Vapor-Liquid Equilibrium Data for Fatty Acids and Fatty Methyl Esters at Low Pressures[1]

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THE increasing application of distillation, rectification, and other contacting equipment in the chemical process industries requires more and more vapor-liquid equilibrium data under various conditions of temperature and pressure. In the following article an attempt is made to obtain some data which can be applied to binary mixtures of the common fatty acids, methyl esters, and also combinations of both.

Where two liquids are mutually soluble, as is the usual case for fatty acids and methyl esters, and their vapor obeys the perfect gas law, the composition of the vapor is given by Raoult's law. This law states that at any particular constant temperature the partial pressure (p_a) of one component of a mixture is equal to the mole fraction (x) of that component multiplied by its vapor pressure in the pure state (P_a) at the temperature of the liquid.

$$p_a = x\, P_a$$
$$p_b = (1 - x)\, P_b$$

However, in general, the composition of the vapor arising from a solution of one liquid in another is an empirical function of the composition of the solution and must be experimentally determined. The data of greatest interest is the relation between liquid composition and vapor composition at constant pressure because the data is actually obtained in this form as the result of experimentation and because the values thus expressed change but slightly with moderate variation in pressure or temperature.

Table I presents physical data for the pure acids and esters studied. The difference in refractive index was not great enough for analysis of various composition of methyl stearate and methyl palmitate and therefore saponification values, determined very precisely in alkali-resistant Corning glass, were selected. Since the same condition prevails for fatty acids, acid values were selected for analysis of binary mixtures of lauric acid and myristic acid. It was also decided to use acid values to analyze mixtures of methyl laurate and lauric acid, the third binary mixture being investigated.

Method

The method used to determine vapor-liquid equilibrium data for the various binary systems was to obtain samples of vapors (as condensed liquids) which were in exact equilibrium with samples of the liquid itself at a total pressure of 4 mm. Hg. There are several important requirements to be followed in order to obtain a true equilibrium sample (1).

1. Apparatus used should be unaffected by the liquid or vapor. For atmospheric and lower pressures on all-glass apparatus of Pyrex is most suitable.
2. The composition of the boiling solution should be constant. This is accomplished by the recycle of condensed vapor into the liquid.
3. There should be no liquid spray in the vapor. This is a serious problem at low pressure with high boiling point compounds which tend to bump. An air leak through a stopcock eliminated most of the bumping during experimental runs. A bulb was fashioned in the vapor line to cut down entrainment as much as possible. Samples were taken after relatively long periods of distillation had elapsed with no bumping.
4. There should be no superheated surface above the boiling liquid to cause total vaporization.

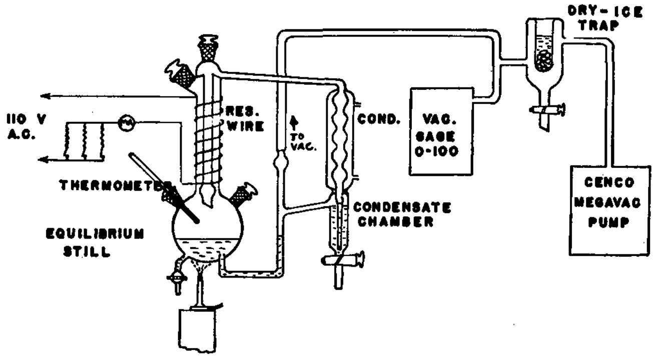

FIG. 2. Diagram of vapor-liquid equilibrium apparatus used at low pressures.

5. There should be no fractionation of the vapors. A vapor jacket around the inner vapor line helps to a certain degree, but additional electric resistance heating was found to be necessary during the runs.
6. The amount of boiling liquid should be large in comparison to the size of the vapor sample obtained. This allows the system to attain equilibrium in a much shorter time.
7. The composition of the liquid should remain constant during the sampling period. The vacuum was broken during the sampling period and the increase in pressure immediately halted all boiling and recycling.

Apparatus

Vapor-liquid equilibrium samples were obtained at a total pressure of 4 mm. Hg. with the still detailed in Figure 1, which still is a modification of the one previously described by Othmer (1). The apparatus is of Pyrex glass throughout, allowing visual observation, and all joints and stoppers are of No-Lub ground-glass construction for use at high vacuum.

