cultural soils. It greatly increases the water-holding capacity. Up to 98% of Boston blue clay was converted to water-stable aggregates by 4% of pitch. One per cent of pitch ($0.02/lb.) gave 10.8% aggregation while 0.1% of Krilium ($1.47/lb.) gave 8.5%.

The cost of soil conditioning with pitch is estimated to be only 15% of the cost in using synthetic polyelectrolytes. Possible methods of application and the use of pitch as a vehicle for trace elements are discussed. Toxicity to plants and effective life in the soil are not known. Field evaluation is urged.

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[Received April 11, 1956]

Phase Behavior of Fatty Acids-Chlorinated Solvent Systems

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THE SOLUBILITY DATA of single fatty acids in a number of solvents and the separation of fatty acids by crystallization reported up to 1937 have been reviewed by Brown (3). Since then additional solubility data for the single acids in solvents for a number of temperatures have been reported by several investigators (4, 5, 6, 7, 8, 11). Melting point and eutectic composition data have been reported for binary systems of saturated and unsaturated acids (15, 16). The review of additional solubility and melting data has been brought up to date by Markley (9) and Bailey (1).

The effect of the presence of one acid on the solubility of another in solvents was first investigated by Waentig and Pescheck (17). Intersolubilization data have been reviewed (9), and more recent data have been presented for binary fatty acid systems in selected solvents (12, 13, 14). No general conclusions on intersolubility can be drawn from the small amount of data now available.

This work presents solubility isotherms for the binary mixtures of palmitic and oleic acids in ethylene dichloride and carbon tetrachloride and stearic and oleic acids in ethylene dichloride and trichloroethylene. These results permit predicting conditions for the separation of the pure saturated from the unsaturated acids and add to the knowledge of intersolubility effects. Solubilities of the three pure acids, palmitic, stearic, and oleic in each of ethylene dichloride, trichloroethylene, and carbon tetrachloride have been determined over a range of temperatures. Also the solubility of palmitic and stearic acids in oleic acid at 30° and 50°C. are included.

Experimental Part

Procedure

The solubility data for the ternary systems were obtained in the apparatus shown in Figure 1. This is a modification of one used by Bailey and coworkers (2). The well-agitated, constant temperature bath was controlled to within 0.1°C. by an interconnected heating and refrigeration system. This bath housed six equilibrium, filtration units mounted together for magnetic stirring of the contents. This arrangement of equilibrium units is shown at the extreme right of Figure 1.

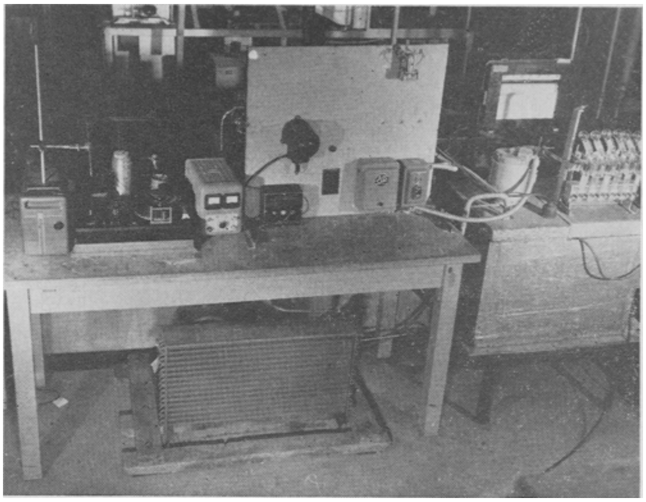

FIG. 1. Experimental apparatus.

