Phase Investigations of Fats. III. Systems Containing Oleic and Palmitic Acids and an Organic Solvent[1]

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Introduction

THE solubility ratios of pairs of certain fatty acids in various solvents have been determined by Foreman and Brown (1), and the magnitude of the solubility effect of one fatty acid on another has been reported by other investigators (2), but no investigations of the intersolubilizing effects of mixtures of oleic and palmitic acids in organic solvents have as yet been reported.

The investigation reported here represents an extension of previously reported work (3) to include the composition of the solid and liquid phases existing in equilibrium in the ternary systems oleic acid-palmitic acid-acetone and oleic acid-palmitic acid-commercial hexane at various temperatures and with varying amounts of the three components present. The utility and value of such data has been explained in a previous publication (3) and will not be repeated here.

Materials

Preparation of Oleic Acid. Oleic acid was prepared from pecan oil by interesterification of the oil with methanol and separation of the methyl oleate by fractional distillation using a Podbielniak heligrid column. The methyl oleate was converted to oleic acid, and the acid was repeatedly crystallized from acetone yielding a product of 99.7% purity based on its iodine value (corrected to 100% oleic acid in the experimental calculations). Alkali isomerization followed by spectrophotometric examination indicated the absence of any acids more highly unsaturated than oleic.

One hundredth of 1% of hydroquinone was added to the oleic acid and the product stored under hydrogen in a refrigerator to prevent oxidation prior to use.

Preparation of Palmitic Acid. Palmitic acid was prepared from commercial Neo-Fat[3] by treatment with concentrated sulfuric acid to remove unsaturated acids, fractional distillation, and repeated crystallization from acetone. The solubility of this acid was determined after each crystallization until a constant solubility value was reached after a total of 14 crystallizations. After drying over P_2O_5 for 18 hours, the palmitic acid melted at 62.8°-63.0°C. The freezing point, determined by a modification of the method proposed by Glasgow *et al.* (4), was found to be 62.75°C.

Solvents. The organic solvents were commercial hexane, boiling range 146°-158°F., which was used without further purification, and acetone, which was purified with caustic silver nitrate by the method of Werner (5).

Experimental

The method used for equilibration of the three-component system, oleic acid-palmitic acid-solvent has been described in previous communications (3, 6) of this series.

In order to ascertain the mutual solubility of each component at various concentrations and at temperatures of 0°, —10°, —20°, —30°, and —40° C., concentrations of fatty acids which ranged from 0% oleic and 100% palmitic acids, to 100% oleic and 0% palmitic acids were investigated. Solvent ratios employed were 5:1, 10:1, and 20:1 (solvent to total acids) by weight. Each original mixture yielded a solid and liquid phase when equilibrated. The composition of these phases, together with the proportions of fatty acids and solvent in each phase at each temperature, are recorded in Tables I and II. These data were plotted in the form of phase diagrams. The limiting boundary of the liquid phase at each isotherm, as well as the composition of the solid phase, is shown in Figures 1 to 10. In addition, the liquid phase area for each isotherm was plotted on an expanded scale as rectangular coordinates to indicate more accurately the nature of the intersolubilizing effect. These areas are shown in Figures 11 and 12, which also include the compositions of unsaturated solutions resulting from complete solubility of the component acids at constant, exact solvent-acids ratios, such compositions represented by theoretical dotted lines labelled 5:1, 10:1, and 20:1.

