Solubility Data for Ternary Liquid Systems

Acetic Acid and Formic Acid Distributed between Chloroform and Water

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LIQUID-LIQUID equilibria were determined at 25° C. and 1 atm. pressure for two Type I ternary systems: acetic acid-chloroform-water (*A-C-W*) and formic acid-chloroform-water (*F-C-W*). Mutual solubility curves were determined by turbidity titration. Tie lines of both systems were obtained by volumetric analyses. Plait points, evaluated according to methods of Othmer and Tobias (*2*) and of Hand (*1*), are in weight per cent; for the system acetic acid-chloroform-water, $A = 36.5$, $C = 52.2$, $W = 11.3$, and for the system formic acid-chloroform-water, $F = 42.8$, $C = 56.0$, $W = 1.2$, where A, C, F, and W represent acetic acid, chloroform, formic acid, and water, respectively. Besides engineering importance of these systems, their solubility data allow analysis of unknown mixtures or solutions.

The methods of determination of mutal solubilities and distribution coefficients of ternary liquid systems have been discussed (*2, 3*); with acetic acid-chloroform-water, titra-

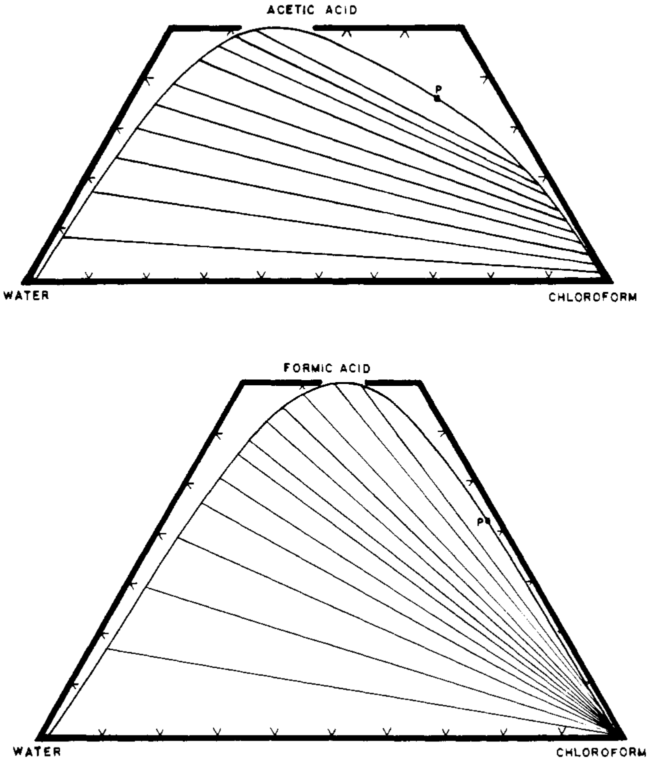

Figure 1. Mutual solubility curves and tie lines for acetic acid–chloroform-water and formic acid–chloroform-water in weight per cent at 25° C.

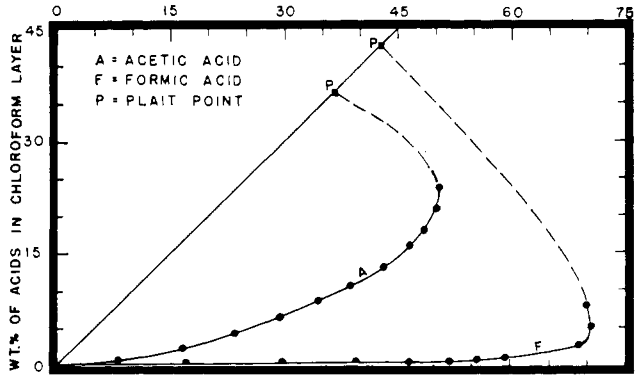

Figure 2. Distribution of acetic acid and of formic acid between water and solvent layers in weight per cent at 25° C.

Table I. Mutual Solubility Data for Ternary Systems

(760 mm. Hg. weight per cent in systems at 25° C. and 760 mm. Hg.)

