ing to 8.20 N in sodium hydroxide and 6.92 N in sodium iodide, which point marks the transition from the dihydrate to anhydrous sodium iodide.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF BRITISH COLUMBIA]

The Density and Transition Points of the n-Paraffin Hydrocarbons

BY WM. F. SEYER, RALPH F. PATTERSON[1] AND JOHN L. KEAYS[2]

The density and transition point of dicetyl ($C_{32}H_{66}$) formed the subject matter of a previous communication to this Journal.[3] Since then, all the even-numbered hydrocarbons, beginning with $C_{16}H_{34}$ and ending with $C_{34}H_{70}$, have been investigated, also $C_{29}H_{60}$ of the odd-numbered series.

Materials.—All of these hydrocarbons excepting $C_{16}H_{34}$ and $C_{29}H_{60}$ were synthesized in the laboratory. Samples of hexadecane were obtained from Messrs. Deanesly and Carelton of the Shell Oil Company, and Professor Parks of Stanford University. Both samples were from lots that had been carefully purified by the donors, but upon comparing the m. ps. of the two, it was found that the m. p. from the former had a slightly higher value than that from the latter. The m. p. of the best material was found to be 18.145 and its setting point 18.3.

The nonacosane was obtained from the Bureau of Standards through the efforts of Dr. B. J. Mair. It had an m. p. of 63.0° but as Piper and his co-workers[4] gave a value of 63.4–6° it was recrystallized until the m. p. rose to 63.5°.

The method employed for synthesizing the desired hydrocarbons depended upon the nature of the material available. Where alcohols served as a starting point the Kraft procedure was followed and where acids, the Peterson electrolytic method was utilized. After the usual preliminary purification the hydrocarbons were treated with sulfuric acid until no color formed upon the addition of the acid. To remove it, the hydrocarbons were washed with hot water. They were then dried and recrystallized from five to twenty times until a constant m. p. and t. p. were obtained.

Tetratriacontane, the highest member so far synthesized, was prepared by the electrolysis of the corresponding acid which in this case was stearic. Considerable difficulty was encountered in the purification of this compound. It could not be obtained completely colorless although it was drastically treated with sulfuric acid and recrystallized from glacial acetic acid over forty times. The reason for this failure may lie in the following statement of Oldham and Ubbelohde.[5] "Owing to the appreciable oxidation of certain liquid paraffins at 130°, it was advisable to hinder the circulation of air over the surface of the paraffin during the purification." It may be that this hydrocarbon was oxidized at the temperatures where purification was attempted.

Melting Points of the Normal Paraffin Hydrocarbons.— A knowledge of the melting points of the normal paraffin hydrocarbons was found to be essential for the present investigation. Piper,[4] et al., claim that the transition point is a more reliable index of purity than the melting point.[4] This may be true for those hydrocarbons having more than twenty-six carbon atoms but for those below this in the series this cannot be so, because there is either no transition point or it is indistinct. As mentioned in the previous article, the melting points, even when done by the method outlined by Piper, et al., were affected by the rate of heating and the personal equation, but experience showed that the setting point was not. It could be reproduced by any worker in the Laboratory to within 0.2 to 0.1° for any one sample by observing the temperature when the first crystal formed during slow cooling (temperature dropping less than 0.5° per minute). Hence, the setting point has been used in this Laboratory for the purpose of establishing the purity of the compounds under investigation. The observed setting points along with the melting and transition points are given in Table II, where N denotes the number of carbon atoms in the chain.

Equations have been developed by Moullin,[6] Taskototos,[7] and Garner[8] for correlating the melting points with number of carbon atoms in the paraffin hydrocarbon chain. None of the equations was found to be satisfactory over the whole range of melting points. Moullin's equation, which is of the form $\log (N - 2) = a + bt$, could be made to fit the curve of melting point against carbon number, if one assumed discontinuities at about $N = 16$ and $N = 33$. N here represents the number of carbon atoms in the chain and a and b are constants. There is also up to $C_{16}H_{34}$ one curve for the odd numbers and one for the even numbers. Above this member, melting points of the odd and even numbered paraffins fall on the same straight line.

