
	904.0	88.24	0.7	1089.2	89.34
	1092.1	92.94	0.7	1283.0	93.79
0.2	390.0	65.88	0.8	489.1	69.56
	753.2	81.82	0.8	749.3	79.85
	889.3	85.61	0.8	884.6	84.05
	1088.2	91.13	0.8	1089.2	89.51
	1284.1	96.01	0.8	1283.0	94.07
0.3	390.0	65.28	0.9	334.8	62.28
	753.2	81.03	0.9	519.8	71.67
	891.3	85.36	0.9	741.1	80.25
	1088.2	90.74	0.9	880.5	84.60
	1284.1	95.36	0.9	1082.4	90.02
0.4	390.0	64.88	1.0	334.8	63.39
	753.2	80.66	1.0	519.8	72.78
	892.5	84.85	1.0	740.7	81.35
	1088.2	90.14	1.0	880.5	85.70
	1284.1	94.77	1.0	1082.4	91.12

obtained. Tables detailing intermediate calculated results are also available from the authors (2).

TERNARY DATA FOR SYSTEM ACETONE–2-PROPANOL–WATER

The ternary system acetone–2-propanol–water is of interest, since it occurs in the process for making acetone by catalytic dehydrogenation of isopropyl alcohol. No data for this system had been previously reported in the literature.

For a systematic study of ternary combinations, a parameter, a, is defined as

$$a = \frac{x_2}{x_1 + x_2} = \text{constant} \qquad (1)$$

Figure 1 illustrates the procedure followed to obtain the data. Each straight line (such as the one for $a = 0.35$), corresponds to a constant value of a. The experimental

Table IV. Vapor-Liquid Equilibrium Data for Three Binary Systems at 75° C

x_1' or x_2'	Acetone–2-Propanol y_1	Acetone–Water y_1	2-Propanol–Water y_2
0.02	...	...	0.28343
0.06	...	...	0.44624
0.10	0.27375	0.71079	...
0.20	0.43894	0.75622	0.55065
0.30	0.54749	0.79124	0.54757
0.40	0.62862	0.80977	0.56021
0.50	0.70996	0.81167	...
0.60	0.76196	0.82069	0.64029
0.70	0.82163	0.83909	0.70155
0.80	0.88267	0.87377	0.77260
0.90	0.93783	0.92054	0.86926
1.00	1.00000	1.00000	1.00000

Table V. Experimental Measurements for System Acetone–2-Propanol–Water

$a = 0.35$

x_1	x_2	π, Mm Hg	t, °C	x_1	x_2	π, Mm Hg	t, °C
0.585	0.315	759.0	61.44	0.26	0.14	753.8	66.36
	0.315	895.0	66.25	0.26	0.14	892.8	71.17
	0.315	1103.7	72.65	0.26	0.14	1097.7	77.53
	0.315	1288.1	77.45	0.26	0.14	1289.0	82.39
	0.315	1477.0	82.00	0.26	0.14	1501.1	87.08
0.52	0.28	759.0	62.39	0.195	0.105	579.9	60.41
	0.28	895.0	67.13	0.195	0.105	746.0	67.57
	0.28	1103.7	73.47	0.195	0.105	879.8	72.41
	0.28	1288.1	78.31	0.195	0.105	1085.8	78.58
	0.28	1477.0	82.61	0.195	0.105	1276.2	83.63
0.455	0.245	759.0	63.40	0.13	0.07	572.1	61.54
	0.245	895.0	68.06	0.13	0.07	745.1	68.82
	0.245	1103.7	74.40	0.13	0.07	882.1	73.51
	0.245	1288.1	79.14	0.13	0.07	1081.7	79.78
	0.245	1477.0	83.49	0.13	0.07	1278.9	85.02
0.39	0.21	753.8	64.36	0.065	0.035	579.9	66.24
	0.21	892.8	60.11	0.065	0.035	746.0	73.43
	0.21	1097.7	75.35	0.065	0.035	879.8	77.96
	0.21	1289.0	80.29	0.065	0.035	1085.8	84.11
	0.21	1501.1	85.06	0.065	0.035	1276.2	89.36
0.325	0.175	753.8	65.40				
	0.175	892.8	70.14				
	0.175	1097.7	76.54				
	0.175	1289.0	81.39				
	0.175	1501.1	86.23				