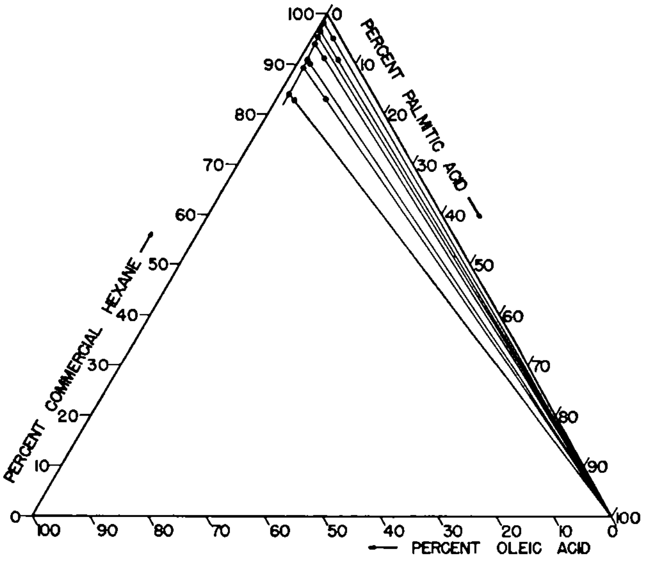

FIG. 1. Phase diagram of oleic acid-palmitic acid-hexane at 0°C.

Discussion

Effect of Different Fatty Acid Ratios. At all temperatures the solubility of palmitic acid in acetone was found to exceed its solubility in commercial hexane, the difference in solubility being greater at the higher temperatures; but increasing amounts of oleic

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[2] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

[3] Neo-Fat is named as part of the specification of the exact experimental conditions and does not imply that this product is particularly endorsed or recommended by the Department of Agriculture over other commercial products having the same or similar composition and properties.

TABLE I

Compositions of the Original Oleic Acid-Palmitic Acid-Commercial Hexane Mixtures and Phases Present at Equilibrium[a]

Temp., °C.	Original mixture			Liquid phase			Solid phase			
							By difference		By calculation	
	Palmitic acid	Oleic acid	Solvent	Palmitic acid	Oleic acid	Solvent	Palmitic acid	Oleic acid	Palmitic acid	Oleic acid
0	3.200	....	96.800	0.125	....	99.875	100.00	0.0	....	....
	3.746	1.249	95.005	0.503	1.303	98.194	100.00	0.0	....	....
	1.239	3.643	95.118	0.836	3.662	95.502	100.00	0.0	....	....
	4.013	4.836	91.151	0.950	5.001	94.049	100.00	0.0	100.00	0.0
	2.207	7.629	90.164	1.154	7.711	91.135	100.00	0.0	100.00	0.0
	8.565	8.565	82.870	1.250	9.234	89.516	100.00	0.0	....	....
	3.087	14.158	82.755	1.528	14.399	84.073	100.00	0.0	....	....
	0.935	3.780	95.285	0.818	3.802	95.380	100.00	0.0	....	....
	0.724	4.038	95.238	0.724	4.038	95.238	....	....	....	....
	0.247	4.581	95.172	0.247	4.581	95.172	....	....	....	....
	....	4.762	95.238	....	4.762	95.238	....	....	....	....
	0.928	8.372	90.700	0.964	8.377	90.659	....	....	....	....
	0.453	9.046	90.501	0.480	9.077	90.443	....	....	....	....
	....	9.229	90.771	....	9.229	90.771	....	....	....	....
	1.367	15.300	83.333	1.367	15.300	83.333	....	....	....	....
	0.879	15.829	83.292	0.879	15.829	83.292	....	....	....	....
	....	16.667	83.333	....	16.667	83.333	....	....	....	....
—10	1.144	....	98.856	0.083	....	99.917	100.00	....	....	....
	2.210	2.526	95.264	0.282	2.638	97.080	100.00	0.0	100.00	0.0
	4.383	4.761	90.857	0.422	4.940	94.638	99.55	0.45	99.32	0.68
	2.509	7.134	90.537	0.537	7.278	92.185	100.00	0.0	....	....
	8.812	8.811	82.377	0.627	9.683	89.690	100.00	0.0	....	....
	3.874	12.951	83.175	0.755	13.460	85.785	100.00	0.0	....	....
—20	1.224	....	98.776	0.024	....	99.976	100.00	....	....	....
	6.897	2.299	90.804	0.140	2.494	97.366	100.00	0.0	....	....
	2.183	6.861	90.956	0.223	7.042	92.735	100.00	0.0	....	....
	0.452	8.671	90.877	0.272	8.686	91.042	100.00	0.0	....	....
	0.270	8.768	90.962	0.270	8.768	90.962	100.00	0.0	....	....
	0.028	9.225	90.747	0.055	8.999	90.946	0.0	100.00	....	....
—30	1.157	....	98.843	0.006	....	99.994	100.00	....	....	....
	1.647	5.337	93.016	0.058	1.776	98.166	30.34	69.66	....	....
	4.690	2.166	93.144	0.058	1.919	98.023	93.13	6.87	....	....
	0.014	5.291	94.695	0.014	1.924	98.062	0.0	100.00	....	....
	0.010	2.866	97.124	0.010	1.910	98.080	0.0	100.00	....	....
—40	0.146	2.757	97.097	0.010	0.271	99.719	5.19	94.81	7.84	92.16
	0.527	....	99.473	0.001	....	99.999	100.00	....	....	....