Acetic Acid–Chloroform-Water			Formic Acid–Chloroform-Water		
Acetic acid	Chloroform	Water	Formic acid	Chloroform	Water
0.0	0.8	99.2	4.9	2.0	93.1
5.8	1.5	92.7	9.8	2.4	87.8
15.4	1.8	82.8	14.6	2.7	82.7
19.5	2.2	78.3	24.2	3.2	72.6
23.1	2.4	74.5	38.4	4.0	57.6
26.3	2.9	70.8	47.6	4.8	47.6
30.2	3.4	66.4	51.3	5.1	43.6
35.0	4.3	60.7	60.5	7.0	32.6
39.0	5.4	55.6	64.3	8.1	27.6
42.1	6.7	51.2	67.3	10.3	22.5
44.6	8.2	47.2	69.7	12.8	17.5
46.5	10.0	43.5	69.6	18.1	12.3
48.3	12.5	39.2	68.5	24.1	7.4
49.3	15.3	35.4	10.0	89.5	0.5
49.5	18.6	31.9	39.7	59.3	1.0
49.4	20.4	30.2	49.0	49.0	2.0
49.3	22.0	28.7	58.1	38.7	3.2
48.5	25.6	25.9	62.6	33.2	4.2
47.4	29.3	23.3	66.1	27.9	6.1
46.1	33.0	20.9	65.8	28.1	4.2
0.0	99.9	0.08			
14.7	84.1	1.2			
16.4	82.3	1.3			
21.4	76.4	2.2			
35.0	71.4	3.6			
29.4	64.7	5.9			
24.0	57.0	9.0			
37.3	50.8	11.9			
40.0	45.7	14.3			
42.1	41.4	16.5			
43.7	37.8	18.5			
45.1	34.8	20.1			
46.1	32.1	21.8			
47.1	29.8	23.1			
47.9	27.3	24.8			
48.5	25.2	26.3			
48.9	23.3	27.8			
49.4	20.1	30.5			
49.5	18.8	31.7			
49.4	16.6	34.0			
49.9	17.1	33.0			
49.8	20.0	30.2			
49.6	21.4	29.0			

Table II. Distribution Data and Densities of Ternary Systems of Acetic Acid–Chloroform-Water and of Formic Acid–Chloroform-Water

(Temperature, 25° C. Pressure, 760 mm. Hg.)

Chloroform Layer		Water Layer		Chlorofrom Layer		Water Layer	
Acetic acid, wt. %	Density, g./cc.	Acetic acid, wt. %	Density, g./cc.	Formic acid, wt. %	Density, g./cc.	Formic acid, wt. %	Density, g./cc.
0.71	1.4725	8.2	1.0108	0.077	1.4788	17.3	1.0415
2.3	1.4620	16.7	1.0220	0.17	1.4789	29.9	1.0738
4.4	1.4500	23.4	1.0325	0.31	1.4784	39.4	1.0984
6.5	1.4360	29.6	1.0413	0.47	1.4783	46.5	1.1145
8.7	1.4237	34.7	1.0507	0.67	1.4770	51.9	1.1335
10.9	1.4100	38.4	1.0584	0.89	1.4740	56.4	1.1360
13.3	1.3970	43.0	1.0677	1.12	1.4727	59.3	1.1565
15.9	1.3791	46.8	1.0753	2.98	1.4649	68.9	1.1981
18.4	1.3629	48.5	1.0868	8.32	1.4428	69.6	1.2459
21.0	1.3457	50.1	1.0996	5.40	...	70.6	...
24.5	1.3152	50.5	1.1181	...	...	...	...

tion of solution with solute was used (*3*), with formic acid-chloroform-water, individual solutions were synthetically prepared and used as titers to obtain sharper end points. Double-distilled water was used; and reagent grade acetic acid, formic acid, and chloroform were carefully fractionated with only the heart cut being used.

Solubility curves with tie lines of the two systems are drawn in Figure 1, with data in Table I. Conjugated phase data are in Table II, and Figure 2 illustrates distribution of the respective acids between the two phases. Densities have been also determined.

The plait point, where the two branches of the solubility curve merge, has the same composition for the water layer as for the chloroform layer, and may be evaluated by several methods with the aid of tie-line data. Since this point exists as one phase, its synthetic preparation confirms distribution data. The plait points of these two systems are indicated in Figure 1.

The effective concentration curves indicate the fraction of acid in the solvent layer on the solvent-free basis *vs.* the fraction of acid in the layer on the solvent-free basis. These curves are shown in Figure 3 and the data in Tables III and IV.

Table III. Effective Concentration Data for Conjugated Phases with Acetic Acid Distributed Between Chloroform and Water Phases at 25° C.

