Summary

The lead chloride–lead bromide system has been studied by means of thermal analysis, conductivity, aqueous preparations and X-ray diffraction. No binary compounds exist in this system other than the preferential-replacement structure, PbCl′Br″, whose existence was demonstrated by the X-ray diffraction data. This "ordered" structure is stable at room temperature but not at the melting point, is isomorphous with lead chloride and lead bromide, and forms a complete series of solid solutions with both.

DETROIT, MICHIGAN RECEIVED APRIL 25, 1949

[CONTRIBUTION FROM THE LABORATORIES OF DISTILLATION PRODUCTS, INC.]

Vapor Pressures of Phlegmatic Liquids. I. Simple and Mixed Triglycerides[1]

BY E. S. PERRY, W. H. WEBER AND B. F. DAUBERT[2]

The vapor pressure measurements of phlegmatic[3] liquids, such as the triglycerides, require a method which imposes a minimum of thermal hazard to the substance under examination. Of the available methods capable of accommodating materials of this kind, the static method of Hickman, Hecker and Embree[4] employing the pendulum tensimeter appeared to be more promising than the dynamic methods proposed by Verhoek and Marshall[5] and Kapff and Jacobs.[6] In application, the dynamic methods have been limited to the vapor pressure measurements of plasticizer-type esters in the range of 10^{-2} to 10^{-4} mm. at 40 to 160°. The pendulum-tensimeter method, however, has been used with substances of lower volatilities which have perhaps even less thermal stability than the ester materials, such as, for example, 1,4-dipropyldiaminoanthraquinone. In addition, the method gives absolute pressure measurements in that the pressure of the vapor is measured directly as a force per unit area. In contrast to the dynamic methods, therefore, the results are independent of the theoretical equations of the kinetic theory and errors introduced by inaccuracies in accommodation coefficients are obviated. For these reasons the pendulum-tensimeter method seemed most generally applicable for the measurements reported below. In the present paper are presented the vapor pressures for a large number of triglycerides, including all of those having an even number of carbon atoms in the acid radical from tributyrin to tristearin; for mixed triglycerides, both saturated and unsaturated; and for several fractionated natural fats. In a subsequent paper[7] there will be presented the vapor pressures of a number of high molecular weight esters of the plasticizer and diffusion pump fluid types.

The theory for the pendulum-tensimeter method has been reported by the original authors,[4] therefore only the final equations will be reproduced here for convenience. The vapor pressure P is calculated from the effective weight of the pendulum M, the area of the orifice A, and the angular displacement θ, according to the relationship: $P = M/A \times \sin\theta$. For our specific apparatus the vapor pressure in mm. mercury is: $P = 1.075/8.96 \times 13.6 \times 10 \times \sin\theta = 0.0882 \times \sin\theta$.

Experimental

Apparatus.—A pendulum-tensimeter similar to that of Hickman, Hecker and Embree,[4] but incorporating the orifice heater recommended by Verhoek and Marshall,[5] was used. A small liquid trap was added to the reflux line to prevent loss of vapor from the boiler. The usual oil-bath was replaced by an air-bath so that the temperature range could be extended. This consisted of an aluminum box approximately 9″ × 9″ × 5″, lagged with asbestos paper. The first air-bath contained a single heater element wound in a flat coil and mounted just off the floor of the box. The heater was shielded and baffled to prevent irregular heating by radiation. Heat distribution in the box was examined by placing 8 thermometers at various points and recording the temperatures of each as the heat was progressively increased to 300°. A satisfactory heat distribution was not obtained by this method regardless of the baffle used and it was finally discarded in favor of one which responded better to the test. The new heater element consisted of a glass rod frame on which was wound asbestos-covered resistance wire equivalent to 1000 watts. The glass frame was cubical in shape and dimensioned so as to leave a half-inch space between it and the walls of the box on all sides. Resistance wire was wound evenly on all 12 rods of the frame. Power was controlled by a variable transformer. Air temperatures measured at various points in the box by means of thermometers as discussed above showed that the total disparity in temperatures was not over 2°. The bath was therefore used as such without any further attempts to better distribute the heat.

The aluminum box with heating element hung from a yoke which straddled the tensimeter and was supported so that it could rotate with the tensimeter. Two Pyrex windows were provided for better illumination and direct observation of the pendulum at the orifice. One window was located on the front wall of the box and the other on the rear wall. The use of the air-bath greatly facilitated the observation of the equilibrium point of the pendulum and thereby increased the reproducibility of the readings. It also extended the effective temperature range to well over 300°.

While collecting data, temperature measurements were made with a well-thermometer which protruded into the

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[1] Communication No. 151 from Laboratories of Distillation Products, Inc.

