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Abstract

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EQUILIBRIUM OF CONDENSED PHASES IN THE NAPHTHALENE-THIONAPHTHENE SYSTEM

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Naphthalene, which occupies second place after benzene among the cyclic products of coal carbonization, is isolated from coal-tar oil (by distillation, crystallization, pressing) with an admixture of thionaphthene. The latter is removed by repeated washing with concentrated sulfuric acid, completed by rectification, and by other methods.

The difficulties associated with separating thionaphthene from naphthalene have long been explained by the closeness of some of their physical properties, which lead, in particular, to the formation of solid solutions. However, up to now we have not encountered in the literature quantitative data that clearly characterize the liquid–crystal phase equilibria in this system.

In G. Frank' s article ([1]), figures are given only for the liquidus line, allowing two intersecting curves to be constructed, from which it is impossible to decide whether naphthalene and thionaphthene form a simple eutectic or solid solutions.

In discussing the problem of separating thionaphthene from naphthalene, V. Svyentoslavsky, in an interesting monograph ([2]), likewise gives no data on phase equilibrium in this system. In work ([2]) it is noted that the experimenters did not have pure thionaphthene.

To resolve the question of the type of phase diagram of the naphthalene–thionaphthene system, the components were first carefully prepared. Thionaphthene was synthesized* from styrene and hydrogen sulfide over a catalyst at a temperature of 600°.

$$\text{styrene} + \mathrm{H_2S} arrow \text{thionaphthene} + 2\mathrm{H_2}.$$

It melted after purification at a temperature of 31.2° (±0.1°). "Pure"naphthalene, in order to remove traces of thionaphthene, was treated with metallic sodium, distilled, and recrystallized; as a result, a preparation was obtained that melted at a temperature of 80.2° (±0.1°).

The processes of crystallization and melting were studied by the method of thermal analysis using a convenient laboratory apparatus ([3]); a series of mixtures of the components was also investigated dilatometrically.

The results of our experiments, characterizing the equilibrium of condensed phases, are collected in Table 1. The diagram constructed from these data —composition (X) versus the temperature of the beginning (t_1) and end of crystallization (t_2)

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* With the participation of V. I. Mil' skii.

shown in Fig. 1. It was found that naphthalene with thionaphthene forms a system of limited solid solutions with a eutectic.

Table 1

Thionaphthene–naphthalene system

Thionaphthene conc., wt. %	Thionaphthene conc., mol. %	Naphthalene conc., wt. %	Naphthalene conc., mol. %	t_1, °C	t_2, °C
100.0	100.0	0.00	0.0	31.2	31.2
97.82	97.7	2.18	2.3	31.0	–
95.90	95.7	4.10	4.3	30.2	30.1
94.40	94.2	5.60	5.8	29.9	29.9
92.05	91.7	7.95	8.3	30.3	30.0
90.04	89.6	9.96	10.4	31.9	30.1
85.10	84.5	14.90	15.5	35.3	30.1
78.29	77.5	21.71	22.5	39.7	30.3
71.41	70.5	28.59	29.5	43.8	30.5
63.84	62.8	36.16	37.2	48.6	–
60.30	59.2	39.70	40.8	50.2	37
53.88	52.8	46.12	47.2	54.2	44
46.39	45.2	53.61	54.8	58.5	50
36.77	35.7	63.23	64.3	64.0	56
26.22	25.4	73.78	74.6	68.8	–
16.47	15.8	83.53	84.2	72.9	70
8.96	8.6	91.04	91.4	76.5	–
4.91	4.7	95.09	95.3	78.1	–
0.00	0.0	100.00	100.0	80.2	80.2

The minimum crystallization (melting) temperature of the solid solutions is 29.9°; it corresponds to a composition of 5.8 mol. % (5.60 wt. %) naphthalene and 94.2 mol. % (94.40 wt. %) thionaphthene.

Fig. 1. Liquid-crystal equilibrium in the naphthalene–thionaphthene system

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When the molten and vigorously mixed mixtures were cooled, crystallization occurred with only a very slight delay. The supercooling of the solid solutions on the naphthalene side was 0.5-1°, and on the thionaphthene side 1.5-2°.

