Vapor-Liquid Equilibria of Water–Lower Fatty Acid Systems

Water–Formic Acid, Water–Acetic Acid and Water–Propionic Acid

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Vapor-liquid equilibrium data for three water-lower fatty acid systems,—water–formic acid, water–acetic acid, and water–propionic acid,—were taken with a vapor recirculation–type still at three pressures: 760, 200, and 70 mm. of Hg. The water–formic acid system has a maximum boiling azeotrope, the composition of which decreases in water content with increasing pressure. At 760 mm. of Hg the azeotrope contains 42.4 mole % water. The relative volatility of water to acetic acid decreases with decreasing pressure. The water–propionic acid system forms a minimum boiling azeotrope at pressures above about 100 mm. of Hg. At 760 mm. of Hg, it contains 95.0 mole % water. The relative volatility of water to propionic acid increases with decreasing pressure for the range of x below the azeotropic compositions. Values of the activity coefficient were calculated for the three systems with allowance for the association of fatty acids in the vapor phase.

VAPOR-LIQUID EQUILIBRIA at atmospheric and subatmospheric pressures were determined for three water-lower fatty acid systems—water-formic acid, water-acetic acid, and water-propionic acid. Treatment of the data for these systems is complicated by the extensive association of fatty acids in the vapor phase.

EXPERIMENTAL

The equilibrium still (Figure 1) was a vapor recirculation type similar to the Braun-type still described by Hipkin and Myers (*8*). It differed from the Braun type in that the vapor jacket was heated by the vapor from the contactor itself. To avoid partial condensation of vapor, the jacket was wound with an auxiliary heating wire, and the entire jacket including the top dome was covered with insulation. The still was made of borosilicate glass; and silicone grease, considered insoluble in the materials tested, was used for sealing the glass cocks. This type of equilibrium still was previously used by Yoshida and Koyanagi (*18*) and gave reliable results.

Experiments were performed at three pressures, 760, 200, and 70 mm. of Hg. Vacuum was maintained by a water-jet pump and a Cartesian-type manostat (*16*), which made possible the regulation of pressure within 1 mm. of Hg.

The formic acid tested was of special grade. The purity was 98.99%, and the impurity was considered to be water, since the density measured at 25° C. was 1.21336 in agreement with the value of 1.2134 in the literature (*5*). The glacial acetic acid used was also of special grade and was found to be 100.00% pure by chemical analysis. The propionic acid for the tests was prepared from special grade acid by fractional distillation in a laboratory packed column. It was difficult to raise the purity above 99.77%, probably because of hygroscopicity. The impurity was regarded as water.

Samples were analyzed for acids by titration with a 0.5*N* aqueous solution of NaOH with phenolphthalein as the indicator. Calculation showed that the errors involved in

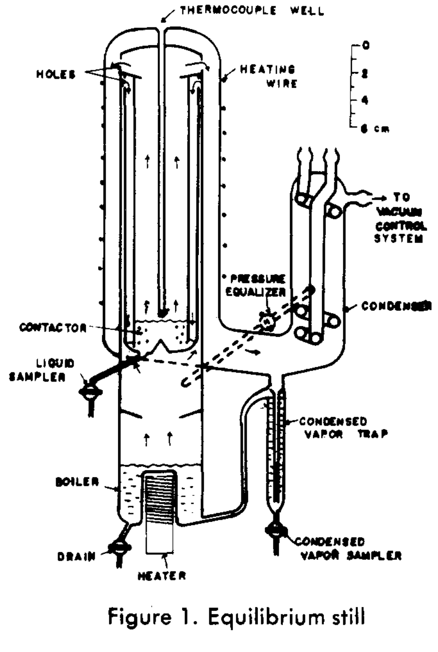

Figure 1. Equilibrium still

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the analysis corresponded to a mole fraction of acid in the sample well below 0.001. For formic acid and acetic acid, analysis should be made as quickly as possible because of hygroscopicity of the sample.

Equilibrium temperatures were measured by means of the copper-Constantan thermocouple inserted in the thermocouple well in the contractor and a potentiometer. The accuracy of temperature measurement was within 0.1° C.