[2] Department of Chemistry, The University of Pittsburgh.

[3] Hickman and Weyerts, THIS JOURNAL, **52**, 4714 (1930).

[4] Hickman, Hecker and Embree, *Ind. Eng. Chem.*, **9**, 264 (1937).

[5] Verhoek and Marshall, THIS JOURNAL, **61**, 2737 (1939).

[6] Kapff and Jacobs, *Rev. Sci. Instruments*, **18**, 581 (1947).

[7] Perry and Weber, THIS JOURNAL, **71**, 3726 (1949).

TABLE I

EXPERIMENTAL DATA AND CALCULATED CONSTANTS OF THE TRIGLYCERIDES

	Material	Temp. (P_1 = 50μ) °C.	°K.	Temp. (P_2 = 1μ) °C.	°K.	A	B	L (cal./mole)	M. p., °C.	Carbon atoms in acid groups	Dühring's rule constant
1	Tributyrin	91	364	45	318	4250	13.37	19,450	....	12	0.920
2	Tricaproin	135	408	85	358	4950	13.82	22,650	....	18	.980
3	Tricaprylin	179	452	128	401	6060	15.12	27,800	....	24	.963
4	Tribenzoin	201	474	148	421	6450	15.30	29,500	75 -76	21	.981
5	Tricaprin	213	486	159	432	6510	15.08	29,800	31.5-32.0	30	.964
6	Trilaurin	244	517	188	461	7190	15.58	32,500	45 -46.5	36	.949
7	Trimyristin	275	548	216	489	7720	15.78	35,300	56 -57	42	1.000
8	Tripalmitin	298	571	239	512	8400	16.40	38,400	64.5-65.5	48	0.983
9	Tristearin	313	586	253	526	8750	16.60	40,000	71 -72	54	
10	1-Capryl-2-lauryl-3-myristin[8]	249	522	189	462	6880	14.90	31,500	36.5-37	36	1.020
11	1-Lauryl-2-myristyl-3-palmitin[8]	275	548	216	489	7720	15.80	35,300	49.5-50	42	0.983
12	1-Myristyl-2-palmityl-3-stearin[8]	297	570	237	510	8250	16.18	37,800	57 -58	48	0.983
13	2-Oleyl-1,3-distearin[9]	315	588	254	527	8660	16.42	39,600	44 -44.5	54	1.033
14	1-Myristyl-2-capryl-3-stearin[8]	274	547	215	488	7750	15.88	35,400	50.5-51.5	42	1.000
15	1-Myristyl-2-lauryl-3-stearin[8]	282	555	223	496	7860	15.84	36,000	53.5-54.5	44	1.034
16	1-Palmityl-2-capryl-3-stearin[8]	280	553	223	496	8090	16.30	37,000	53 -54	44	0.983
17	1-Palmityl-2-lauryl-3-stearin[8]	290	563	232	505	8360	16.55	38,200	56 -57	46	
18	Soybean oil	308	581	254	527	9650	18.30	44,200	....	54	
19	Olive oil	308	581	253	526	9430	17.92	43,100	....	54	

boiler and dipped below the surface of the liquid when the usual charge of 20–30 g. of material was used. With smaller charges of 3 to 10 g., the well was slightly above the liquid surface. However, the stem was entirely within the air-bath and the temperatures of the well-thermometer were in agreement with other calibrated thermometers located in the immediate vicinity, although outside of the well. The temperature of the oil layer in the boiler was thus assumed to be at the temperature of the bath.

Materials.—Most of the simple triglycerides were obtained from the Eastman Kodak Company. The mixed triglycerides, tricaprylin and tricaprin, were synthesized and purified at the University of Pittsburgh.[8,9] The simple triglycerides were further purified by molecular distillation and in some cases the distillation was preceded by a recrystallization from solvents. Because the amounts of the mixed triglycerides available were so small, purification had to be limited to recrystallization only. Distillation in the cyclic molecular still consisted of removing three strip cuts, the first of which amounted to 5% of the original charge and the others 10% each. The 2 succeeding 25% fractions were used for the vapor pressure measurements. The natural fats were also prepared by molecular distillation. The olive oil was an imported U. S. P. grade packaged by Magnus, Mabee and Reynard, Inc. Castor oil from several sources was used; two were refined commercial grades and the third was a U. S. P. grade. The corn and soybean oils were refined commercial products. In all cases, the original oil was first distilled into four equal fractions. The two middle fractions were again molecularly distilled, first removing a 25% strip cut and then collecting the succeeding 50% for examination in the tensimeter.