Samples containing different proportions of the fatty acids and solvents were placed in tubes containing a tin-plated, iron stirring coil. The glass joints were lubricated with a starch-glycerol gel, and the units were mounted on the electromagnet carrier. The samples were first heated to dissolve all solids, then cooled 5°C. below the initial crystallization temperature. This approach from the cold side has been discussed earlier (4, 13) and recommended (13) for reproducible results. An equilibrating period of 8 hrs. was used when it was found that no change in solubility occurred after 6 hrs. After this period the equilibrium cells were rotated in the bath, permitting the filtrate to pass through the coarse, fritted glass filter into a spherical flask collector. The filtrate was analyzed for solvent content, and the unsaturated and saturated fatty acids were determined by the method specified by the American Oil Chemists' Society. The composition of the solid was not determined and can be calculated from the composition of the original mixture and the filtrate composition by assuming closure of the material balance.

Materials

The fatty acids were obtained from the Hormel Foundation, which supplied the following analyses:

	I.N.	M.P.,°C.	Purity %
Palmitic acid	none	63.5	99
Stearic acid	none	69.0	99
Oleic acid	89.8[a]	......	99

[a] Theoretical value is 89.87.

These were obtained in small tubes, sealed under an inert atmosphere to prevent oxidation. They were used directly with no further purification or protection. Solvents of C. P. grade were used without further purification.

Observations

The melting points of the prepared binary acid-solvent mixtures of palmitic, stearic, or oleic acids in ethylene dichloride, carbon tetrachloride, and trichloroethylene were obtained from heating curves, using a 30-ga. copper-constantan thermocouple and a Leeds-Northrup K-2 potentiometer. These results are reported in Table I along with solubilities calculated from other work (11) for some of the systems.

TABLE I
Solubility of Fatty Acids in Chlorinated Solvents [a]

Palmitic acid		Stearic acid		Oleic acid	
Temp. °C.	Wt. %	Temp. °C.	Wt. %	Temp. °C.	Wt. %
Ethylene dichloride					
60	(94.3)	60	(73.7)	9	89.60
50	64.10 (65.2)	50	(41.2)	4.7	79.30
40	(28.4)	40	(9.09)	—3.75	60.00
30	(5.66)	30	1.30 (0.99)	—10.5	23.90
20	(0.06)			—13.0	8.20
				—15.5	2.99
				—18.0	1.89
				—25.8	0.55
Carbon tetrachloride					
30	16.50	60	(76.5)	4.8	72.68
26.3	11.90	50	(51.9)	—4.3	49.77
14.5	3.03	40	(26.7)	—9.0	35.73
5.5	1.00	30	(9.67)	—14.5	24.26
		20	(2.34)	—19.25	13.67
		10	(0.02)	—20.0	6.42
				—21.0	3.04
				—22.5	1.51
Trichloroethylene					
39	38.3	41.5	28.7	9.5	89.58
31.7	23.7	36.0	18.5	3.5	72.93
20.0	9.4	29.3	9.9	—4.5	53.39
10.7	3.84	20.3	3.85	—13.0	35.12
		12.1	1.00	—21.5	19.54
				—26.7	10.12
				—34.5	5.92

[a] Values in parentheses calculated from (11)

For the ternary systems only the initial mixture compositions and the compositions of the resulting saturated solutions were obtained and are reported in Tables II and III. Figures 2, 3, 4, and 5 show the data for the 50°, 30°, and 10°C. isotherms as circles. Curves have been drawn through the data, and that portion of the 10°C. isotherm to points D has been extrapolated. The results for lower temperatures are best shown on Figures 6 and 8. Here too extrapolations to points E and F have been made. Interpolations have been made at 5°, 0°, —5°, and —15°C. along curve DF for the double salt solubility.

