Waste Pickle Liquor

Ferrous Sulfate–Sulfuric Acid–Water

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Data for the ternary system ferrous sulfate-sulfuric acid-water are presented for 0°, 27°, 40°, 60°, and 100° C. Such data are helpful in solving the problem of recovery and utilization of waste pickle liquor. Errors in existing data for binary and ternary systems are also discussed.

The steel industry has worked assiduously to solve the technical problem of recovery and utilization of waste pickle liquor. Numerous processes have been proposed (8, 10, 11, 13, 16, 23, 24). Many of these call for the separation by crystallization of ferrous sulfate in various hydrated forms from the waste solution. To have complete information for engineering calculations, data for the system ferrous sulfate-sulfuric acid-water should be available over the complete range of sulfuric acid concentrations and from 0° to 100° C. This paper presents such solubility data. An enthalpy-concentration diagram for the system ferrous sulfate-water has previously been prepared (20).

The amount of waste pickle liquor produced annually is not known definitely. Hoak (12) estimates it to be in excess of 600 million gallons, and Hodge (14) estimates it from 500 to 800 million gallons. The concentrations vary with pickling processes; typical analyses are given by Hodge. In modern continuous strip picklers a typical analysis would be 7% sulfuric acid, 15% ferrous sulfate, and 78% water. Bramer and Coull (5) estimate nearly a billion gallons of waste pickle liquor annually with an average composition of 5% sulfuric acid and 15% ferrous sulfate.

PRESENT DATA DISCORDANT

The system sulfuric acid-water has been well established (15); sulfuric acid-ferrous sulfate was investigated by Kendall and Davidson (18). The ternary system ferrous sulfate-sulfuric acid-water has been studied by Wirth (26), Kenrick (19), Cameron (7), and more recently by Belopol'skii (1-4) and coworkers and by Bullough, Canning, and Strawbridge (6).

The work of Kendall and Davidson on the binary system ferrous sulfate-sulfuric acid was found to be in error. Kenrick (19) incorrectly reported acid hydrates of ferrous sulfate in the high acid region of the ternary system at room temperature. Cameron reported the existence of ferrous sulfate dihydrate above 70° C., which has since been disproved (2).

Belopol'skii, Kolycheva, and Shpunt (1) reported the solubility relationships in the low acid regions of the system ferrous sulfate-sulfuric acid-water from 10° to 50° C. Belopol'skii and Shpunt (2) reported the solubility in the ternary system for all acid concentrations from 50° to 90° C. Belopol'skii and Urusov (4) reported densities and solubilities in the low acid regions from -20° to -25° C. The work of Belopol'skii and others appears to be reliable and has been checked at certain points in this investigation.

Bullough and coworkers (6) reported the solubilities for the low acid regions of the ternary system at 0°, 25°, 45°, 55°, 60°, 80°, and 100° C. In general, the work of these authors agrees with all previous work and with the work presented here. There is one area of disagreement: data for the low acid region of the 60° C. isotherm are not in agreement with either those of Belopol'skii and coworkers or those of this investigation. Nor does the work of Belopol'skii and coworkers agree with this investigation in this region. The principal difference in these three sets of data for the low acid region of the 60° C. isotherm is the length of time allowed for equilibrium. Bullough and coworkers allowed several weeks, Belopol'skii and Schpunt allowed 36 hours, and this investigation allowed from 1 to 6 days. On this basis, Bullough's data should represent absolute equilibrium more closely, but there are two minor objections to their work. They determined free acid from a total sulfate determination. In the low acid region, this method gives serious magnification of error because of the high ratio of ferrous sulfate to free acid. Also, these workers used anhydrous ferrous sulfate to make up samples, which procedure was found to give consistently low solubilities in this investigation, even in regions where the heptahydrate is the established stable solid phase.