TREATMENT OF DATA

When a nonideal liquid solution is in equilibrium with an ideal gas mixture, the activity coefficient of a component in the liquid is given by

$$\gamma_i = \frac{p_i}{x_i P_i^\circ} = \frac{y_i \pi}{x_i P_i^\circ} \qquad (1)$$

However, the activity coefficients for water-fatty acid systems cannot be calculated by the above equation because of the extensive association of acid molecules in the vapor phase. In this case, γ_i in Equation 1 should be regarded merely as the coefficient of deviation from the Raoult's law, which shall be designated as δ hereafter. Assuming that deviation from ideality in the vapor phase is solely due to association, Hansen *et al.* (*5*) showed that the fugacity of the fatty acid which associates in the vapor phase can be calculated by the following relationship:

$$\ln \frac{f_A}{p_A} = \int_0^{p_A} \left(\frac{1}{p_1 + 2p_2 + 3p_3} - \frac{1}{p_A} \right) dp_A \qquad (2,$$

$$= \int_0^{p_A} \left(\frac{1}{p_1 + 2K_2 p_1^2 + 3K_3 p_1^3} - \frac{1}{p_A} \right) dp_A \qquad (3)$$

$$= \int_0^{p_A} \left(\frac{1}{p_1 (dp_A/dp_1)} - \frac{1}{p_A} \right) dp_A = \ln \frac{p_1}{p_A} \qquad (4)$$

whence,

$$f_A = p_1 \qquad (5)$$

The value of p_1 can be obtained by solving the following equation, which can be readily derived from the definitions of x and K's.

$$K_3(3 - 2x_A)p_1^3 + K_2(2 - x_A)p_1^2 + p_1 - x_A\pi = 0 \qquad (6)$$

There are some differences among the values in the literature of the equilibrium constants K_2 and K_3 for the formation of dimers and trimers from monomers but calculated values of the activity coefficients are affected very little by the differences in K. The only data available on the equilibrium constant for the association of formic acid in the vapor phase were obtained by Taylor (*17*), who gives the constant for dimerization over a temperature range of 50° to 150° C. by the following equation.

$$\log K_2 = 3083/T - 10.743 \qquad (7)$$

The formation of the trimer from formic acid is considered negligible. However, in the case of acetic acid, the formation of the trimer is not negligible. There are several sets of data on the equilibrium constants for this system, but the data of Morcillo (*11*) were used in the present work. The values are

Temp., ° C.	K_2, Mm. of Hg^{-1}	K_3, Mm. of Hg^{-2}
77	330×10^{-4}	900×10^{-7}
98	100	100
128.5	25	20
160.5	7.2	3

Two sets of data for equilibrium constants for the association of propionic acid are available, and the data of Taylor (*17*) were adopted. According to Taylor, the formation of trimer is negligible, and the equilibrium constant for dimer formation for the temperature range of 50° to 150° C. is given by

$$\log K_2 = 3316/T - 10.834 \qquad (8)$$

The activity coefficient was evaluated from Equations 5 and 6 and the defining equation:

$$\gamma_i = f_i / x_i P_i^\circ \qquad (9)$$

Consistency of the measured data was checked by the Herington criterion (*7*) for isobaric data. According to Herington, it can be assumed that the measured data are consistent, if

$$D < J + 10 \qquad (10)$$

where

$$D = \frac{100}{S} \left| \int_0^1 \ln \frac{\gamma_W}{\gamma_A} dx_1 \right| \qquad (11)$$

and

$$J = 150(T_{\max.} - T_{\min.})/T_{\min.} \qquad (12)$$

RESULTS

Tables I, II, and III list the measured values of the equilibrium temperatures, the liquid and vapor compositions in mole fractions along with the calculated values of the coefficient of deviation from the Raoult's law and the activity coefficients at 760, 200, and 70 mm. of Hg for the systems water–formic acid, water–acetic acid, and water–propionic acid, respectively. The $x - y$ values are the raw data and not smoothed values. Figures 2, 3, and 4 show the $x - y$ curves at the three pressures for the three systems, respectively. The smooth curves drawn through the data points indicate the high accuracy obtained in the analysis. As seen from Figure 2, the water–formic acid system has a

