Phase Equilibria in Acetic Acid–Diethylketone–Water System

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An experimental study was made of the vapor-liquid and liquid-liquid equilibrium in the acetic acid–diethylketone–water system at 50°, 60°, and 70°C. Isothermal vapor-liquid equilibria for the binary systems were determined in two types of vapor-recirculating stills. Isothermal liquid-liquid equilibria were determined for the ternary system. The experimental data are presented here.

The acetic acid-diethylketone-water system exhibits marked nonideality. The two acetic acid binaries of this system are miscible in all proportions and do not form azeotropes. The water-diethylketone binary is relatively immiscible, highly nonideal and forms a heteroazeotrope. The ternary of this system contains a region of two coexisting liquid phases. Isothermal vapor-liquid equilibria have been determined for the acetic acid–water system at 25°C by Hansen et al. (*5*) and at 70°, 80°, and 90°C by Arich and Tagliavini (*1*).

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EXPERIMENTAL

Vapor-liquid equilibrium measurements on the two acetic acid binaries, determination of the heteroazeotrope, and measuring the compositions of the coexisting liquid phases of the ternary were the experimental objectives of this investigation.

The acetic acid was Baker reagent grade, assaying at 99.9% by weight, and was used without further purification. The water used was deionized, distilled, and degassed by boiling. Diethylketone was Matheson-Coleman and Bell practical grade, distilled in a 40-plate Oldershaw column at a 10–1 reflux ratio. The first light-boiling portion of about 10% of the starting volume was discarded, and a 70% cut was removed and saved. This was then dried over a 5-Å molecular seive. Analysis by hydrogen ionization chromatograph showed no visible organic impurity. This represents a probable impurity of less than 0.001%.

Vapor-Liquid. Two different types of vapor-recirculating stills were used in this investigation. A still similar to one designed by Scatchard et al. (*6*) was used for runs involving only one liquid phase. This apparatus has two boilers, the bottom one heated with an external electrical heater. Vapors leave this boiler and enter the second boiler through a Cottrell pump which discharges an equilibrium mixture of liquid and vapor onto the thermowell. The original design was modified to prevent liquid buildup in the second chamber through addition of an overflow line back to the first boiler as shown in Figure 1.

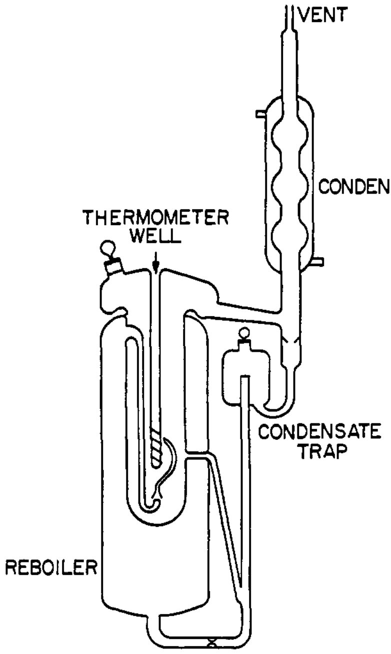

Figure 1. Modified Scatchard equilibrium still

For operation, the still was charged with the desired mixture and the pressure reduced to the expected boiling point. As boiling proceeded, the pressure was adjusted to maintain the desired temperature. When equilibrium was reached, no further adjustment in pressure was required. Boiling was continued for 30 min, after which the heater was turned off, and nitrogen was bled rapidly into the still. Samples of liquid were removed from the second boiler and from the condensate receiver.

For the diethylketone–water system, the still used was designed specifically by Hands and Norman (*4*) for systems whose condensate forms two liquid phases (Figure 2).

The still was charged with 500–600 cc of liquid, and the pressure was reduced to that of the expected boiling point. When boiling began, the pressure was adjusted so as to maintain the desired temperature. The still was equilibrated, with all the condensate being returned directly to the boiler, and the pressure and temperature were recorded. The distillate receiver was then evacuated to system pressure, and the condensate diverted into the receiver. During this time, the pressure was adjusted to maintain as near isothermal operation as possible. After the sample was collected, the condensate was again diverted to the pot. When the system returned to equilibrium, the final pressure was recorded.

With two liquid phases present in the still pot, the still pressure and the composition of each phase remains constant, although the relative amounts of each phase may change. This provides a stable condition for determining the vapor

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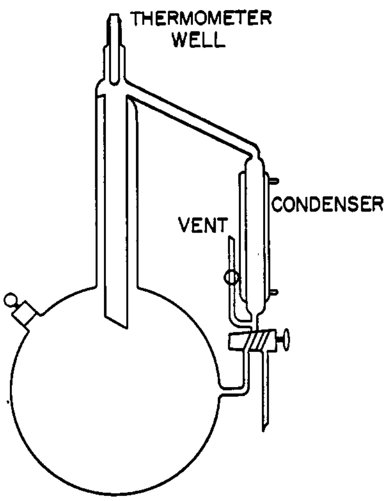

Figure 2. Hands and Norman equilibrium still

pressure of the two-phase region and allows the removal of a sufficient sample of heteroazeotrope to determine the relative volumes of both phases.

