Summary

A laboratory process has been developed which permits the isolation of a highly purified palmitic acid from cottonseed acids through the recrystallization of its cyclohexylamine salt from acetone and subsequent regeneration of the acid. The by-product, predominantly cyclohexylamine salts of the unsaturated fatty acids, can be modified and converted to morpholides which have shown promise as vinyl plasticizers. The morpholine salts can be obtained as a direct by-product by the use of an appropriate mixture of cyclohexylamine and morpholine with the composite acid. By using an amount of cyclohexylamine closely equivalent to the saturated fatty acid content and sufficient morpholine to make up the residual neutralization equivalent of the composite cottonseed acids, the saturated acids can be isolated as cyclohexylamine salts. The stripped mother liquor will consist essentially of the morpholine salts of the unsaturated acids. Pure palmitic acid is obtained by recrystallization of the cyclohexylamine salts. The complete process is applicable to fatty acids from other natural glyceridic oils in which the dominant saturated acid bears a ratio to the other saturated acids closely paralleling that in cottonseed oil. The process is not operable with partially hydrogenated oils.

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Vapor Pressure Equilibrium of Stearic Acid in Triglyceride and in High Paraffin Solutions

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NO VAPOR PRESSURE DATA on solutions of fatty acids are available which would indicate their behavior with respect to Raoult's law. In the literature it is therefore frequently assumed that solutions and mixtures of fatty acids, at least at higher temperatures, are ideal solutions (1, 2). On the other hand, numerous works give evidence of the molecular association of fatty acids in the vapor phase and in solution (3). Recently the degree of association of fatty acids has been determined in the pure state and in high-paraffin solutions at various temperatures by an infrared spectrometric method (4). In view of the association, deviation from ideality may be predicted.

In the present investigation the vapor-pressure equilibrium of stearic acid has been measured at 180°C. in peanut oil and high-paraffin solutions. It has been found that both systems show a positive deviation from Raoult's law. Quantitative relationship could be established between the degree of association of stearic acid and its partial vapor pressure. Evidence of association between triglycerides and fatty acids has been obtained.

Experimental

Vapor Pressure Equilibrium of Stearic Acid in Peanut Oil Solutions. The isothermic deodorizer, which has been described in a previous article (5) and, at moderate rates of flow of steam, has a vaporization efficiency of 1, has been found to be eminently suitable for the measurement of vapor pressures within the desired range of 1 micron to 10 mm. Hg. This deodorizer is essentially an entrainment-distillation apparatus, in which, for the present purposes, water vapor and iso-octane vapor were used as carrier gases. Since the vapor pressure of mercury is known exactly throughout a wide temperature range, it was used to test the apparatus.

The substances distilled over were determined; stearic acid, titrimetrically; mercury, gravimetrically. The pressure was maintained between 100 and 300 mm. by means of a manostat; lower pressures were avoided to prevent evaporation during the heating and cooling periods.

The vapor pressure values found for mercury at 180°C. are recorded in Table I. Their agreement with the literature values of 8.76 (6) and 8.79 (7) is satisfactory as the difference between the mean values is less than 1%. The method of measurement may thus be considered as suitable.

TABLE I
Vapor Pressure Determinations of Mercury at 180°C.

Steam flow rate........	1/h.	93	93	31
Vapor pressure........	mm. Hg.	8.76	8.73	8.65 mean: 8.71 mm.

The vapor pressure of the stearic acid (m.p. 69.9° C.) was determined with steam and also with iso-octane (2,2,4-trimethylpentane) as carrier gas as the latter is indifferent to triglycerides (see later measurements from the point of view of hydrolysis). Practically no difference was found between the two series of measurements, as may be seen from Table II.

The mean value of 0.796 mm. is in good agreement with the recent value of 0.80 mm. found by Pool and Ralston (8). This agreement has more importance because the latter value was obtained from boiling point measurements. Consequently it indicates that stearic acid vapors are not associated at 180°C. in the vapor phase. This conclusion however may not be extended to low fatty acids, which at this temperature have substantially higher vapor pressures and are therefore associated, as pointed out by Jantzen (9).

The vapor pressure of stearic acid in stearic acid/peanut oil solutions was determined under the same conditions as used in the above experiments, with iso-octane vapor as carrier gas. For the calculation the following equation, based upon Raoult's law (10), was used:

$$P'_v = P\frac{(M_o - M) + A\ln(M_o/M)}{(M_o - M) + S}$$

TABLE II

Vapor Pressure Determination of Stearic Acid at 180°C.

Steam flow rate	1/h	15	280	280	....	....	....
Iso-octane-vapor flow rate	1/h	....	....	....	15	15	15
Vapor pressure	mm. Hg.	0.786	0.782	0.808	0.805	0.790	0.808 mean: 0.796 mm.

in which P'_v = observed vapor pressure of the pure volatile substance
P = absolute pressure
M_0, M = moles volatile substance at the beginning and at the end
A = moles oil
S = moles steam or other indifferent vapor used as carrier.