Melting points for most of the triglycerides used are given in Table I.

Procedure.—Most details of the procedure were similar to those recommended by the original authors.[4] Readings were taken after the temperature had reached and maintained a constant value for at least three minutes. Best results were obtained by adjusting the pendulum until it just appeared to float on the vapor, not quite touching the orifice. When sufficient sample was available, a 20- to 30-g. portion was used. With the mixed triglycerides where only limited amounts of material were available, the measurements were made with as little as 3 g. of sample. When using the smaller samples it was necessary to make the readings rapidly so that the material would not all evaporate before the desired temperature range was covered. It was found that results obtained by taking measurements while the temperature rose at the rate of 0.5 to 1° per minute were as good as those taken after the three-minute equilibrating period. This can be verified by an inspection of the results plotted in the figures of the next section. Measurements with all mixed triglycerides were done using this method of temperature increase. Individual temperature readings were taken to 0.5° values. More accurate measurements were not warranted in view of the reproducibility obtained as shown in Figs. 1 to 5.

Results and Discussion

The experimental data for the measurement of all the triglycerides are plotted in Figs. 1 to 5 on the usual log P *vs.* $1/T$ chart. The temperature data given in Table I are not necessarily determined points. These are the temperatures at which the straight lines drawn through the experimental points for each triglyceride intersect the 1- and 50-μ pressure values. This method of listing data was chosen merely as a convenience for permitting accurate reproduction of the vapor pressure curves and thus obviating the necessity of tabulating all of the experimental data in this report. The accuracy of the data, however, can be seen from the curves. In most every case the individual temperature measurements lie on a straight line, with deviations usually not greater than 2° from the line, and in many cases 1°. Data resulting from several independent sets of measurements with the same sample showed that the reproducibility of the curve was within 1°. A 1° variation in the slope of the line corresponds

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[8] Chen and Daubert, THIS JOURNAL, **67**, 1256 (1945).

[9] Jackson, Daubert, King and Longenecker, *ibid.*, **66**, 289 (1944).