The top of the vapor line extends above the level of the tubing leading to the condenser in order to prevent vapor condensate from running back into the still. The volume of the condensate receiver was made 10 ml. to give a sample large enough for varied methods of analysis. Condensed vapor enters the receiver through a tube extending to within one-eighth inch of the bottom of the chamber, and then recycles into the still body.

Figure 2 is a diagram of the set-up used for the equilibrium runs. About 150 ml. of sample was charged into the still body, and the ground glass stoppers and stopcocks were set in place. Stoppers

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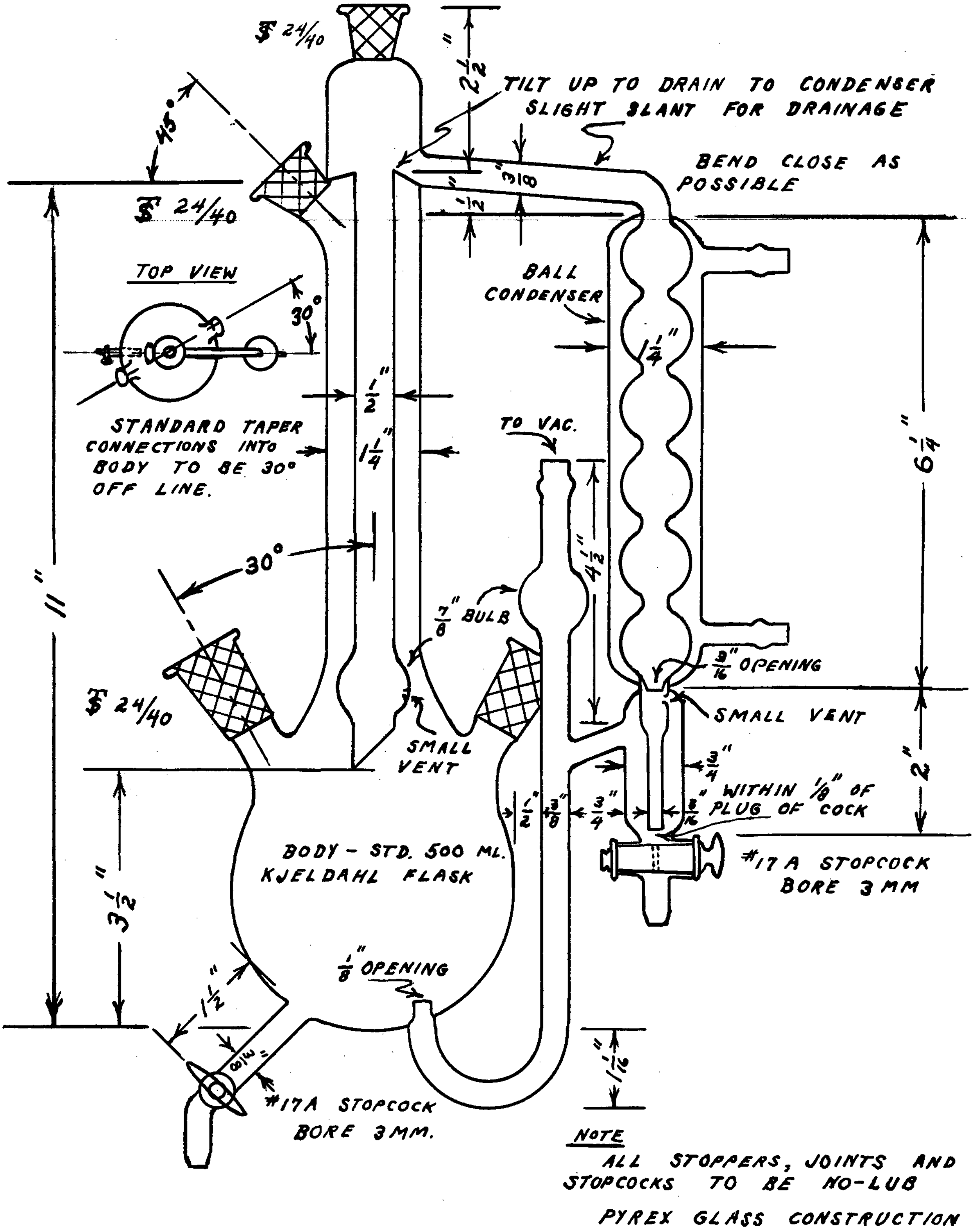