The values of the constants, a and b, obtained by the method of least squares for different sections of the curve are given in Table I. Members lower than C_6H_{14}, for both the odd and even numbered compounds, are not included, as the deviations of observed from calculated m. ps. are too great. The recorded m. p. of $C_{11}H_{24}$ is also out of line.

TABLE I

VALUES OF CONSTANTS a AND b

No. of carbon atoms range:		a	b
$C_6 \longrightarrow C_{16}$ (even)		1.051	0.00481
C_7	C_{15} (odd)	1.067	.00410
C_{16}	C_{34} (odd and even)	1.02	.0065
C_{34}	C_{70}	0.08	.0006

In correlating the melting points of the normal paraffin series with numbers of carbon atoms in the chain, it was attempted insofar as possible to select values obtained by one set of workers. For as has been mentioned above, the m. ps. obtained depend not only upon the purity of the product but also upon the m. p. technique. Further, workers interested in a set of values are sure to develop laboratory methods and gain experience much broader in scope that those who accidentally are led to make measurements only on one compound. Consequently, we have used the selected values of Deanesly and Carleton[9] for the range 6–18, and our own for the range 18–34. For 40, 50, 60 and 70 we selected the melting point given by Carothers,[10] and for 36, 52, 62 and 64 those of Gascard.[11]

(1) Standard Oil Company of British Columbia Research Fellow, 1938–1939.

(2) Standard Oil Company of British Columbia Research Fellow, 1941–1942.

(3) Seyer and Morris, THIS JOURNAL, 61, 1114 (1939).

(4) Piper, et al., Biochem. J., 25, 2072 (1931).

(5) Oldham and Ubbelohde, J. Chem. Soc., 200 (1938).

(6) Moullin, Proc. Camb. Phil. Soc., 34, 459 (1938).

(7) Taskototos, Compt. rend., 143, 1235 (1900).

(8) Garner, Van Bibber and King, J. Chem. Soc., 1533 (1931).

(9) Deanesly and Carleton, J. Phys. Chem., 45, 1104 (1941).

(10) Carothers, Hill, Kirby and Jacobson, THIS JOURNAL, 52, 5279 (1930).

(11) Gascard, Ann. chim., 15, 332 (1921).

From the foregoing data, curves were constructed. Then by means of the smoothed curves a new set of values for the melting points of the paraffin hydrocarbons, up to $N = 70$, was computed as shown in Table II.

Experimental Procedure

The experimental procedure was in general the same as that used in the former measurements with dicetyl. For this, a special dilatometer had to be constructed with a funnel-like opening at the filling end, and to prevent the solid hydrocarbon from working its way upward through the mercury the bulb had to be inverted. However, the difficulties encountered in the measurements of those hydrocarbons lying within the range C_{16} to C_{28} were so great that additional information on the experimental method seemed advisable.

The dilatometer tube, after having been filled, was placed in the constant temperature bath and the capillary heights noted. These heights were plotted against temperature immediately as found. This was done for two reasons. The capillary height–temperature curves resemble, in shape, the density–temperature curve, and therefore, any discrepancy in this, when height was plotted against temperature, would show up at once. Further, the capillary height–density curve shows at a glance the temperature at which any transition points occur and thus indicate what regions must be investigated. The general method of obtaining these curves follows:

The general form of the curve obtained is shown in Fig. 1, where B represents the first transition point and C the second transition or melting point.
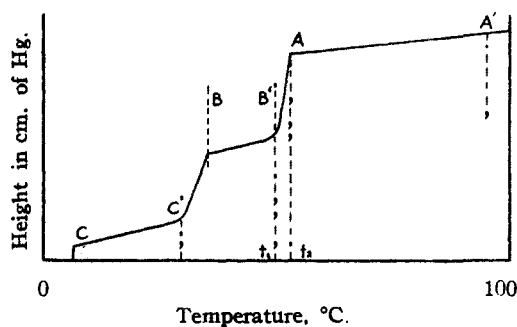

Fig. 1.

Readings were begun near 0°. The bath was kept at this temperature until a constant reading of the mercury level had been obtained. The temperature was then raised several degrees and held constant until equilibrium had been reached. The process was repeated at temperature intervals sufficiently close together to ensure a smooth and continuous curve. The curve given in Fig. 1 is an idealized form of the curve for all members of the aliphatic series greater than 18 and less than 44.