TABLE II
Compositions of Original Palmitic Acid-Oleic Acid-Solvent Mixtures and Resulting Saturated Solutions

Temp. °C.	Original mixture, wt. %			Liquid phase, wt. %		
	Palmitic acid	Oleic acid	Solvent	Palmitic acid	Oleic acid	Solvent
Ethylene dichloride						
50	65.75	8.41	25.84	60.84	9.61	29.55
	62.14	16.88	20.98	56.73	19.30	23.97
	54.80	27.18	18.02	54.36	27.44	18.20
	55.35	32.19	12.46	51.83	34.73	13.44
	59.70	40.30	....	52.80	47.20	....
30	20.16	20.23	59.61	13.25	21.98	64.77
	21.72	40.62	37.66	13.23	45.03	41.74
	24.50	59.10	16.40	13.18	67.98	18.84
	29.63	70.37	....	10.00	90.00	....
10	6.37	13.55	80.08	1.61	14.24	84.15
	7.52	38.01	54.47	3.45	39.68	56.87
	6.87	73.15	19.98	4.03	75.38	20.59
—10	1.01	7.75	91.24	0.18	7.82	92.00
	1.01	13.92	85.07	0.30	14.02	85.68
	0.89	16.88	82.23	0.35	16.97	82.68
—20	0.15	3.24	96.61	0.05	1.35	98.60
	0.06	4.94	95.00	0.03	1.47	98.50
Carbon tetrachloride						
50	58.89	6.64	34.47	55.56	7.18	37.26
	58.00	8.80	33.20	52.90	9.88	37.22
	61.10	29.99	8.91	45.40	42.10	12.50
30	18.22	20.82	60.96	15.44	21.53	63.03
	14.24	45.34	40.42	13.93	45.51	40.56
	13.04	68.67	18.29	12.50	69.10	18.40
10	5.50	22.39	72.11	3.37	22.90	73.73
	5.37	55.95	38.68	3.23	57.22	39.55

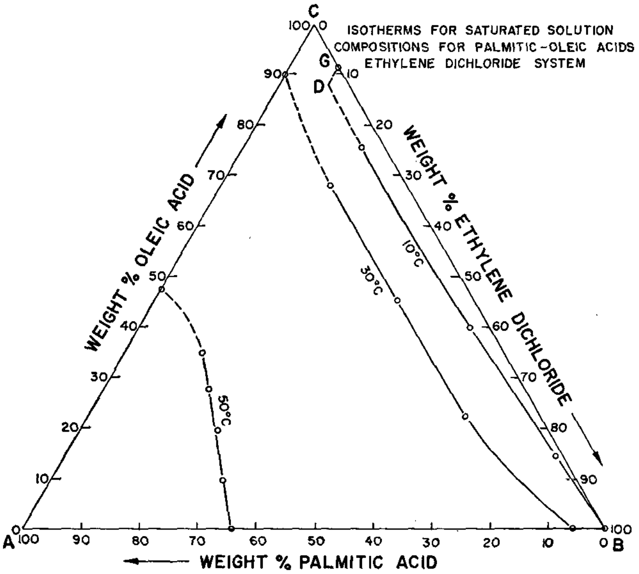

FIG. 2.

It was considered best to show all the results, including those for the low temperature isotherms on a plot of log Y *versus* log X. Y and X are pounds of saturated acid per pound of solvent and pounds of oleic acid per pound of solvent, respectively. These are represented by Figures 6, 7, 8, and 9, which show the useful solvent-total acid ratio lines.

Discussion of Results

Binary Systems

Detailed graphical representation of the binary

TABLE III
Compositions of Original Stearic Acid-Oleic Acid-Solvent Mixtures and Resulting Saturated Solutions