In view of the work of previous investigators, several portions of the ternary system ferrous sulfate-sulfuric acid-water from 0° to 100° C. are still in question. The high acid region of the 0° C. isotherm has not been established, and the heptahydrate to monohydrate transition point at 0° C. is not agreed upon by Cameron or by Bullough and coworkers. At 25° C. the work of Cameron and coworkers and Bullough does not agree on the heptahydrate to monohydrate transition point. The data reported by Kenrick in the high acid region of the 25° C. isotherm must be checked because of the variety of acid hydrates he found in this region, and because his data for the low acid region of the isotherm are in complete disagreement with later workers. The high acid region of the 40° C. isotherm has not been established. The low acid region of the 60° C. isotherm is in question regarding the stable solid phase present. The 100° C. isotherm is not established above 50% sulfuric acid.

EXPERIMENTAL TECHNIQUE

All chemicals used were of reagent grade. Samples were made up in sealed glass test tubes and attached to a revolving wheel (equilibrium wheel) which was on a horizontal axis (21, 25). The wheel was submerged in a constant temperature bath filled with either oil, water, or water-methanol mixture, depending upon the temperature of the bath. After remaining attached to the revolving equilibrium wheel for a period of 24 hours or more the sample tube was removed from the bath, the top was broken, and the contents were filtered off rapidly in a filter maintained at the temperature of the experiment.

The work in the tetrahydrate region was performed by the technique reported for work on sodium sulfite (21). All samples were made up in 0.66% sulfuric acid solution in a nitrogen atmosphere to prevent hydrolysis and

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oxidation. Like the system mercuric acetate–acetic acid–water (22), hydrolysis of the salt occurs in pure water with the formation of a precipitate.

Analysis. The composition of the solid phase was determined by Schreinemakers' method involving analysis of the wet residue, analysis of the liquid phase, and extrapolation of a straight line through these two points to the composition of the solid phase. In some cases, the solid phase composition was checked by first drying the residue with acetone prior to analysis.

Samples containing more than 1% ferrous sulfate were analyzed for iron using potassium permanganate. Samples containing less then 1% ferrous sulfate were analyzed for iron by colorimetric methods.

The analysis of free acid in samples containing ferrous sulfate was a difficult problem. Of nine methods of analysis tried, the best method found was to sequester the iron with potassium flouride and titrate the free acid directly (17). There is a decided advantage in determining free acid directly. In many cases, the ratio of ferrous sulfate to free acid in a sample may be 10 or 30 to 1. It is obvious that extreme care must be taken if the free acid is to be determined by obtaining the total sulfate and subtracting the ferrous sulfate equivalent.

RESULTS

Only the smoothed curves and smoothed data are presented in this paper. In the interpretation of the original data visual observations of the solid phase present and the solubilities of the stable and metastable phases were given consideration. The data for the ternary system are given in Table I. The low acid region and the high acid region of the various isotherms are plotted with different scales for the percentage of ferrous sulfate in solution because of the extreme difference in solubility in these two portions of the ternary system.

0° C. Isotherm. The data are shown in Figure 1. Ferrous sulfate heptahydrate, ferrous sulfate monohydrate, and anhydrous ferrous sulfate were identified as the stable solid phases present. By application of binary data to the ternary system, two other solid phases may be shown to exist. These two solid phases are the monohydrate of sulfuric acid and anhydrous sulfuric acid. The monohydrate of sulfuric acid appeared only once in the samples taken, and repeated efforts failed to cause it to appear again. Fourteen days at 0° C. were allowed for some of the samples to reach equilibrium, but the monohydrate of sulfuric acid was still not observed. Samples were not made up in which anhydrous sulfuric acid would be expected as a stable solid phase. Although the solid phase sulfuric acid monohydrate was not established, dotted lines (BACDE) are added to Figure 1 to show how the diagram would look. A sample whose composition falls in the area ABC would have a liquid phase composition along AB and a solid phase composition of C (sulfuric acid monohydrate). A sample whose composition falls in the area CDE would have a liquid phase composition along DE and solid phase composition of C. Points A and D are the invariant point liquid phase compositions encountered when two solid phases are present (ferrous sulfate monohydrate and sulfuric acid monohydrate). A distinct minimum is apparent in the branch representing ferrous sulfate monohydrate. This minimum was noted by Belopol'skii and Shpunt (2) in each isotherm investigated by them from 50° to 90° C. A similar minimum was found to occur in the monohydrate branch of each isotherm investigated in the present work.