In the regions A–A', B–B', and C–C', equilibrium was reached within a few minutes, but not so in the curve sections A'–B, and B'–C. As the regions of sharp transition were approached, the time required for the mercury level to reach a constant value increased rapidly. In the 0.1–0.2° interval between t_1 and t_2 (that is, at a temperature just below the setting point) it required from one to two weeks for equilibrium to be established. During this time it was necessary to control the temperature as closely as possible.

When the highest possible mercury level had been reached, the temperature was lowered by suitable increments, readings taken, and the values plotted in order to provide a check on the previous curve. It was found that on a descending temperature scale, the points A, B', B or C' for any given sample could be determined with an accuracy limited only by the rigidity of temperature control, the accuracy of temperature measurement, and the patience of the observer. In those regions where the densities were

Table II

N	M. p. computed, °C.	M. p. observed, °C.	Dev., °C.	S. p. observed, °C.	T. p. observed, °C.
6	−94.0	−95.4	−1.4		
7	−89.7	−90.6	−0.9		
8	−56.7	−56.9	+ .2		
9	−54.1	−53.7	+ .4		
10	−29.7	−29.7	.0		
11	−27.6	−25.6	+2.0		
12	−10.0	− 9.6	+0.4		
13	− 6.3	− 6.2	+ .1		
14	5.5	5.5	.0		
15	10.5	10.0	− .5		
16	18.0	18.3	+ .3	18.3	None
17	22.5	21.0	−1.5		
18	28.3	28.1	−0.2	28.1	26.8
19	32.0	31.4	− .6		
20	36.4	36.2	− .2	36.2	32.0
21	39.8	40.4	+ .6		
22	44.2	44.1	− .1	44.1	40.0
23	46.5	47.0	+ .5		
24	49.6	50.6	+1.0	50.7	47.9
25	52.5	53.3	+0.8		
26	55.6	55.8	+0.2	55.8	48.8
27	58.1	59.1	+1.0		
28	61.2	61.2	0.0	61.2	54.0
29	63.6	63.3	− .3	63.2	57.1
30	65.6	65.7	+ .1	65.4	60.0
31	68.7	68.0	− .7		
32	70.2	69.5	− .7	69.5	63.5
33	71.6	72.0	+ .4		
34	73.0	72.9	− .1	72.9	68.4
35	74.4	75.0	+ .6		
36	75.6	76.0	+ .4		
37	76.9	74.4	−2.5		
38	78.0	77.6	−0.4		
39	79.2	78.8	− .4		
40	80.4	80.7	+ .3		
41	81.5	81.7	+ .2		
42	82.6	82.9	+ .3		
43	83.6	83.8	+ .2		
44	84.8	86.4	+1.6		84.8
50	90.5	92.1	+1.6		
54	94.0	95.0	+1.0		
60	98.7	98.9	+0.2		
62	100.2	100.5	+ .3		
64	102.2	102.6	+ .4		
70	105.4	105.3	− .1		

Table III

n	Density at m. p.	Density at t. p.
16	0.774	
18	.774	0.839
20	.779	.867
22	.779	.869
24	.801	.867
26	.779	.872
28	.779	.878
30	.782	.880
32	.784	.878
34	.785	.883
29	.780	.796

linear functions of the temperature, determinations were made in about five-degree intervals. Elsewhere, the intervals were much smaller varying from 1 to 0.1°, depending upon rate of change of density in that particular region. The densities at the melting and transition points are given in Table II. Here n denotes the number of carbon atoms in the compound.

Discussion of Results

When the densities are plotted against the temperatures, a family of curves is obtained such as shown in Fig. 2. It is at once evident that the dilatometer method yields information which both amplifies and substantiates results arrived at by X-ray examinations of some of these hydrocarbons.

