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Abstract

Full Text

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DOUBLE SYSTEMS OF TWO-RING MOLECULES INVOLVING THIONAPHTHENE

(Presented by Academician I. I. Chernyaev, VII 1, 1960)

Phase equilibria in systems including thionaphthene have scarcely been covered in the literature. It is of interest to determine the type of phase diagrams in combinations of thionaphthene with such second components as are either very close to it in the structure of the molecular skeleton—indene, indole—or differ from it in a regular way—isoquinoline, 2-methylnaphthalene, 3-methylisoquinoline, 2,6-dimethylnaphthalene. The presence of the selected substances in coal and in petroleum-refining products determines the applied orientation of the work.

Fig. 1. Sections of molecular models: S_1 and S_1'—thionaphthene, S_2—indene, S_3—indole, S_4—isoquinoline, S_5—3-methylisoquinoline, S_6—2-methylnaphthalene, S_7—2,6-dimethylnaphthalene.

Components of the systems. Thionaphthene and 2-methylnaphthalene were synthetic, while the other five substances were of coke-chemical origin. All of them were first carefully purified. As a result of the preparation, specimens were obtained with melting-crystallization temperatures within $\pm 0.1^\circ$, as indicated in Table 1.

Methods for studying double systems. Four methods were used. The dependence T, X between the composition X (in percent) of mixtures and the equilibrium temperature T of the condensed phases was determined: a) by thermal analysis on an apparatus assembled according to scheme ([1]); b) by visual observations on the same laboratory apparatus; c) a series of specially prepared mixtures was studied with the aid of a dilatometer connected to an ultrathermostat of the Vobser type; d) the behavior of the components in the liquid phase was determined by recording the refractive index n_D^t for mixtures

of composition X in an Abbe refractometer.

The types of phase diagrams established as a result of the experiments—continuous solid solutions and eutectic systems—are in good agreement with the structural characteristics of the components; Fig. 1 presents sections of models of their molecules.

In the original literature, structural measurements are described for 2,6-dimethylnaphthalene; the models of the remaining 6 molecules in Fig. 1 were constructed from averaged or similar data, with allowance for ([2,3]). The centers of the skeletal atoms of the molecules in Fig. 1 lie in one plane. We take the valence bonds and angles as follows: a) in benzene and naphthalene rings: CC 1.4; CH 1.08 Å, $\angle\alpha$ 120°; b) in the 5-membered ring of thionaphthene, according to thiophene ([4]): C′C″ 1.35; CC′ 1.44; CS 1.74; CH 1.08 Å; $\angle\beta$ 91°; $\angle$SC′C″ 112°; $\angle$C″C′C 113°; c) in the 5-membered ring of indene, according to fluorene ([5]): CC 1.50; C′C″ 1.40; C″CH_2 1.52 Å; $\angle\gamma$ 106°; $\angle$CC′C″ 108°; $\angle$C′C″CH_2 109°; d) in the 5-membered ring of indole, according to pyrrole ([6]): CC′ 1.44; C′C″ 1.35 Å; C 1.42, $\angle\delta$ 108°; $\angle$CC′C″ 108°; $\angle$C′C″ 110°; e) the nitrogen-containing ring in isoquinoline and 3-methylisoquinoline, according to pyridine ([6]): C′C″ 1.39; C″N 1.37 Å; $\angle$CC′C″ 121°; $\angle\delta$ 119°.

The outer contours of the molecular models in Fig. 1 were constructed using intermolecular approach radii (Å): R_C 1.8, R_S 1.85, R_N 1.57, R_H 1.17; the contour of the hydrogen atoms in methyl groups is conventionally shown by a dashed line. As for the "thickness" of the molecular models, it is on average equal to $2R_C \sim 3.6$ Å. A certain "bulge" is noticeable for the region of the sulfur atom of thionaphthene—$2R_S \sim 3.7$ Å, and, correspondingly, a smaller thickness corresponding to nitrogen atoms—$2R_N \sim 3.2$ Å. From the models, the cross-sectional areas S Å^2 and volumes V Å^3 of the molecules were calculated; their ratios are given below.