FIG. 1. Vapor-liquid equilibrium still.

were coated with colloidal graphite, and stopcocks with high temperature lubricant before insertion in the apparatus. Vacuum was obtained with a Cenco Megavac pump, and a Zimmerli gauge with a range of 0-100 mm., graduated in 0.1 mm. Hg., was used to measure the pressure. A dry-ice trap was installed in the system to catch vapors which may have escaped from the still.

The vacuum pump was turned on and a pressure of 4.0 ± 0.2 mm. was maintained during all the runs. Chips were added to prevent bumping, and the still was heated with a small Bunsen burner. Sufficient air leaked through the stopcock used for taking liquid samples that no additional air leak was necessary. Current in the Inconel resistance wire around the vapor neck was adjusted until no refluxing took place

TABLE I

Physical Data for Fatty Acids and Methyl Esters

	Mol. Wt.	Acid Value	Sap. Value	M. P. °C.	B. P. °C. @ 4.0 mm.	Refractive Index
Methyl Laurate	214.34	0	26.17	5	113	1.4215 ^{45}
Methyl Myristate	242.39	0	23.14	19	141	1.4271 ^{45}
Methyl Palmitate	270.44	0	20.74	29.5	163	1.4317 ^{45}
Methyl Stearate	298.50	0	18.79	38	184	1.4346 ^{45}
Lauric Acid	200.31	28.01	28.01	43.2	154	1.4183 ^{82}
Myristic Acid	228.37	24.57	24.57	53.9	174	1.4308 ^{60}
Palmitic Acid	256.42	21.88	21.88	61.8	192	1.4273 ^{80}
Stearic Acid	284.47	19.72	19.72	68.8	210	1.4299 ^{80}

in the vapor line. Aluminum foil and asbestos cement were used around the top of the vapor line to cut down heat losses. Recycling was allowed to take place for at least a half hour in all cases, which was more than sufficient to obtain constant temperature in the still body. Air alone was observed to be sufficient to condense hot vapors although hot water was used in several cases to prevent solidification in the vapor condensate line.

A series of mixtures of two components that differed by about 10 mole per cent were run, and equilibrium samples of liquid and vapor were taken after breaking the vacuum. This stopped all boiling, and 10 ml. samples were withdrawn and stoppered in labeled bottles.

Preparation of Materials

Pure methyl ester was obtained by treating a neo-fat fatty acid with K Mn O_4 to remove unsaturates, esterifying with methanol and sulfuric acid, removing the excess methanol and distilling the ester from a Claisen flash at 1-2 mm. pressure. The methyl ester was fractionated through a jacketed Pyrex glass column packed for two feet with glass Raschig rings, operating at a reflux ratio of 16-1, and a pressure of about 3 mm. Hg. Samples selected for future runs were checked for their boiling point and refractive index.

A pure fatty acid was prepared by saponifying a pure methyl ester with KOH, splitting out the fatty acid with HCl, washing repeatedly until free of mineral acid, and drying for several days in a vacuum desiccator.

Analysis of Samples

Saponification Values: About 1.5 grams of methyl ester was accurately weighed into a saponification flask of Corning alkali-resistant glass, approximately 30 ml. of neutral alcohol was added, and then 20 ml. of N/2 alcoholic KOH was carefully aliquoted with a pipette. The sample was refluxed on a hot plate for exactly one hour, the condenser was washed down with neutral alcohol, and the sample back-titrated with N/5 HCl using thymol blue as an indicator. An automatic burette was used, titration was always begun from the same initial reading, and samples were titrated to the same color tint in all cases. A blank was run with every batch of determinations.