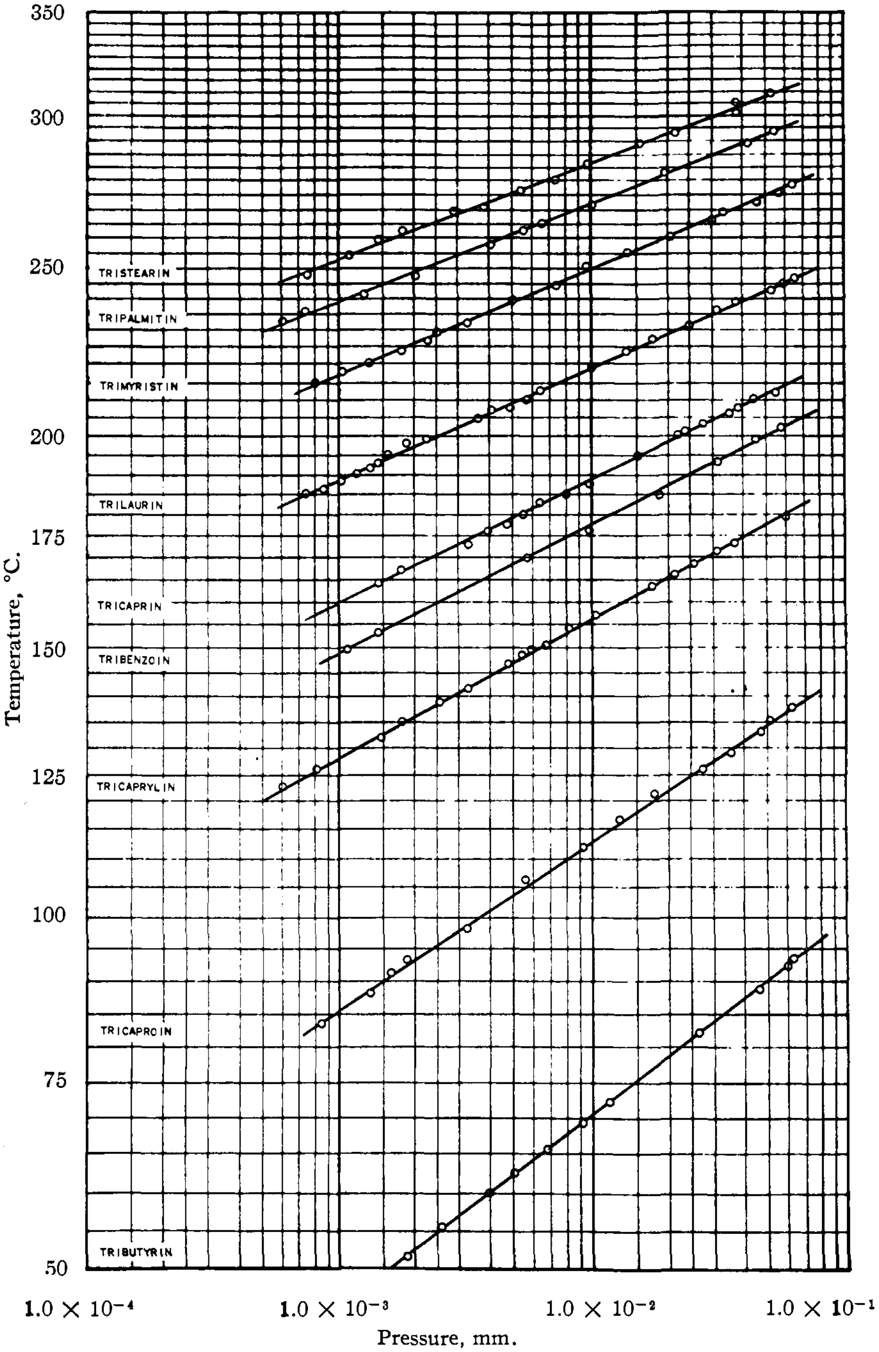

Fig. 1.—Experimental vapor pressure data.

to about a 2% change in the latent heats of vaporizations.

The curves connecting the points for each triglyceride can be expressed by the general equation: $\log P = -A/T + B$, where A represents the slope of the line and B is the y-intercept. These constants have been calculated for each material using the temperatures corresponding to pressures at 50 and 1 μ. The values are recorded in Table I. The latent heats of vaporization L in cal./mole are related to A as follows: $A = L/2.3R$, where R is the universal gas constant. The latent heats for each material have been calculated and are given in column 6 of Table I.

It will be noticed that the slopes of the curves for all triglycerides show a gradual increase as the number of carbon atoms in the acid chain increase. The degree of linearity obtained between latent heats of vaporization and molecular weight is shown by the plot of Fig. 6 in which the computed latent heats for the triglycerides are plotted against the total number of carbon atoms of the fatty acid side-chains. The points on the curve are numbered in accordance with the listing of Table I for the purpose of reference to the triglyceride in question. The adherence to straight line agreement is only fair but the general trend is clearly shown. Tribenzoin (point 4), containing 7 carbon atoms per acid group, 6 of which form an aromatic ring, shows a definite departure from the curve. This is not unexpected since it is known that aromatic groupings usually have lower vapor pressures than do the same number of carbon atoms arranged in open-chains. The vapor pressure–temperature relationship of tribenzoin lies between that for tricaprylin and tricaprin, perhaps being very close to that for an aliphatic triglyceride having 9 carbons in the acid chains.

The vapor pressure curves for the mixed triglycerides are given in Figs. 2, 3 and 4, according to the sequence of the acid groupings in each molecule. These data indicate that the vapor pressure appears to be independent of the group

