CHEMISTRY

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1957

SovietRxiv

Abstract

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CHEMISTRY

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INVESTIGATION OF SYSTEMS OF NORMAL PARAFFIN HYDROCARBONS C_{30}–C_{34} and C_{30}–C_{36}

We have already noted ([1]) the scientific and practical significance of studying phase diagrams of systems of high-molecular-weight *n*-paraffin hydrocarbons, and we have also presented the results of a study of two binary systems: eicosane–triacontane ($C_{20}H_{42}$—$C_{30}H_{62}$) and triacontane–dotriacontane ($C_{30}H_{62}$—$C_{32}H_{76}$). Eicosane and triacontane form a system of the eutectic type, whereas triacontane and dotriacontane interact with the formation of continuous solid solutions.

In the present article we give data obtained in the further study of *n*-paraffin systems by differential-thermal and microstructural methods.

Phase diagrams of the binary systems of *n*-paraffins: triacontane–tetratriacontane ($C_{30}H_{62}$—$C_{34}H_{70}$) and triacontane–hexatriacontane ($C_{30}H_{62}$—$C_{36}H_{74}$) have not been described in the literature.

Triacontane and tetratriacontane were obtained by Kolbe electrosynthesis ([2–3]); hexatriacontane was synthesized by the Wurtz method. The starting and final products were repeatedly recrystallized from a number of solvents, the final recrystallization being carried out from ethyl alcohol.

The degree of purity of the hydrocarbons obtained was determined on a precision thermographic apparatus. It was 98.88 mole % for triacontane and 98.87 mole % for tetratriacontane.

The purity of hexatriacontane was not determined by the precision method, since only a very small amount of this hydrocarbon was available to us.

As is known, all long-chain *n*-paraffins undergo reversible polymorphic transformations ([4–7]). The temperatures of the polymorphic transformations and the melting temperatures for the synthesized preparations were determined from heating curves:

Hydrocarbon	Temperature of polymorphic transformation, °C	Melting point, °C
Triacontane	59.0	66.2
Tetratriacontane	68.9	73.0
Hexatriacontane	73.0	74.0

The data given are very close to those in the literature.

Thermograms were recorded on a Kurnakov photo-recording pyrometer. The sample weight during recording was 0.05 g. The accuracy of temperature reading was about 0.2°. The data presented in Tables 1 and 2 are averages of several parallel determinations for each mixture. The discrepancy of temperature values in parallel experiments ranged from ±0.2 to ±0.5°. The heating (or cooling) rate was 0.6–0.7 deg/min. The heating curves of mixtures of the systems studied were completely identical to their cooling curves both in the number of recorded

phase transformations, and in temperature values; for this reason only the data obtained during crystallization of the mixtures are given.

Table 1

Results of thermal analysis of the system $C_{30}H_{62}$—$C_{34}H_{70}$

No.	$C_{34}H_{70}$, wt. %	Crystallization temperature, °C (beginning)	Crystallization temperature, °C (end)	Transformation temperature $\alpha \rightarrow \beta$, °C (beginning)	Transformation temperature $\alpha \rightarrow \beta$, °C (end)
1	98.0	72.7	71.1	68.5	67.2
2	93.1	72.5	70.9	68.3	65.7
3	90.0	72.0	68.9	66.8	63.7
4	76.6	71.6	67.6	65.3	60.1
5	70.0	71.1	67.8	65.6	60.0
6	63.0	70.2	66.2	63.7	58.9
7	50.0	69.5	65.0	62.0	57.6
8	40.0	68.8	63.6	59.7	55.5
9	29.2	67.8	63.1	59.3	55.7
10	22.0	67.5	63.5	58.9	56.0
11	14.6	66.6	62.1	57.8	55.0
12	5.0	66.4	63.1	58.0	55.1
13	2.0	66.3	64.7	58.8	56.8