TABLE II

Saponification Value-Composition Data for Known Mixtures of Methyl Palmitate-Methyl Stearate

Saponification Value as % KOH	Mole Per Cent Methyl Palmitate	Mole Per Cent Methyl Stearate
20.59	100.0	0.0
20.46	90.8	9.2
20.26	81.5	18.5
19.89	62.3	37.7
19.51	42.4	57.6
19.12	22.0	78.0
18.87	9.9	90.1
18.64	0.0	100.0

Saponification values were run in duplicate and the average did not differ by more than 0.02 saponification units from the two determinations. Samples of known composition were also weighed out and saponification values determined (Table II). The saponification values versus mole percentage of the methyl esters of the known mixtures were plotted as a calibration curve and used in the subsequent determination of the sample compositions. The object of such careful analysis was to determine compositions with a precision of 1 mole per cent.

Acid Values: About 1.5 grams of fatty acids or a fatty acid-methyl ester mixture was accurately weighed into a saponification flask of Corning alkali-resistant glass, approximately 30 ml. of neutral alcohol was added and the sample warmed on a hot plate. The sample was titrated in a water bath at a temperature of 50-55° C., using N/5 KOH which was added from a water jacketed burette at a temperature of 25-26° C. A mixture of thymol blue and phenolphthalein was used as an indicator with the appearance of a green tint taken as the end point, and all samples were titrated to the same green tint.

Acid values were run in duplicate, and the average did not differ by more than 0.02 acid value units from the two determinations. Samples of known composition were also weighed out and acid values determined (Tables III and IV). Plots of acid value versus mole percentage for known mixtures were used in the subsequent determination of the sample compositions.

The analysis of mixtures of fatty acids by means of acid value is complicated by polymerization when fatty acids are refluxed at their boiling point for periods of time such as occur during the obtaining of vapor-liquid equilibrium samples. Several liquid residues after equilibrium runs were analyzed before and

TABLE III

Acid Value-Composition Data for Known Mixtures of Lauric Acid-Myristic Acid

Acid Value as % KOH	Mole Per Cent Lauric Acid	Mole Per Cent Myristic Acid
27.72	100.0	0.0
26.90	77.2	22.8
26.09	53.2	46.8
25.28	27.7	72.3
24.47	0.0	100.0

TABLE IV

Acid Value-Composition Data for Known Mixtures of Methyl Laurate-Lauric Acid

Acid Value as % KOH	Mole Per Cent Methyl Laurate	Mole Per Cent Lauric Acid
0.01	100.0	0.0
6.96	73.9	26.1
13.97	48.6	51.4
20.86	24.5	75.5
27.97	0.0	100.0

after a vacuum distillation, and the increase in acid value after distillation plotted versus time. A correction from this plot was applied to the liquid samples obtained during the equilibrium runs since the vapor samples did not contain any of the polymerized material.

Results

Methyl Palmitate-Methyl Stearate. Vapor pressure-temperature data for pure methyl esters have been reported by Althouse and Triebold (2) and by Norris ~~and Terry (3). The logarithm of vapor pressure was~~ plotted versus the reciprocal of the absolute temperature in order to obtain the data on a straight line (Figure 3). Vapor pressure data from Figure 3 were used to compute Raoult's law vapor-liquid compositions. The compositions of experimental vapor-liquid equilibrium samples were obtained from a plot of saponification value versus mole percentage for known mixtures of methyl palmitate-methyl stearate, and are presented in Table V.

The experimentally determined vapor-liquid equilibrium data and the calculated Raoult's law data were plotted in Figure 4. There was a good agreement between the experimental data and the calculated ideal data which shows that the system follows Raoult's law closely and almost within experimental error.

The vapor liquid equilibrium data were evaluated by the method of Carlsen and Colburn (4). Their work showed that a plot of the logarithm of the activity coefficient against the composition of each component of a binary system is remarkably sensitive to errors in experimental measurement. The activity coefficient is a measure of the deviation from Raoult's law and is expressed by the following equation:

TABLE V

Experimental Vapor-Liquid Equilibrium Data for Methyl Palmitate-Methyl Stearate at 4 mm. Pressure

Temperature t, °C. (Approx.)	Mole % Methyl Palmitate		Deviation Factors	
	Liquid X	Vapor y	γ_1	γ_2
163	100.0	100.0	......	......
163	87.2	94.0	1.13	1.13
165	77.6	89.6	1.10	1.06
167	64.7	83.8	1.06	0.90
169	54.0	74.4	1.06	1.01
171	43.2	67.4	1.07	0.95
174	31.4	53.8	1.03	0.95
176	25.3	42.4	0.92	1.00
~~178~~	~~19.0~~	~~35.9~~	~~0.99~~	~~0.97~~
181	12.1	24.4	0.94	0.94
183	0.0	0.0	......	......

