The Density and Transition Points of Dotriacontane (Dicetyl)

BY W. F. SEYER AND WM. MORRIS

Introduction

The reasons for the following work were twofold: first, to determine as accurately as possible the transition temperatures of the hydrocarbon, dotriacontane; and, second, to discover whether this compound could be obtained in the pure state from cetyl alcohol. Piper and his co-workers[1] have prepared this hydrocarbon from n-hexadecanol which itself had been synthesized from purified ethyl palmitate and have determined both its melting and transition points. They stressed the fact that the melting point of dicetyl prepared from natural cetyl alcohol was invariably higher than that of their compound because of the presence of higher alcohols and for the same reasons the transition points were necessarily lower.
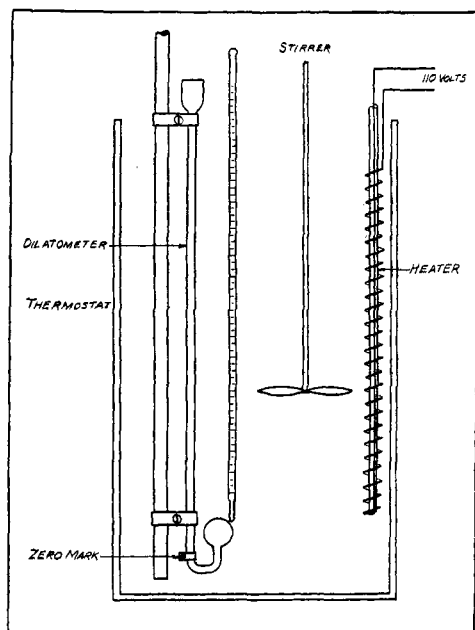

Fig. 1.

The lack of agreement among the recorded values of the transition points can be ascribed as partly due to the difficulty of measuring these accurately by the methods so far tried.[2]

The matter is made still more complicated by the existence of two or more transition points.

Thus Piper and co-workers[1] have shown that not only is it possible for normal paraffins to have two transition points but these may have different values depending upon whether the sample is being heated or cooled. Since Garner, von Bibber and King[3] found the heats of transition to be comparatively large it occurred to the authors that there should be a correspondingly large volume change accompanying the process and that therefore a dilatometer method of determining the transition points might be made an accurate one. Further, if this were found to be the case it would become a simple matter to compare the purity of various samples of dotriacontane.

Materials.—Three samples of dicetyl were used in the investigation. Sample 1 was obtained from Eastman Kodak Co. and used without further purification. Sample 3 was part of a lot whose preparation was described previously.[4] Sample 2 was a part of No. 3 that was subjected to five more recrystallizations from acetic acid followed by four from ethyl ether. As a knowledge of the m. p.'s was important, they were determined with some care by the method utilized by Piper and co-workers.[1] It was noted that the rate of heating, unless below a certain minimum, affected the m. p.'s. This rate for the particular apparatus used was found to be 0.5° per minute. The melting of the three samples was as follows: Sample 1, 69.3 to 69.4°; No. 2, 69.6 to 69.7°; and No. 3, 69.8 to 69.9°. The thermometers used read to 0.1° and had all been calibrated against a standard resistance thermometer. All temperatures were corrected for stem immersion.

The Dilatometer.—Small-bore Pyrex capillary tubing was examined until a suitable length of uniform bore was found. Three pieces of this tubing were used with lengths about 35 cm. Their diameter was measured by drawing mercury into the tube, determining the length of the column and then weighing it after its removal. From these figures and using the well-known corrections for the ends of the mercury column the cross sectional areas given in Table I were calculated.

Next a thick-walled glass bulb about 1.5 cm. in diameter was blown from Pyrex tubing. It was weighed and then 1 g. or less of dicetyl was melted and run in through a small funnel. The bulb was connected by a short piece of heavy rubber tubing to a system evacuated to a pressure of the order of 10^{-4} mm. The hydrocarbon was melted and allowed to solidify repeatedly so as to remove any occluded gases. After evacuation the bulb was again weighed, sealed to the calibrated capillary tube and then the whole apparatus was filled with mercury by distillation.

(1) Piper, Chibnall, Hopkins, Pollard, Smith and Williams, *Biochem. J.*, **25**, 2072 (1931).

(2) West, THIS JOURNAL, **59**, 742 (1937).

(3) Garner, von Bibber and King, *J. Chem. Soc.*, **1**, 1533 (1931).

(4) Seyer and Fordyce, THIS JOURNAL, **60**, 827 (1938).