Pressures were controlled by means of a Cartesian manostat to ±0.1 mm Hg. A slight amount of dried nitrogen was bled through the manostat to the vacuum pump to permit proper operation of the pressure controller. The pressure was measured with a mercury manometer and the meniscus viewed with a cathetometer which could be read to 0.05 mm Hg. Ambient temperature was recorded, and the mercury column height was corrected for temperature and for acceleration constant to obtain absolute pressure.

Temperatures were measured with a total immersion thermometer inserted in a mercury-filled well. The thermometer was standardized and calibrated to 0.01°C. The readings were taken with thermometer NP16491 immersed to 50°C. The magnitude of the stem correction ranged to 0.21°C.

Liquid-Liquid. The solubility envelope for the system water-diethylketone-acetic acid was determined by the cloud-point method in an apparatus similar to that described by Smith and Bonner (7). The apparatus was jacketed, and water from a constant-temperature bath circulated through it (Figure 3).

Figures 4 and 5 present x-y diagrams of the systems at 70°C.

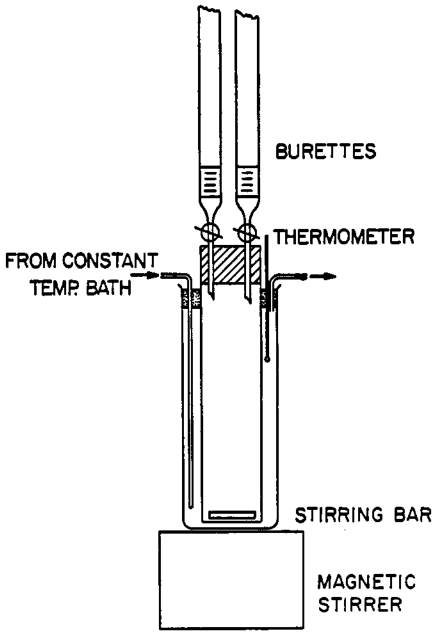

Figure 3. Cloud-point titrator

Tie lines were determined by titration for acetic acid of coexisting phases which had achieved equilibrium for 24 hr in a constant-temperature bath. These were then located on the solubility envelope (Figure 6).

ANALYSIS

Compositions of the binary acetic acid systems were determined by titration of weighed samples with 0.1N sodium hydroxide to the phenolphthalein end point.

In the miscible region of the diethylketone–water system refractive-index determinations were made on known synthetic

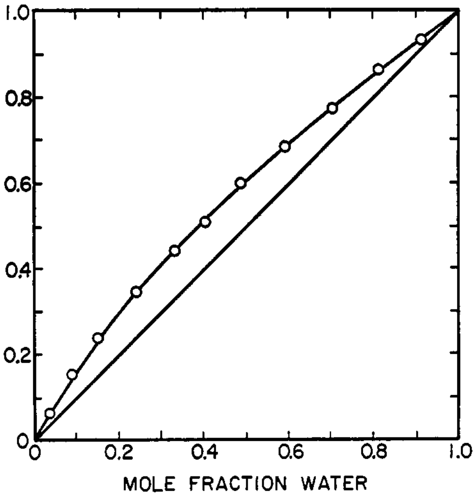

Figure 4. x-y Diagram of water–acetic acid system at 70°C

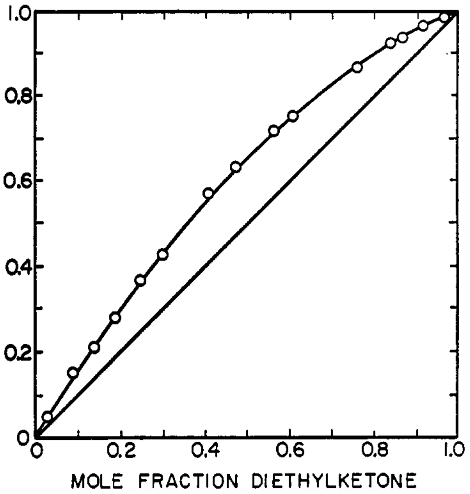

Figure 5. x-y Diagram of diethylketone–acetic acid system at 70°C

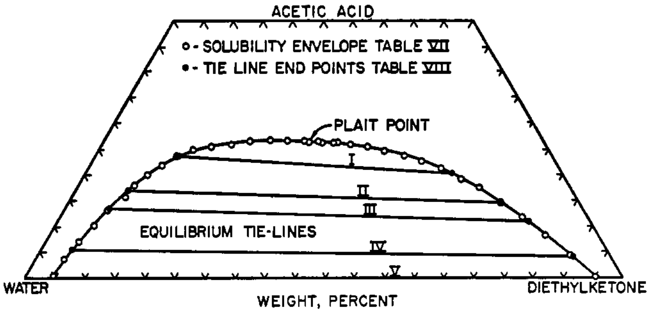

Figure 6. Composition diagram diethylketone–water–acetic acid system at 70°C

solutions. In the water-rich region, this proved to be an extremely sensitive method of analysis, and the data are given in Table I. A plot of these data indicates a precision of ±0.02 wt % diethylketone or 0.00005 mol fraction.