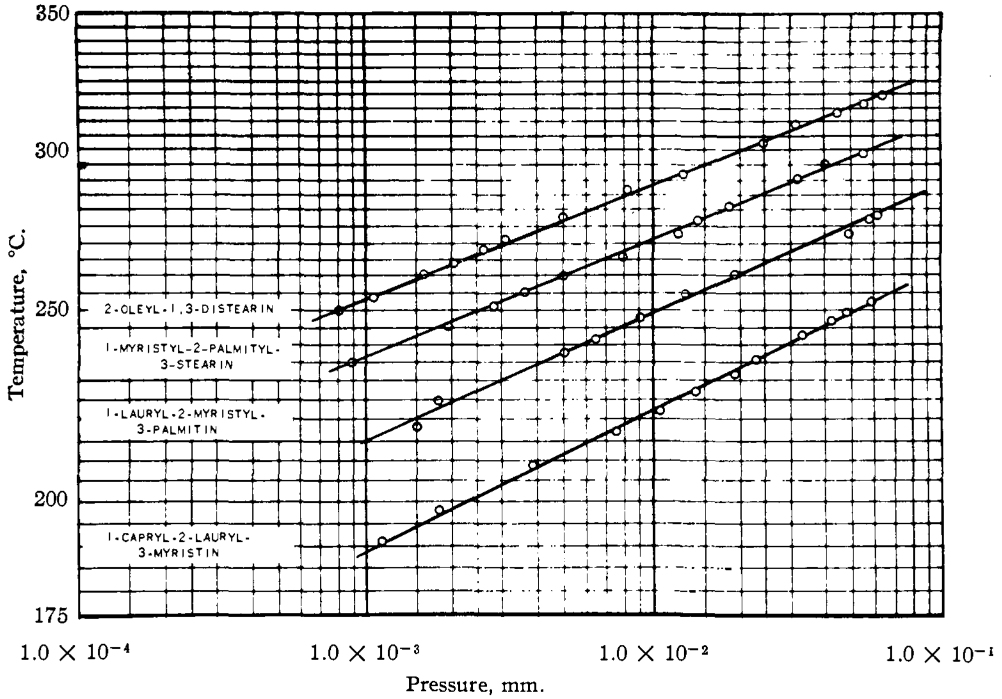

Fig. 2.—Experimental vapor pressure data.

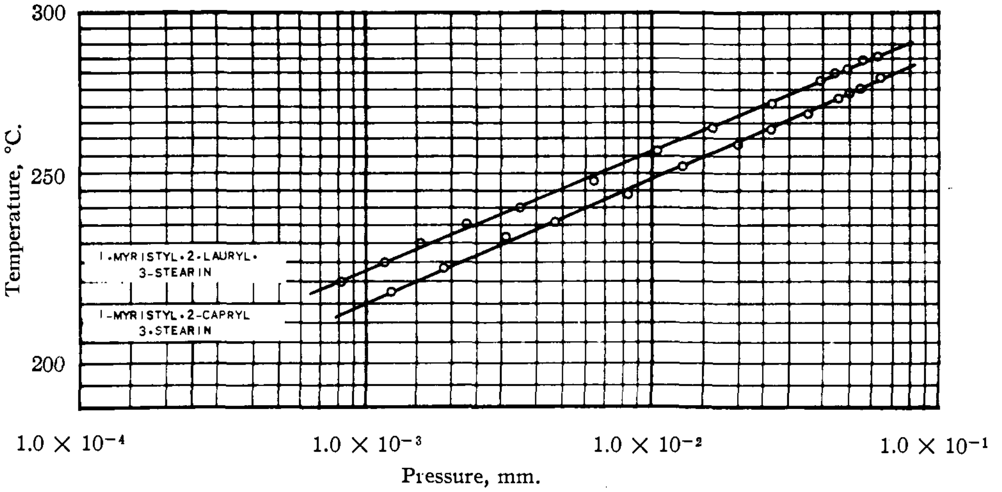

Fig. 3.—Experimental vapor pressure data.

arrangement and the individual chain-length of the acid groups. The principal influence is, perhaps, the total number of carbons in the molecule. For example, the three compounds: trimyristin, 1-lauryl-2-myristyl-3-palmitin and 1-myristyl-2-capryl, 3-stearin—all of which have a total of 42 carbon atoms in the acid groups—have comparable latent heats, as shown by the coincidence of points 7, 11 and 14 of Fig. 6. Likewise, the latent heat for tripalmitin is comparable to that for 1-myristyl-2-palmityl-3-stearin —points 8 and 12. Other correlations of this kind are evident from Fig. 6 or Table I. The effect of one double bond per triglyceride molecule has very little, if any, influence on the vapor pressure, as is shown by comparison of results for 2-oleyl-1,3-distearin with tristearin. The vapor pressure values for tristearin are very slightly higher than those for the oleyl distearin which, if significant, is at variance with the relative order of vapor pressures as would be deduced from boiling point data of saturated compounds and their unsaturated analogs. From the distillation of mixtures of quite pure methyl oleate and methyl stearate, Weitkampf and Brunstrun[10] have shown

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[10] Weitkampf and Brunstrun, *Oil and Soap*, **18**, 47 (1941).