The data of previous workers are in good agreement with data presented here for those portions of the isotherm for which other data are available.

27° C. Isotherm. The smoothed data for the 27° C. isotherm are also presented in Figure 1. Ferrous sulfate heptahydrate, ferrous sulfate monohydrate, and anhydrous ferrous sulfate were found to be the stable solid phases in the ternary system. The solid phases $2FeSO_4\cdot H_2SO_4\cdot H_2O$, $FeSO_4\cdot H_2SO_4$, and $FeSO_4\cdot 3H_2SO_4$ reported by Kenrick (19) were not observed during this investigation.

40° C. Isotherm. These smoothed data, presented in Figure 1, show that ferrous sulfate heptahydrate, fer-

Table I. The System $FeSO_4$–H_2SO_4–H_2O

0° C.			27° C.			40° C.			60° C.			100° C.		
H_2SO_4, %	$FeSO_4$, %	Solid phase[a]	H_2SO_4, %	$FeSO_4$, %	Solid phase[a]	H_2SO_4, %	$FeSO_4$, %	Solid phase[a]	H_2SO_4, %	$FeSO_4$, %	Solid phase[a]	H^2SO^4, %	$FeSO_4$, %	Solid phase[a]
0.0	14.0	7	0.0	23.7	7	0.0	28.7	7	0.0	37.5	7(m)	0.0	22.5	1
									0.0	36.5	1(m)			
									0.0	35.6	4			
									9.5	27.3	4,1			
10.0	10.0	7	10.0	17.6	7	10.0	21.9	7	10.0	27.0	1	10.0	18.0	1
						18.2	19.5	7,1						
20.0	6.1	7	20.0	13.8	7				20.0	17.4	1	20.0	13.6	1
						21.5	19.0	7,4(m)						
						25.0	15.5	4(m)						
			26.6	11.8	7,1									
30.0	3.3	7				30.0	9.2	1	30.0	9.5	1	30.0	9.2	1
40.5	3.5	7,1	40.0	3.4	1	40.0	3.5	1	40.0	4.7	1	40.0	5.2	1
50.0	0.60	1	50.0	0.60	1	50.0	0.60	1	50.0	0.67	1	50.0	1.8	1
60.0	0.08	1	60.0	0.12	1	60.0	0.13	1	60.0	0.29	1	60.0	0.66	1
70.0	0.05	1	70.0	0.07	1	70.0	0.07	1	70.0	0.16	1	70.0	0.38	1
80.0	0.06	1	80.0	0.12	1	80.0	0.13	1	80.0	0.29	1	80.0	0.42	1
			88.7	0.26	1,0	87.3	0.26	1,0	85.3	0.52	1,0	86.8	1.06	1,0
90.3	0.24	1,0				90.0	0.11					90.0	0.62	0
95.0	0.04	0	95.0	0.05	0				95.0	0.22	0			
100.0	< 0.01	0	100.0	0.01	0	100.0	0.03	0	100.0	0.10	0	100.0	0.29	0

[a] 7 = $FeSO_4\cdot 7H_2O$; 4 = $FeSO_4\cdot 4H_2O$; 1 = $FeSO_4\cdot H_2O$; 0 = $FeSO_4$
(m) = metastable region

