Composition of Vapors from Boiling Binary Solutions

Systems Containing Formic Acid, Acetic Acid, Water, and Chloroform

A description of the equipment used in this study appears in the July 1960 issue of *Industrial and Engineering Chemistry* on page 625.

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VAPOR-LIQUID equilibria of the following binary systems have been investigated using a new adiabatic still, and data have been correlated by standard methods: formic acid–water, acetic acid–water; acetic acid–chloroform; formic acid–acetic acid.

Expermental determinations have been used with data of the binaries to develop the following ternary systems: acetic acid–chloroform–water; formic acid–chloroform–water; acetic acid–formic acid–water; acetic acid–formic acid–chloroform.

These data have been obtained in an effort to understand the operation of some industrially important azeotropic distillation systems which are described further in patent applications.

The binary vapor-liquid equilibrium data have been correlated thermodynamically by the logarithmic plotting technique of Othmer-Ricciardi-Thakar, and the consistency of the data have also been evaluated by the methods of Redlich and Kister and of Gilmont, Weinman, Kramer, Miller, Hashmall, and Othmer.

The phenomena of molecular association and the use of the pseudo molecular weights has been successfully applied in the thermodynamic interpretation of the vapor-liquid equilibria of the binary systems containing formic acid as one component. Moderate success has also been obtained with the systems containing acetic acid.

APPARATUS AND OPERATING PROCEDURE

The experimental equipment has been described (*9*), both for completely and partially miscible systems. The operating procedure was similar to that previously described (*7, 12*). Pressure was controlled at 760 ± 1 mm. of mercury by balancing a slight inflow of air against a slight withdrawal in a large surge bottle, regulated by a Cartesian manostat.

The still was charged with solutions of approximately the desired composition; and the pressure control system properly adjusted during the initial boil-up period. The system was allowed to run undisturbed to a steady state, as evidenced by constancy of the boiling temperature, followed by an additional 30 minutes at least at these conditions. Temperatures were measured with thermometers calibrated to 0.2° C., which were checked against thermometers calibrated by the National Bureau of Standards. Standard corrections were applied. At the termination of a run, boiler heat was turned off, the pressure control system was vented, and the condensate receiver stopcock turned to block off the recycle line. After preliminary drainage to waste, samples were withdrawn into pre-evacuated glass sample "bombs" connected directly to the still sample cocks or into vials thoroughly chilled in crushed ice. Samples were placed in a water bath maintained at 25 ± 0.1° C. prior to analysis. The still was then prepared for the next run.

Operation of the unit modified for partially-miscible systems differed slightly in the start-up and sampling procedure. Because the condensate receiver is positioned slightly higher than the main still body, liquid would not fill it completely without at the same time blocking the vapor path to the condenser unless the stirrer was functioning properly—i.e., giving a slight lifting action to maintain a full head of liquid in the receiver and out the overflow while sucking all liquid out of the inlet line. The recirculation system was first primed by filling the receiver with part of the total charge while operating the stirrer. The entire contents of the receiver was withdrawn into a special separatory funnel having a fine capillary bore stopcock and drainage tube which accurately separated the two layers. When the pot contained two layers of boiling liquid, samples of each were withdrawn immediately upon phase separation after ebullition ceased.

MATERIALS

U.S.P. grade chloroform, usually containing about 1% ethyl alcohol as a decomposition inhibitor, was purified by first washing with concentrated sulfuric acid followed by washing with potassium carbonate solution. The thoroughly washed material was then distilled in a glass batch-rectifying column, and the center cut taken as product. Glacial acetic acid was fractionated in the presence of acetic anhydride to yield an anhydrous product. Anhydrous grade formic acid was purified further by freezing out crystals from a center cut carefully distilled and fractionated. Laboratory de-ionized water was distilled twice before using. The analytical techniques are not described here (*3*).

VAPOR-LIQUID EQUILIBRIUM DATA

Binary Systems. Vapor-liquid equilibrium data for all of the binary systems are presented in Table I and Figures 1 to 6.

The formic acid–water system (Figure 1) is one of negative deviation from Raoult's law and has a maximum boiling azeotrope. The data agree well with that determined at a slightly lower pressure (*8*), and the observed azeotropic composition of 23.0 weight % agrees exactly with another published value (*2*).

Acetic acid–water data and formic acid–acetic acid data agree well with earlier results (*4,12*) and (*1*), respectively. Acetic acid–chloroform (Figure 4) and formic acid–chloroform (Figure 5) systems have not been previously reported. The latter exhibits positive deviations from Raoults's Law; and it is observed that the repulsive forces between formic acid molecules and chloroform molecules are almost sufficient to cause partial miscibility. A minimum-boiling azeotrope of 90 weight % chloroform exists at 59.1° C.

The chloroform-water system, of the partial-miscibility type, has solubility limits so low that total immiscibility is approached. These limits have been published and are as follows:

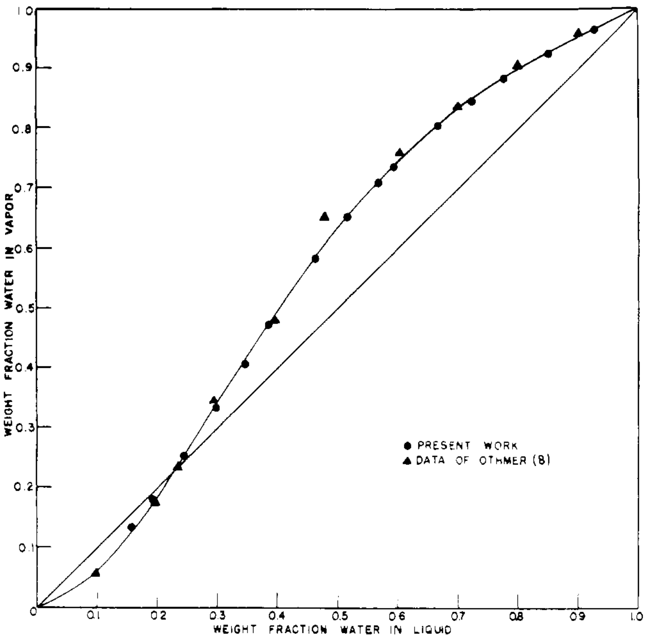

Figure 1. Formic acid–water

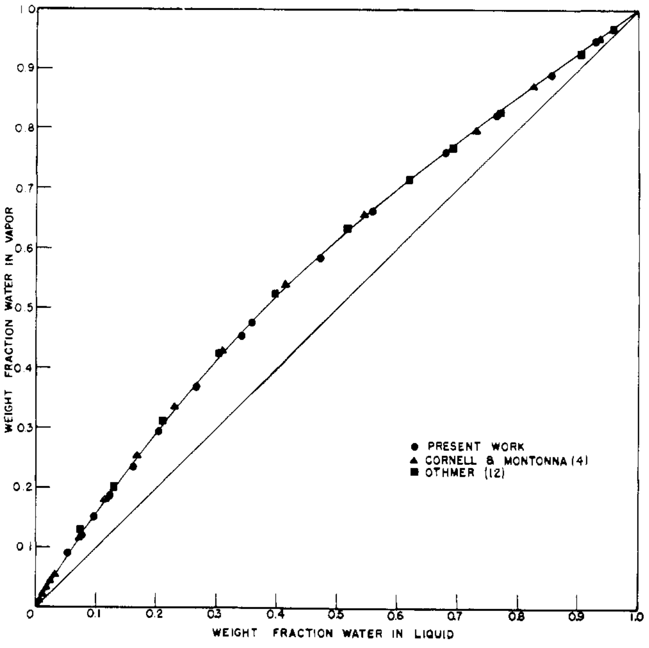

Figure 2. Acetic acid–water

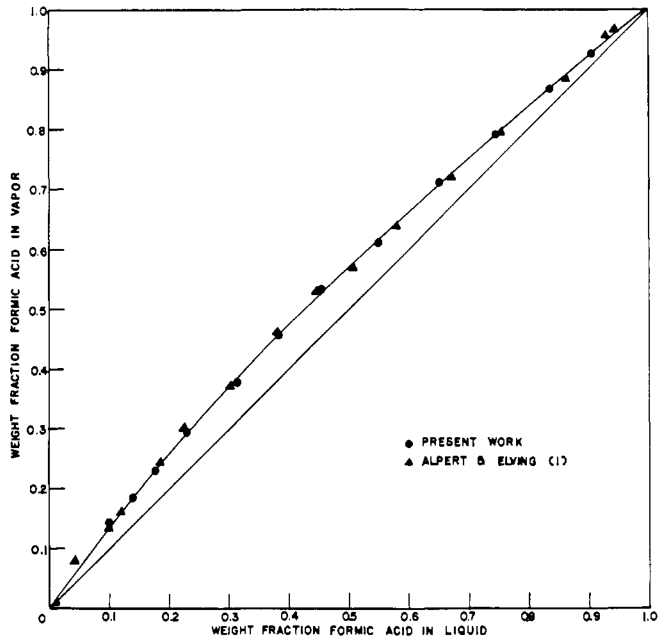

Figure 3. Formic acid–acetic acid

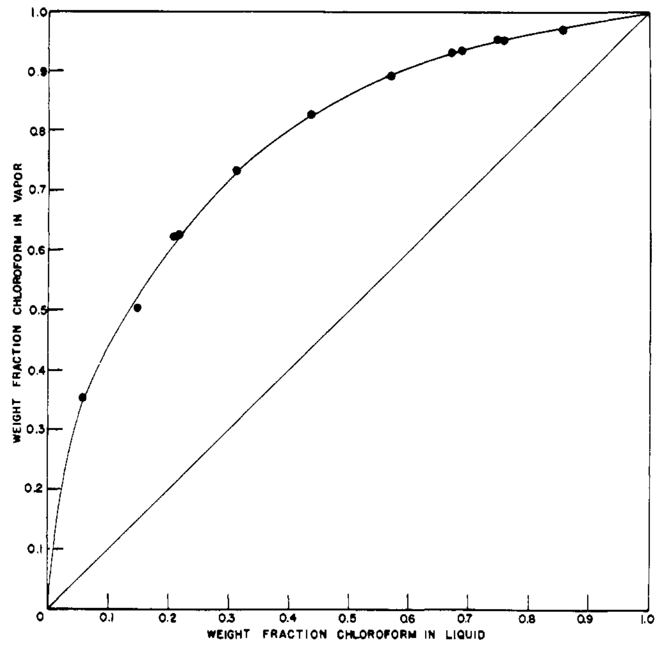

Figure 4. Acetic acid–chloroform

Temp., ° C.	Wt. % Cholorform in Water	Wt. % Water in Chloroform
25	0.75	0.08
56.1	0.8	0.17

The heterogeneous azeotrope has been experimentally verified to consist of 2.8 weight % water in the vapor at 56.1° C.

Ternary Systems. The acetic acid-chloroform-water system is a Type I ternary; experimental solubility limit and tie-line data at 25° C. were presented by Othmer and Ku (*10*). The data are successfully correlated by the methods of Hand (*6*) and Othmer and Tobias (*13*). The improved vapor-liquid equilibrium still modified for partially-miscible systems was used to investigate the phase equilibria of this system at boiling temperatures. For liquid compositions within the partial-miscibility region, an experimental run defined the compositions of the two equilibrium (conjugate) liquid layers at the boiling temperature as well as the composition of the vapor in equilibrium with these layers. In this region, for three components and three phases, the phase rule gives two degrees of freedom. Hence, fixing the pressure leaves one degree of freedom, which can be either boiling temperature or one composition variable—e.g., weight % acetic acid in one of the conjugate liquid layers. This shows that for any over-all liquid composition lying on a particular boiling-temperature tie line, one and only one equilibrium vapor composition exists (Figure 7).