Table I. Data for Water–Formic Acid System

t ° C.	x_W	y_W	δ_W	δ_A	γ_W	γ_A
760 mm. of Hg						
102.3	0.0405	0.0245	0.5575	0.9658	0.8321	0.9830
104.6	0.155	0.102	0.5586	0.9446	0.7859	0.9857
105.9	0.218	0.162	0.6042	0.9182	0.8156	0.9744
107.1	0.321	0.279	0.6780	0.8772	0.8558	0.9592
107.6	0.409	0.402	0.7537	0.8269	0.8829	0.9367
107.6	0.411	0.405	0.7557	0.8255	0.8839	0.9350
107.6	0.464	0.482	0.7966	0.7898	0.9041	0.9160
107.1	0.522	0.567	0.8473	0.7483	0.9441	0.8990
106.0	0.632	0.718	0.9206	0.6520	0.9755	0.8546
104.2	0.740	0.836	0.9730	0.5673	0.9985	0.8262
102.9	0.829	0.907	0.9866	0.5090	0.9976	0.8216
101.8	0.900	0.951	0.9893	0.4732	0.9933	0.8464
200 mm. of Hg						
62.8	0.055	0.0235	0.5027	0.9524	0.8073	0.9703
66.5	0.168	0.0835	0.4970	0.8880	0.7411	0.9405
68.9	0.278	0.177	0.5736	0.8412	0.7982	0.9281
69.8	0.320	0.223	0.6034	0.8198	0.8147	0.9222
71.2	0.396	0.327	0.6713	0.7580	0.8551	0.8982
72.3	0.536	0.548	0.7925	0.6332	0.9104	0.8476
71.4	0.637	0.703	0.8900	0.5510	0.9641	0.8168
70.5	0.713	0.803	0.9464	0.4800	0.9906	0.7892
69.4	0.796	0.883	0.9774	0.4156	0.9984	0.7706
69.2	0.812	0.896	0.9765	0.4023	0.9961	0.7973
68.2	0.900	0.950	0.9774	0.3774	0.9830	0.8506
70 mm. of Hg						
38.4	0.094	0.031	0.4526	0.9748	0.7488	0.9895
43.3	0.244	0.110	0.4781	0.8282	0.7172	0.9190
44.5	0.291	0.157	0.5395	0.8003	0.7787	0.9102
47.0	0.392	0.287	0.6447	0.7077	0.8584	0.8709
48.2	0.496	0.448	0.7466	0.6284	0.9159	0.8448
48.5	0.598	0.624	0.8493	0.5323	0.9610	0.8102
47.4	0.734	0.816	0.9607	0.4139	1.0089	0.7692
46.3	0.826	0.900	0.9906	0.3560	1.0112	0.7730
45.7	0.907	0.953	0.9872	0.3216	0.9940	0.8327

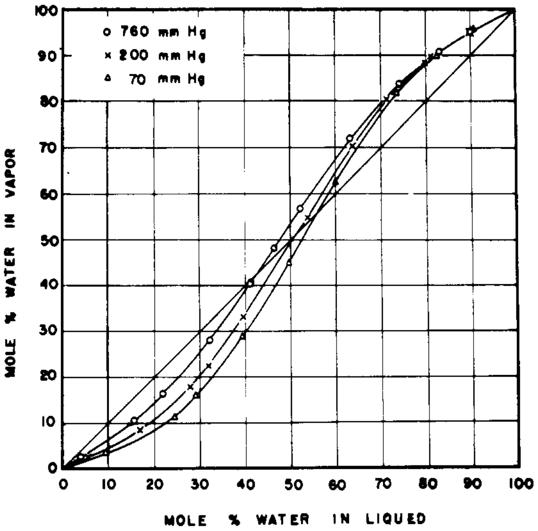

Figure 2. $x - y$ plot for water–formic acid

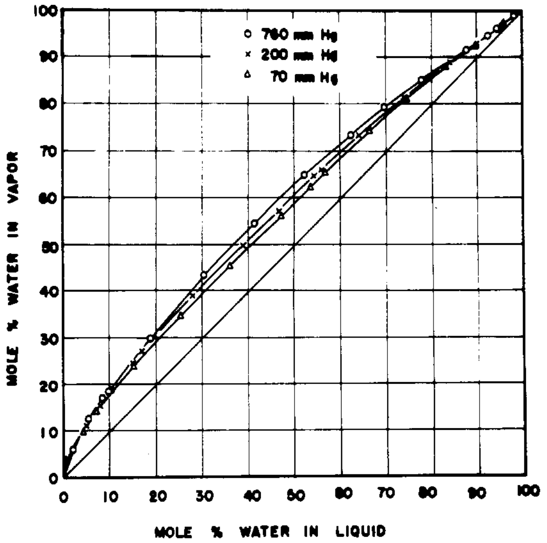

Figure 3. $x - y$ plot for water–acetic acid

maximum boiling azeotrope, the composition of which decreases in water content with increasing total pressure. The azetropic data for the water–formic acid system read from Figure 2 are summarized in Table IV.