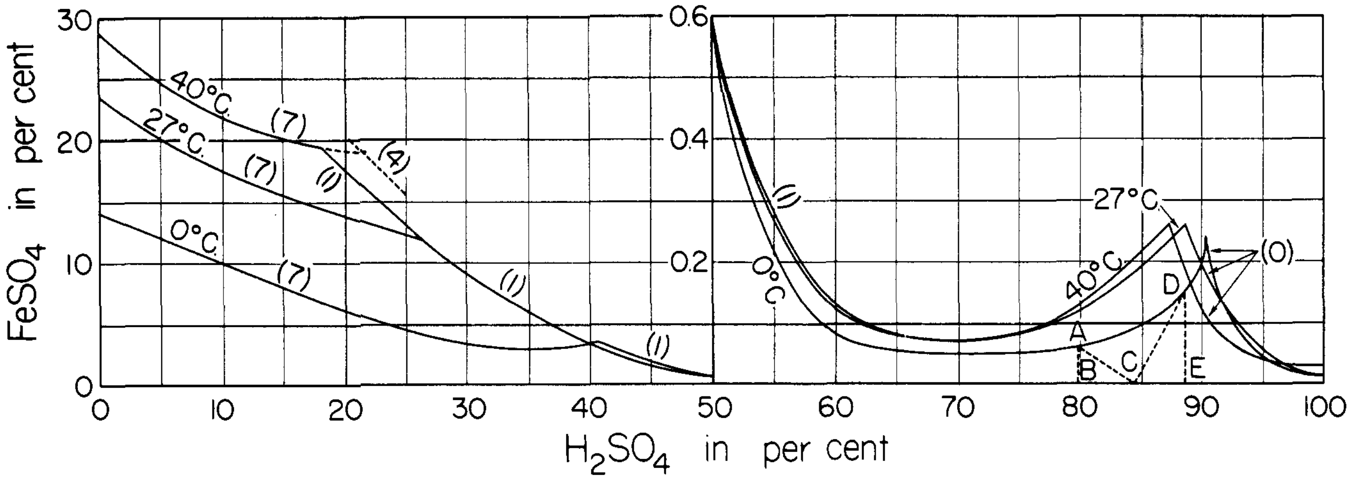

Figure 1. System ferrous sulfate-sulfuric acid-water at 0°, 27°, and 40° C.

rous sulfate monohydrate, and anhydrous ferrous sulfate were the stable solid phases. Ferrous sulfate tetrahydrate was observed as a metastable solid phase.

60° C. Isotherm. The smoothed data for the 60° C. isotherm are presented in Figure 2. Ferrous sulfate tetrahydrate, ferrous sulfate monohydrate, and anhydrous ferrous sulfate were found to be the stable solid phases. Ferrous sulfate heptahydrate, ferrous sulfate tetrahydrate, and ferrous sulfate monohydrate all appeared as metastable solid phases. This is an extremely difficult region in which to attain complete equilibrium, as evidenced by the length of time Bullough and coworkers allowed for equilibrium to be established. In fact, they do not report having ever obtained the monohydrate as the stable solid phase when using heptahydrate to prepare their samples.

There is complete agreement between all investigators on the remaining portions of the 60° C. isotherm.

100° C. Isotherm. The smoothed data for the 100° C. isotherm are also presented in Figure 2. Ferrous sulfate monohydrate and anhydrous ferrous sulfate were found to be the stable solid phases for this isotherm. Bullough's work is in fair agreement with the work presented here.

Tetrahydrate Region. Because of the disagreements concerning the tetrahydrate region, it was investigated further by Mrs. K. C. Hellwig. All samples were made from ferrous sulfate heptahydrate. Because it was necessary to have 0.66% sulfuric acid in the sample to prevent hydrolysis, a series of samples was run at 51.70° C. to determine the effect of sulfuric acid on the solubility of the salt. The results were:

H_2SO_4, %	$FeSO_4$, %	Solid Phase
0.66	33.14	$FeSO_4 \cdot 7H_2O$
1.00	32.84	$FeSO_4 \cdot 7H_2O$
1.50	32.47	$FeSO_4 \cdot 7H_2O$

These data extrapolate to a solubility of 33.68% ferrous sulfate at 0.0% sulfuric acid, or an increase of 0.54% ferrous sulfate from the 0.66% sulfuric acid used in