Experimental Procedure.—The loaded dilatometer was clamped rigidly to a stand whose base was a heavy lead plate. This plate rested firmly on the bottom of a Pyrex jar 40 cm. high and 20 cm. in diameter (Fig. 1). For temperatures above 20° the bath was filled with petrolatum oil which was heated by a coil of nicrome wire. The heater itself was connected to a thermoregulator not shown in the figure. Below 20° water replaced the oil. In this case the heater was enclosed in a glass tube while the cooling was done by a constant stream of ice water. The temperature of the bath over the range covered could be maintained constant to within 0.03°. Readings were always made through the same vertical portion of the jar's surface. This portion showed no optical defect as was proved by reading the column height of mercury at room temperature both within and without the bath. A calibrated cathetometer reading to 0.05 cm. was used to obtain the heights of the mercury column.

It will be noted from Fig. 1 that the dilatometer bulb was inverted. The reason for this was to prevent the hydrocarbon from working its way upward in the capillary tube. Preliminary measurements showed this would occur whenever the temperature approached the m. p. of the hydrocarbon.

The question that arose at the outset was whether the mercury did actually fill all the voids between the dicetyl crystals even though it had been introduced under a high vacuum. No decisive answer can be given except to say that after repeated meltings and solidifications the mercury and hydrocarbon became so intimately mixed that reproducible readings could be obtained at any temperature whether it was approached either from above or below, i. e., by cooling or heating. From four to six hours were required in nearly every case before equilibrium was attained. In all three experiments in order to cover the temperature range decided upon, mercury had to be removed before the melting point was reached. This mercury after removal was weighed carefully, and its volume calculated. After all the readings had been obtained it was still necessary to calibrate the bulb and to check the cross section of the capillary tube.

This was done by alternately heating and cooling the bulb until enough glacial acetic acid had been introduced to dissolve all the hydrocarbon. The empty dilatometer was then weighed, evacuated and then filled by distillation to the zero mark with mercury. The apparatus was next weighed and the height of the mercury above the zero mark observed at some fixed temperature. By measuring the height of the mercury column at different temperatures above that at 20° it was possible to obtain both an accurate knowledge of the volume of the bulb and that of the capillary tube. From this latter volume the cross sectional area of the tube was again calculated. It is given in Table I under heading (A) and as will be noticed agrees very well with the area measured previously (B). The volume of the bulbs at the zero mark is also given.

TABLE I

Sample	Dicetyl, g.	Vol. of bulbs, cc.	Area of tubes, sq. cm. × 10⁻³	
			A	B
1	1.1927	4.91542 at 80°	3.43	3.427
2	0.6989	3.56978 at 80°	5.21	5.211
3	1.1927	2.67434 at 20°	4.86	4.861

All weighings were corrected for buoyancy of air. Corrections for the expansion of the glass were also made where necessary. The calculated densities at the different temperatures for each sample no. 2 are given in Table II along with the observed heights above the zero mark. The results have been placed in chronological order to emphasize the fact that they are independent of how the temperature was approached.

TABLE II
Sample No. 2

t, °C.	h, cm.	d^4_4
20.00	6.255	0.9439
30.00	7.985	.9386
40.10	9.565	.9343
45.00	10.295	.9326
50.25	11.340	.9290
55.10	12.530	.9243
60.10	13.670	.9200
62.00	14.235	.9175
64.00	21.000	.8780
63.50	19.940	.8826
63.00	14.705	.9151
63.30	15.020	.9134
65.00	21.215	.8773
67.00	22.095	.8733
68.00	22.900	.8693
69.00	24.430	.8613
69.20	24.960	.8585
69.40	31.105	.8260
69.50	39.775	.7843
70.00	39.885	.7840
75.00	41.060	.7807
80.00	42.220	.7776
85.00	43.380	.7744

Discussion of Results

By plotting some of the density figures against temperatures the curves in Fig. 2 have been obtained. While three solid phases A, B, C, exist, only two are evident from the figure. The method of measurement was not sufficiently sensitive to detect any difference between the density of the solid phase A and that of the liquid. The existence of this phase was inferred from the fact that it was opaque while both that of the liquid and the solid phase B were transparent. In all cases the transition point from phase B to A was only about 0.1° below the melting point of the sample.