The $x - y$ data for the water–acetic acid system plotted in Figure 3 indicate that there is no azeotrope for this system. Over the range of x between 0.03 and 0.916, the relative volatility of water to acid decreases with decreasing pressure. Difficulties are involved in the accurate determination of terminal relative volatilities. Figure 4 shows that the water–propionic acid system forms the minimum boiling azeotrope at pressures above about 100 mm. of Hg and that the relative volatility of water to acid increases with decreasing pressure over the range of x below the azeotropic compositions. The azeotropic data read from Figure 4 are summarized in Table V.

Table II. Data for Water–Acetic Acid System

t ° C.	x_W	y_W	δ_W	δ_A	γ_W	γ_A
760 mm. of Hg						
116.5	0.022	0.058	1.506	1.012	2.482	0.994
114.6	0.054	0.123	1.382	1.030	2.167	0.994
113.4	0.086	0.168	1.233	1.050	1.872	1.002
113.5	0.099	0.183	1.163	1.042	1.745	1.003
113.1	0.101	0.188	1.186	1.050	1.775	1.000
110.6	0.189	0.298	1.093	1.096	1.514	1.038
107.8	0.303	0.433	1.088	1.125	1.390	1.083
106.1	0.413	0.545	1.064	1.132	1.273	1.141
104.4	0.522	0.649	1.064	1.137	1.210	1.208
103.1	0.624	0.735	1.055	1.146	1.151	1.307
102.3	0.696	0.792	1.049	1.140	1.120	1.434
101.6	0.778	0.851	1.031	1.141	1.076	1.591
100.8	0.876	0.914	1.012	1.206	1.030	1.918
100.5	0.923	0.944	1.003	1.287	1.012	2.160
100.4	0.945	0.960	0.999	1.287	1.005	2.330
100.1	0.985	0.989	1.000	1.314	1.000	2.860
200 mm. of Hg						
77.7	0.011	0.0385	2.160	1.064	4.100	1.018
75.9	0.050	0.111	1.480	1.101	2.380	1.032
75.3	0.078	0.153	1.343	1.100	2.109	1.029
73.6	0.148	0.246	1.218	1.142	1.784	1.052
73.2	0.168	0.272	1.208	1.148	1.740	1.055
71.7	0.280	0.391	1.108	1.175	1.475	1.098
70.6	0.389	0.499	1.073	1.197	1.334	1.151
69.8	0.467	0.573	1.062	1.205	1.270	1.202
69.2	0.543	0.647	1.059	1.198	1.219	1.260
69.0	0.560	0.662	1.060	1.200	1.198	1.270
68.1	0.642	0.734	1.064	1.208	1.168	1.375
67.7	0.742	0.816	1.040	1.169	1.112	1.522
67.2	0.842	0.888	1.019	1.191	1.039	1.820
67.0	0.901	0.929	1.006	1.216	1.022	2.113
66.5	0.955	0.969	1.009	1.188	1.016	2.653
70 mm. of Hg						
53.1	0.006	0.0365	3.943	1.052	4.783	1.017
52.1	0.0435	0.0965	1.512	1.075	2.506	1.021
51.2	0.072	0.140	1.386	1.109	2.236	1.030
49.8	0.152	0.237	1.190	1.151	1.776	1.058
48.7	0.254	0.347	1.102	1.172	1.524	1.096
47.9	0.360	0.453	1.056	1.187	1.367	1.136
47.3	0.471	0.561	1.031	1.186	1.246	1.191
46.7	0.534	0.622	1.040	1.193	1.222	1.259
46.5	0.566	0.653	1.038	1.183	1.205	1.317
45.9	0.663	0.742	1.043	1.175	1.160	1.419
45.6	0.744	0.811	1.031	1.148	1.106	1.486
45.2	0.831	0.878	1.015	1.138	1.059	1.759
45.0	0.896	0.925	1.005	1.150	1.036	2.067
44.6	0.959	0.973	1.010	1.072	1.015	2.532