Table 1

Double systems of thionaphthene (X_B—wt. %, X_M—mol. % thionaphthene, t_1—temperature at the start of crystallization, t_2—end of crystallization)

X_B	X_M	t_1	t_2	X_B	X_M	t_1	t_2	X_B	X_M	t_1	t_2
Thionaphthene–indene											
100,00	100,0	31,2	–	56,46	52,9	18,0	15	18,43	16,4	4,2	2
89,47	88,1	28,1	27	48,84	45,3	15,2	12	10,14	9,0	1,0	0
80,79	78,5	25,6	24	42,90	39,4	13,1	10	4,75	4,1	−0,2	−1
73,91	71,1	23,6	22	26,61	23,9	6,9	5	0,00	0,0	−1,7	–
67,22	64,0	21,6	19								

X_B	X_M	t_1	t_2	X_B	X_M	t_1	t_2	X_B	X_M	t_1	t_2
Thionaphthene — indole											
100,00	100.0	31,2	—	67,33	64,3	34,1	33	22,90	20,5	42,5	40
93,25	92,3	31,6	31	59,60	56,3	35,0	34	13,42	11,9	46,5	43
87,38	85,8	31,9	31	44,14	40,8	37,0	35	6,09	5,3	49,8	47
75,60	73,0	33,3	32	34,79	31,7	39,0	37	0,00	0,0	53,0	—
Thionaphthene — isoquinoline											
100,00	100,0	31,2	—	46,70	45,8	27,8	26	21,53	20,9	26,6	—
91,56	91,2	30,2	29	33,56	32,6	27,2	25	15,36	14,8	26,1	24,5
78,30	77,7	29,6	28	64,90	64,0	28,8	—	4,50	4,0	25,1	24
70,16	69,4	29,2	27,5	58,21	57,3	28,6	27	0,00	0,0	24,7	—
Thionaphthene — 2-methylnaphthalene											
100,00	100,0	31,2	—	60,10	61,5	−4,2	−4,2	21,10	22,1	19,5	−4,2
88,37	88,9	23,0	−6	54,78	56,2	−1,1	−4,2	12,65	13,3	25,2	−4,2
79,43	80,4	15,8	−5	50,08	51,5	1,8	−4,2	6,24	6,6	30,0	−5
73,48	74,6	10,3	−4,2	43,21	44,6	5,9	−4,2	0,00	0,0	34,4	—
69,50	70,8	6,7	−4,2	31,55	32,8	13,0	−4,2				
Thionaphthene — 3-methylisoquinoline											
100,00	100,0	31,2	—	73,04	74,4	13,2	13,2	42,81	44,4	39,9	13,2
93,81	94,2	27,7	13	69,94	71,3	16,1	13,2	31,76	33,2	47,8	—
89,16	89,8	24,4	13	66,40	67,8	20,0	13,2	20,37	21,5	54,6	—
83,37	84,3	20,8	13,2	56,56	58,2	28,2	13,2	9,58	10,7	60,4	—
78,07	79,2	17,0	13,2	47,54	49,2	36,0	13	0,00	0,0	65,7	—
75,55	76,6	14,9	13,2								
Thionaphthene — 2,6-dimethylnaphthalene											
100,00	100,0	31,2	—	78,30	80,8	41,2	22,5	42,10	45,9	81,5	22
96,40	96,9	28,1	22,5	73,25	76,1	48,0	22,5	33,16	36,7	88,5	22
93,19	94,1	26,0	22,5	64,37	67,8	59,9	22,5	18,27	20,7	99,1	—
90,94	92,2	24,1	22,5	54,96	58,7	70,2	22,5	9,31	10,6	105,0	—
88,65	90,1	22,5	22,5	47,71	51,5	77,0	22	0,00	0,0	110,0	—

Fig. 2

Figure 2: Fig. 2

83,54	85,6	32,5	22,5	–

The results of determining the phase-equilibrium temperature as a function of composition for six systems involving thionaphthene are collected in Table 1. Corresponding-

their phase diagrams t, X are shown in Fig. 2, where the lines n_D^t, X (two dots –dash) are also plotted, one for each system.