Temp. °C.	Original mixture, wt. %			Liquid phase, wt. %		
	Stearic acid	Oleic acid	Solvent	Stearic acid	Oleic acid	Solvent
Ethylene dichloride						
50	48.53	13.21	38.26	41.04	15.13	43.83
	46.44	28.71	24.85	36.56	34.00	29.44
	40.37	46.80	12.83	31.61	53.68	14.71
	39.72	60.28	....	32.48	67.52	....
30	22.40	19.00	48.60	6.57	22.30	70.53
	18.14	41.73	40.13	6.60	47.58	45.82
	18.21	64.86	16.93	5.16	75.21	19.63
	21.73	78.27	....	2.60	97.40	....
10	2.72	20.26	77.02	1.00	20.62	78.38
	3.45	44.61	51.94	1.50	45.51	52.99
	3.91	69.76	26.33	1.50	71.51	26.99
—10	0.30	4.03	95.67	0.004	6.496	93.50
	0.43	6.15	93.42	0.02	6.08	93.90
	0.44	9.03	90.53	0.03	10.57	89.40
—20	0.25	3.48	96.27	0.002	1.398	98.60
	0.13	5.00	94.87	0.02	2.08	97.90
Trichloroethylene						
50	55.11	10.87	34.02	43.22	13.81	42.96
	50.43	25.00	24.57	36.80	31.87	31.33
	50.82	40.22	8.96	29.76	57.45	12.79
30	15.61	21.98	62.41	11.39	23.08	65.53
	13.85	45.82	40.33	8.81	48.50	42.69
	13.02	68.43	18.55	6.87	73.27	19.86
10	4.70	23.96	71.34	2.41	24.54	73.05
	4.06	51.40	44.54	1.64	52.70	45.67
	4.22	76.20	19.58	0.73	78.97	20.30

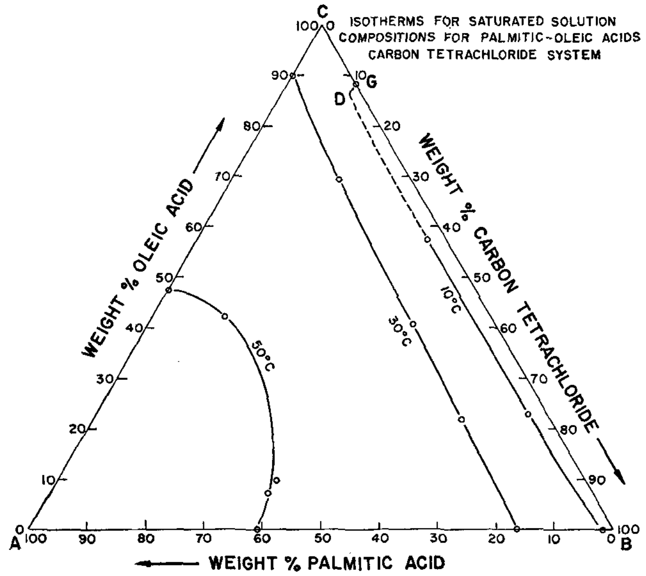

Fig. 3.

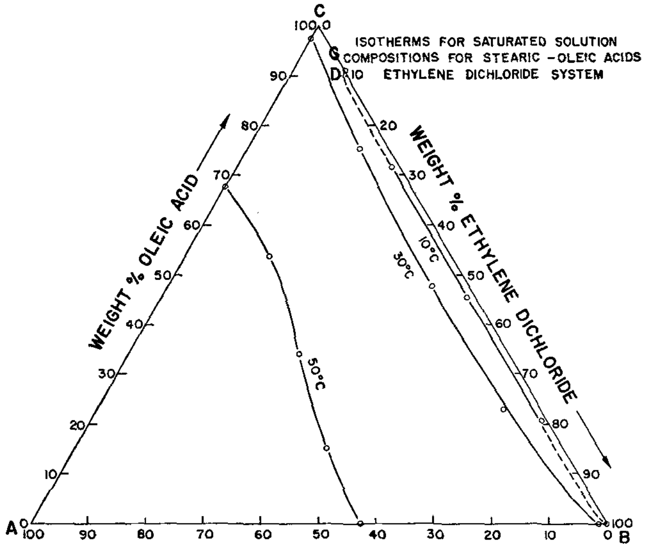

Fig. 4.