[a] Compositions are expressed in gram-weight-per cent of total solution.

acid in the original mixtures resulted in a greater maximum solubility of palmitic acid in commercial hexane than in acetone.

At 0°C. (Figures 11 and 12) the solubility of palmitic acid was 0.125 g./100 g. commercial hexane, and 0.650 g./100 g. acetone. With the addition of about 90% of oleic acid to the original acid mixtures, the solubility of palmitic acid increased to a maximum of 1.56 g./100 g. of commercial hexane, and to 1.35 g. /100 g. of acetone at the lowest solvent ratio.

At —10°C., the solubility of palmitic acid, initially 0.083 g./100 g. commercial hexane and 0.289 g./100 g. acetone, increased to a maximum of 0.835 g./100 g. commercial hexane, and 0.61 g./100 g. acetone, in the presence of approximately 95-96% of oleic acid.

At both 0° and —10°C., oleic acid was completely soluble in both solvents down to the lowest solvent ratio employed. The solid phases at these temperatures contained only palmitic acid.

At —20°C. the solubility of palmitic acid was slightly increased by the addition of oleic acid up to the concentration at which the latter acid separated from solution as a result of saturation of the liquid

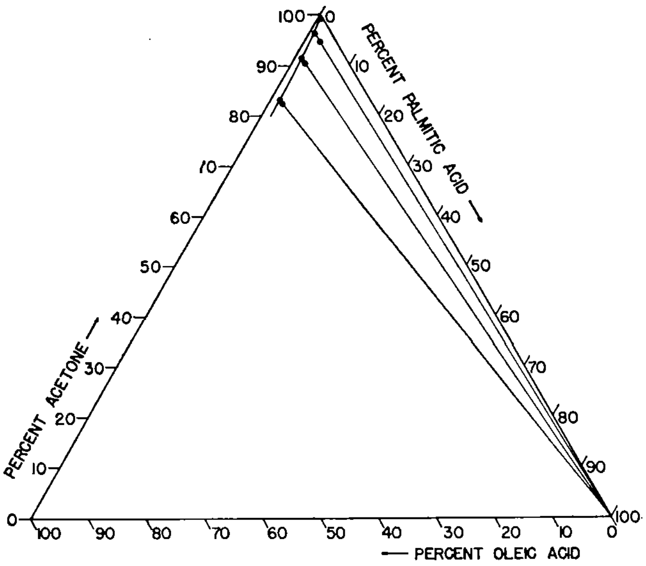

FIG. 2. Phase diagram of oleic acid-palmitic acid-acetone at 0°C.