Table III. Data for Water–Propionic Acid System

t ° C.	x_W	y_W	δ_W	δ_A	γ_W	γ_A
760 mm. of Hg						
131.8	0.040	0.252	2.242	1.082	2.852	0.9973
121.1	0.115	0.471	2.018	1.150	2.382	0.9904
113.2	0.232	0.633	1.738	1.222	1.952	1.059
107.3	0.382	0.733	1.487	1.380	1.612	1.211
101.0	0.758	0.882	1.121	1.992	1.156	2.060
99.9	0.892	0.925	1.033	2.965	1.058	3.462
99.8	0.950	0.950	0.9934	4.293	1.016	5.542
99.9	0.979	0.974	0.9988	5.286	1.002	7.895
200 mm. of Hg						
95.0	0.033	0.253	2.418	1.050	3.215	0.9721
85.4	0.100	0.507	2.305	1.116	3.161	1.219
75.2	0.278	0.704	1.734	1.312	2.189	1.421
71.4	0.417	0.778	1.505	1.451	1.814	1.617
67.9	0.724	0.880	1.141	1.958	1.214	1.970
67.7	0.753	0.888	1.112	2.061	1.174	2.040
66.9	0.891	0.929	1.022	3.065	1.042	2.757
66.4	0.951	0.956	1.005	4.328	1.011	3.220
66.4	0.980	0.978	0.9980	5.301	1.000	4.770
70 mm. of Hg						
71.7	0.029	0.240	2.299	1.030	3.154	0.9536
63.2	0.072	0.459	2.579	1.150	4.414	1.220
50.6	0.290	0.736	1.870	1.407	2.709	1.476
45.5	0.683	0.875	1.212	1.944	1.514	1.976
44.7	0.887	0.930	1.034	3.217	1.078	3.074
44.5	0.951	0.959	1.008	4.371	1.021	3.823
44.5	0.981	0.9825	1.002	4.812	1.004	4.179

Table IV. Azeotropic Data for the Water–Formic Acid System

Pressure, mm. of Hg	Boiling Pt. ° C.		Composition of Azeotrope		Boiling Temp. of Azeotrope, ° C.
	Water	Acid	Mole % water	Wt. % water	
760	100.0	100.8	42.4	22.4	107.6
200	66.5	60.9	51.6	29.5	72.3
70	44.5	35.5	56.6	33.8	48.6

Table V. Azeotropic Data for the Water–Propionic Acid System

Pressure, mm. of Hg	Boiling Point, ° C.		Composition Azeotrope of		Boiling Temp. of Azeotrope ° C.
	Water	Acid	Mole % water	Wt. % water	
760	100.0	141.1	95.0	82.2	99.8
200	66.5	102.8	96.5	87.2	66.4

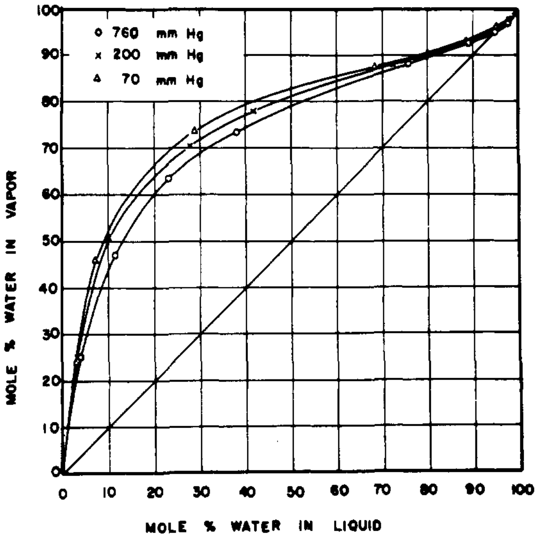

Figure 4. x–y plot for water–propionic acid

DISCUSSION

Water–Formic Acid System. Values of the coefficient of deviation from the Raoult's law, δ, are given in Table I as well as the true activity coefficient, γ, with allowance for the association of the acid in the vapor phase. Calculations based on the δ values indicated that the data are inconsistent with the Herington criterion, but similar calculations with the activity coefficient γ are consistent (Table VI). A similar conclusion was reached by Herington with the data of Marek and Standart (*10*) on the water-acetic acid system.

