Table II. Equilibrium Data

Temp., °C.	Refractive Index		Mole Fraction Methanol	
	Liquid	Vapor	Liquid	Vapor
64.1	...	...	1.000	1.000
65.5	1.36761	1.33103	0.754	0.999
68.0	1.38677	1.33421	0.590	0.998
77.5	1.40824	1.33175	0.360	0.995
89.2	1.41712	1.33135	0.250	0.995
101.0	1.42131	1.33382	0.185	0.985
110.0	1.42426	1.33853	0.142	0.960
131.5	1.42719	1.34424	0.100	0.922
147.2	1.42914	1.35597	0.075	0.845
166.0	1.43137	1.38433	0.032	0.610
171.1	1.43172	1.39182	0.027	0.540
180.3	1.43240	1.40748	0.015	0.368
188.6	1.43273	1.42363	0.010	0.152
199.0	...	...	0.000	0.000

The activity coefficients, $\gamma = (y/x)/(p^{\circ}/p)$, were calculated but are not reported. The nature of the system is such that one of the phase compositions is within 0.02 mole fraction of a pure material for nearly all points. Any normal experimental error in composition determination causes exaggerated errors in the activity coefficients. It was felt that the comparison of the data with that calculated from Raoult's Law is more significant.

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Vapor-Liquid Equilibria for the Methyl Oleate and Methyl Stearate Binary System

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The methyl oleate-methyl stearate vapor–liquid equilibrium behavior deviates only slightly from the ideal. The total pressure technique, using a modified U–tube manometer, gave precise vapor pressure measurements.

PRECISE DETERMINATIONS of the vapor pressures of pure methyl oleate and methyl stearate and of known mixtures of these compounds have revealed that the system exhibits nearly but not quite ideal vapor-liquid equilibrium behavior. The nonidealities are negative deviations from Raoult's law. The equilibrium data reported here are in qualitative agreement with gas chromatographic behavior of these compounds. A binary mixture of methyl oleate and methyl stearate separates normally in gas chromatography on a saturated hydrocarbon substrate, but on a polyester substrate, a reversal of volatility occurs because of interaction of the oleate double bond with ester groups.

The equilibrium data were obtained by the total pressure technique. A special adaptation of an ordinary U-tube manometer was used to make the precise pressure measurements that were necessary in order to reveal the slight nonidealities present in the methyl oleate–methyl stearate system. The relative volatility α, defined as the ratio of the vapor pressures of the pure components, ranges from about 1.08 to 1.15.

EXPERIMENTAL

The need for high precision can be appreciated by plotting values of y-x *vs.* x for the actual nonideal system and for the same system assuming ideal behavior and also for a system which has a larger separation factor. This is shown in Figure 1. To define differences due to nonideal behavior in the oleate–stearate system, analytical techniques sensitive to 0.1% or better are required. It is difficult or impossible to achieve this on rather small samples. However, quite precise measurements of the vapor pressures can be made and this was a main reason for using the total pressure approach.

Apparatus. A U-tube manometer, suitably modified, was used successfully to measure the low pressure–high temperature equilibrium pressures. A drawing of the manometer is shown in Figure 2. The problems which arise in low pressure–high temperature work with organic materials prevented the use of presently available equilibrium stills.

Successful precise equilibrium measurements in the range 30 to 700 mm. of Hg pressure on fatty acids, esters, and alcohols in this laboratory were first made (*9*) using a Cottrell-type equilibrium still developed by Williams (*11*). Sumantri (*15*) and Supina (*10*) determined that this type of unit had an upper operating limit with fatty acids and esters of about 180° C. and a lower limit at 20 to 30 mm. of Hg. In the region below 20 mm. of Hg, the pressure drop through the Cottrell tube may account for three or more centigrade degrees of superheating, thus limiting the usefulness of this type of still for low pressure measure-

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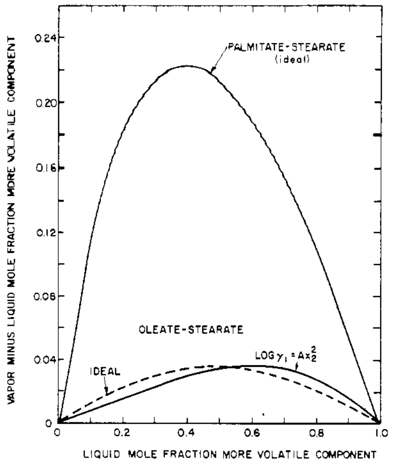

Figure 1. Comparison of vapor-liquid equilibrium relation for methyl oleate–methyl stearate with corresponding hypothetical ideal system, and with methyl palmitate–methyl stearate system

ments. The upper temperature limit of 180° C. stems largely from the fact that wall temperatures much greater than 180° C. are necessary to transfer a sufficient amount of heat to operate the still at 180° C. These wall temperatures are high enough to cause decomposition of the fatty esters and acids.