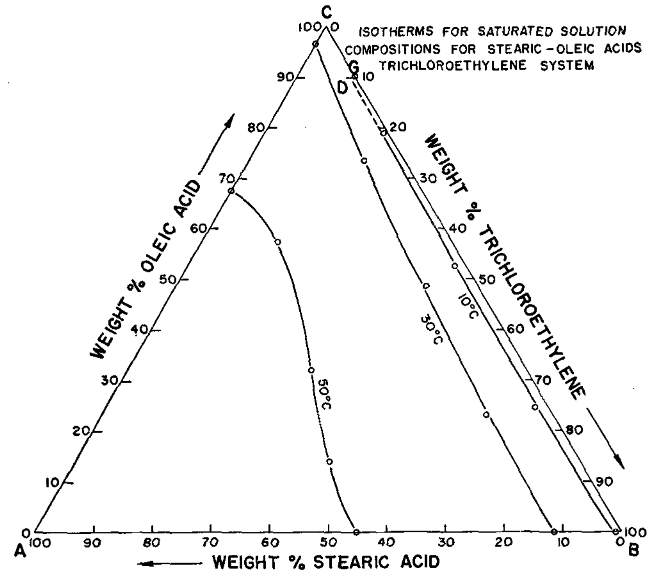

Fig. 5.

solubility data reported in Table I has been made elsewhere (10). The results may be summarized here. Plots of mole fraction of fatty acid *versus* 1/T show that the degree of nonideality increases with the solvents in the order of trichloroethylene, carbon tetrachloride, and ethylene dichloride for all acids investigated. Experimental solubilities were less than the ideal solubility. In addition, the range of ideal behavior is larger for oleic than for palmitic or stearic acids and larger for stearic than for palmitic acid in each of the three solvents. The solubility curves thus plotted have a characteristic sigmoid shape. Finally it can be said that ethylene dichloride may be attractive as a solvent for the separation of palmitic and stearic acids from oleic acids, provided other factors are favorable.

Ternary Systems

Intersolubilization. The intersolubilization of the saturated fatty acids by oleic acid increases for 50°C. isotherms for all acid-solvent systems except palmitic-oleic acids-carbon tetrachloride. This comparison is made by using a constant ratio of saturated acid to solvent in the Figures 2, 3, 4, and 5. Intersolubilization is measured by the deviation of the solubility curve from a line drawn from the binary solubility point on the base line AB to the apex C. With carbon tetrachloride the intersolubilization is negative up to 11% oleic acid, is zero at about 21% oleic, and then increases over the balance of the concentration range. For the 30°C. isotherms this intersolubilization increases over the entire range in the case of palmitic acid-carbon tetrachloride or to a particular concentration and thereafter decreases, such as, at 65%, 45%, and 64% oleic acid for palmitic acid-ethylene dichloride, stearic acid-ethylene dichloride, and stearic acid-trichloroethylene, respectively. For the 10°C. isotherms the intersolubilization increases up to a flat maximum of 65%, 43%, 40%, and 35% oleic acid and then decreases to the double salt equilibrium concentration for palmitic acid-ethylene dichloride, palmitic acid-carbon tetrachloride, stearic acid-ethylene dichloride, and stearic acid-trichloroethylene, respectively. For the lower temperatures of —10° and —20°C. the intersolubilization because of oleic acid increases up to 0.571%, 0.057%, and 0.065%; 0.020% saturated acid corresponds to that in equilibrium with the two solids for palmitic acid-ethylene dichloride and stearic acid-ethylene dichloride systems, respectively. It should be remembered that extrapolations are involved over parts of the composition range, and the values at these low temperatures should be used with caution. The effect of the saturated acids on the solubility of oleic acid below 13.6°C. is relatively small except in stearic-oleic acids-ethylene dichloride at —20°C. whereas the effect of oleic acid on the solubility of the saturated acids is quite considerable in the several solvents. The solvent certainly does affect intersolubilization as is shown in the comparison of Figures 2 and 3 and 4 and 5 for palmitic and stearic acids, respectively.