Compared with the present data, the previous data of Othmer (*12*) on the same system at 750 mm. of Hg. give lower values of y for the range of x below the azeotrope composition and higher values of y for the range of x above the azeotrope composition, probably because of defects in the liquid recirculation-type equilibrium still. The data of Chalov (*2*) and of Sheinker (*15*) on the equilibrium and azeotropic composition at reduced pressures do not appear to be very reliable. The azeotropic compositions obtained in the present work agree well with those in the literature (*9*).

Table VI. Checking Consistency of Data for the Water-Formic Acid System

Pressure, mm. of Hg	$D\delta$	D	J
760	22.3	3.36	3.06
200	29.3	5.41	5.40
70	29.6	5.90	6.37

The pressures at which the azeotrope will disappear can be estimated by plotting the logarithms of the vapor pressure of azeotropes, given in Table IV, and those of water and formic acid against the logarithms of the corresponding water vapor pressure, on a Cox chart. The straight line for the azeotrope intersects with the straight line for formic acid at about 2700 mm. of Hg and with the straight line for water at a pressure around 10^{-3} mm. of Hg. This indicates that the azeotrope will disappear on the acid side at about 2700 mm. of Hg and on the water at an unpractical pressure of 10^{-3} mm. of Hg.

Water-Acetic Acid System. Values of the coefficient of deviation from the Raoult's law δ and the activity coefficients with allowance for association of the acid γ are given in Table II. Figures 5 and 6 show values of δ and γ plotted against the liquid composition x, respectively. Again the calculations based on δ values do not satisfy the Herington criterion, whereas similar calculations with the γ values indicate that the data are consistent with the Herington criterion (Table VII).

There are a number of data on this system at the atmospheric pressure. The present data at the atmospheric pressure agree well with the data of Perry (*3*) for the values of x above 0.3 and with the data of Altsheler *et al.* (*1*) for the lower values of x. Three sets of isobaric data on this system at pressures including reduced pressures are available, Gilmont and Othmer (*4*), Othmer *et al.* (*13*), and Rick *et al.* (*14*). The latter report was not accessible to the authors. The data of Gilmont and Othmer seem unreliable in view of the fact that their data at 760 mm. of Hg deviate considerably from most of the data in the literature at the same pressure. The data of Othmer *et al.* are somewhat better, but data for x below 0.3 are completely lacking. To compare the accuracy of the data of Othmer *et al.* with that of the present data the values of $(y - x)$ were plotted against x. Curves for the present data show more smoothness and regularity than those for the data of Othmer *et al.* The plots of log δ *vs.* x for the present data also show more regularity than those for the data of Othmer *et al.*

Water–Propionic Acid System. Again with this system, the activity coefficients with allowance for the association of the acid conform better to the Heringron criterion than the coefficients of deviation from the Raoult's law (Table VIII).

All of the isobaric data available in the literature on this system are for the atmospheric pressure. Comparison

Table VII. Checking Consistency of Data for the Water–Acetic Acid System

Pressure, mm. of Hg	$D\delta$	D	J
760	39.0	5.00	7.28
200	38.2	1.58	5.96
70	24.6	2.02	4.96

Table VIII. Checking Consistency of Data for the Water–Propionic Acid System

Pressure, mm. of Hg	$D\delta$	D	J
760	36.0	13.5	16.5
200	27.2	12.0	16.0
70	26.7	13.0	15.7