It is apparent that the impurities in the samples 1 and 3 show their greatest effect at the beginning of the transition region. Indeed one cannot speak of a transition point for these cases at all but only of a transition region as the lines along which transition takes place are not at right angles to the temperature axis. For sample 2 this is almost the case and it must therefore be regarded as the purest of the three samples.
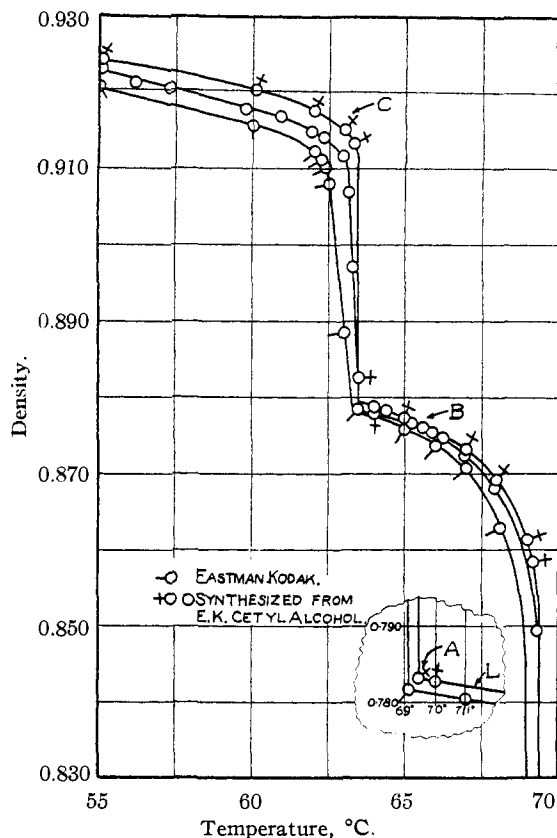
If that part of the line which is parallel to the

Fig. 2.—-O, sample no. 1; -O, sample no. 2; O, sample no. 3.

ing the nomenclature adopted by Piper and co-workers these have been designated A, B and C. The letter L signifies as usual the liquid phase. The phase A, as far as this hydrocarbon is concerned, exists only over a temperature range of 0.1°. As has been mentioned before, the existence of this phase was inferred from the change in optical properties of the hydrocarbon upon cooling the liquid. This region was investigated with some care but all efforts to define it more closely were unsuccessful because the thermostat was difficult to adjust to any exact temperature. At 69.50° the hydrocarbon could be held in the solid phase for any length of time but raising the temperature 0.1 to 69.60 ± 0.03° always caused melting to take place. The clear melt upon cooling invariably set to an opaque solid. The phases B and C on the other hand were transparent and opaque, respectively. Contrary to the findings of the experimenters quoted above no difference was found in the transition temperatures whether they were approached by heating or cooling the substances. This was probably due to the fact that it took considerable time for the bath temperature to change more than a degree. Nevertheless there is agreement between the present results and some of theirs. Thus they give the figures 69.2–69.4° for the second transition point on heating, while that found in the
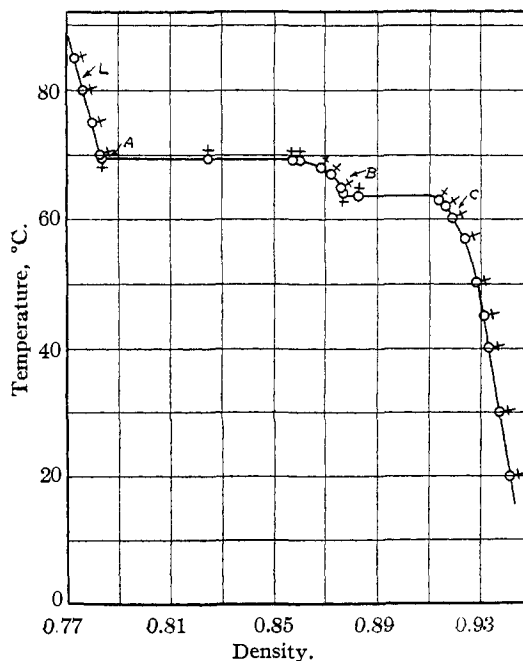
density axis is produced it cuts the temperature axis at 63.5°. This may then be regarded as the transition point for phase C to B. This sample had a melting point of 69.6° identical with that found by Piper and his co-workers.[1] From the above facts one is therefore led to believe that it is possible to prepare very pure dicetyl from cetyl alcohol if only sufficient recrystallizations are made. A further examination of the figure reveals the fact that the initial transition stage of B to C, upon cooling, is not nearly so sensitive to impurities as the converse C to B, upon heating. This also applies to the transition from B to A phase. It may be remarked here that the phase A, although opaque, must resemble the liquid phase very closely because not only has it the same coefficient of expansion, as far as the present measurements go, but the transition point appears to be lowered by the impurities present to about the same extent as the melting point.