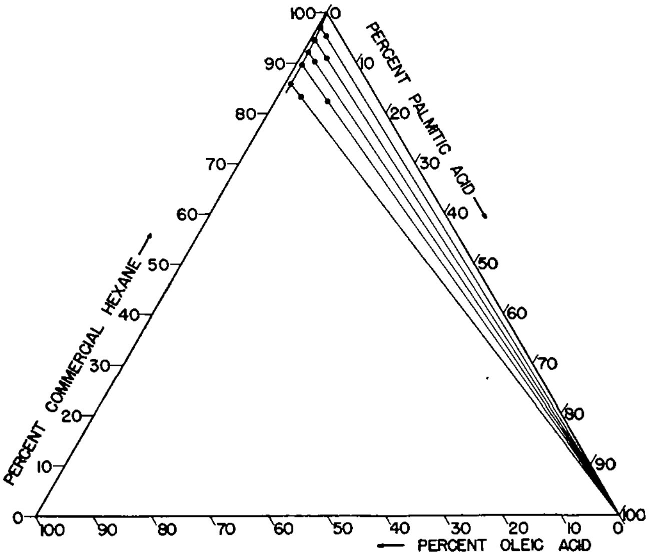

FIG. 3. Phase diagram of oleic acid-palmitic acid-hexane at —10°C.

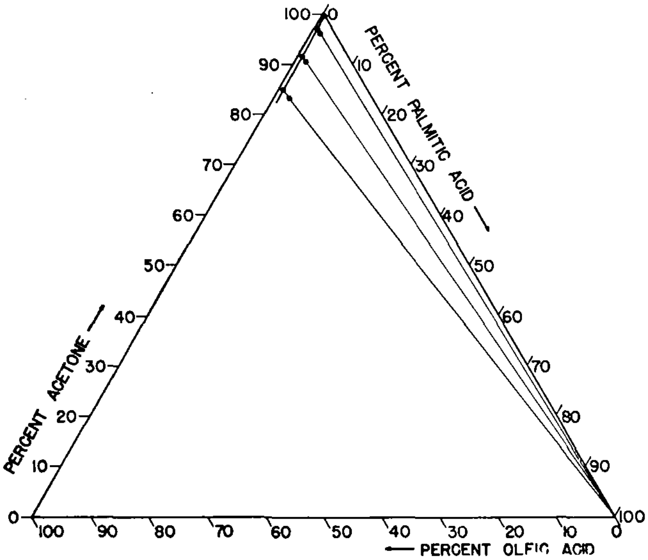

FIG. 4. Phase diagram of oleic acid-palmitic acid-acetone at —10°C.

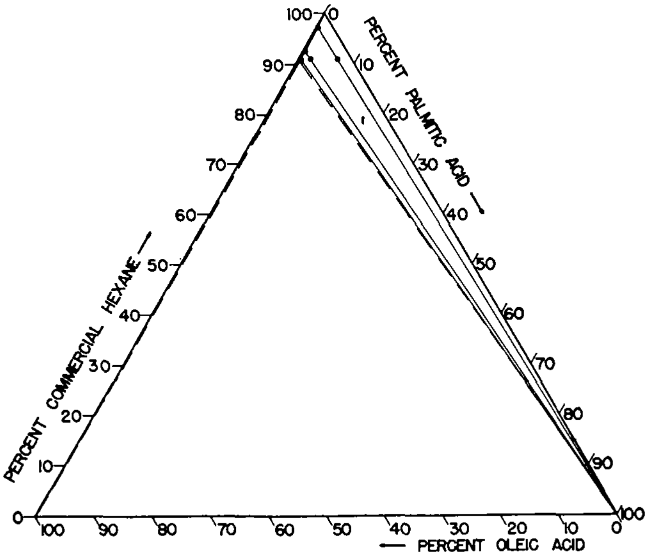

FIG. 5. Phase diagram of oleic acid-palmitic acid-hexane at —20°C.

phase. This saturation point occurred when oleic acid was present in excess of 9 g./100 g. commercial hexane, or 5.5 g./100 g. acetone. The liquid phase, when saturated with both acids, remained constant in composition as the original mixtures increased in oleic acid until the concentration of palmitic acid became low enough to be completely soluble, at which point the liquid phase boundary formed a closed contour. The fields within which original mixtures, at equilibrium, resulted in palmitic acid in the solid phase are designated as "1" in Figures 5 to 8; those mixtures which yielded saturated liquid phases, with both acids also in the solid phases, are designated as "2." Original mixtures which gave solid phases containing only oleic acid are within the field at the extreme left of these figures.