The P'_v values found for different stearic acid concentrations (mean of initial and final concentrations) are recorded in Table III and represented in Figure 1 by curve a. It will be seen that, with solutions having a stearic acid concentration higher than *ca.* 20%, the P'_v values are slightly higher than the vapor pressure of pure stearic acid (P_v) whereas, for lower concentrations, greater deviations are found which increase with increasing dilution.

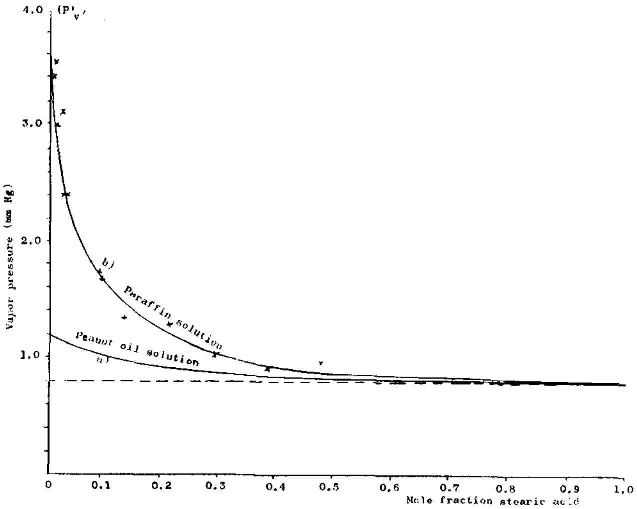

FIG. 1. Vapor pressure equilibrium of stearic acid in peanut oil and paraffin solutions.

These measurements indicate that the molecules of stearic acid are associated in the liquid phase and that in solutions containing less than 20% stearic acid dissociation occurs. Full confirmation of this conclusion was obtained from infrared spectroscopic measurements which enabled the degree of association in high-paraffin solutions to be determined (4).

Vapor Pressure Equilibrium of Stearic Acid in High-Paraffin Solutions. The degree of association of a dissolved fatty acid is dependent on the polarity of the solvent (11). Peanut oil is a polar solvent with a dielectric constant of 3.18. It may be expected that in a nonpolar solvent the degree of association of stearic acid and consequently the vapor pressure equilibrium will be different from those found in triglyceride solution. Such nonpolar solvents suitable for measurements at 180°C. are high paraffins, which have a dielectric constant of 2.10.

Vapor pressure measurements similar to those in peanut oil solution have been carried out at 180°C. in high-paraffin solutions.

Commercial paraffin wax (m.p. 56°C.), which consists of straight-chain high paraffins with very little variation in chain lengths (average $C_{26}H_{54}$) was used as solvent.

The method described above was applicable by reason of the relatively low vapor pressure of the paraffin itself, for which, using the same method, a value of 0.45 mm. Hg. was measured at 180°C. This very small pressure was taken into account by introducing the number of gram-moles paraffin distilled off (N) into the steam distillation equation given above.

$$P'_v = P\frac{(M_0 - M) + A \ln (M_0/M)}{(M_0 - M) + S + N}$$

After titration of the distilled stearic acid and extraction with light petroleum, N was determined gravimetrically. Moreover in the calculation of the number of gram-moles paraffin (A) half of the paraffin distilled off (N) was substracted. It was found however that, above 0.3 mole fraction stearic acid, the paraffin distilled off can be entirely disregarded and that, with more dilute solutions, the deviation falls within the experimental error.

The results so obtained, which are, in fact, theoretical vapor pressures of the pure acid (P'_v) calculated from the partial vapor pressures by Raoult's law, are recorded in Table IV and represented in Figure 1 by the individual points of curve b.

TABLE IV

Vapor Pressure Equilibrium of Stearic Acid in High Paraffin Solutions

Mol. fraction	P'_v (in mm. Hg.)
0.470	0.96
0.379	0.91
0.288	1.02
0.207	1.29
0.127	1.34
0.090	1.67
0.083	1.74
0.031	2.40
0.023	2.41
0.021	3.12
0.0109	3.0
0.0109	3.53
0.0064	3.42

The vapor pressures found with dilute solutions are surprisingly high. Graphical extrapolation to infinite dilution gives a vapor pressure as high as 3.9 mm.

On comparison of this value with that obtained from peanut oil solution—1.20 mm. at infinite dilu-

TABLE III

Vapor Pressure Equilibrium of Stearic Acid in Peanut Oil Solutions

Mol. fraction	0.0146	0.0235	0.083	0.1338	0.215	0.345	0.386	0.503	0.625	0.690	0.853
P'_v mm. Hg.	1.16	1.15	1.04	0.97	0.90	0.85	0.82	0.83	0.84	0.83	0.79

tions—it is apparent that stearic acid is strongly solvated in peanut oil.