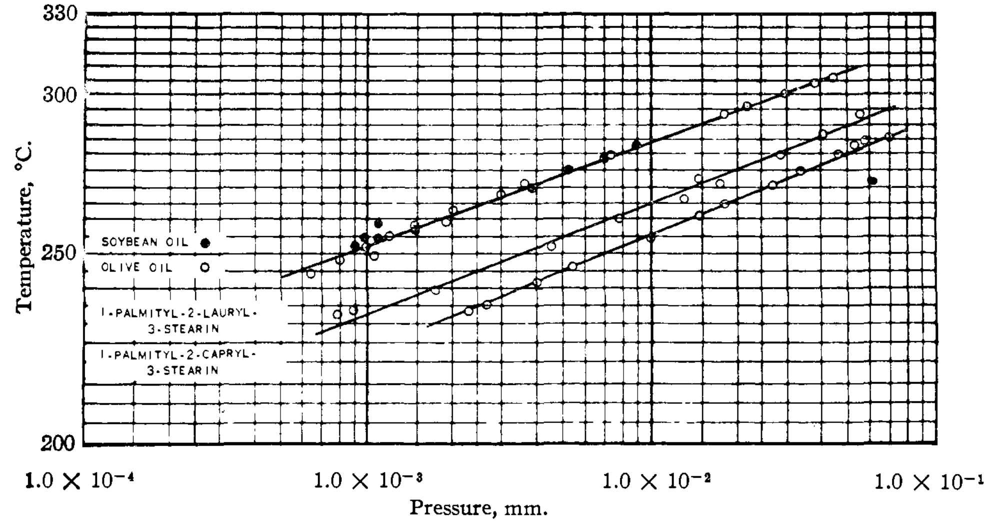

Fig. 4.—Experimental vapor pressure data.

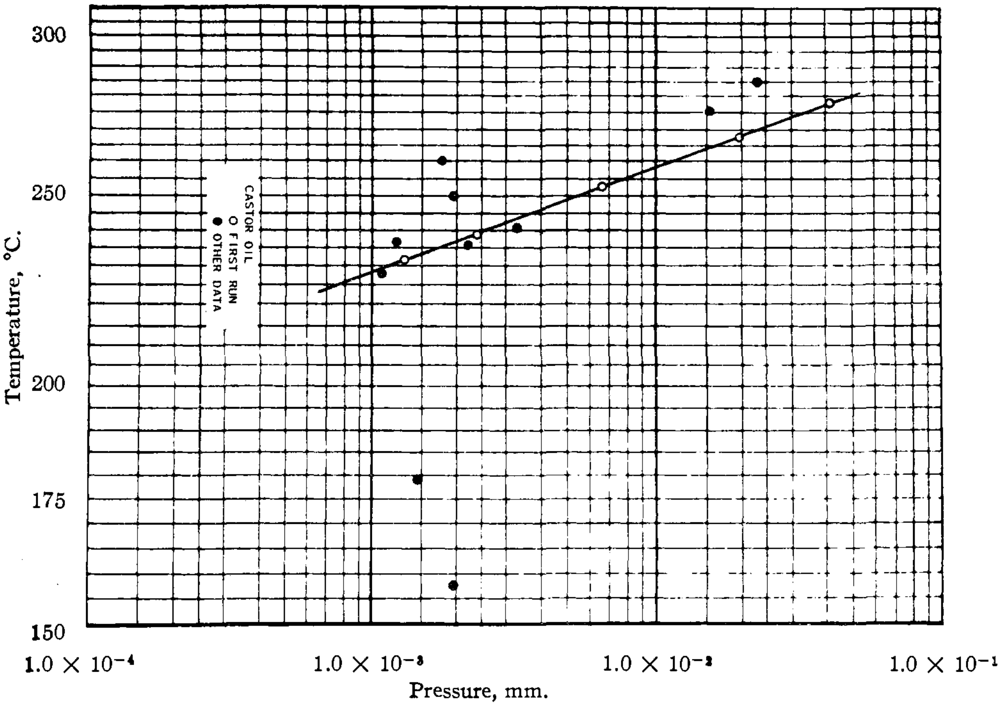

Fig. 5.—Experimental vapor pressure data.

that the boiling points of the unsaturated acids appear to be perhaps 2 to 3° lower than those of the corresponding saturated acids. The more recent work of Norris and Terry[11] shows conclusively that the vapor pressures of the methyl ester of fatty acid of equal carbon atoms increase with increasing unsaturation. For example, the vapor pressure of methyl stearate is lower than that of its unsaturated analog, methyl oleate, and the latter, in turn, is lower than that of methyl linoleate. It would be expected, therefore, that the vapor pressure of tristearin should be lower than that of the oleyl distearin. The influence of only one double bond in the large oleyl distearin molecule may not be as effective in altering its vapor pressure as one double bond would be in a smaller molecule like the fatty acid molecule.

The attempt to determine the effect of additional unsaturation on vapor pressure was not successful with synthetic triglycerides owing to the abnormal behavior encountered with triolein and its *trans*-isomer, trielaidin, in the tensimeter. Although synthesized and purified by the

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[11] Norris and Terry, *Oil and Soap*, **22**, 41 (1945).