The boiling-temperature tie-line data are also correlated by the Othmer-Tobias technique (Figure 8). The ternary vapor-liquid equilibrium data are represented on triangular coordinates with parametric curves of equilibrium vapor

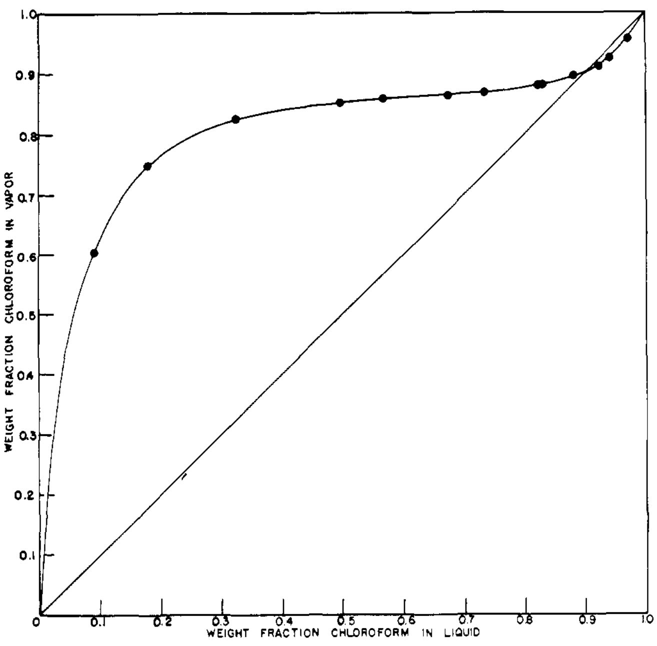

Figure 5. Formic acid–chloroform

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compositions superimposed on a base grid of liquid composition in Figures 9 and 10, and the data presented in Table II. The curves were obtained by cross-plotting the experimental data and the use of graphical interpolation. Liquid boiling point isotherms are shown in Figure 11.

Formic acid-chloroform-water system is also a Type I ternary (*10*); the experimental data are presented in Table II and Figures 12 to 15.

Acetic acid-formic acid-water (Table III and Figures 16 and 17) and acetic acid-formic acid-chloroform (Table IV and Figures 18 and 19) systems are completely miscible.

CORRELATION OF DATA

The molecular association of acetic acid and of formic acid requires modified techniques for correlating and checking the thermodynamic consistency of vapor-liquid equilibrium data. This subject and a method for coping with it is discussed in detail elsewhere (*5*). The logarithmic plotting technique of Othmer, Ricciardi, and Thakar (*11*) has been applied to the binary system data presented herein. The experimental vapor-liquid equilibrium data plotted in

(*Text continued on page 307*)

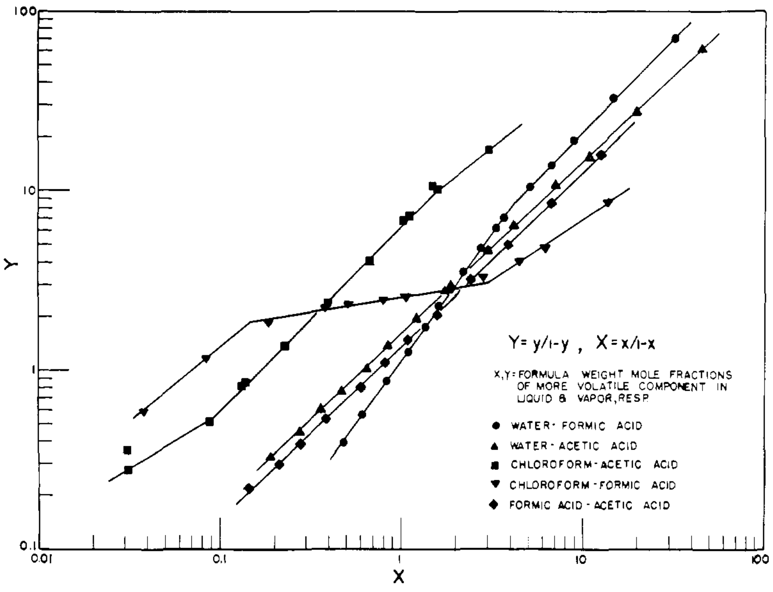

Figure 6. Logarithmic plot correlation of binary system data

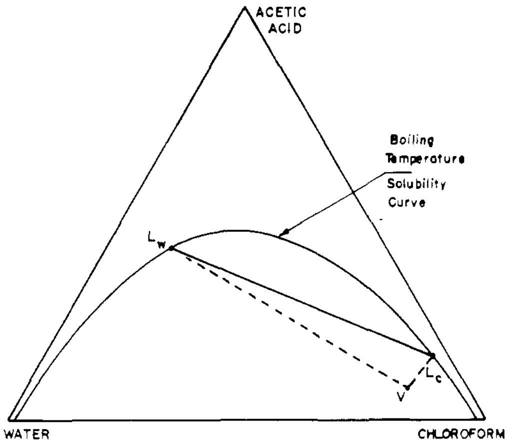

Figure 7. Composite phase diagram for general case

V = vapor in equilibrium with liquid of any over-all composition along tie line $L_w - L_c$

