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Abstract

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STUDY OF SYSTEMS OF n-PARAFFIN HYDROCARBONS C_{20}–C_{30} AND C_{30}–C_{32}

Over the last decade, natural petroleum paraffins have been subjected to comprehensive study by chemical and physicochemical methods. The application of classical techniques of organic chemistry, in combination with X-ray, differential-thermal, mass-spectrometric, and other methods, has made it possible to establish that the hydrocarbons entering into petroleum paraffins are not uniform in their chemical nature. The principal part of them consists of normal long-chain hydrocarbons from $C_{17}H_{36}$ and higher; branched hydrocarbons, cycloparaffins, and alkylbenzenes are present in smaller amounts ($^{1-4}$).

The industrial use of petroleum paraffins for organic synthesis is considerably hindered by the absence of adequate methods for separating hydrocarbons into the above-mentioned types. At the same time, in order to solve a number of problems connected both with the development of methods for separating solid petroleum paraffins and with the identification and determination of the degree of purity of isolated and synthesized hydrocarbons, a thorough study is required of the properties of individual n-paraffins, as well as of their interaction with one another and with hydrocarbons of other classes.

A number of binary systems of n-paraffins with long chains were studied by Piper and co-workers (^{5}), Mazee (^{6}), Seyer (^{7,8}), Smith (^{9}), Yuganova (^{10}), and others. A theoretical generalization of the available experimental material on binary systems of n-paraffin hydrocarbons was made by V. M. Kravchenko (^{11}).

However, the binary systems of long-chain n-paraffins studied so far do not cover the entire range of components entering into petroleum paraffins. The reason for this apparently lies in the great difficulties encountered by investigators in obtaining individual long-chain paraffins of high purity.

The impossibility of completely removing impurities from n-paraffin hydrocarbons and the presence of various phase transformations in the solid state ($^{5,12-16}$) make the interpretation of data obtained by classical methods of physicochemical analysis extremely complicated. Data on the interaction of n-paraffins with hydrocarbons of other classes are almost entirely lacking.

The present paper presents the results of a study of the state diagrams of binary systems of n-paraffins: $C_{20}H_{42}$–$C_{30}H_{62}$ and $C_{30}H_{62}$–$C_{32}H_{66}$, by differential-thermal and microstructural methods. We have found no information on these systems in the literature.

Eicosane and triacontane were obtained by Kolbe electrosynthesis ([17,18]). Dotriacontane was synthesized by Wurtz' s method. The synthesized hydrocarbons –

hydrocarbons were purified by repeated recrystallization from a series of solvents. The final product was recrystallized from ethyl alcohol.

n-Eicosane. Found, %: C 84.76; 84.80; H 15.24; 15.20
$C_{20}H_{42}$. Calculated, %: C 85.00; H 15.00

n-Triacontane. Found, %: C 85.34; 85.38; H 14.75; 14.67
$C_{30}H_{62}$. Calculated, %: C 85.20; H 14.80

n-Dotriacontane. Found, %: C 85.28; 85.24; H 14.70; 14.80
$C_{32}H_{66}$. Found, %: C 85.26; H 14.77

The degree of purity of the hydrocarbons, kindly determined by N. I. Lyashkevich on a precision thermographic apparatus, was as follows: eicosane 99.14 mole %, triacontane 98.88 mole %, and dotriacontane 99.78 mole %.

The heating and cooling curves were recorded with a Kurnakov photo-recording pyrometer. A differential platinum-gold-palladium thermocouple with a wire diameter of 0.2 mm was used. The sample weight in recording the thermograms was 0.05 g. To observe the microstructure, an apparatus consisting of a microscope, a heating-cooling stage, and a thermocouple was used ([19]).

From the heating curves, the melting temperatures and the temperatures of the polymorphic transformation of the hydrocarbons were determined.

	Transformation temp., °C	Melting temp., °C
Eicosane	none	37.5
Triacontane	59.0	66.2
Dotriacontane	64.0	69.5

The very close agreement of the above melting temperatures, and especially of the polymorphic-transition temperatures, with the literature data ([5,12–16]) also indicates a sufficiently high degree of purity of the hydrocarbons.

Table 1 gives the temperatures of phase changes in the system *n*-$C_{20}H_{42}$—*n*-$C_{30}H_{62}$, and Fig. 1 presents its phase diagram.

Table 1

Results of thermal analysis of the system $C_{20}H_{42}$—$C_{30}H_{62}$

Mixture No.	$C_{30}H_{62}$, wt. %	Crystallization of excess component, °C	Polymorphic transformation, °C	Crystallization of eutectic, °C	Phase transition below crystallization of eutectic, °C	Mixture No.	$C_{30}H_{62}$, wt. %	Crystallization of excess component, °C	Polymorphic transformation, °C	Crystallization of eutectic, °C	Phase transition below crystallization of eutectic, °C
1	2.00	–	—	36.0	29.0	11	40.70	53.1	—	35.5	29.0
2	4.70	—	—	35.5	29.5	12	50.50	56.5	—	35.5	29.0
3	5.00	—	—	36.0	30.0	13	58.00	57.5	—	35.5	29.0
4	6.40	—	—	36.0	29.0	14	61.10	59.0	—	35.5	29.0
5	7.00	—	—	36.0	30.0	15	70.00	61.0	59.0	34.5	29.0
6	8.00	36.5	—	36.5	29.0	16	80.00	62.0	59.0	34.5	29.5
7	10.90	37.0	—	35.5	29.0	17	90.00	65.0	59.5	35.0	—
8	17.60	44.0	—	35.5	29.0	18	95.00	64.2	58.5	—	—
9	20.0	46.0	—	35.5	30.0	19	98.00	64.5	58.5	—	—
10	31.90	50.2	—	35.5	29.0						