The straight, approximately parallel lines sloping to the right at the bottom of the figure represent the change in density with temperature of the various hydrocarbons in the liquid state. For this group of lines the following equation has been determined

$$d_t = 0.7615 + 0.00205n - 0.0006368t$$

where d_t is the density at $t°$, n the number of carbon atoms in the chain and t the temperature. Values of the density near the m. p. calculated by means of this equation agree to within less than 1% of those given in Beilstein. From the fact that the lines are straight and all have the same slope, one must conclude that the molecules in the liquid state under these conditions are parallel to one another, and that there is thus some degree of order or arrangement. This type of order has been given the name, "cybotaxis." It appears then that in the liquid state the behavior of the n hydrocarbon molecule, with respect to temperature, is the same whether it be even or odd numbered, or whether the chain be long or short. From the observations of Mueller,[12] it would appear safe to assume that hexagonal packing occurs in the liquid just above the m. p. as it does in the solid phase, just below the m. p. The difference between the two phases would then be only that in the liquid phase the molecules would be farther apart than in the solid and that the terminal groups would no longer be in one plane. While movement in the liquid could take place by the molecules sliding over one another in a direction parallel to their long axis, it is more likely that movement occurs by a rolling of the molecules over one another at right angles to

the long chain axis. It is this type of motion which probably gives these long chain hydrocarbons their characterisic property as lubricants.

This orderly arrangement must, however, show signs of disappearing as the temperature approaches the b. p. A few preliminary measurements made with hexadecane indicated that a noticeable departure from linearity begins to occur at 100°. At a temperature then somewhere near the b. p. molecular agitation will become so great as to disturb the orderly arrangement and one would then expect the expansions per degree for the different hydrocarbons to differ from one another. Their differences should be a function of molecular weight or chain length. Hence, in the orderly liquid state, expansion must be largely at right angles to the long axis rather than in the chain itself or in the gaps between the terminal atoms between the molecules just as was found to be the case in the different solid phases.

Upon cooling the liquid, the setting point is reached. It is apparent that there is a slight increase in density at this point in going from C_{16}
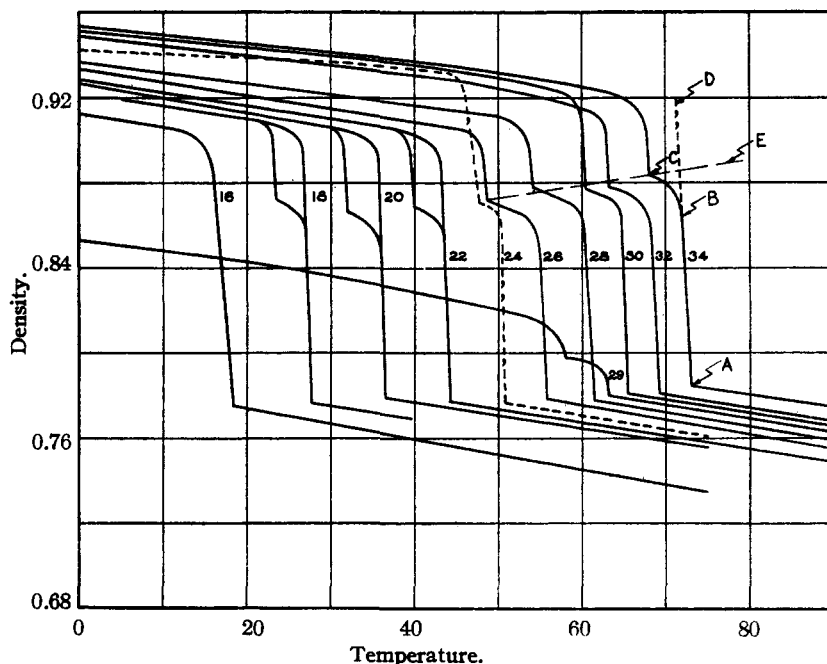

Fig. 2.

(12) A. Mueller, *Proc. Roy. Soc.* (London), A138, 515 (1932).

to C_{34}. At the s. p., crystallization begins, and there is a large change in density with a relatively small change in temperature as this process takes place. It would appear, at first sight, that no change in temperature should take place during this change in phase but experience shows this not to be the case. Considerable pains were taken to measure the density in this region by successively lowering the temperature through intervals of 0.1° over periods of time, amounting to several days. It is worth while to note that

the slope of the lines from the s. p. (A) to the point (B) is practically the same for all the even numbered hydrocarbons, except C_{16} which shows no transition point. At the point (B), crystallization can be said to be completed and the rate of change of density with respect to temperature begins to fall off rapidly until the transition point (C) is reached. The solid phase existing in the region BC corresponds to Mueller's A modification with the "long spacing." In this case, X-ray work shows the molecule to be standing at right angles to the basal plane, the 001 plane. Here at the point (C), a new solid phase appears and the difference between this and the previous one, according to the above-mentioned investigator, and Piper, et al.,[4] is that the molecule in the crystal cell is now tilted with respect to the basal plane.