$$\gamma = \frac{P\,y_1}{p_1\,x_1}$$

where P is the total pressure
p_1 the vapor pressure of pure component 1
x_1 the mole % of component 1 in the liquid
y_1 the mole % of component 1 in the vapor

Deviation factors are presented in Table V for methyl palmitate-methyl stearate. These values vary around 1.00 and do not show any general trend, either positive or negative, as in the usual case of non-ideal solutions. It was quite difficult to obtain good deviation data since it is a function of the vapor

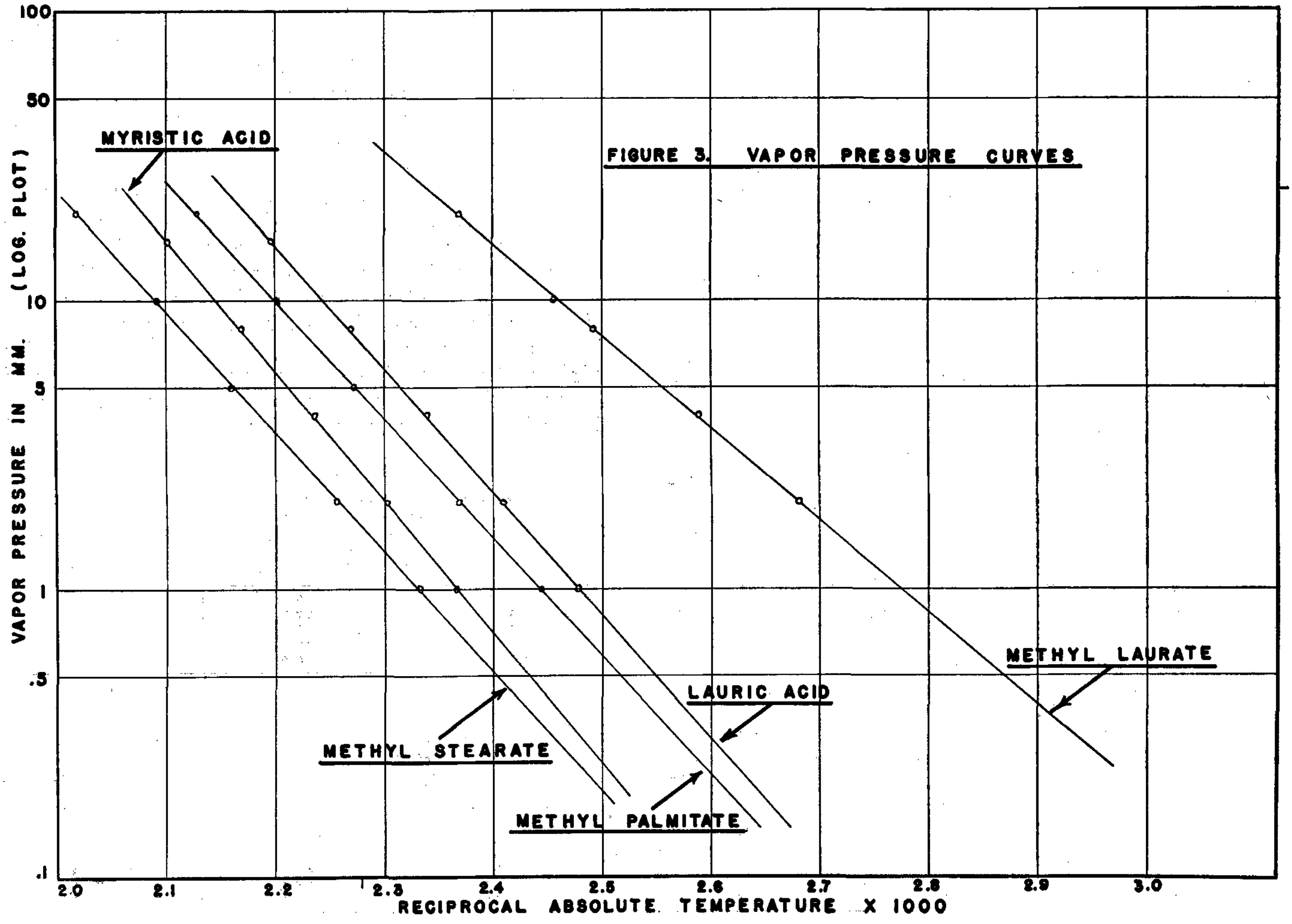
FIGURE 3. VAPOR PRESSURE CURVES

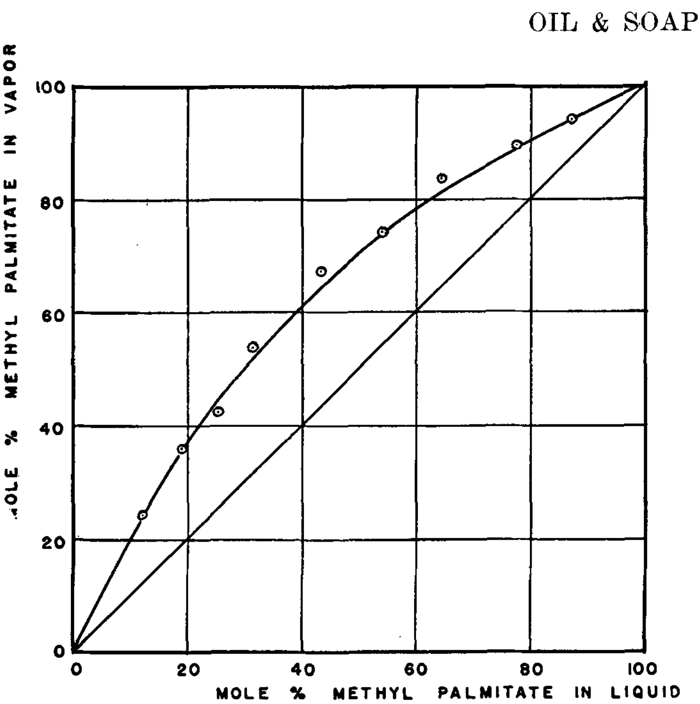

FIG. 4. Vapor composition vs. liquid composition for methyl palmitate-methyl stearate at 4 mm. pressure.
Solid line, calculated from Raoult's law.
Circles, experimental data.

pressure of the pure ester, which vapor pressure is a function of the temperature, and the temperature during the experimental run varied appreciably with small changes in pressure. However, the deviation factors were close enough to 1.0 to say that the system obeyed Raoult's law at a pressure of 4.0 ± 0.2 mm. Hg.

Lauric Acid-Myristic Acid. Vapor pressure-temperature data for pure fatty acids have been reported by Pool and Ralston (5). These data were plotted on a $^1/T$ — log P plot to obtain the data on a straight line (Figure 3). Vapor pressure data from Figure 3 were used to compute vapor-liquid compositions by Raoult's law.

Since the analysis was based on small differences in acid value, the formation of any small quantity of a polymer with a zero acid value will have a correspondingly large effect on the analysis. Two equilibrium liquid samples were totally distilled under vacuum, and acid values were run on the samples before and after distillation. The increase in acid value was plotted versus time, and a straight line running through the origin was obtained. The average increase of acid value as % KOH was 0.07% per hour, and this corresponded to an average rate of polymer formation of 0.23% per hour at 155-170° C. for mixtures of lauric acid and myristic acid.

Corrections to the liquid equilibrium samples obtained during the experimental runs were obtained from the above plot and applied to the acid values depending upon the time of refluxing. The compositions of experimental equilibrium samples were then obtained from a plot of acid value versus mole percentage for known mixtures of lauric acid-myristic acid, and are presented in Table VI.

The experimentally determined vapor-liquid equilibrium data and the calculated Raoult's law data were plotted in Figure 5, and a noticeable deviation was obtained. Deviation factors show a noticeable negative trend as in the usual case of a non-ideal solution, and the system can be considered non-ideal or not obeying Raoult's law at a pressure of 4.0 ± 0.2 mm. Hg.