Preliminary work on methyl oleate and stearate indicated that the best way to get the low pressure, vapor-liquid equilibria was by using a static type of apparatus (*12*). This static type of apparatus avoids the problems that are encountered with the dynamic equilibrium stills. The problems are superheating, which is encountered when boiling occurs and is invariably accompanied by bumping at low pressures; pressure drop, which is more serious when circulating a rarefied vapor; and decomposition, which causes erroneous results and takes place at increasing rates as the temperature is increased. In a manometer, a static device, there is no circulation and hence no pressure drop. There is no boiling, which reduces the likelihood of superheating, and decomposition can be made less of a problem since no heat of vaporization need be supplied; therefore, a vapor bath operating at the equilibrium temperature can be used to maintain the temperature.

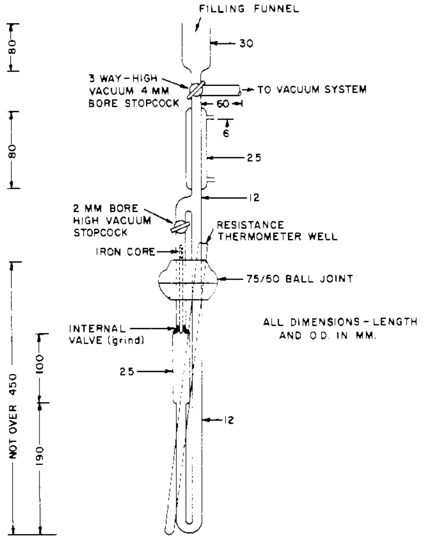

Figure 2. Modified U-tube manometer for measuring equilibrium vapor pressure by static method

The manometer used in the present study functioned as a closed end manometer while measurements were being made. At other times it was simply a U-tube with the liquid of interest in it. It was operated in the range from 0.8 to 15 mm. of Hg without difficulty. As with any closed end manometer, the pressure on the closed end side was equal to the vapor pressure of the manometer fluid at any temperature. To measure this pressure in the closed end, the pressure in the open end was raised until it equaled the pressure in the closed end. The equality of pressures was determined by observing when the liquid levels in both arms of the manometer were equal. Once the pressures were equalized, a measurement of the pressure could be made by using a second pressure gage connected into the line leading to the open side of the manometer.

The reason for fixing the manometer so that both arms could be open was to facilitate and indeed make possible complete degassing of the liquid while in the manometer. It was not possible to do this with a true closed end manometer which had no provision for evacuating the closed end side. Enough gas was adsorbed on the glass walls to cause appreciable and erratic pressures. This gas could be removed by prolonged degassing for periods of about 24 hours at temperatures above 150° C. in the manometer used in this study.

The internal valve was actuated by a magnet and was installed to prevent vapors from the material in the manometer rising into and condensing in the part of the manometer which is outside the vapor bath. This would mean that not all of the system was at constant temperature or for that matter, at constant pressure.

Procedure. Eleven to 15 ml. of material were charged to the manometer with care being exercised to avoid contamination with stopcock grease. A vapor bath was used to maintain the high temperatures needed. A sensitive mercury manometer controlled an on-off pressure regulator on the vapor bath which enabled temperatures to be held constant to 0.01° C. Equilibrium temperature measurements were made with a platinum resistance thermometer and a Mueller bridge.

A diagram of the experimental unit is shown in Figure 3. The operation of the unit involved a sequence of steps and slow, careful, painstaking effort was required to achieve good results. The initial steps involved filling the manometer with material whose vapor pressure is to be measured. An inert gas atmosphere was used with compounds sensitive to atmospheric contamination.

The vapor bath operated in the 400 to 700 mm. of Hg region, so a liquid having the needed boiling points in this pressure range was used to fill the vapor bath. This liquid should be fairly pure, as impure liquids will fractionate and thus not give steady boiling temperatures. After filling the manometer and vapor bath, the units were put

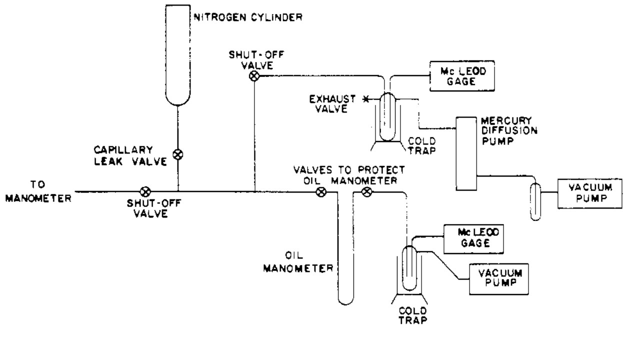

Figure 3. Diagram of experimental unit

together, and the various vacuum lines and necessary utilities were connected.