Effect of Solvent-Acid Ratios. For fixed fatty acid mixtures the increasing of the amount of solvent for systems in the single solid phase region improves the solubility of oleic acid (at temperatures below 13.6°C.), and may increase or decrease the solubility of the saturated acids. In Figure 2 at 10°C. an in-

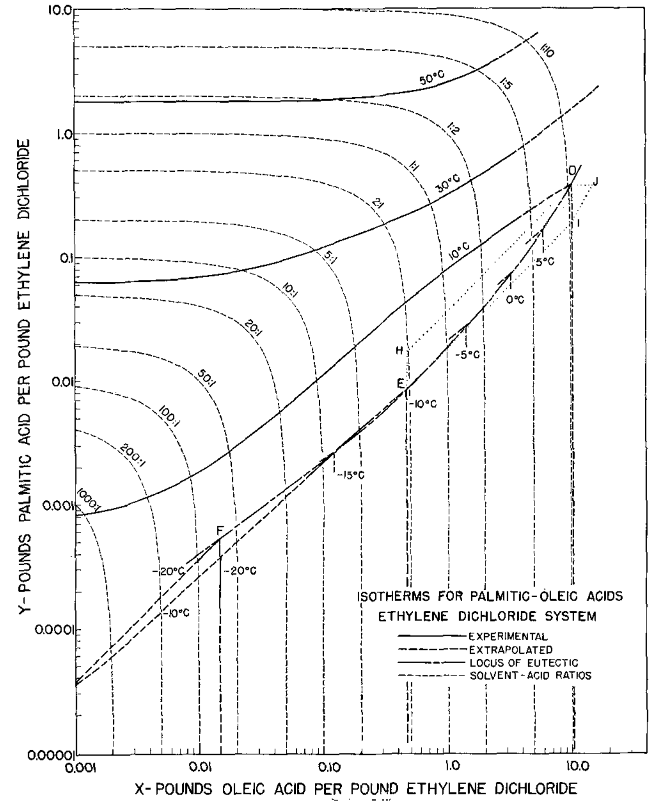

FIG. 6.

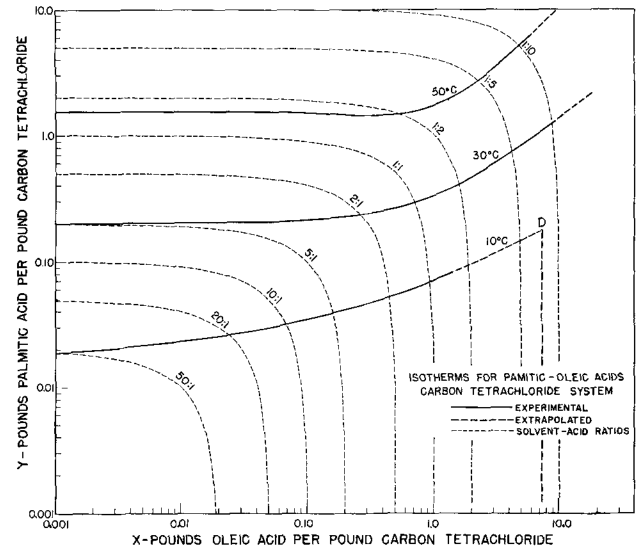

FIG. 7.

crease in the solvent-acid ratio causes an increase in the solubility of oleic acid in the region CDG. Similarly the solubility of palmitic acid increases with the solvent-acid ratio to 4.2% palmitic acid and then decreases to nearly zero at high solvent compositions in the region ADB. Similar statements may be made at other temperatures for both palmitic-oleic and stearic-oleic acid mixtures in the several solvents except for the 30°C. isotherm for carbon tetrachloride and trichloroethylene. In these latter cases the solubility of the saturated acid increases over the entire solvent-acid ratio range.