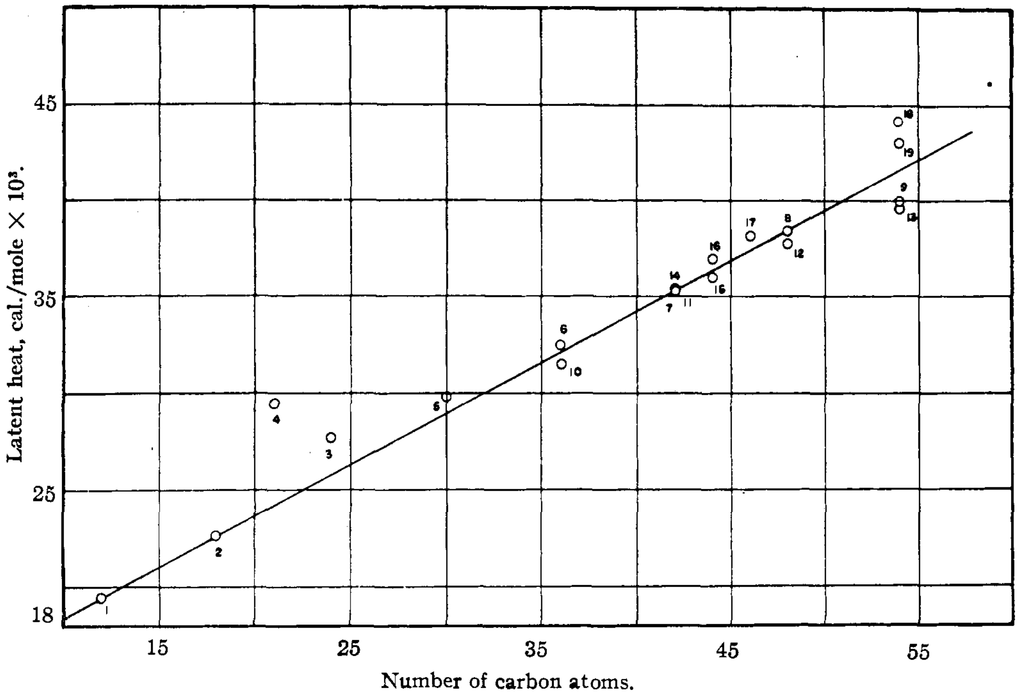

Fig. 6.—Relationship between molecular weights and latent heats.

same general methods used for the other triglycerides, these substances appeared to decompose in the tensimeter. The data followed no general trend and variations of 25 to 50° at one temperature were not uncommon. This was indeed surprising because of the known thermal stability of triolein in regard to its distillability. Since similar results were obtained from three individual preparations it appeared that the difficulty could be inherent in this type of triglyceride.

Of interest, however, is the fact that distilled olive oil responds normally to measurement by the method. Although the principal fatty acid constituent of this fat is oleic acid which makes it very similar to triolein, good reproducible vapor pressure data can be obtained with it by the tensimeter method. The pressure–temperature relationship for olive oil is plotted in Fig. 4. The regularity with which the points fall on a straight line is not only evidence of the accuracy of the data but shows that the olive oil triglycerides sustain the treatment of the tensimeter and hereby differ from the behavior of the synthetic triolein or trielaidin. The vapor pressures for olive oil are higher than those for tristearin which, on the basis of its unsaturation, is in agreement with the results of Norris and Terry.[11]

There was cause to surmise from these results that perhaps the olive oil fractions contained a natural inhibitor which protects it. Olive oil, however, is known to contain only minute quantities of tocopherols, its natural stability being due to the high percentage of stable fatty acids, such as oleic, which comprise its structure. The fractionation in the molecular still, in addition, would have completely removed any tocopherols from the fractions tested. In spite of these facts, an experiment was undertaken in which 25 mg. of tocopherols was added to 6 g. of the synthetic triolein in hopes of arresting the undesirable reactions taking place in the tensimeter. The presence of the tocopherols, however, made no improvement over the previous results.

The vapor pressures obtained with the fractionated soybean oil are also plotted in Fig. 4. The data fall on a straight line which, within experimental limits, follows the course of the olive oil line and thereby exhibits identical vapor pressures. The greater degree of unsaturation which exists in soybean oil, however, is not manifested in showing higher vapor pressures for this fat over the more saturated olive oil, which would be expected. When compared to tristearin, the two lines are not parallel but cross at the lower range and diverge 5° at 50 μ. Tristearin, in general, has lower vapor pressures over this range than soybean oil, but not of the order which would be expected from the differences in saturation. Perhaps these differences expected from pure substances are minimized in natural material where the molecules are heterogeneous combinations of many related constituents such as the number of different triglycerides which can exist in a natural fat.