TABLE VI

Experimental Vapor-Liquid Equilibrium Data for Lauric Acid-Myristic Acid at 4 mm. Pressure

Temperature t. °C. (Approx.)	Mole % Lauric Acid		Deviation Factors	
	Liquid x	Vapor y	γ_1	γ_2
154	100.0	100.0	......	......
156	84.0	95.5	1.05	0.77
159	67.4	83.7	0.95	1.10
162	51.4	72.1	0.92	1.07
164	43.5	61.7	0.85	1.14
169	23.4	32.7	0.66	1.16
169	22.1	34.2	0.73	1.09
174	0.0	0.0	......	......

Methyl Laurate-Lauric Acid. Vapor pressure-temperature data from Figure 3 were used to compute vapor liquid compositions by Raoult's law. The compositions of experimental equilibrium samples were obtained from a plot of acid value versus mole percentage for known mixtures of methyl laurate-lauric acid, and are presented in Table VII.

TABLE VII

Experimental Vapor-Liquid Equilibrium Data for Methyl Laurate-Lauric Acid at 4 mm. Pressure

Temperature t.°C. (Approx.)	Mole % Methyl Laurate		Deviation Factors	
	Liquid x	Vapor y	γ_1	γ_2
113	100.0	100.0	......	......
116	87.2	98.4	0.99	1.22
120	70.2	96.1	1.00	0.99
125	52.5	92.5	1.03	0.88
130	37.5	85.7	1.04	0.93
137	23.4	74.6	1.06	0.90
141	14.4	62.4	1.23	0.94
146	9.1	46.9	1.18	0.95
154	0.0	0.0	......	......

The experimentally determined vapor-liquid equilibrium data and the calculated Raoult's law data were plotted in Figure 6. There was a good agreement between the experimental and the calculated

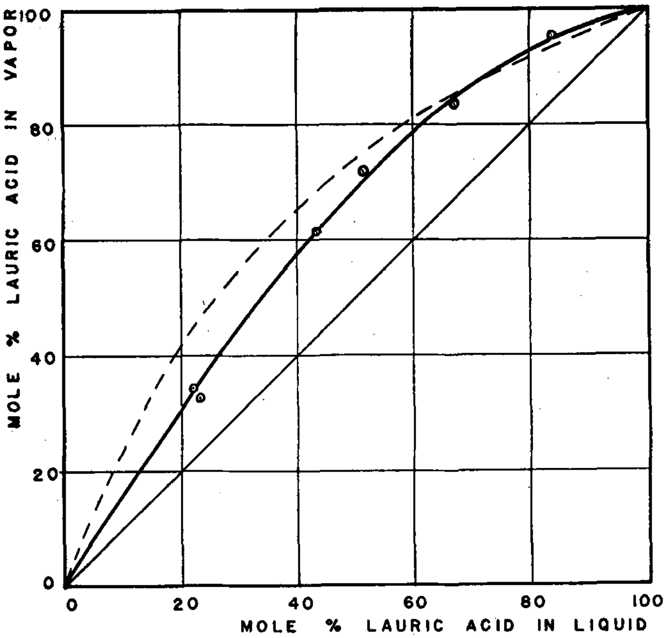

FIG. 5. Vapor composition vs. liquid composition for lauric acid-myristic acid at 4 mm. pressure.
Solid line, experimental data.
Dashed line, calculated from Raoult's law.