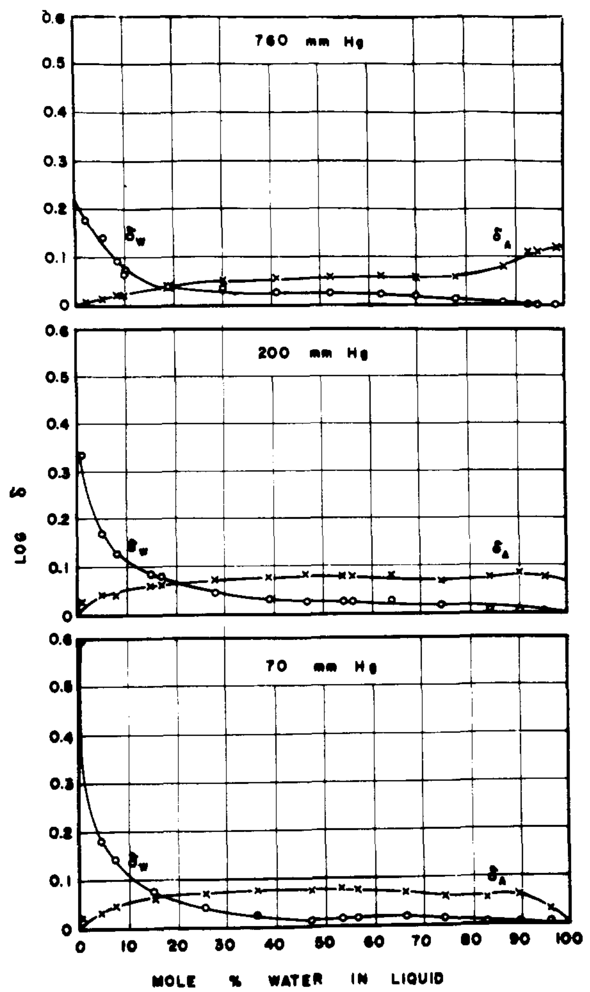

Figure 5. Coefficient of deviation from Raoult's law, water–acetic acid

of the present data with the atmospheric data of Othmer (*12*) taken with a liquid recirculation-type still shows that Othmer reported lower values of y for the values of x below 0.4 and slightly higher values of y for x above 0.4.

For the water-acetic acid and water-propionic acid systems, Hansen *et al.* (*6*) reported isothermal data at 25° C. from partial pressure measurement experiments. They correlated the activity coefficients with allowance for association of the acids with the modified Van Laar equation. Since the present data are isobaric and not isothermal and the standard states for the activity coefficients are temperature dependent, there are no reasons to suppose that the present data should fit the Van Laar equation. There is no evidence that with a recirculation-type apparatus the retention time for vapor is long enough to attain the association equilibria. The final conclusion on the consistency of the data should be deferred until the rates of association of these fatty acids are studied.

NOMENCLATURE

D = function defined by Equation 11
$D\delta$ = function similar to D with δ in place of γ
f_A = fugacity of fatty acid
J = function defined by Equation 12
K = equilibrium constant
K_2 K_3 = equilibrium constants for the association of acid to form dimer and trimer, respectively, defined: $K_2 = p_2/(p_1)^2$; $K_3 = p_3/(p_1)^3$
N = normality