Table I. Vapor-Liquid Equilibria for Binary Systems at 760 Mm. of Mercury

Formic Acid–Water			Acetic Acid–Water			Formic Acid–Acetic Acid			Acetic Acid–Chloroform			Formic Acid–Chloroform		
Temp., °C.	Wt. % Water		Temp., °C.	Wt. % Water		Temp., °C.	Wt. % Formic Acid		Temp., °C.	Wt. % Chloroform		Temp., °C.	Wt. % Chloroform	
	Liquid	Vapor		Liquid	Vapor		Liquid	Vapor		Liquid	Vapor		Liquid	Vapor
100.0	100	100	100.0	100	100	100.6	100	100	61.2	100	100	61.2	100	100
100.4	92.6	96.5	100.1	92.9	94.7	101.2	90.5	92.6	64.9	85.7	97.1	59.2	94.1	92.6
101.0	85.1	92.6	100.3	85.5	89.1	101.9	83.6	86.6	67.8	75.9	95.2	59.1	88.1	89.6
101.5	77.7	88.2	100.5	76.5	82.3	102.9	74.5	79.2	69.9	68.8	93.6	59.2	82.1	88.1
102.0	72.3	84.4	100.8	68.0	76.1	104.0	65.1	71.1	68.1	74.8	95.4	59.2	83.1	88.1
102.5	66.6	80.2	101.3	56.1	66.2	105.3	54.9	61.1	70.5	67.1	93.2	59.6	67.4	86.4
103.3	59.4	73.6	101.8	47.2	58.5	106.6	45.5	53.4	74.4	57.1	89.2	60.4	49.7	85.2
103.7	56.7	70.9	102.8	35.9	47.7	107.9	38.3	45.6	81.4	43.8	82.7	62.0	32.6	82.6
104.4	51.6	65.3	103.0	34.3	45.5	109.4	31.4	37.8	88.8	31.3	73.2	69.0	18.0	75.0
105.1	46.3	58.3	104.1	26.7	37.0	110.8	22.9	29.4	95.7	20.9	62.1	79.5	9.1	60.4
106.1	38.6	47.2	105.3	20.4	29.5	112.3	17.6	23.0	101.7	5.8	41.7	59.7	97.3	95.8
106.6	34.7	40.6	106.4	16.3	23.5	113.3	14.0	18.6	106.8	5.8	35.3	59.1	92.2	91.2
107.1	29.9	33.3	107.6	12.4	18.7	114.2	10.0	14.4	95.4	21.7	62.6	59.5	73.6	86.9
107.4	24.5	25.3	108.8	9.8	15.2	118.1	0	0	101.3	14.9	50.4	59.9	56.8	85.9
107.3	19.3	18.0	110.0	7.8	11.9				118.1	0	0	100.6	0	0
106.8	15.8	13.3	111.4	5.4	9.0									
100.6	0	0	118.1	0	0									

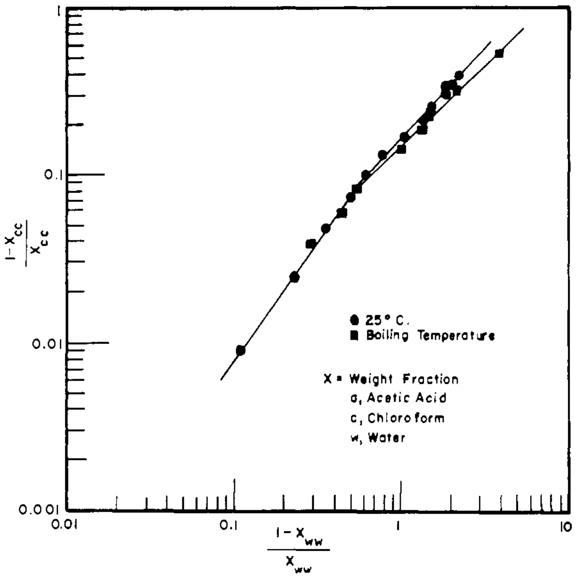

Figure 8. Liquid-liquid distribution data

ogarithmic plot correlation of acetic acid–chloroform–water at 25° C. and boiling point