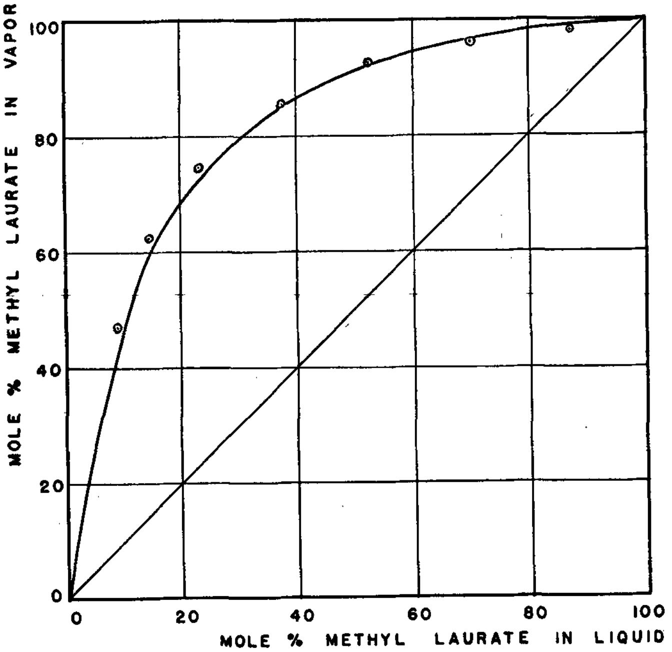

Fig. 6. Vapor composition vs. liquid composition for methyl laurate-lauric acid at 4 mm. pressure.
Circles, experimental data.
Solid line, calculated from Raoult's law.

ideal data. Deviation factors do not show any definite positive or negative trend from a value of 1.0, and the system can be said to obey Raoult's law at a pressure of 4.0 ± 0.2 mm. Hg.

Conclusions

The experimental vapor-liquid equilibrium data obtained with a mixture of methyl esters, and a mixture of a fatty acid and the corresponding methyl ester, were in agreement with calculated Raoult's law data at a pressure of 4.0 ± 0.2 mm. Hg.

The system lauric acid-myristic acid was observed to be non-ideal or not obeying Raoult's law at a pressure of 4.0 ± 0.2 mm. Hg. An average rate of polymer formation of 0.23% per hour at 155-170° C. was determined for mixtures of lauric acid and myristic acid.

The above work shows the feasibility of obtaining useful vapor-liquid equilibrium data for fatty materials at low pressures.

Acknowledgment

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Nomographs for Determining Relative Bleaching Costs of Adsorbents

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ONE of the problems confronting the refiner or chemist is to determine the relative merits of various bleaching adsorbents. It is frequently found, for example, that the more expensive absorbents are more economical to employ because their use effects a savings in handling costs and in lower loss of oil in the press cake.

The accompanying monographs offer a rapid method for evaluating these differences between bleaching adsorbents. Two operations are involved: first, the determination of cost of adsorbent itself plus adsorbent handling cost, and second, the determination of value of oil lost in the press cake. The sum of these two items offers a basis for comparing adsorbents and is taken as the bleaching cost. Motive power and other costs incident to bleaching are assumed to be constant for all adsorbents. For convenience the computations are based upon bleaching one ton of oil.

The procedure is as follows:

(1) *Cost of adsorbent itself plus adsorbent handling cost.*

Determine the cost of the adsorbent per ton as used. Add to this the cost of handling one ton of adsorbent. The example following illustrates how the cost of handling may be determined. Any plant can establish its own handling costs by substituting in the example its specific conditions.

(a) Unloading car — trucking to storage and stacking. (Requires 8 trips for one man, at $0.70 per hour, handling 5 bags at a time. Assuming 5 minutes per round trip, this would equal 40 minutes, or)	$0.47
(b) Trucking from storage to bleach tanks. (Requires 8 trips for one man, at $0.70 per hour, handling 5 bags at a time. Assuming 2 minutes per round trip, this would equal 16 minutes, or)	$0.18
(c) Opening bags and dumping into bleach tanks. (Requires one man, at $0.70 per hour, 20 minutes to open 40 bags and dump into tank at ½ minute per bag, or)	$0.23
(d) Dressing press. (Requires one man, at $0.70 per hour, one hour to dress a 1,000-pound press, or about 2 hours per ton of clay as charged)	$1.40
(e) Opening and cleaning press. (Requires one man, at $0.70 per hour, one hour to open and clean a 1,000-pound press, or about 2 hours per ton of clay as charged)	$1.40
(f) Trucking spent clay and bags away. (Requires 7 trips for one man, at $0.70 per hour, handling 400 pounds per trip. Assuming 5 minutes per trip and 2,800 pounds of used clay per ton of clay as charged, this would equal 35 minutes, or)	$0.41
(Total handling, 5.85 man-hours at $0.70 per hour = $4.09)	
(Assuming 10% of the sum of the above items for overhead, or)	$0.41
Total Clay Handling Cost per Ton of Clay as Charged	$4.50