The vacuum pump was started with precautions to avoid sudden surges. The oil manometer must be protected from such surges which blow the manometer oil into the vacuum lines. Next the vapor bath pressure system and heater were started. The vapor bath pressure was controlled by a mercury manometer which had an adjustable probe and acted as an on-off switch controlling a bleed valve. A sketch of this vacuum system is shown in Figure 4. This system can be set to hold any pressure from atmospheric down to less than 1 mm. of Hg by means of the movable probe.

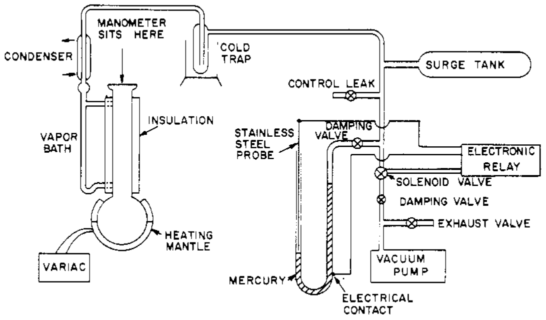

Figure 4. Diagram of vacuum system

The final operation consisted of making a pressure measurement after the system had been degassed for 24 hours and then allowed to reach a steady state at the desired temperature. The levels in the modified manometer were equalized by bleeding nitrogen through a capillary into the open side. The levels were checked with a telescope with a hairline mounted on a cathetometer. The sequence of events was to adjust the levels to equality, read the temperature, read the pressure on the oil manometer, read the temperature again, and recheck the equality of the oil levels. The levels were not allowed to differ by more than 0.05 mm. of the hot fluid and the temperatures had to agree within less than 0.01° C. from one reading to the next. After making such a determination the vapor bath pressure was adjusted to yield a higher temperature and the entire procedure was repeated after steady state had been reached.

The materials used in this study (Applied Science Laboratories, State College, Pa.) were highly purified and the gas chromatographic analysis indicated that only trace amounts—*i.e.*, less than 0.1%—of the nearest boiling isomers were present.

VAPOR PRESSURE

Vapor pressures of purified methyl oleate and methyl stearate were determined in the range of 0.8 to 15 mm. of Hg. The values are listed in Table I. Included in the table are values of the constants A, B, and C for the Antoine equation:

$$\mathrm{Log}_{10}\, p = A - \frac{B}{t + C}$$

for each compound. The equations with the respective constants will reproduce the experimental temperatures for the various pressures to a root mean square deviation of ±0.060° C. for methyl oleate and ±0.063° C. for methyl stearate.

Boiling temperatures determined by earlier investigators were compared at 1 mm. of Hg. The values are listed in Tables II and III for methyl stearate and methyl oleate, respectively. Also given are the values for the present work. Five earlier investigators give methyl stearate boiling temperatures at 1 mm. of Hg that cover a range of 9.1° C. Values given by four investigators for methyl oleate boiling temperatures cover a range of 6.4° C.

The first value listed in Table II was measured in the initial stages of the present investigation in a pot still equipped with a reciprocating stirrer (*6*). Boiling temperatures were determined at other pressures in this pot still, and the constants for the Antoine equation as calculated from experimental data were A = 5.90665, B = 1352.70, and C = 70.2761. The experimental temperatures could be reproduced with a root mean square deviation of ±0.34° C. Boiling temperatures for methyl stearate as measured in the pot still and with the manometer are compared in Table IV by listing temperatures calculated at integral values of the pressure. The relatively large discrepancy at 1 mm. of Hg arises because of pressure drop effects in the pot still at pressures of 1 mm. of Hg or less (*6*).

EQUILIBRIUM STUDY

Various methods have been used for calculating partial pressures of the components in binary liquid mixtures from experimental knowledge of the liquid mole fractions and total pressure alone. A number of authors have discussed the theory (*3, 4*) and the apparatus (*8*).

The total pressure method was used in the present work, and the data were interpreted using Raoult's law and the Margules equations, which are integrated forms of the constant temperature Gibbs-Duhem equation.