Table 2

Results of thermal analysis of the system $C_{30}H_{62}$—$C_{36}H_{74}$

No.	$C_{36}H_{74}$, wt. %	Crystallization temperature, °C (beginning)	Crystallization temperature, °C (end)	Transformation temperature $\alpha \rightarrow \beta$, °C (beginning)	Transformation temperature $\alpha \rightarrow \beta$, °C (end)
1	98.0	73.0	71.9	70.2	68.4
2	95.0	71.8	71.1	70.2	66.8
3	88.3	71.7	69.4	68.6	62.4
4	80.0	70.6	67.4	66.6	57.6
5	70.0	70.0	67.2	64.8	56.6
6	60.2	69.4	66.2	62.4	56.0
7	48.0	68.3	64.2	61.0	55.2
8	36.4	67.0	63.1	58.1	54.4
9	28.0	67.0	63.0	59.2	55.0
10	20.0	65.5	62.6	57.6	54.1
11	9.6	65.8	63.5	57.7	54.4
12	2.0	66.1	64.8	57.7	56.3

The results of thermal analysis of the binary triacontane–tetratriacontane system are given in Table 1, and its phase diagram is shown in Fig. 1.

Fig. 1. Phase diagram of the system n-$C_{30}H_{62}$–n-$C_{34}H_{70}$

Fig. 2. Phase diagram of the system n-$C_{30}H_{62}$–n-$C_{36}H_{74}$

Triacontane and tetratriacontane form a system with continuous solid solutions (see Fig. 1). The polymorphic modifications of n-paraffins that separate from the melt during crystallization and are usually designated by the letter α form a continuous solid solution, correspondingly also designated as the α-solid solution. With a certain lowering of temperature, the α-solid solution passes into a continuous solid solution formed by β-modifications, which are stable at lower temperatures down to room temperature. With further lowering of the temperature, the β-solid solution undergoes no changes.

The liquidus line of the phase diagram in the system $C_{30}H_{62}$—$C_{34}H_{70}$ is an almost straight line. This circumstance was noted earlier in Piper' s studies for certain other systems of long-chain n-paraffins ([8]).

The straight-line character of the liquidus line indicates that addition of the

second component to the higher-melting hydrocarbon causes only a very slight lowering of the melting point. Thus, addition to tetratriacont-

the addition of 10% triacontane causes the temperature at the onset of crystallization to decrease by only 1.0°. The temperature at the end of crystallization decreases more noticeably. The temperature interval between the onset of solidification of this mixture and the end of solidification, at the given cooling rate, is 3.1°.

This circumstance shows that it is very difficult to judge the degree of purity of *n*-paraffin preparations from determinations of the melting or solidification point carried out by the capillary method with the aid of a thermometer, since in this case it is almost impossible to determine both the onset and the end of crystallization, and the mean temperature obtained will differ very little from the melting temperature of the pure hydrocarbon, despite the considerable content of a second component in it.

The point of polymorphic transformation undergoes a considerably greater decrease in the crystallization temperature upon addition of the second component. In the mixture considered above (10% $C_{30}H_{62}$ and 90% $C_{34}H_{74}$), it is 2.1° relative to pure $C_{34}H_{70}$. The temperature interval in which the transition of the α-solid solution to the β-solid solution occurs in this mixture is 3.6°, which also indicates the greater sensitivity of the transition temperature to an impurity than that of the crystallization temperature.

Table 2 gives the results of thermal analysis of the triacontane–hexatriacontane system. Its phase diagram is presented in Fig. 2.

This system is analogous to the preceding one. Over the entire concentration range the components form a series of continuous solid solutions. At higher temperatures the solid solution formed by the α-modifications of the hydrocarbons is stable. Upon lowering the temperature, over a fairly broad interval, the α-solid solution transforms into the β-solid solution, which, upon further cooling of all mixtures of the system, undergoes no changes.

The liquidus line on the phase diagram of this system also differs very little from a straight line. The transformation temperature decreases considerably as the percentage content of triacontane in the mixtures increases. When triacontane is added to $C_{36}H_{74}$, the line of the onset of transformation drops sharply downward, becoming somewhat leveled in the left-hand part of the diagram.

The largest temperature interval of transformation corresponds to mixtures containing from 60 to 80% $C_{36}H_{74}$. Thus, for a mixture containing 70% hexatriacontane and 10% triacontane, it is 8.2°.

Thus, *n*-paraffins $C_{30}H_{62}$–$C_{34}H_{70}$ and $C_{36}H_{62}$–$C_{36}H_{74}$ form systems with continuous solid solutions, which in the solid state undergo type I transformations according to Roseboom.

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Received
11 IV 1957

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Note: Figure translations are in progress. See original paper for figures.