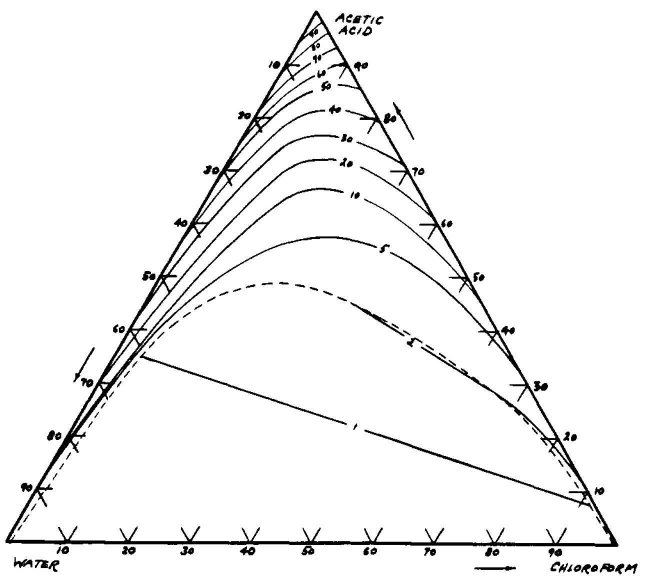

Figure 9. Vapor-liquid equilibria, acetic acid–chloroform–water

Acetic acid vapor curves, weight per cent

Table II. Vapor-Liquid Equilibria for Partially Miscible Ternary Systems

Temp., ° C. 760 Mm.Hg.	Liquid Phase						Vapor Phase, Wt. %		
	Wt. % in Water Layer, L_w			Wt. % in Chloroform Layer, L_c					
	Acetic Acid-Chloroform-Water								
	Acetic acid	Chloroform	Water	Acetic acid	Chloroform	Water	Acetic acid	Chloroform	Water
56.1	0	0.8	99.2	0	99.8	0.2	0	97.2	2.8
56.8	19.7	2.4	77.9	3.1	96.3	0.6	0.7	95.9	3.4
57.2	27.4	3.0	69.6	5.4	94.4	0.2	0.9	95.5	3.6
57.5	31.4	3.7	64.9	5.5	92.4	2.1	0.8	95.3	3.9
58.5	42.1	7.6	50.3	10.3	87.5	2.2	1.3	94.8	3.9
59.0	45.7	11.0	43.3	14.5	84.0	1.5	1.5	94.9	3.6
59.2	47.0	12.7	40.3	15.6	81.6	2.8	1.5	94.7	3.8
60.0	47.4	23.1	29.5		Sample no good		2.0	94.1	3.9
59.8	44.3	35.1	20.6	28.5	65.1	6.4	2.0	94.7	3.3
59.3	49.0	19.4	31.6	21.5	75.9	2.6	1.9	94.7	3.4
60.4	14.9	84.3	0.8	Monophase			1.6	95.4	3.0
66.9	35.8	63.5	0.7				5.6	92.2	2.2
77.0	64.7	29.9	5.4				13.7	82.3	4.0
94.4	79.4	6.2	14.4				41.5	44.5	14.0
80.9	68.3	11.5	20.2				16.6	74.3	9.1
97.1	80.6	4.0	15.4				39.5	48.2	12.3
	Formic Acid-Chloroform-Water								
	Formic acid	Chloroform	Water	Formic acid	Chloroform	Water	Formic acid	Chloroform	Water
56.1	0	0.8	99.2	0	99.8	0.2	0	97.2	2.8
56.9	46.9	4.8	48.3	0.9	98.8	0.25	3.2	94.8	2.0
57.1	54.1	5.8	40.1	1.1	98.4	0.5	3.6	94.9	1.5
57.9	66.9	14.4	18.7	4.3	95.6	0.1	5.8	93.0	1.2
58.1	67.7	17.3	15.0	5.0	94.8	0.2	6.6	92.6	0.8
58.2	66.9	17.4	15.7	5.3	94.1	0.6	9.7	88.8	1.5
57.6	63.0	9.6	27.4	2.8	97.0	0.2	4.1	94.5	1.4
58.3	68.0	20.6	11.4	6.8	93.0	0.2	7.0	92.0	1.0
58.8	59.9	34.2	5.9	15.1	84.6	0.3	10.4	88.9	0.7
56.6	35.7	4.0	60.3	1.33	97.9	1.8	3.7	93.7	2.6
56.5	30.3	3.5	66.2	0.39	98.9	0.7	3.7	93.8	2.5
59.5	64.7	30.0	5.3	Monophase			13.0	86.9	0.1
64.6	75.7	18.2	6.1				15.4	83.1	1.5
69.3	81.2	12.7	6.1				20.5	77.1	2.4
99.8	73.9	0.2	25.9				52.6	29.8	17.6

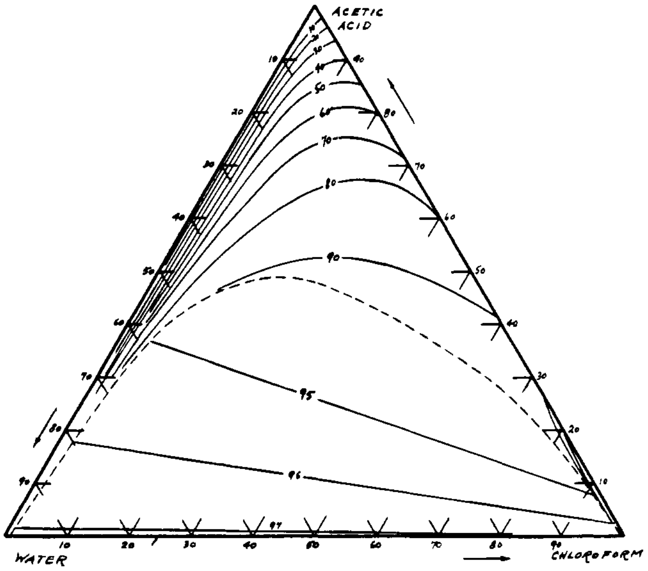

Figure 10. Vapor-liquid equilibria, acetic acid–chloroform–water

Chloroform vapor curves, weight per cent

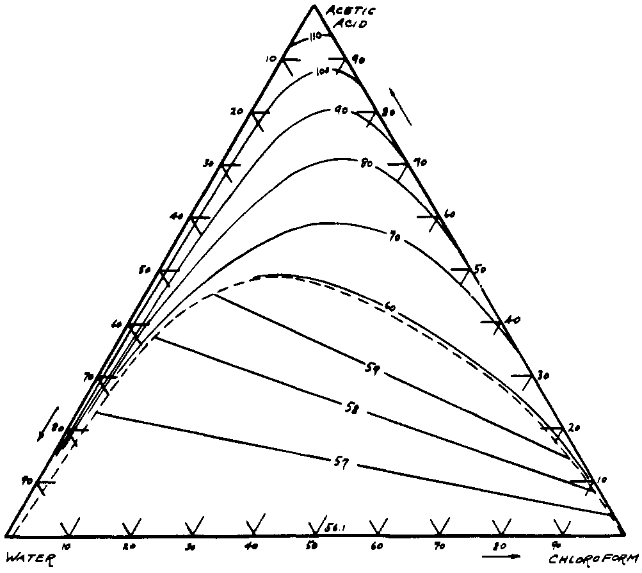

Figure 11. Liquid boiling temperatures of acetic acid–chloroform–water, ° C.

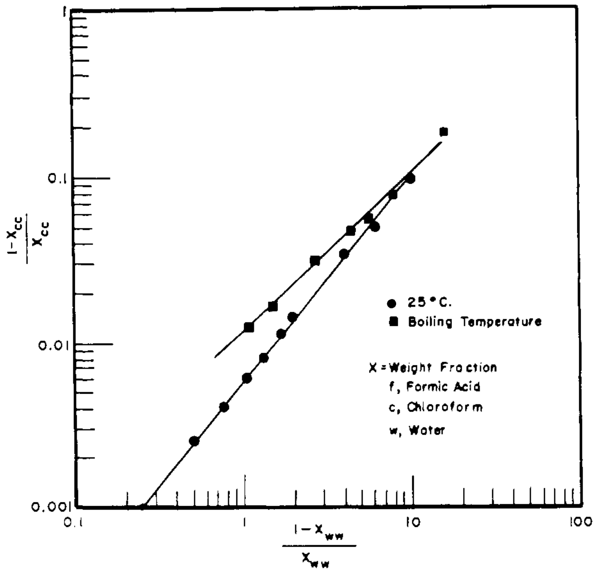

Figure 12. Liquid-liquid distribution data

Logarithmic plot correlation of formic acid-chloroform-water at 25° C. and boiling point