In the two solid phase regions, ADC, below 13.6°C. an increase in the solvent-acid ratio for a fixed saturated-unsaturated acid mixture produces a constant solution composition D, E, or F and a changing proportion of solid saturated and solid unsaturated acid, depending on the composition of the original acid mixture. This may be looked upon as an increase in solubility of the unsaturated acid and a decrease in solubility of the saturated acid if the original acid mixture is to the right of the extension of line BD to the AC axis as in Figure 2. If the original acid mixture lies to the left, this may be considered as a decrease in solubility of the unsaturated acid and an increase in solubility of the saturated acid with an increasing solvent-acid ratio.

It is however possible to add sufficient solvent, to move from the two solid phase regions to one or the other of single solid phase regions and thereby achieve separation of the pure components. This is illustrated by taking an acid mixture containing 3.65% palmitic and 96.35% oleic acids in the region of two solid salts at a solvent-acid ratio of 1:10.538 at —10°C. in Figure 6. By adding solvent until the solvent acid ratio is 2.076:1, pure saturated palmitic acid is precipitated.

Separation of Fatty Acids. A cyclic process may be devised which utilizes a combination of temperature and solvent-acid ratio changes to yield pure saturated and unsaturated acid components. The success of such a process will depend on other aspects connected with economics, such as nucleation and crystallization rates, crystal size and habit, costs of equipment and processing materials. The example is based on phase equilibria alone and indicates that a mixture containing 96.04% oleic acid and 3.96% palmitic acid theoretically may be separated into pure oleic and pure palmitic acids.

Consider 44.55 lbs. of a feed mixture containing

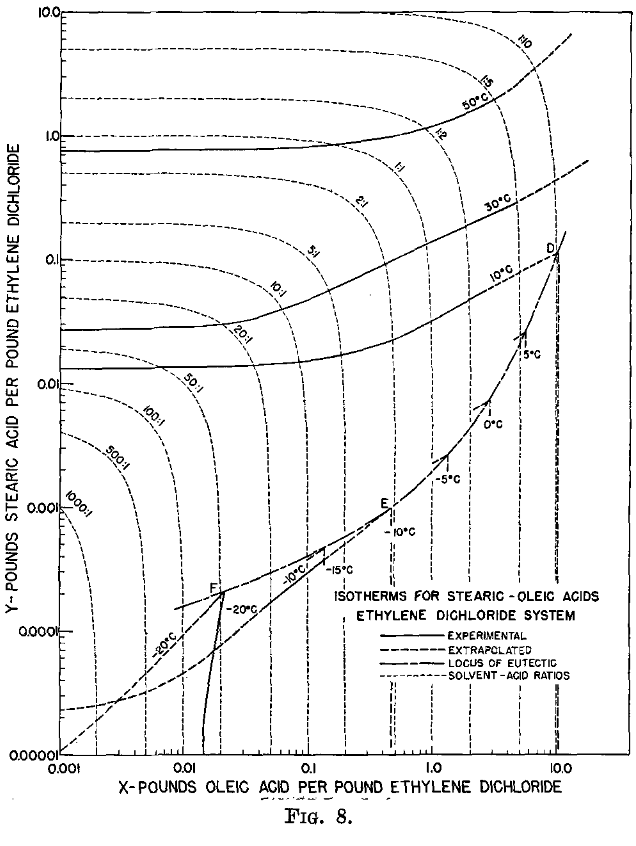

FIG. 8.