Acetic Acid in					
Water Phase			Chloroform Phase		
A	$A + W$	$\frac{A}{A+W}$	A	$A + W$	$\frac{A}{A+W}$
8.2	98.1	0.08	0.7	99.9	0.01
16.7	97.7	0.17	2.3	99.5	0.02
23.4	97.4	0.25	4.4	99.8	0.04
29.6	96.3	0.31	6.5	99.7	0.07
34.7	95.5	0.36	8.7	98.7	0.09
38.4	94.4	0.41	10.9	99.5	0.11
43.0	93.0	0.46	13.3	99.0	0.13
46.8	90.3	0.52	15.9	98.9	0.16
48.5	88.8	0.55	18.4	98.4	0.19
50.1	85.8	0.58	21.0	98.7	0.21
...	82.5	...	...	...	...
50.5	82.5	0.61	24.5	96.6	0.25
45.0	65.0	0.69	30.0	94.0	0.32
39.0	52.0	0.75	34.0	91.0	0.37
36.5	47.5	0.77	36.5	89.0	0.41

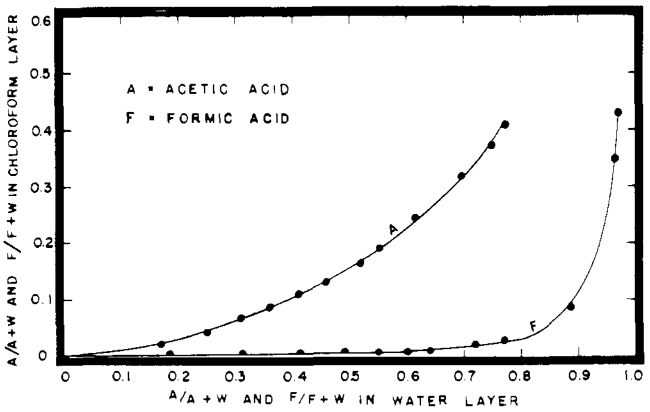

Figure 3. Effective concentration in both systems

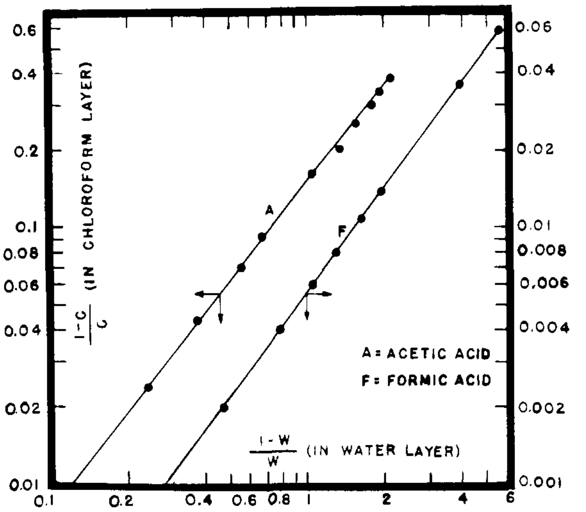

Figure 4. Plot of logarithmic coordinates of $\frac{100-C}{C}$ (in chloroform layer) *vs.* $\frac{100-W}{W}$ (in water layer) at 25° C.

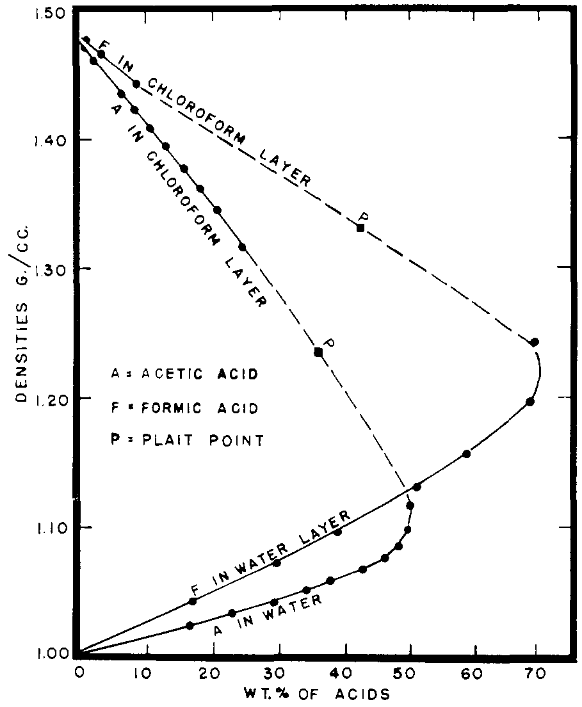

Figure 5. Densities at 25° C. of conjugated phases of both systems

Table IV. Effective Concentration Data for Conjugated Phases with Formic Acid Distributed Between Chloroform and Water Phases at 25° C.