Table III. Vapor-Liquid Equilibria for Acetic Acid-Formic Acid-Water

Temp., ° C., 760 mm.Hg.	Liquid, Wt. %			Vapor, Wt. %		
	Acetic Acid	Formic Acid	Water	Acetic Acid	Formic Acid	Water
107.6	80.3	7.3	12.4	73.8	8.1	18.1
105.8	62.1	16.1	21.8	56.9	14.8	28.3
105.2	42.8	26.8	30.4	39.2	22.8	38.0
105.8	33.0	37.4	29.6	32.3	32.0	35.7
106.6	16.8	55.0	28.2	17.5	50.1	32.4
107.0	19.6	57.2	23.2	20.3	54.3	25.4
107.1	11.9	63.1	25.0	13.0	60.0	27.0
107.2	10.8	66.3	22.9	11.9	64.0	24.1
107.2	22.7	61.3	16.0	23.3	61.8	14.9
106.5	15.5	72.2	12.3	15.6	74.4	10.0
105.9	13.2	76.5	10.3	12.8	79.2	8.0
104.8	8.4	83.3	8.3	9.0	84.6	6.4
103.6	5.6	87.5	6.9	5.6	89.5	4.9
106.6	3.0	62.6	34.4	3.2	56.6	40.2
105.6	2.6	55.1	42.3	3.4	44.8	51.8
104.0	6.1	41.0	52.9	5.9	29.0	65.1
102.0	3.5	23.9	72.6	3.7	13.2	83.1
102.0	13.1	19.0	67.9	11.1	10.9	78.0
102.4	19.0	21.4	59.6	11.6	12.4	76.0
103.4	38.1	18.6	43.3	32.4	13.5	54.1
104.6	56.5	12.2	31.3	49.8	9.6	40.6
106.6	58.2	21.0	20.8	53.5	20.4	26.1
107.4	61.1	22.2	16.7	57.1	21.6	21.3
108.3	71.7	15.0	13.3	67.4	15.3	17.3
109.2	69.4	21.6	9.0	63.6	25.9	10.5
109.0	65.5	27.9	6.6	59.2	33.0	7.8
110.3	74.6	20.2	5.2	68.9	24.6	6.5
107.1	49.3	45.8	4.9	43.6	51.3	5.1
107.2	29.2	56.1	14.7	28.3	57.7	14.0
106.7	26.0	62.2	11.8	25.0	64.8	10.2
105.8	18.3	72.2	9.5	17.3	74.5	8.2
107.0	24.2	62.0	13.8	24.3	64.1	11.6
106.1	15.4	73.5	11.1	15.9	74.5	9.6
105.6	13.7	75.7	10.6	12.4	78.8	8.8
104.7	10.0	80.8	9.2	9.2	83.3	7.5
106.9	8.1	76.5	15.4	8.1	78.7	13.2
107.2	11.5	62.5	26.0	11.9	60.4	27.7
107.0	26.2	50.9	22.9	26.3	49.7	24.0
107.2	40.5	40.5	19.0	39.3	40.6	20.1
107.9	57.7	28.1	14.2	55.0	28.9	16.1