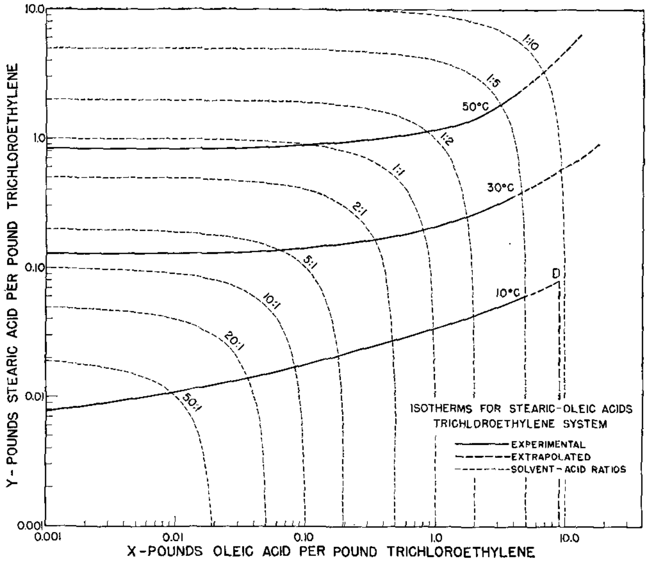

FIG. 9.

96.04% oleic and 3.96% palmitic acid added to 100 lbs. of a recycled stream containing 91.18 lbs. of 98.21% oleic acid at a solvent-acid ratio of 1:10.335 and at temperature greater than 10°C. This recycled stream is represented by point I in Figure 6. After the addition of the feed, the mixture contains 135.73 lbs. of 97.50% oleic acid at a solvent-acid ratio of 1:15.385, represented by J. This mixture when cooled to 10°C. yields 42.79 lbs. of pure oleic acid crystals. The solution at D saturated with respect to both oleic and palmitic acids contains 92.94 lbs. of 96.35%oleic acid at a solvent acid ratio of 1:10.536. To this mixture are added 184.17 lbs. of ethylene dichloride, which brings the solvent-acid ratio to 2.076:1.

The mixture is next cooled to —10°C. and 1.77 lbs. of palmitic acid crystals separate, leaving 91.18 lbs. of 98.21% oleic acid in solution in equilibrium with the two salts at E. The solvent-acid ratio at E is 2.155:1. The solution is warmed above 10°C. and 184.17 lbs. of ethylene dichloride is removed by vaporization, bringing the solution to point I with the composition as given before. The process cycle IJDHEI (Figure 6) is completed, and the 96.04% oleic acid feed mixture is separated into 42.79 lbs. of oleic acid and 1.77 lbs. of palmitic acid. The preparation of the pure acids depends on the successful washing of the adhering mother liquor from the crystal fractions.

Summary

1. The solubilities of oleic acid in ethylene dichloride, carbon tetrachloride, and trichloroethylene, palmitic acid in carbon tetrachloride and trichloroethylene, and stearic acid in trichloroethylene have been determined. The solubility of oleic is less than palmitic, and that of palmitic is less than that of stearic in all solvents. Except for oleic acid above —10°C. the solubilities of the acids decrease in the solvents in the order trichloroethylene, carbon tetrachloride, and ethylene dichloride.

2. Ethylene dichloride would be an excellent solvent for the separation of the fatty acids, based on a comparison of their actual with their ideal solubility (mole fraction) variation with the reciprocal of the temperature in the various solvents.

3. Ternary solubilities at 50°, 30°, and 10°C. are presented for palmitic and oleic acids in ethylene dichloride and carbon tetrachloride, and stearic and oleic acids in ethylene dichloride and trichloroethylene. In addition, solubilities at —10° and —20°C. are presented for palmitic and oleic as well as stearic and oleic acid in ethylene dichloride. The 10°, —10°, and —20°C. isotherms give the extrapolated compositions of the solutions in equilibrium with both saturated and unsaturated acids.

4. The intersolubilizing effect of oleic acid on palmitic acid is greater than on stearic acid in the several solvents. Intersolubilization is greater with ethylene dichloride as a solvent.

5. The separation of a binary mixture into its pure constituents may be achieved by a cyclic process, which involves both temperature and solvent-acid ratio changes. This cyclic process is especially suitable for isolating pure oleic acid.

Acknowledgment

The authors wish to acknowledge the chemical analyses performed by the Analytical Section of the General Mills Research Laboratories.

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[Received September 25, 1956]