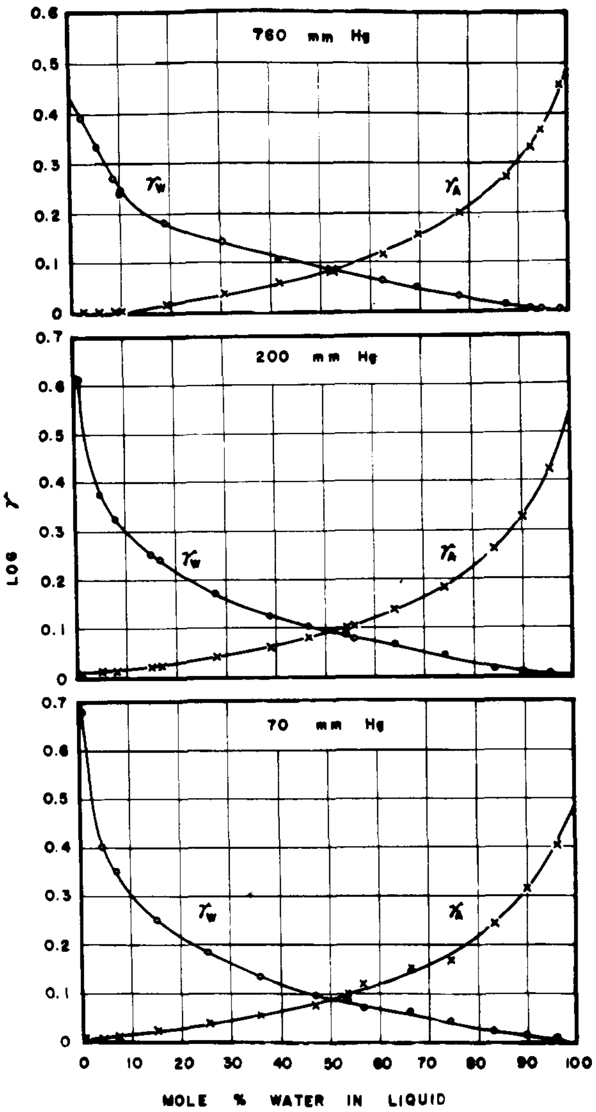

Figure 6. Activity coefficient vs. liquid composition, water–acetic acid

P^0 = vapor pressure of pure component, mm. of Hg
p = partial pressure, mm. of Hg
S = area above the axis of ln (γ_w/γ_A) plus the area below it, without regard to sign
T = temperature, ° K.
x = mole fraction of lower boiling component in liquid
y = mole fraction of lower boiling component in vapor
γ = activity coefficient defined by Equation 9
δ = coefficient of deviation from Raoult's law defined by Equation 1
π = total pressure, mm. of Hg

Subscripts

1, 2, 3, = monomer, dimer, trimer, respectively
A = fatty acid
W = water
i = i component

LITERATURE CITED

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Phase Equilibrium for System Methylethylketone, Cyclohexane, and Water

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Experimental solubility and tie-line data have been determined for the system cyclohexane, water, and methyl ethyl ketone. The reliability of the experimental results were assessed by the correlations of Othmer and Tobias, and Hand; in addition, a distribution curve was predicted thermodynamically and was compared with the experimental distribution curve. The results were satisfactory in all experiments.

THE SEARCH for a suitable liquid system possessing Type II phase equilibria for studying a solvent extraction problem resulted in consideration of the methyl ethyl ketone (MEK)-cyclohexane–water system. This system is similar to those of methyl ethyl ketone–water with either of *n*-hexane or *n*-heptane which were studied by Treybal and Vondrak (*9*). However, this system presented the challenge of separating by solvent extraction two organic liquids which formed an azeotrope and also had practically the same vapor pressure–temperature relation. Further points that commended the system: Although it is one of low interfacial tension, the rate of coalescence of the phases was rapid enough that the system could be used in extraction column studies, and finally, the large difference in the boiling point between methyl ethyl ketone–water permits easy regeneration of the ketone from the extract phase. Hence the phase equilibria were investigated at 25° C. and 1.0 atmosphere pressure and the results obtained are reported below.

EXPERIMENTAL

Materials. The methyl ethyl ketone and cyclohexane were distilled in a 50-tray Oldershaw fractionating column operating with a 10 to 1 reflux ratio. Fractions having the physical properties given in Table I were collected for the phase equilibrium experimental work. Water used was distilled water with the usual physical properties and collected from an all-glass still.

Determination of Solubility Curves. Ternary solubility curves were determined by cloud point titrations using the cell and the method recommended by Smith and Bonner (*7*). In this series of experiments, homogeneous mixtures of the ketone and hydrocarbon were placed in the cell which was maintained at 25° C. The contents were agitated and titrated with distilled water until the cloud point was observed.

Cyclohexane is completely immiscible with water and aqeuous solutions of the ketone in water. Therefore, the aqueous phase is a binary containing no cyclohexane, so that the results presented in Table II give the solubilities of the three components in the organic phase only. In each case the results reported are the mean of two estimations, but scatter was negligible and never greater than 0.1%. Four determinations were made of the solubility of methyl ethyl ketone in water, and the maximum variation in the titration was 0.02 ml. Thus, 15.0 ml. of water required 5.80 ml. of the ketone to produce a turbidity corresponding to a solubility of 23.7% methyl ethyl ketone in water. A solubility of 35.0% is reported in Perry (*2*), and for this reason four estimations were carried out.

In each determination the titration was performed slowly so that the contents of the cell were always at 25.0° C. Furthermore, a bead of mercury was placed in the exit throat of the cell so that there was no unmixed pocket in the cell. Finally the agitation was continued for about 15 minutes after the cloud point had been detected to ensure permanency of the faint turbidity. In the experiments estimating the solubility of methyl ethyl ketone in water, the agitation was continued for about 1.0 hour to be sure the turbidity was permanent.

Determination of Tie Lines. In these experiments heterogeneous mixtures of methyl ethyl ketone, cyclohexane, and water were placed in the Smith-Bonner cell and agitated for 4 to 6 hours at 25° C. Following this, the agitation was stopped and mixture allowed to separate into two clear