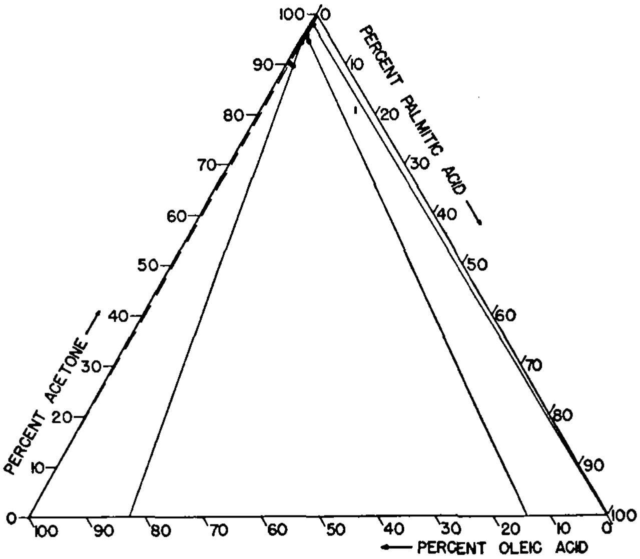

FIG. 6. Phase diagram of oleic acid-palmitic acid-acetone at —20°C.

The maximum solubility of palmitic acid in commercial hexane was about 0.06 g./100 g. at —30°C., and 0.01 g./100 g. at —40°C. These values were slightly lower in acetone. Oleic acid was soluble in commercial hexane to the extent of 1.9 g./100 g. at

TABLE II

Compositions of the Original Oleic Acid-Palmitic Acid-Acetone Mixtures and Phases Present at Equilibrium[a]

Temp. °C.	Original mixture			Liquid phase			Solid phase			
							By difference		By calculation	
	Palmitic acid	Oleic acid	Solvent	Palmitic acid	Oleic acid	Solvent	Palmitic acid	Oleic acid	Palmitic acid	Oleic acid
0	....	....	....	0.650	....	99.350	100.00	....	100.00	....
	2.560	2.560	94.880	0.825	2.583	96.592	100.00	0.0	....	....
	1.698	7.482	90.820	1.103	7.436	91.461	100.00	0.0	....	....
	1.686	15.406	82.908	1.343	15.276	83.381	100.00	0.0	....	....
—10	0.801	....	99.199	0.289	....	99.711	100.00	0.0	....	....
	0.670	2.450	96.880	0.379	2.377	97.244	100.00	0.0	....	....
	0.779	7.736	91.485	0.462	7.745	91.793	100.00	0.0	....	....
	2.381	14.046	83.573	0.621	14.298	85.081	100.00	0.0	....	....
—20	0.319	....	99.681	0.094	....	99.906	100.00	0.0	....	....
	0.590	1.545	97.865	0.134	1.543	98.323	98.00	2.0	100.00	0.0
	1.182	3.945	94.873	0.153	3.822	96.025	85.93	14.07	....	....
	1.062	9.382	89.556	0.156	5.212	94.632	17.06	82.94	17.64	82.36
	0.871	8.000	91.129	0.164	5.356	94.480	18.61	81.39	....	....
	0.035	9.612	90.353	0.036	5.600	94.364	0.0	0.0	0.0	0.0
—30	0.539	....	99.461	0.038	....	99.962	100.00	....	100.00	....
	0.307	....	99.693	0.032	....	99.968	100.00	....	100.00	....
	1.879	1.253	96.868	0.065	1.241	98.694	97.91	2.09	....	....
	0.244	2.410	97.346	0.060	1.967	97.973	28.87	71.13	....	....
	0.039	2.584	97.377	0.039	1.978	97.983	0.0	100.00	....	....
—40	0.232	2.167	97.601	0.013	0.674	99.313	12.74	87.26	13.25	86.75
	0.539	1.589	97.872	0.009	0.658	99.333	33.90	66.10	35.67	64.33

[a] Compositions are expressed in weight (gram)-per cent of total solution.