Abnormal behavior was encountered with castor oil. The first experiments with a commerical grade of castor oil of unknown origin labeled "Stripped" gave results which fell with good regularity on a straight line, as shown in Fig. 5. The position of the line, however, was some 25° below that for soybean oil or tristearin which did not seem reasonable in view of the structure of the castor oil molecule. Assuming that the sample used had received some unknown treatment either by the refiner or in stripping, several other samples were tried. A commercial grade of refined oil (Baker Castor Oil Co.) having acetyl values of 146.5 and 146.3 before and after distillation, respectively, gave very erratic results which extended over an abnormal temperature range, as can be seen from the plot in Fig. 5. After treatment in the tensimeter, the acetyl value was found to be 143 ± 2%, the uncertainty being due to errors introduced because of the small sample available for analysis. The degree of dehydration, however, seemed small to account for the large disparity in the data. Other undesirable reactions must occur, although the fact that the greatest variations are at the lower temperatures makes it difficult to offer an explanation on the basis of thermal effects. The examination of two other samples of castor oil, one a U.S.P. product and the other a refined grade, yielded similar results.

It was not possible to get data when using corn oil because of the tendency of the pendulum to stick to the orifice. Apparently the corn oil polymerized too rapidly to be successfully handled in the tensimeter and that oil which reached the orifice was sufficiently tacky to cause the diaphragm of the pendulum to stick. The orifice heater aggravated this condition perhaps by even further overheating the oil. After several attempts to collect data with fresh samples of corn oil, these measurements were abandoned.

The constants for Dühring's rule[12] for the triglycerides have been determined and are listed in the last column of Table I. The constants were computed from the absolute temperatures at the 2 pressures, 50 μ and 1 μ for contiguous members of the series in the order listed in Table I. The constant as determined is the ratio of the absolute temperature difference for one triglyceride at 2 pressures to that for the other triglyceride at the same 2 pressure values. Expressed more precisely, the relationship has the following form: $T'_A - T_A/T'_B - T_B$ = constant, where $(T'_A - T_A)$ equals the absolute temperature of one triglyceride at 50 and 1 μ, respectively, and $(T'_B - T_B)$ equals the corresponding temperatures for the other triglycerides. The Dühring constant is calculated from the temperature data of the indicated material with that of the material next lower in the list. For example, the value 0.920 is the ratio of the difference of the two temperatures for tributyrin to that for tricaproin. The constancy of this quantity is good over the entire series investigated, as can be noted from the computed values in Table I.

Summary

The vapor pressure–temperature relationships for 9 simple triglycerides, 10 mixed triglycerides and 4 natural fats have been determined by the pendulum-tensimeter method. In most every instance a straight-line relationship between temperature and pressure was obtained. Abnormal behavior with 2 unsaturated synthetic triglycerides and 2 natural fats was encountered. Latent heats of vaporizations for each material are calculated, and constants for Dühring's rule are also computed.

[12] Roehl, *Ind. Eng. Chem.*, **30**, 1320 (1938).

ROCHESTER 13, NEW YORK RECEIVED FEBRUARY 24, 1949

[CONTRIBUTION FROM THE LABORATORIES OF DISTILLATION PRODUCTS, INC.]

Vapor Pressures of Phlegmatic Liquids. II. High Molecular Weight Esters and Silicone Oils[1]

BY E. S. PERRY AND W. H. WEBER

The vapor pressures of a number of simple and mixed triglycerides have been reported in a previous paper.[2] At the time of these measurements there was available in this Laboratory a number of molecularly distilled phthalate and sebacate esters whose pressure–temperature relationships could be determined by the pendulum-tensimeter method.[3] A knowledge of the vapor pressures of this class of materials is of importance in certain aspects of their use as plasticizers and vacuum pump fluids. Therefore, the determination of their vapor pressures seemed advisable and worthy of publication.

The pressure–temperature curves for a few of these esters, particularly dibutyl phthalate, di-2-ethylhexyl phthalate, and di-2-ethylhexyl sebacate, have been obtained by others[3 4,5,5a] using both

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[1] Communication No. 152 from Laboratories of Distillation Products, Inc.

[2] Perry, Weber and Daubert, THIS JOURNAL, **71**, 3720 (1949).

[3] Hickman, Hecker and Embree, *Ind. Eng. Chem.*, **9**, 264 (1937).

[4] Verhoek and Marshall, THIS JOURNAL, **61**, 2737 (1939).

[5] Kapff and Jacobs, *Rev. Sci. Instruments*, **18**, 581 (1947).

[5a] A recent publication on this subject by Small, Small and Cowley, *Trans. Faraday Soc.* (London), **44**, 810 (1948), has come to the authors' attention since the original manuscript of this paper was submitted for publication. Their dynamic method gave results which are in closer agreement than previously published results (from dynamic methods) to those of the present paper.