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Abstract

Full Text

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CHEMISTRY

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SYSTEMS OF 3-METHYLISOQUINOLINE WITH BENZENE, NAPHTHALENE, 2-METHYLNAPHTHALENE AND INDOLE

(Presented by Academician I. I. Chernyaev, 7 IX 1959)

Few data have been published on phase equilibria in systems involving nitrogen-containing components of coal tar. Phase diagrams including 3-methylisoquinoline, in general, have not been encountered by us.

Among the five substances taken by us for this work, the sample of 2-methylnaphthalene was of synthetic origin; the other four were coking-chemical products.

Fig. 1. Sections of molecular models: S_1—3-methylisoquinoline, S_2 and S_2'—benzene, S_3—naphthalene, S_4—2-methylnaphthalene, S_5—indole

All of them were subjected to careful purification; for the preparation of mixtures, fractions were used that melted and crystallized within an interval of $\pm 0.1^\circ$; the melting temperatures of the purified preparations are given in Table 1.

The liquid-crystal equilibrium was studied by thermal analysis, accompanied by visual observations; a laboratory apparatus according to scheme ([1]) was used. A number of mixtures were also investigated with the aid of a specially constructed dilatometer connected to an ultrathermostat. The characterization of some molten mixtures was obtained by determining the refractive index n_D with an Abbe-type refractometer.

The parameters of the crystal lattice of 3-methylisoquinoline are not known to us. In discussing the types of phase diagrams found, we shall take into account the chemical interaction of the components and compare the shape and dimensions of models of their molecules.

Figure 1 shows sections of molecular models; in particular, the similarity of 3-methylisoquinoline and 2-methylnaphthalene is visible. The models in Fig. 1 were constructed from known ([2,3]) data (averaged) for valence bonds (Å): C–C_{ar} 1.4, C_{ar}–H 1.08, C_{ar}–C_{al} 1.5, C–N 1.37, C–NH 1.42; for valence angles: $\angle\alpha$ 120°, $\angle\beta$ 119°, $\angle\gamma$ 108°, and inter-

Table 1

Binary systems of 3-methylisoquinoline with benzene, naphthalene, 2-methylnaphthalene, indole (x_w–wt. %, x_m–mol. % of 3-methylisoquinoline, t_1 –temperature at the beginning of crystallization, t_2–end of crystallization)

x_w	x_m	t_1	t_2	x_w	x_m	t_1	t_2
3-methylisoquinoline–benzene				**3-methylisoquinoline–naphthalene**			
100.00	100.0	65.7	65.7	45.55	31.3	19.1	−3.3
94.82	90.9	61.2	3.5	37.68	24.8	12.2	−3.3
88.13	80.2	55.4	–	28.91	18.2	2.2	−3.3
81.75	70.9	50.3	–	23.29	14.2	−3.3	−3.3
73.07	59.7	43.1	3.5	20.40	12.3	−2.4	−3.3
67.31	52.9	38.1	–	16.94	10.0	−1.0	−3.3
61.20	46.3	32.7	−3.3	0.00	0.0	5.5	5.5
53.30	38.4	25.9	−3.3	–	–	–	–
3-methylisoquinoline–naphthalene				**3-methylisoquinoline–naphthalene**			
100.00	100.0	65.7	65.7	49.38	46.6	44.8	35.5
90.38	89.3	59.0	–	36.71	34.2	55.9	35.5
88.67	87.5	57.3	50	29.80	27.5	61.6	35.5
82.65	81.0	53.4	40	21.15	19.4	68.0	35.5
75.50	73.4	48.0	35.5	15.61	14.2	72.0	41
69.22	66.8	43.0	35.5	13.65	12.4	73.0	47
61.16	58.5	37.0	35.5	10.55	9.5	74.0	56
59.00	56.3	35.5	35.5	4.69	4.2	78.0	69
56.48	53.7	37.9	35.5	0.00	0.0	80.2	80.2

x_w	x_m	t_1	t_2	x_w	x_m	t_1	t_2
3-methylisoquinoline–2-methylnaphthalene				**3-methylisoquinoline–2-methylnaphthalene**			
100.00	100.0	65.7	65.7	50.41	50.3	40.0	37.7
92.47	92.4	62.5	60	44.12	44.0	37.5	34.8
87.16	87.0	59.9	57	37.41	37.3	34.6	31.6
86.10	86.0	59	56	30.70	30.6	31.3	29
81.28	81.2	57	54	26.51	26.4	28.8	28.6
74.89	74.8	53.8	51	22.58	22.4	28.8	28.6
70.04	69.9	51	48	17.92	17.8	29.8	29
62.15	62.1	46.9	43.8	8.35	8.2	39.7	31
56.10	56.0	43.5	41	0.00	0.0	34.4	34.4
55.00	54.8	43	40	–	–	–	–
3-methylisoquinoline–indole				**3-methylisoquinoline–indole**			
100.00	100.0	65.7	65.7	54.50	49.5	–	46
95.16	94.2	62	58	54.00	49.1	46.7	45
89.43	87.4	57	49	53.22	48.2	–	44
87.98	85.7	55.7	–	51.74	46.7	46.0	43
85.76	83.1	53	40	51.24	46.3	45.8	–
81.52	78.3	47.3	–	47.68	42.7	44.1	22
76.81	73.1	40.2	34.2	38.50	33.9	37.2	22
73.82	69.8	34.2	34.2	32.28	28.0	30.5	22.3
69.63	65.2	38.8	34.2	28.40	24.5	24.6	22.3
65.49	60.8	41.7	34.2	26.83	23.1	22.3	22.3
62.08	57.2	44.1	34	25.10	21.5	24.6	22.3
58.17	53.2	45.9	34	22.62	19.3	26.3	22.3
55.70	50.7	46.9	43	16.90	14.3	35.2	22
55.23	50.3	47.0	46	9.80	8.2	42.6	–
54.70	49.7	46.8	–	0.00	0.0	53.0	53