The measured vapor pressures of the mixtures exhibited negative deviations from Raoult's law—*i.e.*, the vapor pressures for the mixtures were less than those calculated from Raoult's law and the vapor pressures of the pure components. Table V lists the calculated and measured total pressures for two binary mixtures. It is important to consider whether the differences are real. Since the deviations from Raoult's law are negative, decomposition may be ruled out as a reason for their appearance. The decomposition products would be relatively volatile and would cause the measured vapor pressures to be higher than the calculated pressures.

The possibility exists that polymerization could cause the discrepancies. Polymerization would decrease the total pressure and thus give the appearance of negative deviations. Only 2% of the oleate would need to be polymerized to give the observed results if the polymer were assumed to have negligible vapor pressure. However, the formation of such polymer is considered to be very unlikely. Swern and others have shown that the oleate double bond enters

Table I. Vapor Pressure Data

Methyl Oleate			Methyl Stearate		
Press., mm. Hg	Temp., ° C.		Press., mm. Hg	Temp., ° C.	
	Expl.	Calcd.		Exptl.	Calcd.
1.040	155.57	155.57	0.821	154.01	153.98
1.541	162.77	162.83	1.028	158.04	158.10
2.188	169.56	169.58	1.870	169.52	169.47
2.247	170.18	170.11	1.991	170.72	170.70
2.940	175.46	175.49	2.849	177.82	177.90
3.235	177.51	177.44	4.000	185.07	184.98
4.727	185.37	185.40	5.430	191.52	191.57
6.320	191.35	191.73	5.673	192.52	192.53
7.258	194.74	194.83	9.737	204.91	204.80
8.498	198.46	198.42	11.226	208.09	208.15
10.147	202.46	202.55	13.019	211.67	211.70
11.743	205.96	206.01			
13.247	208.93	208.92			
15.038	212.07	212.02			

Antoine Equation Constants

Methyl Oleate	Methyl Stearate
A = 8.1067992	A = 8.7443153
B = 2728.0494	B = 3239.3514
C = 181.66082	C = 212.86733

Table II. Boiling Temperatures of Methyl Stearate at 1 Mm. of Hg.

Investigator	Temperature, ° C.
This work: pot still	158.7
This work: manometer	157.6
Ackerman (*1*)	152.0
Norris (*7*)	155.5
Bonhorst (*2*)	161.1
Scott (*13*)	158.2
Liang (*5*)	152.2
Stage (*14*)	158.0

Table III. Boiling Temperatures of Methyl Oleate at 1 Mm. of Hg

Investigator	Temperature, ° C.
This work: manometer	154.85
Ackerman (*1*)	148.0
Norris (*7*)	152.5
Scott (*13*)	154.4
Liang (*5*)	152.3

Table IV. Methyl Stearate Boiling Temperatures Determined by Two Methods

	Temperature, ° C.	
Pressure, Mm. Hg	Manometer	Pot still
1	157.6	158.7
2	170.8	171.0
3	179.0	178.9
4	185.0	184.7
5	189.8	189.5
6	193.8	193.5
7	197.2	197.0
8	200.3	200.1
9	203.0	202.9
10	205.4	205.4
12	209.7	209.9
14	213.5	213.9

Table V. Vapor Pressure for Two Mixtures of Methyl Oleate and Methyl Stearate

		Pressure, Mm. Hg	
Mole Fraction Methyl Oleate	Temp., ° C.	Measured	Calculated
	Mixture 1		
0.4401	196.18	6.993	7.134
0.4401	200.64	8.513	8.674
0.4401	208.25	11.808	11.980
	Mixture 2		
0.7121	197.78	7.837	7.950
0.7121	204.72	10.580	10.716

into an olefinic polymerization reaction very slowly even when in a reactive system composed of methallyl oleate and vinyl acetate with 1% of benzoyl peroxide as a catalyst at temperatures above 100° C. (*16*). It does not seem that the methyl oleate–methyl stearate system in the absence of a catalyst and air would form any polymer during the brief periods of the present experiments.

The apparatus was constructed entirely of glass and was thoroughly degassed and flushed with nitrogen before every run. Furthermore, any appreciable rate of polymerization or decomposition would probably cause a drift of pressure with time. No such changes with time were noted during any of the experiments.

The Margules equations were used to express the data and subsequently to calculate activity coefficients. These equations are derived from the constant temperature form of the Gibbs-Duhem equation:

$$x_1\left(\frac{\partial \ln\gamma_1}{\partial x_1}\right)_{T,P} + x_2\left(\frac{\partial \ln\gamma_2}{\partial x_1}\right)_{T,P} = 0$$

The Margules equations were selected for the expression of the nonidealities because the ratio of the molar volumes of the two materials making up the binary is close to unity. The oleate-stearate binary fulfills the criterion. The densities of the oleate and stearate at 95° C. are 0.8197 and 0.8100, respectively, so that the ratio of molar volumes would be almost unity at this temperature. An increase in the temperature tends to cause the ratio to approach unity even more closely.