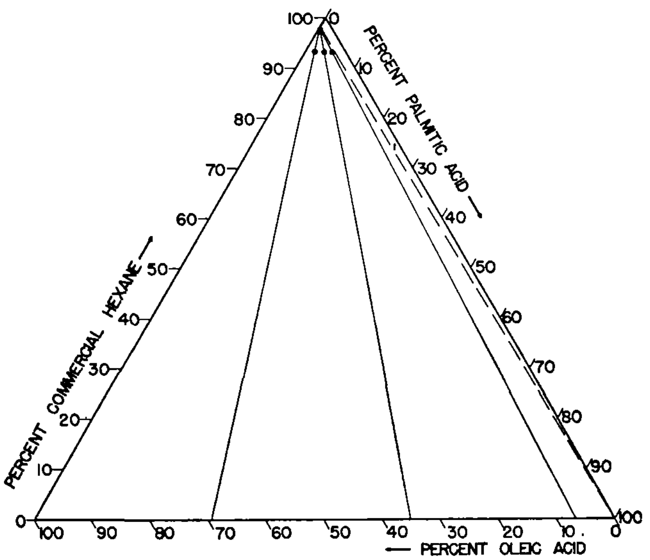

Fig. 7. Phase diagram of oleic acid-palmitic acid-hexane at —30°C.

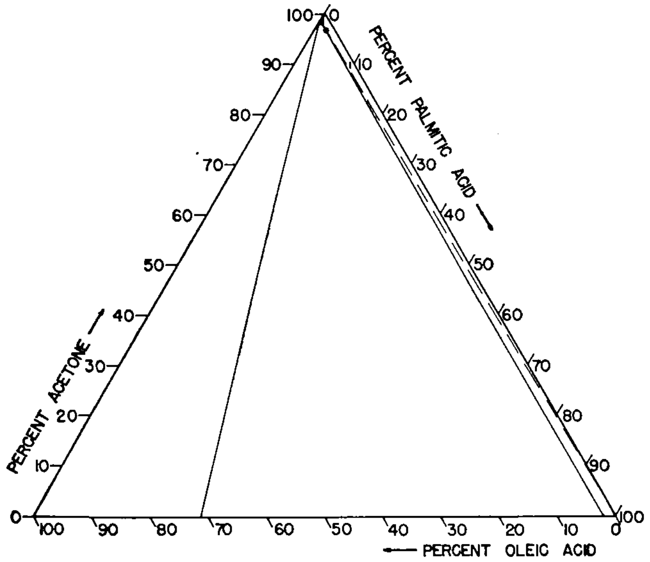

Fig. 8. Phase diagram of oleic acid-palmitic acid-acetone at —30°C.

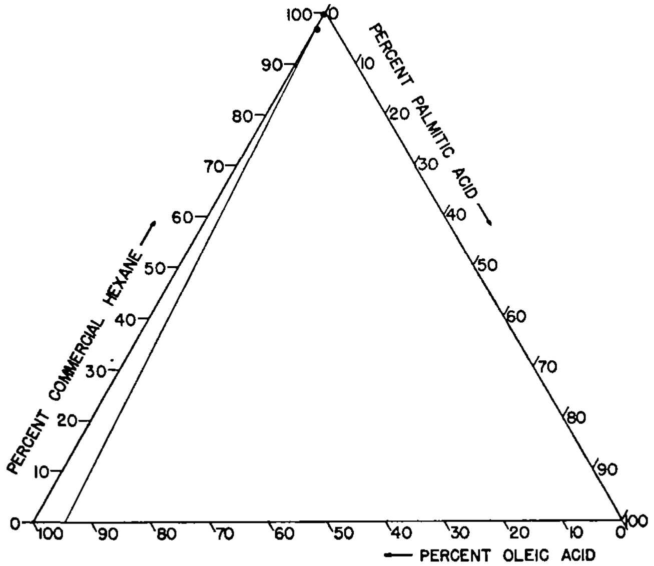

Fig. 9. Phase diagram of oleic acid-palmitic acid, commercial hexane at —40°C.