Thionaphthene–indene system. Continuous solid solutions were found. The mixtures crystallized (melted) within narrow temperature limits not exceeding 3°. In the phase diagram t, X, Fig. 2, 1, the line for the onset of crystallization passes with very slight convexity ($\sim 2°$ in the middle part) toward the limiting straight line (7), which can be drawn between the melting points of the components. Equally close to the limiting line is the slightly concave line for the end of crystallization. The ratios of the structural characteristics of the components are: $S_1/S_2 \sim 1.4$, $V_1/V_2 \sim 1.1$. The diagram n_D^{32}, X in Fig. 2, 1 is rectilinear, type I according to V. Ya. Anosov (8).

Fig. 2. Diagrams t, X and n_D^t, X for systems of thionaphthene with indene (1), indole (2), isoquinoline (3), 2-methylnaphthalene (4), 3-methylisoquinoline (5), and 2,6-dimethylnaphthalene (6).

Thionaphthene–indole system. In Fig. 2, 2, a diagram t, X is presented, characterizing a series of continuous solid solutions with the greatest divergence of the temperatures of the beginning and end of crystallization, $\sim 4°$, at a thionaphthene content of $\sim 15\%$. The lines for the beginning and end of crystallization are also close to, and somewhat (by 5–6° in the middle part) concave relative to, the limiting straight line. Here $S_1/S_3 \sim 1.05$, $V_1/V_3 \sim 1.06$. The line n_D^{60} is rectilinear, type I.

In the thionaphthene–isoquinoline system (Fig. 2, 3), a series of continuous solid solutions was found. The lines for the beginning and end of crystallization, respectively convex and concave, are symmetrically situated on the two sides of the limiting straight line, the deviation from which in the middle part is about 1°. In general, the diagram t, X is a very narrow "cigar," positioned almost horizontally, since the melting points of the components differ by only 6°. Here $S_1/S_4 \sim 1.03$, $V_1/V_4 \sim 1.05$, and the combination of the "convexity" of thionaphthene and the "concavity" of isoquinoline. The line n_D^{35} is close to a straight line.

Thus, in two of the three thionaphthene-containing systems, a very rare type of phase diagram has been found, illustrating the approach of the line t, X

to the rectilinear limit, where continuous solid solutions are found with the participation of second components similar in structure, at $\Delta S \sim 3$–5% and $\Delta V \sim 1$–6%.

The three systems of thionaphthene with homologs of naphthalene and isoquinoline are eutectic. For them, as a rule, secondary eutectic arrests were observed on the temperature–time curves, marked accordingly on the diagrams t, X. We shall give the determined coordinates of the eutectic points: temperature (t_e°, C) and content (X_e, mole %) of thionaphthene; indicate the observed supercooling (Δt, °C) of the components crystallizing under intensive stirring; and note the values of ΔS and ΔV for the components.

System thionaphthene–2-methylnaphthalene, Figs. 2, 4:
t_e 4.2°, X_e 61.5 mole %, Δt of thionaphthene $\sim$ 2–3°, Δt of 2-methylnaphthalene $\sim$ 3–4°, $\Delta S \sim 18\%$, $\Delta V \sim 22\%$.

System thionaphthene–3-methylisoquinoline, Figs. 2, 5:
t_e 13.2°, X_e 74.4 mole %, Δt of thionaphthene 6–8°, Δt of 3-methylisoquinoline 8–10°, $\Delta S \sim 15\%$, $\Delta V \sim 19\%$.

System thionaphthene–2,6-dimethylnaphthalene, Figs. 2, 6:
t_e 22.5°, X_e 90.1 mole %, Δt of both components 2–3°, $\Delta S \sim 28\%$, $\Delta V \sim 36\%$.

Consequently, the eutectic type of the three thionaphthene-containing systems is explained by a considerable difference in the shape (Fig. 1) and sizes of the molecules of the components: $\Delta S > 14\%$ and $\Delta V > 20\%$.

The previously studied system thionaphthene–naphthalene is characterized by a phase diagram t, X ([9]), the type of which may be regarded as intermediate between the eutectics and the solid solutions described in the present communication. The n_D^t diagrams for the investigated eutectic thionaphthene-containing systems in Figs. 2, 4–6 are very close to rectilinear, type I, i.e., no interaction of the components in the liquid phase is observed.

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