In attempting to fit the total pressure–constant temperature data to the Margules equations:

$$\text{Log}\gamma_1 = Ax_2^2 + 3Bx_1x_2^2 - Bx_2^3$$

$$\text{Log}\gamma_2 = Ax_1^2 + Cx_1^3 - 3Cx_2x_1^2$$

it was found that the constants in the Margules equations were equal when the best fit was obtained. This meant that the simple form of the Margules equations:

$$\text{Log}_{10}\gamma_1 = Ax_2^2$$

$$\text{Log}_{10}\gamma_2 = Ax_1^2$$

could be used to express the variation of the activity coefficients with liquid composition and that this variation is therefore symmetrical. The treatment assumes constant temperature and pressure and equal molar volumes and an ideal vapor phase.

These requirements are very closely satisfied for the system and conditions in question. The computation was made at 199° C., and at this temperature, the difference in the vapor pressures of the two components is only 1.1 mm. of Hg. The ratio of the molar volumes is about 1.01 and the vapor phase at 10 mm. of Hg and 199° C. would be expected to be very nearly ideal.

The activity coefficients at 199° C. are shown in Figure 5 and were calculated using $A = -0.0346$ in the reduced Margules equations. The vapor and liquid composition at

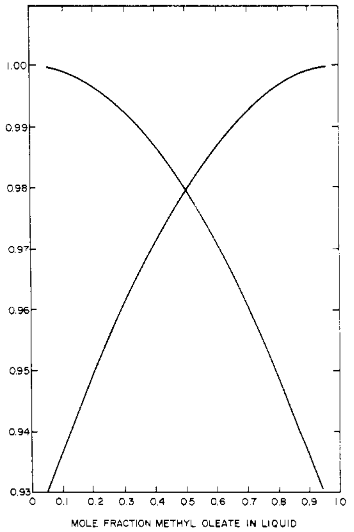

Figure 5. Activity coefficients of methyl oleate and methyl stearate at 199° C.

199° C. are listed in Table VI. The Margules equations were written in the form:

$$\gamma_1 = e^{[2.30259\,(A x_2^2)]} \quad \gamma_2 = e^{[2.30259\,(A x_1^2)]}$$

These expressions were substituted into the expression:

$$\pi = Po_1 x_1 \gamma_1 + Po_2 x_2 \gamma_2$$

The only unknown in the resulting expression is the constant A. At a temperature of 199° C., the vapor pressure for the binary mixture containing 0.4401 mole fraction methyl oleate was 7.915 mm of Hg, and this value was used along with the vapor pressure of the pure components at 199° C. to compute the desired value of A as −0.0346. This fixes the values of the γ_1 and γ_2, and the vapor compositions for any x, or x_2 at 199° C. as:

Table VI. Methyl Oleate and Methyl Stearate Equilibrium Vapor and Liquid Compositions at 199° C.

Mole Fraction Methyl Oleate In	
Liquid	Vapor
0.1	0.1071
0.2	0.2153
0.3	0.3233
0.4	0.4303
0.5	0.5350
0.6	0.6369
0.7	0.7349
0.8	0.8285
0.9	0.9169

$$\gamma_1 = \frac{Po_1 x_1 e^{[2.30259\,(-0.0346)\,x_2^2)]}}{\pi}$$

$$y_2 = 1 - y_1$$

where the subscript 1 applies to methyl oleate.

ACKNOWLEDGMENT

The authors wish to thank the National Science Foundation and the National Institutes of Health for substantial financial assistance.

NOMENCLATURE

A, B, C = constants in Antione equation
= constants in Margules equations
p = vapor pressure of pure component at temperature t in Antoine equation, mm. Hg
P = total pressure of system in Gibbs-Duhem equation
PO_1 = vapor pressure of pure methyl oleate
PO_2 = vapor pressure of pure methyl stearate
t = temperature of pure component at pressure p in Antoine equation, ° C.
T = temperature of system in Gibbs-Duhem equation
x_1 = mole fraction of methyl oleate in liquid
x_2 = mole fraction of methyl stearate in liquid
y_1 = mole fraction of methyl oleate in vapor
y_2 = mole fraction of methyl stearate in vapor
α = relative volatility, defined as ratio of the vapor pressures of methyl oleate and methyl stearate
γ_1 = activity coefficient of methyl oleate
γ_2 = activity coefficient of methyl stearate
π = total pressure of methyl oleate-methyl stearate system

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