Formic Acid in					
Water Phase			Chloroform Phase		
F	$F + W$	$\frac{F}{F+W}$	F	$F + W$	$\frac{F}{F+W}$
17.3	97.3	0.18	0.077	99.9	0.0008
29.9	96.6	0.31	0.17	99.7	0.0017
39.4	95.7	0.41	0.31	99.6	0.0031
46.5	95.5	0.49	0.47	99.6	0.0047
51.9	95.1	0.55	0.67	99.6	0.0067
56.4	94.2	0.60	0.89	99.4	0.0090
59.3	93.6	0.64	1.12	99.2	0.011
66.9	91.0	0.72	2.48	99.0	0.024
68.9	89.3	0.77	2.98	99.3	0.030
69.6	78.6	0.89	8.32	98.3	0.084
70.6	80.1	0.89	5.40	98.5	0.055
50.0	52.0	0.96	35.00	99.0	0.35
42.6	44.0	0.97	42.60	98.6	0.43

Straight lines are shown in Figure 4 by the plot on logarithmic paper according to the equation developed by Othmer and Tobias (2).

$$\log \frac{100 - W}{W} \text{ (in water layer) } = n \log \frac{100 - C}{C} \text{ (in chloroform layer) } + \text{ a constant}$$

Densities at 25° C. of the respective equilibrium layers were determined, and data are shown in Table II and in Figure 5.

ACKNOWLEDGMENT

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Phase Equilibria in Hydrocarbon Systems

Volumetric and Phase Behavior of Ethane–*n*-Pentane System

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A KNOWLEDGE of the volumetric and phase behavior of hydrocarbon mixtures is of value in connection with the production and refining of petroleum. Equilibrium data of this nature are essential to the evaluation and application of experimental results relating to the molecular transport of components under nonequilibrium conditions. Because information appears to be available concerning the volumetric or phase behavior of mixtures of ethane and *n*-pentane, the volumetric and phase behavior of the ethane–*n*-pentane system was studied at temperatures from 40° to 460° F. and for pressures up to 10,000 p.s.i.

Ethane has been investigated experimentally in detail. The volumetric behavior was carefully studied by Beattie and coworkers (*1*, *3*) and supplemented by other more recent investigations (*15*). The critical state has recently been carefully evaluated by Schmidt and Thomas (*30*) as well as by Beattie and coworkers (*2*). The phase behavior of the methane-ethane-*n*-pentane system was studied over a limited range of temperatures (*4*). The volumetric and phase behavior of mixtures of ethane with other hydrocarbons, as well as water, carbon dioxide, nitrogen, and hydrogen sulfide has been studied in some detail (*8, 9, 11, 13, 16, 20, 22, 24*). This listing of references is by no means exhaustive and has been included only to indicate the extent to which the characteristics of ethane as a pure substance and in mixtures have been investigated.

Likewise, *n*-pentane has been studied in some detail. Its volumetric and phase behavior was investigated over a reasonable range of pressures and temperatures (*26*). Shepard and coworkers (*31*) determined a number of the physical properties with accuracy at atmospheric pressure. The latent heat of vaporization (*23*), and the Joule-Thomson coefficients (*12*) and related coefficients (*6, 10*) have been measured along with the isobaric heat capacity of this gaseous hydrocarbon (*29*). The behavior of *n*-pentane in mixtures has been the subject of some study (*4, 6, 7, 10, 19, 25, 28, 32*).

APPARATUS AND METHODS

The equipment employed in this investigation was described in detail (*27*). A mixture of ethane and *n*-pentane was confined within a stainless steel pressure vessel. The volume of the chamber available to hydrocarbons was changed by introducing or withdrawing mercury in known amounts. Attainment of equilibrium was hastened by the use of a mechanical agitator, and the molal volume and pressure were determined for a series of states for each of a number of systematically chosen temperatures. The quantity of ethane and *n*-pentane introduced into the vessal was determined by weighing bomb techniques (*27*) with a probable uncertainty of not more than 0.05%.

The temperature of the sample was determined from that of a strongly stirred oil bath which surrounded the stainless steel pressure vessel. A stain-free platinum resistance thermometer was employed to measure the temperature of the oil bath. This instrument was compared with a similar instrument calibrated by the National Bureau of Standards. Intercomparison of three such calibrated instruments indicates that the temperature of the sample was related to the international platinum scale with an uncertainty of less than 0.03° F.

Pressures were measured by means of a piston-cylinder combination incorporated into a balance (*27*) which was calibrated against the vapor pressure of carbon dioxide at the ice point (*5*). Experience with this equipment (*17*) over a period of years indicates that the pressure of the sample was established with a probable error of 0.05% or 0.1 p.s.i., whichever was the larger measure of uncertainty. The total volume of the chamber available to hydrocarbons