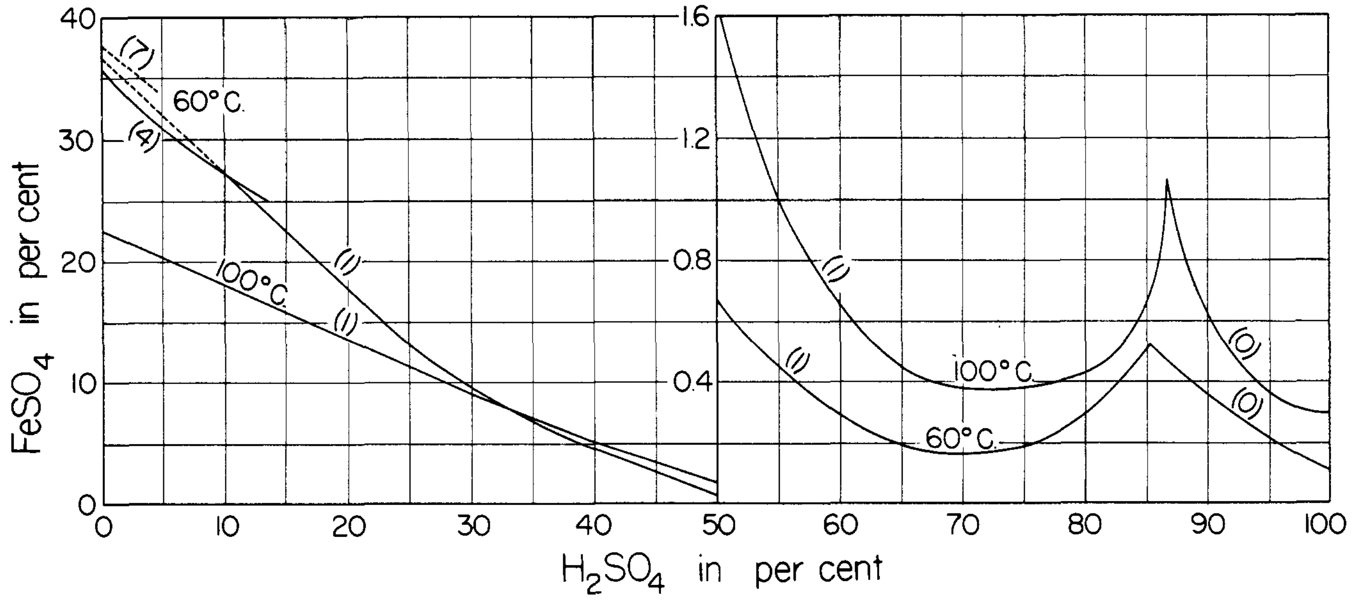

Figure 2. System ferrous sulfate-sulfuric acid-water at 60° and 100° C.

Table II. The Systems $FeSO_4$-H_2O and $FeSO_4$-H_2SO_4

Temp., °C.	$FeSO_4$-H_2O		$FeSO_4$-H_2SO_4	
	$FeSO_4$, %	Solid phase[a]	$FeSO_4$, %	Solid phase[a]
0.0	14.0	7		
10.0	17.5	7	<0.005	0
20.0	21.2	7	0.005	0
25.0	23.0	7		0
30.0	24.8	7	0.015	0
40.0	28.7	7	0.040	0
50.0	32.8	7	0.070	0
56.0(U)	35.4	7,4		
59.0(Um)	37.0	7,1		
60.0(m)	37.5	7		
60.0	35.6	4	0.105	0
60.0(m)	36.5	1		
61.7(U)	35.7	4,1		
70.0	32.3	1	0.15	0
80.0	28.6	1	0.20	0
90.0	25.2	1	0.25	0
100.0	22.5	1	0.30	0

[a] 7 = $FeSO_4 \cdot 7H_2O$; 4 = $FeSO_4 \cdot 4H_2O$; 1 = $FeSO_4 \cdot H_2O$; 0 = $FeSO_4$
U = transition temperature
m = metastable region

all samples. The solubility determined in 0.66% sulfuric acid solution was increased by 0.5% to give the solubility in pure water. To produce the tetrahydrate, the heptahydrate was heated to about 60° C. and then cooled to 51.70° C. The tetrahydrate persisted below and above its transition temperature. To produce the monohydrate, the tetrahydrate was heated to about 80° C., then cooled to 66.10° C. Six days were allowed for the solution to come to equilibrium with the solid phase. The data for this region are:

Temp., °C.	$FeSO_4$, %		Solid Phase
	In 0.66% H_2SO_4	In H_2O	
51.70	33.03	33.53	$FeSO_4 \cdot 7H_2O$
51.70(m)	34.91	35.41	$FeSO_4 \cdot 4H_2O$
57.65	34.93	35.43	$FeSO_4 \cdot 4H_2O$
62.00	35.33	35.83	$FeSO_4 \cdot 4H_2O$
66.10(m)	35.63	36.13	$FeSO_4 \cdot 4H_2O$
66.10	33.30	33.80	$FeSO_4 \cdot H_2O$

m = metastable region

A large-scale plot of these data with those in Table I allowed smooth curves to be drawn and transition points to be read from the graph. These are:

Temp., °C.	$FeSO_4$, %	Solid Phase
56.0(U)	35.45	$FeSO_4 \cdot 7H_2O + FeSO_4 \cdot 4H_2O$
59.0(Um)	37.0	$FeSO_4 \cdot 7H_2O + FeSO_4 \cdot H_2O$
61.7(U)	35.7	$FeSO_4 \cdot 4H_2O + FeSO_4 \cdot H_2O$

U = transition temperature; m = metastable region.

Binary System Ferrous Sulfate-Water. Table II and Figure 3 present the smoothed data for the solubility of ferrous sulfate in water. It is understood that this system probably can exist as such only at low temperatures (as was the case with mercuric acetate) and that ordinarily the solution must contain some sulfuric acid (0.66%) to prevent hydrolysis and oxidation.

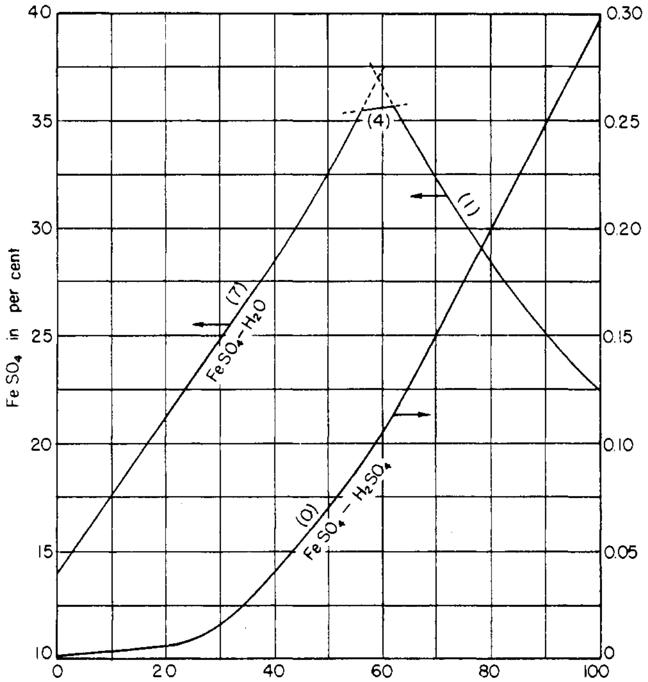

Figure 3. Solubility of ferrous sulfate in water and in sulfuric acid

Binary System Ferrous Sulfate-Sulfuric Acid. Table II and Figure 3 present the smoothed data obtained by extrapolation of the ternary data to 100% sulfuric acid. The data of this investigation show the previous work of Kendall and Davidson (18) to be in error.

EFFECT OF SUPERSATURATION

There is a strong tendency to supersaturation along the ferrous sulfate monohydrate branches of the five isotherms presented here. The degree of this supersaturation is brought out by comparing the work of Bullough and coworkers who allowed up to 15 days for equilibrium to be established; Belopol'skii and coworkers who allowed 36 hours; and this work, which allowed but 24 hours in the low acid region of the 60° C. isotherm. During investigation of the high acid region of the 0° C. isotherm, supersaturation along the ferrous sulfate monohydrate branch was observed to exist for periods of 14 days and longer. In this instance, the phase transition was between ferrous sulfate monohydrate and sulfuric acid monohydrate. In this case the supersaturation would be expected because of low temperature and high viscosity.