molecular radii (Å): R_C1.8, R_H1.17, R_N1.57. The "thickness" of all the models is close to that of benzene (section S_2 in Fig. 1), $\sim$ 3.6 Å. From these data the cross-sectional areas S Å^2 and volumes V Å^3 of the molecular models were found.

The results of thermal analysis and dilatometric experiments, supplementing one another, are summarized in Table 1 and presented in Fig. 2 in the form

diagrams of t, x (t–equilibrium temperature, x–concentration). In Fig. 2 the "two dots–dash" lines and the diagrams n_D^t, x are also plotted.

Fig. 2. Diagrams tx and n_D^t, x of the systems of 3-methylisoquinoline with benzene (1), naphthalene (2), 2-methylnaphthalene (3), indole (4).

Figure 2: Fig. 2. Diagrams tx and n_D^t, x of the systems of 3-methylisoquinoline with benzene (1), naphthalene (2), 2-methylnaphthalene (3), indole (4).

System 3-methylisoquinoline–benzene. The phase diagram (Fig. 2, 1) and the tabular data characterize a eutectic type of equilibria. The eutectic contains 14.2 mole % of the heterocycle and crystallizes at -3.3°. A simple eutectic corresponds to a very considerable difference in the shape (Fig. 1) and sizes of the components: $S_1/S_2 \simeq 1.58$ and $V_1/V_2 \simeq 1.67$.

The diagram has a slight convexity with respect to the composition axis (i.e., it is close to type I according to V. Ya. Anosov ([4])), with a relatively insignificant deviation from a straight line. This deviation is possibly connected with slight solvation.

In the system 3-methylisoquinoline–naphthalene limited solid solutions were found, forming a eutectic at 35.5° with a heterocycle content of 56.3 mole % (Table 1, Fig. 2, 2). Here the ratios of the cross sections and volumes of the molecular models do not exceed 10%: $S_1/S_3 \sim 1.06$, $V_1/V_3 \sim 1.09$. The diagram n_D^{80}, x is an inclined straight line, type I.

System 3-methylisoquinoline–2-methylnaphthalene. The mixtures investigated crystallized (melted) within narrow temperature limits, of the order of 1–2° on the side of 2-methylnaphthalene and 3–4° on the side of the heterocycle. The phase diagram (Fig. 2, 3) illustrates solid solutions with a minimum at 28.5° and a 3-methylisoquinoline content of $\sim$ 24 mole %. The difference of this type of phase equilibria from the preceding ones is in good agreement with the decrease in the structural differences of the components: $S_1/S_4 \sim 0.97$, $V_1/V_4 \sim 0.97$. The diagram n_D^{70}, x here is also type I, but with a rare feature –it is horizontal, i.e., it proves the optical similarity of the components in the liquid phase.

System 3-methylisoquinoline–indole. A molecular compound $1 : 1$ was found, which is in equilibrium with the melt at $\sim 47^\circ$ (point M in Fig. 1, 4); for its crystallization, prolonged holding of supercooled melts was required (a day or more), unless seeds–crystals of the previously formed complex–were used. On the phase diagram (Fig. 2, 4) two eutectics are marked–$e_1 \sim 34^\circ$ and $e_2 \sim 22.5^\circ$, formed by limited solid solutions of the molecular compound with the initial components. The formation of the compound is the result of interaction of the unshared pair of electrons of the nitrogen of 3-methylisoquinoline with the hydrogen of the imino group of indole. Comparison of the shapes S_1 and S_5 (Fig. 1) shows that there are no steric obstacles to complex formation (here $S_1/S_5 \sim 1.20$, $V_1/V_5 \sim 1.16$). An analogous compound was found in the isoquinoline–indole system ([5]).

Fig. 2. Diagrams tx and n_D^t, x of the systems of 3-methylisoquinoline with

benzene (1), naphthalene (2), 2-methylnaphthalene (3), indole (4).

The diagram n_D^{70}, x in Figs. 2, 4 consists of two intersecting lines close to straight lines—type III—and reflects the presence of a molecular compound in the liquid phase.

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