This method was not suitable in the diethylketone-rich region and for this portion of the vapor-liquid equilibria, pot bottom composition was determined by charging the still with a known quantity of diethylketone and water and adjusting for the amount of condensate removed.

When two liquid phases were present in the condensate, the sample was placed in a constant-temperature bath, agitated periodically, and the phases were allowed to separate. The volume of each phase was determined. The overall composition was easily determined, since the density and composition of each phase were known from literature values (*3*) and through determinations made during this investigation.

The liquid composition in the diethylketone-rich region is subject to cumulative errors in analyses of vapor. Furthermore, since the liquid composition is changing as the vapor sample is being collected, true equilibrium is not attained. The vapor composition is regarded as being in equilibrium with the arithmetic average of the initial and final liquid compositions. This is not accurate but is reasonable. A plot of vapor pressure as a function of vapor and liquid compositions gives a reasonably smooth curve. The data for the 70°C isotherm are included in Table II. See also Tables III–VIII and the 10 tables deposited with the American Chemical Society Microfilm Depository Service.

Table I. Refractive Index vs. Composition

System: diethylketone-water

n^{30}_D	Wt % DEK
1.33196	0.00
1.33284	0.81
1.33361	1.60
1.33436	2.38
1.33509	3.14
1.33583	3.90
1.33655	4.64
1.33668[a]	4.78

[a] Saturation value—weight percent determined by extrapolation.

Table II. Vapor-Liquid Equilibria Data

System: diethylketone–water at 70°C

Wt % diethylketone			*P*, mm Hg	
Liquid				
Initial	Final	Vapor	Initial	Final
0				233.7
[a]	0.005	0.09		234.5
0.45	0.10	7.3	269.6	241.8
0.82	0.45	19.6	309.8	269.6
1.05	0.82	53.9	313.2	309.8
1.51	1.05	71.4	358.1	313.2
2.45	1.51	81.8	388.7	358.1
4.54[b]		84.36		462.5
95.80[b]		84.36		462.5
96.10	96.37	85.08	453.7	441.4
96.37	96.54	87.88	441.4	435.6
96.54	96.73	87.53	435.6	427.9
96.73	96.90	86.92	427.9	418.5
96.90	97.17	87.95	428.1	420.7
97.17	97.73	88.12	420.7	400.5
97.73	97.87	92.45	400.5	396.8
97.87	98.41	90.75	396.8	393.2
98.41	98.60	91.95	381.2	355.6
98.60	98.96	95.89	337.3	320.6
98.96	99.13	95.88	320.6	309.5
99.13	99.25	97.30	309.1	299.5
100.00				260.3

[a] Run to equilibrium on Scatchard still. [b] Solubility limit.

Table III. Determination of Heteroazeotrope Compositions

System: water–diethylketone

Temp, °C	Sample no.	Vol. of equil. phase, ml[a]	
		H_2O layer	DEK layer
50	1	1.14	9.06
	2	0.81	6.44
	3	1.17	8.89
60	1	1.26	9.34
	2	1.26	9.31
70	1	1.37	9.63
	2	1.26	9.04
	3	1.25	8.75
	4	1.34	9.30
	5	1.30	9.20

[a] The distillate sample was allowed to reach equilibrium in a constant-temperature bath at 30°C. The volumes of the layers were then measured. The water layer contains 4.78 wt % diethylketone with a specific gravity of 0.9901. The diethylketone layer contains 98.17 wt % diethylketone with a specific gravity of 0.8108. The average of the runs gives the following compositions for the heteroazeotropes:

Temp	Y_W	Y_D	*P*, mm Hg
50°	0.445	0.555	195.0
60°	0.459	0.541	304.8
70°	0.470	0.530	462.5