The similarity of the shapes of the curves in this solid phase is obvious. This suggests that the manner of crystal packing must be the same for all the even numbered n-hydrocarbons, and that expansion or contraction must be largely in a plane at right angles to the long chain axis. Unlike the liquid state, however, the density is now a function of molecular weight. This can be explained easily by assuming that the distance between the terminal carbon atoms is the same for all the members. This value calculated from Mueller's table of the "long spacing" is 2.6 Å., about twice the distance between two carbon atoms in the molecule. Hence, the longer the chain the less is the part the end effect plays in the density factor. There is evidence that at some low temperature all the density lines will merge. Only more accurate methods of density measures, than those employed, will prove this. The density curves of C_{24} and C_{30} for the (C) or tilted phase do not quite conform to the general pattern. In the case of the latter compound, measurements were checked on two separate samples with the same results. Some doubt exists as to the true values of the former although the density at the m. p. and at the t. p. fall in line with those of the others.[13] It is interesting to note both Mueller[12] and Kolvoort[14] found this (C_{24}) hydrocarbon to behave somewhat differently than the other members of the even numbered series. While the m. p. of both samples were the same the t. p. recorded by them was between 40–41° whereas our sample showed the expected value of 47.9. It appears that C_{24} forms a kind of boundary between the set of hydrocarbons to the left and the set to the right.

The difference between the two groups lay in their behavior with ascending or descending temperatures. In the case of the group to the right, comprising the members C_{26}, C_{28}, C_{30}, C_{32} and C_{34}, points on the curves could be retraced either upon heating or cooling. This condition

(13) R. Yatabe, unpublished M.Sc. Thesis.
(14) Kolvoort, J. Inst. Pet. Tech., 24, 338 (1938).

also applied to C_{24}, but not for C_{22}, C_{20} and C_{18}. Points on the curve for C_{16}, which has no t. p., could also be checked, irrespective of whether the temperature was going up or down. Those hydrocarbons to the left of C_{24} showed no t. p. upon heating but only upon cooling. The curves obtained upon cooling were of the same form as all the other members of the series and were reproducible. Upon heating these compounds the C phase did not convert to the B but melted directly, and the curves drawn represent limiting conditions. Indications were noted which implied that if the heating were done slowly enough some of the B modifications might be formed before melting took place. Density points would then lie somewhere within the enclosed region as shown in the figure.

If the line AB is produced to the point D and the distance from this line to the t. p. is measured along the temperature axis, it will be seen that this distance decreases as we pass from C_{26} to C_{34}. This indicates that at some higher member in the series than C_{34} the transition point will again disappear. Measured from the figure this distance decreases 0.03° per carbon atom, and consequently at about C_{45} or C_{46} the t. p. should coincide with the m. p. Mueller states that this should occur at C_{44}. This is also shown by the slope of the line EC.

Probably the most striking fact in connection with the figure is the great difference in density in the solvent phase between C_{29}, the only odd hydrocarbon measured and that of its neighboring even-numbered members. While too much stress must not be laid on the behavior of this one member at this time, nevertheless it is well to mention that the density points all fell on a smooth curve, whether the temperature was rising or falling. Since the type of packing is the same for the even and odd members of the paraffin series in this molecular weight range, the difference in density must be ascribed largely to the difference in the gap distance between the molecules of the odd- and even-numbered hydrocarbons.

Summary

1. The densities of the even-numbered n-paraffin hydrocarbons from C_{16} to C_{34} have been measured.

2. The density measurements indicate that the structure in the liquid and solid states is the same for all members of the series.

3. The odd numbered hydrocarbon C_{29} has a solid phase much less dense than the neighboring even-numbered members.

4. The transition points of hydrocarbons C_{24} to C_{34} could be observed with either heating or cooling, while the transition points of C_{18}, C_{20} and C_{22} were observed only on cooling.