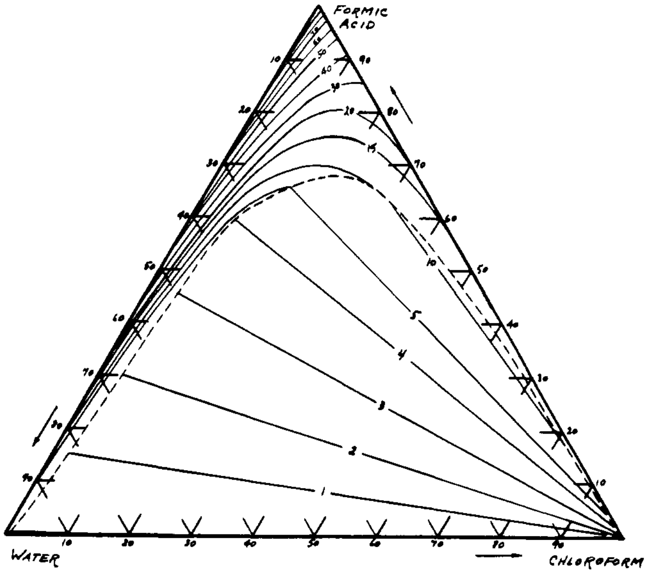

Figure 13. Vapor-liquid equilibria of formic acid–chloroform–water

Formic acid vapor curves, weight per cent

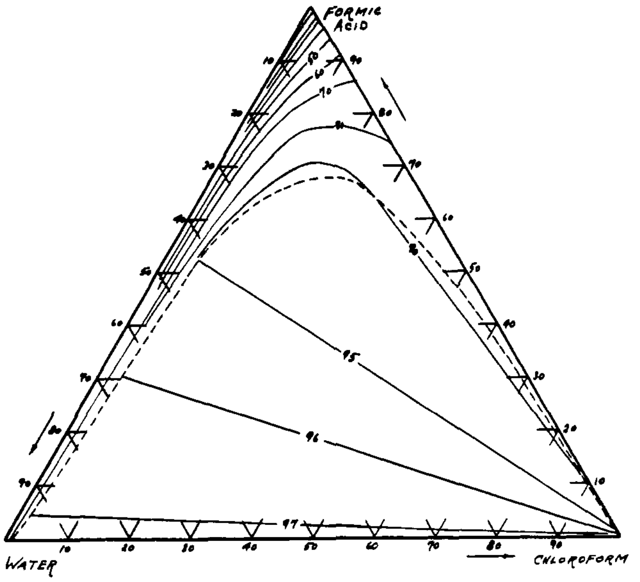

Figure 14. Vapor-liquid equilibria of formic acid–chloroform–water

Chloroform vapor curves, weight per cent

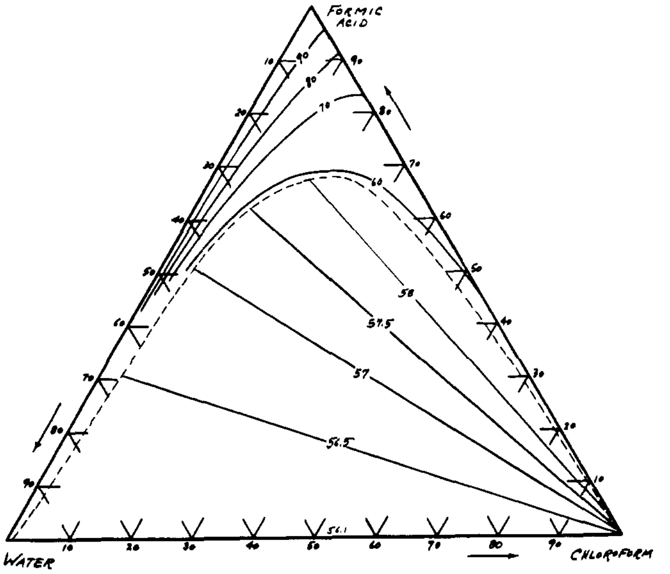

Figure 15. Liquid boiling temperatures of formic acid–chloroform–water, °C.

Table IV. Vapor-Liquid Equilibria for Acetic Acid-Formic Acid-Chloroform

Temp., ° C., 760 Mm.Hg.	Liquid Phase, Wt. %			Vapor Phase, Wt. %		
	Acetic Acid	Formic Acid	Chloro-form	Acetic Acid	Formic Acid	Chloro-form
63.4	13.0	32.5	54.5	1.8	13.6	84.6
65.5	20.3	23.7	56.0	3.0	12.0	85.0
72.7	38.1	18.3	43.6	9.5	8.0	82.5
79.9	52.2	15.9	31.9	15.6	8.4	76.0
81.5	54.0	16.3	29.7	17.2	8.8	74.0
83.8	56.0	14.9	29.1	19.5	8.0	72.5
90.4	67.7	11.2	21.1	27.4	8.6	64.0
96.1	70.8	16.1	13.1	36.0	14.0	50.0
96.6	72.7	14.1	13.2	36.1	13.0	50.9
96.5	68.0	21.5	10.5	35.5	16.8	47.7
90.9	57.1	29.1	13.8	25.4	19.7	54.9
89.4	49.8	33.7	16.5	22.1	22.0	55.9
92.5	46.5	45.3	8.2	22.6	31.9	45.5
92.5	42.0	50.3	7.7	20.7	33.9	45.4
98.3	40.9	54.7	4.4	26.5	46.5	27.0
99.7	29.0	69.2	1.8	21.2	62.5	16.3
94.4	38.0	54.0	8.0	22.1	38 9	39.0
97.1	43.9	50.2	5.9	26.9	40.4	32.7
98.8	36.9	61.1	2.0	24.1	51.8	24.1
89.8	43.6	45.4	11.0	19.0	28.5	52.5
92.4	42.0	49.5	8.5	21.0	33.0	46.0
96.0	42.3	52.3	5.4	23.9	40.3	35.8
94.4	40.0	53.4	6.6	22.4	37.7	39.9
84.8	37.6	47.6	14.8	13.7	25.9	60.4
72.8	30.0	36.6	33.4	7.0	15.3	77.7
72.3	35.0	25.8	39.2	8.5	12.0	79.5
67.2	23.5	17.0	59.5	5.2	8.6	86.2
70.8	34.3	12.9	52.8	7.9	6.9	85.2
61.5	7.0	8.5	84.5	2.2	6.2	91.6
61.0	5.3	28.8	65.9	0.9	13.6	85.5
60.3	5.4	17.4	77.2	3.0	9.0	88.0
64.0	13.0	40.5	46.5	3.0	14.4	82.6
68.1	13.0	60.8	26.2	2.7	20.3	77.0
80.7	7.5	83.6	8.9	1.7	38.8	59.5
93.2	12.9	84.6	2.5	7.6	59.1	33.3
97.4	16.5	82.7	0.8	12.3	67.2	20.5
95.8	26.2	71.3	2.5	15.9	55.1	29.0
76.4	20.1	62.0	17.9	6.4	24.0	69.6
88.4	25.8	65.7	8.5	11.1	39.3	49.6
71.9	22.6	50.8	26.6	4.3	20.5	75.2

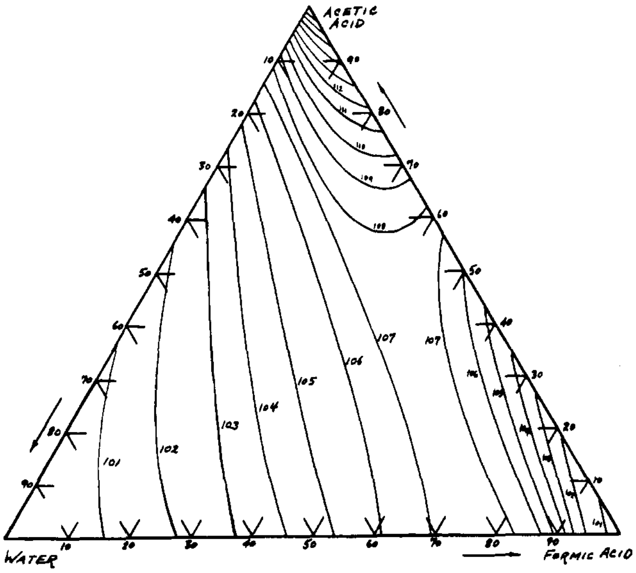

Figure 17. Liquid boiling temperatures of acetic acid–formic acid–water, °C.