Table IV. Specific Gravity and Refractive Index vs. Composition

System: diethylketone–acetic acid

Wt %, HAC	n^{30}_D	Specific gravity at		
		50°C	60°C	70°C
0.000	1.38758	0.7875	0.7779	0.7684
6.144	1.38717	0.7998	0.7901	0.7803
11.308	1.38656	0.8109	0.8022	0.7921
20.425	1.38528	0.8271	0.8172	0.8086
29.980	1.38376	0.8464	0.8368	0.8274
39.111	1.38213	0.8661	0.8557	0.8470
46.100	1.38069	0.8804	0.8700	0.8608
56.233	1.37863	0.9041	0.8938	0.8842
65.782	1.37656	0.9260	0.9188	0.9059
76.301	1.37408	0.9519	0.9414	0.9307
86.423	1.37187	0.9781	0.9672	0.9570
100.00	1.36839	1.0155	1.0050	0.9940

Table V. Vapor-Liquid Equilibria Data

System: diethylketone–acetic acid at 70°C

Wt %				*P*, mm Hg
Liquid		Vapor		
DEK	HAC	DEK	HAC	
100.00	0.00	100.00	0.00	260.3
97.45	2.55	99.08	0.92	259.5
93.62	6.38	97.44	2.56	245.7
90.04	9.96	95.44	4.56	245.2
88.23	11.77	94.39	5.61	242.1
81.96	18.04	90.41	9.59	232.2
68.76	31.24	81.25	18.75	216.6
64.69	35.31	78.25	21.75	211.3
56.29	43.71	70.95	29.05	203.5
49.92	50.08	65.49	34.51	194.2
38.24	61.76	51.10	48.90	178.1
32.34	67.66	45.02	54.98	173.8
25.22	74.78	35.35	64.65	166.9
18.95	81.05	27.07	72.93	160.1
12.44	87.56	19.92	80.08	152.9
4.44	95.56	6.87	93.17	144.6
0.00[a]	100.00	0.00	100.00	138.2

[a] Extrapolated value.

Table VI. Vapor-Liquid Equilibria Data

System: water–acetic acid at 70°C

Wt %				
Liquid		Vapor		P,
Water	HAC	Water	HAC	mm Hg
0.00[a]	100.00	0.00	100.00	138.2
0.73	99.27	0.14	99.86	139.6
1.23	98.77	1.85	98.15	143.1
3.09	96.91	5.15	94.85	158.9
5.14	94.86	8.61	91.39	168.3
8.92	91.08	13.68	86.32	179.1
13.13	86.87	19.29	80.71	187.4
16.93	83.07	23.85	76.15	193.1
22.33	77.67	30.98	69.02	200.3
30.47	69.53	39.32	60.68	208.5
41.70	58.30	51.12	48.88	215.9
56.81	43.19	65.28	34.72	223.6
75.85	24.15	81.41	18.59	228.6
100.00	0.00	100.00	0.00	233.7

[a] Extrapolated value.

Table VII. Ternary Solubility Data

System: water–acetic acid–diethylketone

Wt % at 70°C			
Water	HAC	Water	HAC
95.46	0	37.14	26.37
91.32	3.80	34.84	26.16
87.13	7.25	32.28	25.90
83.24	10.39	29.71	25.46
79.58	13.24	27.18	24.79
75.22	15.64	24.62	23.91
72.58	18.12	22.07	22.77
69.30	20.18	19.69	21.31
65.95	21.95	17.38	19.54
62.69	23.47	15.22	17.39
59.28	24.64	13.13	14.86
55.75	25.51	10.91	11.94
52.21	26.06	8.82	8.53
48.87	26.43	6.61	4.58
45.63	26.57	4.20	0.00
42.59	26.58		
39.94	26.58		
37.36	26.42		
35.08	26.27		
39.41	26.44		

ACCURACY

The limits of error in the experimental data have been estimated to be: pressure, ±0.1 mm of mercury, and temperature, ±0.02°C.

Table VIII. Equilibrium Solubility Data

System: water–acetic acid–diethylketone

Water-rich layer, wt % at 70°C			DEK-rich layer, wt % at 70°C		
Water	HAC	DEK	Water	HAC	DEK
62.60	23.31	14.09	18.15	20.15	61.8
62.04	23.66	14.30	18.67	20.53	60.8
74.28	16.92	8.80	12.95	14.55	72.5
74.05	17.05	8.90	12.93	14.47	72.6
79.38	13.32	7.30	10.44	11.06	78.5
79.16	13.44	7.40	10.39	11.01	78.6
89.47	5.33	5.20	6.32	4.18	89.5
89.44	5.36	5.20	6.21	4.09	89.7

The accuracy of composition determination varies with the type of analysis used. For the acetic acid–binary systems, +0.002 mol fraction; for the diethylketone–water system in the region of 0–4.8 wt % diethylketone, ±0.00005 mol fraction. In the diethylketone–water system where two liquid phases exist in the condensate (most of the region), the accuracy of the vapor-phase composition is estimated to be ±0.02 mol fraction. Since the heteroazeotrope was determined by averaging of multiple samples, the accuracy of this determination is ±0.01 mol fraction.

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