The system is eutectic. In all mixtures containing from 61.0 to 100% triacontane, an effect corresponding to the polymorphic transformation of the given-

hydrocarbon. The magnitude of the effect, as was to be expected, increased as the percentage content of triacontane in the mixtures increased. In the phase diagram, the polymorphic transformation of triacontane corresponds to the line (ab).

The eutectic of the system has the composition 93.0 wt.% eicosane and 7.0 wt.% triacontane and lies at a temperature of 35.5°C. In mixtures containing 95.0 and 98.0% triacontane, the thermograms show no effect corresponding to crystallization of the eutectic, but its separation was observed when micropreparations were examined in polarized light. The liquidus line characterizing the precipitation of primary crystals of eicosane is drawn as a dashed line, since on the differential curves the effect corresponding to crystallization of the excess ($C_{20}H_{42}$) merged with the effect of crystallization of the eutectic, owing to the closeness of the temperatures of the two processes. It should be noted that on the cooling curves of mixtures of this system, at a temperature of 29-30°, i.e., below the crystallization temperature of the eutectic, a phase transition

Fig. 1 and Fig. 2: phase diagrams

Figure 1: Fig. 1 and Fig. 2: phase diagrams

was observed, the thermal effect of which increased regularly as the percentage content of eicosane in the mixtures increased (Fig. 1, line (vg)). However, this effect was completely absent from the heating curves. On the basis of observations of the microstructure of specimens on a heating-cooling stage in polarized light, it may be assumed that the observed phase transition at 29-30° belongs to the category of irreversible transformations, which are observed in (n)-paraffin hydrocarbons and their derivatives with a moderate chain length (fewer than 22 carbon atoms) containing impurities (($^{\{15\},}$ {20})). However, in contrast to the published data, the observed phase transition, although irreversible, apparently does not belong to slow transformations occurring during storage of the specimens, since the heating curves were recorded immediately after the cooling curve had been recorded and nevertheless the corresponding effect was absent from the heating curves. Still, a final judgment about the nature of the phase transition at 29-30° cannot be made on the basis of thermal and microstructural analyses. An X-ray structural study is apparently necessary, as well as a comprehensive detailed investigation of the polymorphism of (C_{20}H_{42}), both maximally purified and containing impurities. For pure eicosane, no reversible polymorphic transformations were observed, which corresponds to the assumption

Fig. 1

Fig. 2

Fig. 1. Phase diagram of the system (n)-(C_{20}H_{42})—(n)-(C_{30}H_{62}); (a)—(b)—reversible polymorphic transformation of (n)-(C_{30}H_{62}); (v)—(g)—presumed irreversible transformation of (n)-(C_{20}H_{42}) (observed only on cooling)
Fig. 2. Phase diagram of the system (n)-(C_{30}H_{62})—(n)-(C_{32}H_{66})

Hoffman' s data (15) on the existence of rotational transitions in individual *n*-paraffin hydrocarbons containing only 22 or more carbon atoms in the chain.

Table 2 gives the data from a thermal study of the system n-$C_{30}H_{62}$—n-$C_{32}H_{66}$, and Fig. 2 presents its phase diagram.

Table 2

Results of thermal analysis of the system n-$C_{30}H_{62}$—n-$C_{32}H_{66}$

Mixture no.	$C_{32}H_{66}$, wt. %	Temperature, °C: onset of crystallization	Temperature, °C: end of crystallization	Temperature, °C: onset of transformation	Temperature, °C: end of transformation
1	98.00	69.5	68.8	63.6	63.0
2	95.00	69.0	68.2	63.3	62.6
3	85.00	68.6	67.6	62.9	61.9
4	74.33	68.5	67.6	62.5	60.5
5	65.00	67.9	66.0	61.5	59.5
6	62.43	67.9	66.0	61.6	59.2
7	47.43	67.2	66.0	60.9	58.7
8	42.85	67.6	66.0	60.7	58.4
9	29.04	67.0	65.6	60.0	58.2
10	20.00	66.6	65.5	59.4	58.0
11	15.00	66.7	65.6	59.3	58.0
12	8.40	66.8	65.6	59.5	57.6
13	4.90	66.4	65.6	58.9	58.0
14	2.00	66.1	65.7	58.8	58.2

The α-modifications of triacontane and dotriacontane separating from the melt form a continuous series of solid solutions. As the temperature is lowered, the α-solid solution passes into a β-solid solution, which is formed by the polymorphic modifications of the hydrocarbons that are stable below the transition point.

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