To give a detailed picture of the behavior of the pure dicetyl from 10 to 90°, Fig. 3 has been drawn. There are three solid phases and follow-

Fig. 3.—L, liquid phase.

present work is 69.5°. No transition point corresponding to 65.2–65.4°, which they obtained on heating, was found in the present case but the transition point between the B and C modifications, 63.5°, does approach their value of 63.9°, which was their second transition point upon cooling.

It appears that *n*-dotriacontane like *n*-hexacosane can occur in three forms. The equation for the expansion of the C form cannot be expressed by any simple equation. In the case of the liquid over the range studied, the relationships are linear and given by the equation $d = 0.8275 - 0.00064t$ where d is the density at any temperature t.

Summary

1. It has been shown that the dilatometer method can be used to measure accurately the transition points of solid paraffin hydrocarbons such as dicetyl.

2. Pure dicetyl can be prepared from cetyl alcohol if sufficient recrystallizations are made.

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The Adsorption of Ethyl Iodide on a Plane Surface of Iron at 20°

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Although the adsorption of gases on powdered iron and on promoted iron catalysts has been studied intensively, practically no attention has been paid to adsorption on iron surfaces which are substantially plane. As the great majority of iron surfaces commonly used can be considered plane, at least from a macroscopic point of view, and as the condition of the surface presumably influences the behavior of iron and steel in pickling, in galvanizing and tinning, in painting, in lubrication, and in corrosion, a knowledge of adsorption phenomena on such surfaces is greatly to be desired. As a preliminary to a general study of the subject, measurements have been made of the adsorption at 20° of ethyl iodide on a surface of cold-rolled steel. The surface was studied in two conditions: (1) after degreasing, and (2) after degreasing and subsequent reduction in hydrogen at 450°. Ethyl iodide was selected because it is an effective inhibitor in pickling solutions and at the same time has a vapor pressure which enables it to be used conveniently in adsorption measurements.

Apparatus.—The method employed was identical with that described in earlier measurements on mica.[1] The apparatus, however, had been improved in two ways: the ratio of the volume of the adsorption bulb and trap to that of the remainder of the system had been changed to give higher accuracy, and the single McLeod gage had been replaced by a double one, one arm of which covered the range 10^{-6} to 0.2 mm., the other the range 0.2 to 2.0 mm. With these improvements pressure was determined with an accuracy of 1% over the range 10^{-6} to 2 mm. The volume of C, the main part of the system, was 521.8 cc.; the volume of A, the adsorption bulb and trap, and of B, the blank system, was 457.3 and 458.4 cc., respectively.

Materials.—Ethyl iodide from the Eastman Kodak Company was redistilled under reduced pressure and the constant boiling fraction was collected in a bulb which was subsequently connected to the gas manifold through a U-tube and vacuum stopcock. Dissolved or entrapped air was removed by first freezing the iodide in the U-tube and bulb with a mixture of carbon dioxide snow and alcohol, and then, by alternate warming of bulb and U-tube with the vacuum pump on, distilling the iodide back and forth until the pressure as read by the gage had fallen below 10^{-4} mm., which is approximately the vapor pressure of the iodide at this temperature. Ethyl iodide was then introduced into the adsorption system by allowing the U-tube to warm up with the stopcock to the gas manifold open. In spite of precautions to keep the iodide in the dark a very slight discoloration appeared after several weeks. When such discoloration was noted, a fresh sample was prepared. Measurements made with a trace of discoloration present gave, however, the same results as those made with a fresh sample.

Hydrogen, taken from a tank, was freed of traces of water vapor and oxygen by passing it through sulfuric acid and calcium chloride, then over hot platinized asbestos and finally over activated alumina and phosphorus pentoxide. Direct determination showed that hydrogen is not measurably adsorbed on the plane surface of iron at room temperature, hence its use caused no interference in the measurements with ethyl iodide.

Iron Surface.—The adsorbent was a bundle of cold-rolled flat steel wire in strips 0.076 mm. in thickness, 110 mm. in length and 19 mm. in width. These strips were not bound together but were packed into the adsorption bulb in an upright position. The total area, determined by measuring the dimensions of each strip, was 11,129

(1) Armbruster and Austin, THIS JOURNAL, 60, 467 (1938).