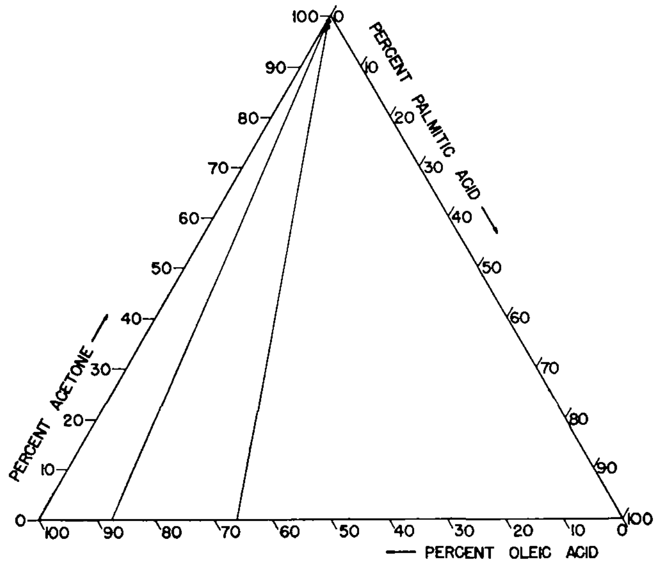

Fig. 10. Phase diagram of oleic acid-palmitic acid- acetone at —40°C.

—30°C., and 0.3 g./100 g. at —40°C. In acetone, these values were 2 g./100 g. and 0.6 g./100 g. at —30°C. and —40°C., respectively.

The intersolubilizing effects noted in this work confirm the observations reported by Waentig and Pescheck (2), who state that at all temperatures the mutual solubility effect decreases with increasing concentration of the second component.

Effect of Different Solvent-Fatty Acid Ratios. The chief effect of increasing the amounts of solvent in oleic-palmitic acids mixtures at 0° and —10°C., those temperatures at which oleic acid was completely soluble, was the increase in maximum solubility of palmitic acid. At a constant solvent-acids ratio, increasing proportions of oleic to palmitic acid increased the solubility of the latter acid to its maximum for both solvents; further addition of oleic acid resulted in liquid phases unsaturated with respect to either acid hence no solid phase appeared. Lowering

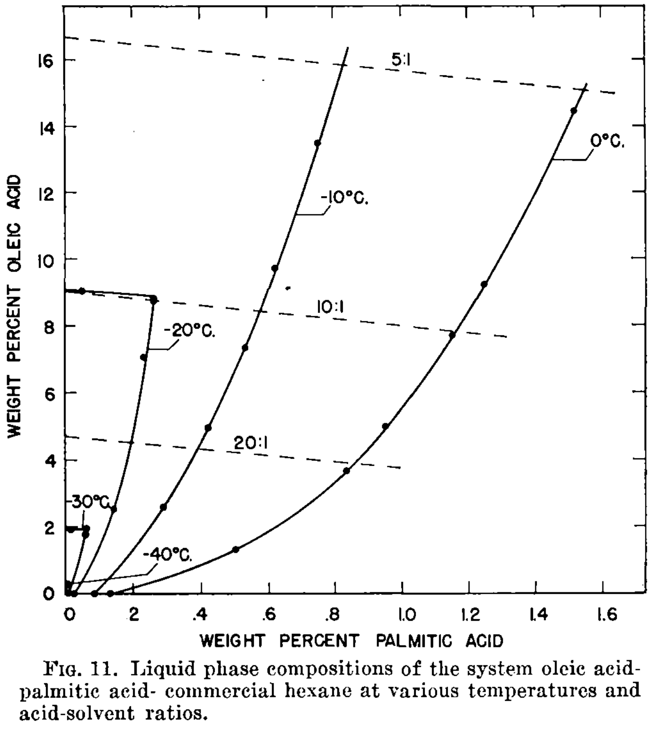

Fig. 11. Liquid phase compositions of the system oleic acid-palmitic acid- commercial hexane at various temperatures and acid-solvent ratios.