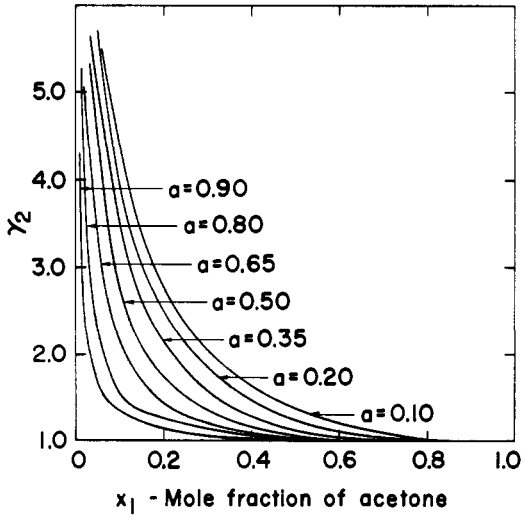

Figure 3. Activity coefficient for system acetone–2-propanol–water at 75° C

Table VI. Vapor Liquid Equilibrium Data for Ternary System Acetone–2-Propanol–Water at 75° C

$a = 0.35$

x_1	x_2	y_1	y_2	π, Mm Hg
0.585	0.315	0.7321	0.1837	1190.9
0.52	0.29	0.7002	0.1658	1160.0
0.455	0.245	0.6724	0.1531	1127.1
0.39	0.21	0.6517	0.1431	1086.2
0.325	0.175	0.6337	0.1376	1046.8
0.26	0.14	0.6175	0.1366	1011.6
0.195	0.105	0.5988	0.1361	961.6
0.13	0.07	0.5733	0.1463	925.0
0.065	0.035	0.5096	0.1511	792.9

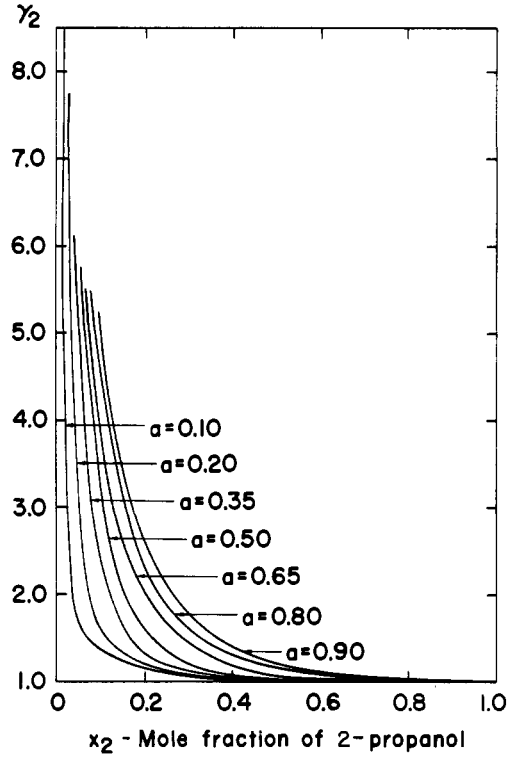

Figure 4. Activity coefficient for system acetone–2-propanol–water at 75° C

measurements were conveniently taken along each line (a = 0.10, 0.20, 0.35, 0.50, 0.65, 0.80, and 0.90). The range of pressures involved was between 300 and 1500 mm Hg. Hg.

Because of the considerable amount of space required for presentation of all the data obtained, only a sample (for a = 0.35) is presented here. Similar data for the other