Considerable supersaturation can be obtained at 100° C. when a homogeneous solution is evaporated until monohydrate crystallizes out (6), a result of importance if the solution is then to be cooled for crystallization of the heptahydrate.

Ferrous sulfate heptahydrate, ferrous sulfate tetrahydrate, ferrous sulfate monohydrate, anhydrous ferrous sulfate, sulfuric acid monohydrate, and anhydrous sulfuric acid must be considered the stable solid phases in the ternary system ferrous sulfate-sulfuric acid-water between 0° and 100° C. All the solid phases containing ferrous sulfate were observed to have metastable branches beyond their stable branches.

Ferrous sulfate tetrahydrate is stable over a short temperature range; because other phases are metastable over this same temperature range, the tetrahydrate would not be observed in industrial processing steps unless considerable effort was made to secure it.

Because of the unusual shape of the 100° C. isotherm, it would be interesting to determine if more than one crystal structure of ferrous sulfate monohydrate is formed at this temperature.

Edge (9) reports that ferrous sulfate monohydrate is completely insoluble at 290° F. (143° C). The study of this system at higher temperatures and pressures would give data for processing under these conditions.

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Liquid-Liquid Equilibrium Relations in Systems Involving Oleic Acid

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Interest in the solvent method for refining fats and oils commercially is relatively new and little published data are available. This report gives qualitatively, the mutual solubility of 35 solvents and their solubility in oleic acid, plus mutual solubility and tie-line data at 25° C. for oleic acid with five pairs of immiscible solvents—three in which propylene glycol is paired with n-heptane, cyclohexane, and xylene; and two in which furfural is paired with n-heptane and cyclohexane. Two methods for correlating tie-line data are given and evaluated.

Although refining and fractionation of fats and oils by means of solvents have been practiced for a long time, commercial application is relatively recent (9). Examples of this method include furfural extraction described by Gloyer (7, 8) and the use of liquid propane as a selective solvent—e.g., in the Solexol process (14). Because of increasing interest in solvent extraction of fats and oils commercially, and as a result of exploratory experiments, it seemed desirable to consider the use of multicomponent solvent mixtures to separate undesirable coloring material from fatty mixtures such as foots, tallow, or fatty acid stocks. A literature survey showed that reasonably promising solvent combinations could not be postulated with existing solubility data and it was necessary to determine in the laboratory some solubility relationships between fatty materials and commercial solvents.

In order to obtain reproducible data and because of the lack of information on pure fatty acids, oleic acid was selected as the fatty material. The problem was then to determine the solubility of oleic acid with two non-consolute solvents; these were selected either on the basis of solubility tables of fatty acids with non-aqueous solvents by Markley (10) or from a general list of 100 common solvents by Mellan (12). In making selections from the latter, an attempt was made to choose solvents that are commercially used with fats and oils and also to select at least two solvents in each of the classifications given by Durrans (5). After thirty-five solvents were selected, their solubility both mutually and with oleic acid was qualitatively determined in order to select pairs of solvents that were immiscible with each other but miscible with oleic acid (Table I).

From these data (Table I) 16 immiscible solvent pairs were selected, and the binodal curves of the following ternary systems were determined at 25° ± 2° C. (16):

Oleic acid -
Furfural - n-pentane
Propylene glycol - n-pentane
Furfuryl alcohol - n-pentane
Methanol - cyclohexane
Furfural - cyclohexane
Furfuryl alcohol - cyclohexane
Propylene glycol - carbon tetrachloride
Propylene glycol - cyclohexane
Propylene glycol - o-dichlorobenzene
Propylene glycol - p-chlorotoluene
Propylene glycol - benzene
Propylene glycol - ethylene dichloride
Propylene glycol - tetrachloroethylene
Propylene glycol - toluene
Propylene glycol - trichloroethylene
Propylene glycol - xylene

From these 16 ternary systems five were selected as follows for detailed study. The solubility isotherm and several tie lines were determined at 25° C.

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