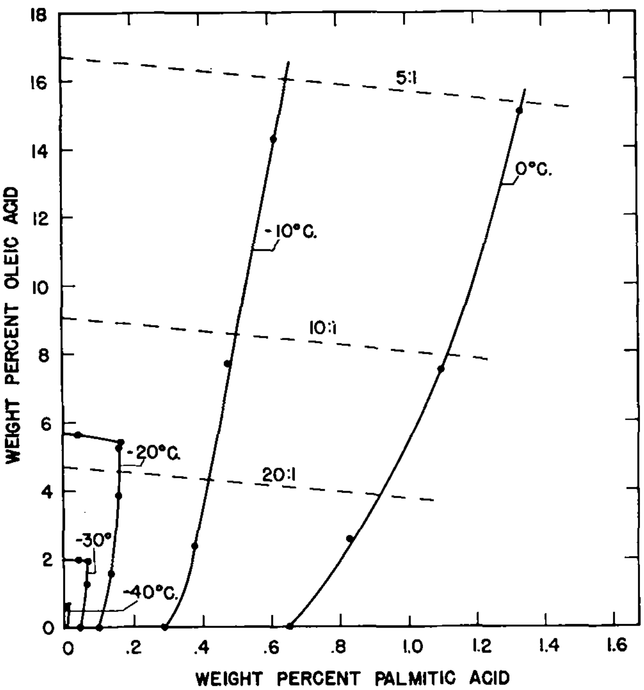

Fig. 12. Liquid phase compositions of the system oleic acid-palmitic acid-acetone at various temperatures and acid-solvent ratios.

of the solvent-acids ratio when an unsaturated condition prevailed caused the liquid phase to become saturated with palmitic acid, thus decreasing the amount of this acid in the liquid phase. Compositions of the liquid phases, at the maximum solubilities of palmitic acid and on a solvent-free basis, are contained in Table III, from which it can be observed that lowering the temperature from 0° to —10°C. decreased the palmitic acid content of the liquid phases approximately 4 to 11%, depending upon solvent ratio.

At temperatures of —30° and —40°C. the solubility of each acid was proportional to the amount of solvent present as neither acid was completely soluble at these temperatures, and at solvent-fatty acid ratios up to 20:1.

The general behavior of these systems were the same as those reported in a previous publication (3).

TABLE III

Liquid Phase Compositions at Maximum Solubilities of Palmitic Acid With Three Solvent Acid Ratios (on solvent-free basis)

Temp. °C.	Fatty acids[1]	Commercial hexane			Acetone		
		5:1	10:1	20:1	5:1	10:1	20:1
0	Oleic Palmitic	90.6 9.4	87.2 12.8	82.0 18.0	92.0 8.0	87.8 12.2	80.4 19.6
—10	Oleic Palmitic	95.0 5.0	93.7 6.3	91.6 8.4	96.5 3.5	94.8 5.2	91.8 8.2

[1] The values are per cent of total acids.

From the family of curves obtained it is possible to predict the degree of separation obtainable in any mixture of oleic and palmitic acids, with either acetone or commercial hexane as the solvent, provided equilibrium exists in the system.

Summary

1. The ternary systems, oleic acid-palmitic acid-commercial hexane and oleic acid-palmitic acid-acetone, containing varying amounts of the three components have been equilibrated at 0°C., —10°C., —20°C., —30°C., and —40°C.
2. From compositional data of the liquid and solid phases in equilibrium at each isotherm, ternary phase diagrams have been constructed. From these diagrams it is possible to predict the degree of separation which can be obtained with any given mixture of oleic and palmitic acids, using either acetone or commercial hexane as solvent.
3. The liquid phase boundaries have been established for each isotherm investigated and have been constructed on an enlarged scale.
4. The intersolubilizing effect of oleic acid on palmitic acid is greater in commercial hexane than in acetone although each acid is more soluble in acetone than in commercial hexane.

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