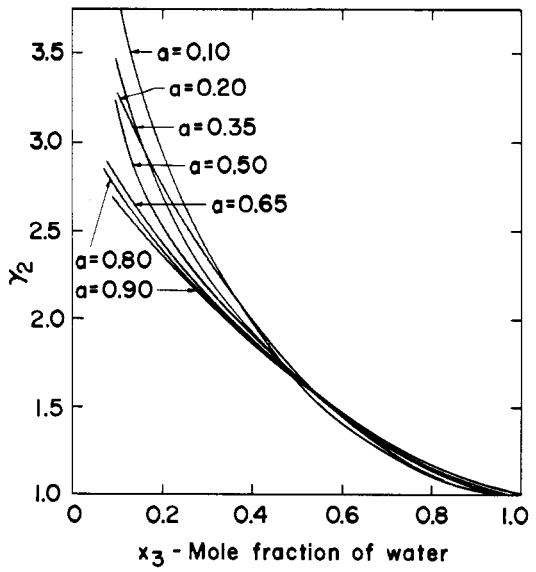

Figure 5. Activity coefficient for system acetone–2-propanol–water at 75° C

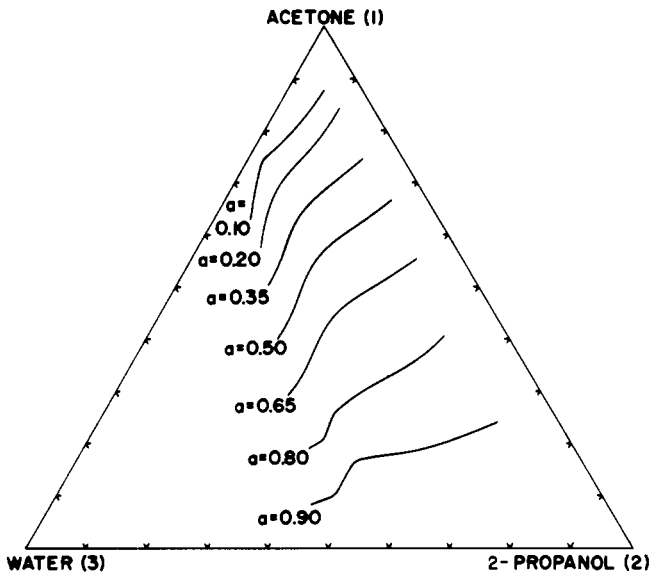

Figure 6. Triangular diagram for system acetone–2-propanol–water at 75° C

six values of a have been filed with the ASIS National Auxiliary Publications Service. The experimental data are presented in Table V, and the vapor-liquid data in Table VI. Figure 2 is a sample of the total pressure curves for $a = 0.35$. Similar sets of curves are available for the other values of a (2). Figures 3, 4, and 5 present the activity coefficient γ_1, γ_2, and γ_3 *vs.* x_1, x_2, and x_3 for the different values of parameter a.

The thermodynamic consistency of the ternary data was checked by the test of McDermott and Ellis (3), and the deviations are shown in Table 8 (filed with ASIS) for the case of $a = 0.35$. The data may be considered satisfactory, deviations being usually less than ± 0.01. All the calculations in this work were performed by an IBM 360 (model 50).

Figure 6 is a triangular diagram, with vapor compositions plotted along the sides of the triangle, and showing curves corresponding to constant values of parameter a.

ACKNOWLEDGMENT

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NOMENCLATURE

a = parameter for liquid compositions of ternary mixtures, Equation 1, dimensionless

B_{12}, B_{13}, B_{23}, C_{12}, C_{13}, C_{23}, D_{12}, D_{13}, D_{14} = Redlich-Kister coefficients, dimensionless (Subscripts 1, 2, and 3 denote acetone, 2-propanol, and water, respectively, throughout this article)

C = Redlich-Kister coefficient for ternary system, dimensionless

t = bubble point temperatures, ° C

x_1, x_2, x_3 = mole fractions of components 1, 2, and 3, respectively, in liquid phase, for case of a ternary mixture, dimensionless

x_1', x_2', x_3' = mole fractions of components in liquid phase, for case of a binary mixture, dimensionless

y_i = mole fraction of more volatile component in vapor phase (i = 1, 2, 3), dimensionless

Greek Letters

γ_i = activity coefficient of component i in liquid phase (i = 1, 2, 3), dimensionless

ϕ_i = correction coefficient for vapor phase, relative to component i (i = 1, 2, 3), dimensionless

π = total pressure, mm Hg

LITERATURE CITED

(1) Delmas, J., M.S. thesis, Laval University, Quebec, Canada, 1967.

(2) Drolet, J. F., M.S. thesis, Laval University, Quebec, Canada, 1969.

(3) McDermott, C., Ellis, S. R. M., *Chem. Eng. Sci.*, **20**, 293 (1965).

(4) Prengle, H. W., Jr., Palm, G. F., *Ind. Eng. Chem.*, **49**, 1769–74 (1957).

(5) Ramalho, R. S., Bui, V. T., *Can. J. Chem. Eng.*, **48** (3), 1970.

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