It was seen from the relatively very high heats of dissociation and standard entropy changes (4) that only very slight association occurs between paraffin and stearic acid. It may therefore be assumed that in infinite dilution monomeric stearic acid is dissolved in an unassociated state and that its vapor pressure at 180°C. would most probably be 3.9 mm., were this substance to exist in a free, unassociated state.

Quantitative Relationship Between the Degree of Association and Vapor Pressure. The degree of association of stearic acid in high-paraffin solutions has recently been determined (4) for high concentrations and temperature ranges. It has been attempted to calculate with the aid of these data the vapor pressure of the pure dimeric acid and the vapor pressure equilibrium of stearic acid obtained in high-paraffin, as represented by Figure 1b.

Vapor Pressure of the Dimeric Acid. The degree of association[1] of pure stearic acid at 180°C. is 0.887 (4); from this it follows that the mole proportions are

$$m_1 = 0.1130 \text{ and } m_2 = 0.4435$$

while the mol. fractions are

$$x_1 = 0.202 \text{ and } x_2 = 0.798.$$

According to the above measurements, the vapor pressure of pure monomeric acid is 3.9 mm. Hg.; its partial vapor pressure in the pure acid, at 180°C., is then

$$P_{v_1} = 3.9 \times 0.202 = 0.788 \text{ mm. Hg.}$$

As the vapor pressure of the pure acid is 0.80 mm., the partial vapor pressure of the dimer can be indirectly found:

$$P_{v_2} = 0.80 - 0.788 = 0.012 \text{ mm. Hg.}$$

and its vapor pressure in the pure state is

$$P_{v_2} = \frac{0.012}{0.798} = 0.015 \text{ mm. Hg.}$$

As this is an indirect calculation, the error may be greater than with the vapor pressure of the monomer.

Normal pure stearic acid is therefore a mixture of monomeric and dimeric molecules, which, at 180°C., have vapor pressures of 3.9 mm. Hg. and 0.015 mm. Hg., respectively.

It is interesting to note that the vapor pressure at 180°C. of methylstearate, which is not associated, is 3.5 mm. Hg., a value which is very close to that found for monomeric stearic acid.

Vapor Pressure of Stearic Acid in Solution. Similar calculations were made for stearic acid in solutions, using the values $P_{v_1} = 3.9$ mm. Hg. and $P_{v_2} = 0.015$ mm. Hg., although the vapor pressure of the dimer can be disregarded over the whole concentration range.

The curve for the P'_v values thus obtained is shown in Figure 1, curve b; the individual points represent the P'_v values from vapor pressure measurements shown in the table. The agreement between the results from these two entirely different approaches is excellent; the points coincide with the curve. This indicates the suitability and accuracy of the infrared spectrophotometric method for the measurements of degrees of association and of the dynamic method for vapor-pressure measurements.

The Association of Fatty Acids and Triglycerides. In nonpolar solvents the dissociation of the dimer molecules is almost complete in high dilutions. The fact that in peanut oil the vapor pressure in high dilutions is lower than in paraffin indicates that in the former solvent the stearic acid is associated with triglyceride molecules. A part of the free monomeric molecules is bound to the nonvolatile solvent, resulting in a lower vapor pressure.

Actually there is a double equilibrium in peanut oil solutions, one between fatty acid molecules and the other between triglycerides and fatty acid molecules.

Schematically:

I—dimeric fatty acid $\leftrightarrows$ monomeric fatty acid

II—monomeric fatty acid + triglyceride $\leftrightarrows$ fatty acid/triglyceride complex.

The positive deviation measured in the peanut oil solution is therefore the resultant of a strong positive deviation and a less strong negative deviation. It is to be expected that the association between the fatty acid molecules is stronger than between the fatty acid and the triglycerides because the hydrogen bridges between $C = O$ and $H - O$ dipoles in fatty acids form an exceptionally strong ring structure which cannot be formed between triglycerides and fatty acids, where formation of only half the ring is possible.

Despite the weaker bonds the influence of the triglycerides is considerable as, in dilute solution, these are present in great excess, causing the equilibrium of reaction II to be shifted strongly to the right.

Actually, in the case of infinite dilution, only solvation occurs and no association of fatty acids.

Summary

The vapor pressure equilibrium of stearic acid has been determined at 180°C. in peanut oil and high-paraffin solutions. Positive deviation from Raoult's law has been observed in both of the systems; it was however essentially stronger in the nonpolar high-paraffin.

Extrapolation of the vapor pressures obtained in paraffin to infinite dilution indicated that monomer stearic acid in free state would have a vapor pressure of 3.9 mm. Hg. at 180°C. in comparison with 0.80 mm. of the pure stearic acid itself, which is a mixture of monomer and dimer molecules.

Quantitative relationships could be established between degree of association and vapor pressure. For pure dimeric acid at 180°C. a vapor pressure of 0.015 mm. Hg. has been calculated.

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[1] The degree of association expresses the fraction of the original molecules which are associated.