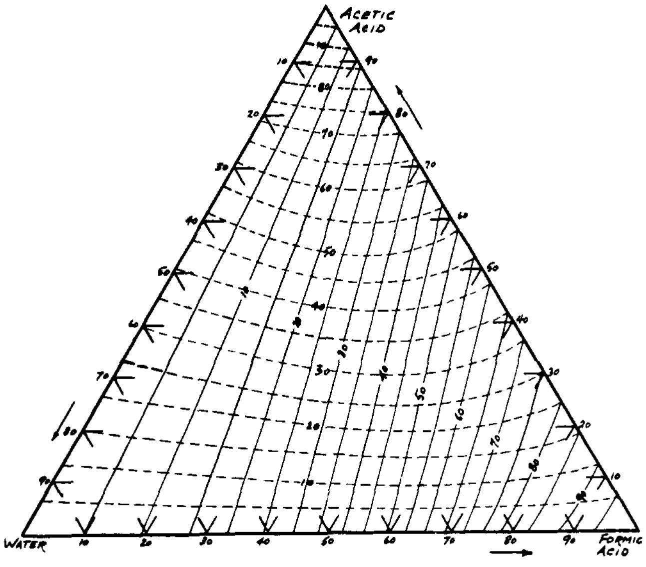

Figure 16. Vapor-liquid equilibria of acetic acid–formic acid–water

——— Weight % of formic acid in vapor

— — — Weight % acetic acid in vapor

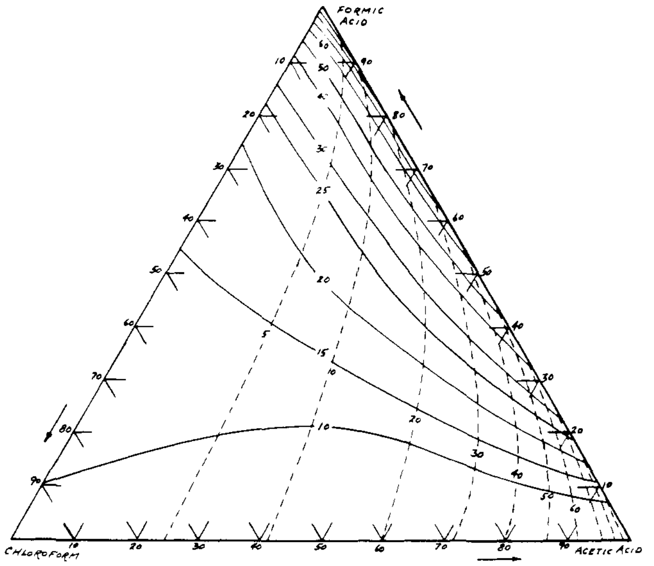

Figure 18. Vapor-liquid equilibria of acetic acid–formic acid–chloroform

——— Weight % formic acid in vapor
— — — Weight % acetic acid in vapor

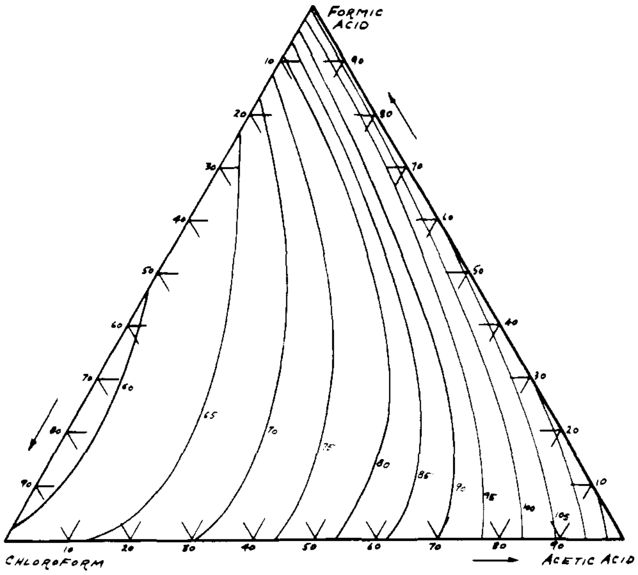

Figure 19. Liquid boiling temperatures of acetic acid–formic acid–chloroform, °C.

this manner are shown in Figure 6 and indicate good linear relationships for each of the systems.

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Collision Integrals for the Viscosity of Polar Gases

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MANY CALCULATIONS have been made of the thermodynamic properties of both nonpolar and polar gases, and of the transport properties of nonpolar gases for several intermolecular potential functions. The only calculation of transport properties for polar gases reported to date was that for viscosity by Krieger (*3*).

Calculations for polar gases usually have been made with the Stockmayer potential function (*7*)

$$E(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^{6}] - \mu^{2}r^{-3}f(\Theta_1 \times \Theta_2 \times \phi) \qquad (1)$$

which expresses the energy variation as a function of molecular separation, r, and certain parameters ϵ, σ, and μ. Parameters ϵ and σ represent the maximum depth in the potential "well," and the molecular separation for zero intermolecular energy, respectively; μ is the dipole moment.

The Krieger Model. The function f includes the effect of relative orientation of the two polar molecules specified in terms of certain angles Θ_1, Θ_2, ϕ. Krieger found Equation 1 was too difficult to employ in the calculation of viscosity and set $f(\Theta_1, \Theta_2, \phi) = 2$, an assumption implying that molecules only collide in the end-on position. Making this assumption, Krieger computed the viscosity to be given by

$$10^{7}\eta = 266.93\,(MT)^{1/2}/W[T/\Theta,.\delta] \qquad (2)$$

where η is the viscosity in poises, T is absolute temperature, Θ is reduced temperature, ϵ/k, M is molecular weight, and $W[T/\Theta,\ \delta]$ is a collision intregal dependent upon the reduced temperature, T/Θ, and the reduced dipole moment, δ, defined by

$$\delta = 1/2\,\frac{\mu^{2}}{\epsilon\sigma^{3}} \qquad (3)$$