In Fig. 1, the ideal-solubility curves of the components of the system, calculated from I. F. Schröder' s equation (4), are plotted with a dashed line: $\ln X = Q(1/T - 1/T_1)/R$, where Q (cal/mol) is the heat of fusion, T is the absolute saturation temperature of a solution of concentration X in mole fractions; $R = 1.987$ cal/mol. In the calculation, the heat of fusion of naphthalene was taken as $Q = 4610$ cal/mol (5), found calorimetrically for a naphthalene preparation with m.p. 80.0°, and the heat of fusion of thionaphthene as $Q = 2826.8$ cal/mol (6). The ideal-solubility curves and the experimentally found t, X diagram in Fig. 1 diverge very strongly. The experimental eutectic point is shifted upward relative to the ideal eutectic (e) by $\Delta t \approx 14°$ and toward thionaphthene by $\Delta X \approx 17$ mol. %. Such a considerable deviation of these points may be explained by the influence of the formation of solid solutions of naphthalene with thionaphthene, whose liquidus line tends toward a straight line (see the analogy in (7)).

Fig. 1. Liquid–crystal equilibrium in the naphthalene–thionaphthene system

Averaged structural data for naphthalene (8) indicate equality of the intermolecular C–C bonds, 1.4 Å, and of the valence angles formed by them, ∠C—C=C = 120°. Supplementing these quantities with the values of the intermolecular radii $R_C = 1.72$ Å and $R_H = 1.17$ Å, one can find the cross-sectional area of the flat model of the naphthalene molecule: $S \approx 50$ Å^2.

In a new work (9), for the C–C bond in naphthalene the values from 1.354 to 1.421 Å are given, and the valence angles ∠C—C=C from 119 to 121°. The question arises how, taking these new data into account, S of the naphthalene molecule changes at constant R_C and R_H. Calculation shows that the order of magnitude of ΔS is less than 1 Å^2 (in the analogous case for anthracene, with $R_C = 1.72$ Å and $R_H = 1.17$ Å, $\Delta S \approx 0.4$ Å^2 (10)).

Such a small change in the value of S makes it possible, as before (10, 11), to use averaged structural data for constructing sections (S and S') of a model of the naphthalene molecule (Fig. 2).

We have not found characteristics of the structure of thionaphthene in the literature. In Fig. 2 the sections of its model (S_1 and S_1') have been constructed approximately: by combining one six-membered ring of naphthalene with the five-membered ring of thiophene (the latter has been studied [12]). For thionaphthene the dimensions are $C'—C'' = 1.35$ Å, $C—C'' = 1.44$ Å, $C—S—1.74$ Å, $C—H = 1.08$ Å, $\angle C—S—C = 91°$, $\angle S—C'—C'' = 112°$, $\angle C'—C''—C = 113°$

Fig. 2. Sections of schematic models of naphthalene molecules (S and S') and thionaphthene (S_1 and S_1')

Figure 2: Fig. 2. Sections of schematic models of naphthalene molecules (S and S') and thionaphthene (S_1 and S_1')

[11]. The intermolecular radii in Fig. 2 are: $R_C = 1.72$ Å, $R_H = 1.17$ Å, $R_S = 1.85$ Å.

Fig. 2. Sections of schematic models of naphthalene molecules (S and S') and thionaphthene (S_1 and S_1')

The ratio of the areas of the large sections of the molecular models is $S/S_1 \approx 5\%$; when superposed, S_1 fits completely within the contour S. From a comparison of the smaller sections of the models S' and S_1' it is seen that the sulfur atom in thionaphthene extends only slightly beyond the boundary of the corresponding portion of the contour of the naphthalene molecule.

The small discrepancies noted in the dimensions and shapes of the sections of the molecular models of naphthalene and thionaphthene explain the limited isomorphism found in these substances.

The t, X diagram in Fig. 1, for the most part (40–100% naphthalene), shows that the points on the liquidus line coincide with the limiting straight line that can be drawn between the melting points of the components. In the smaller part of the t, X diagram (0–40% naphthalene) there is a slight deviation of the liquidus curve from the limiting straight line, not exceeding 5° at the minimum point. This portion of the t, X diagram, corresponding to a relatively increased content of thionaphthene, may be explained by the specific influence of the latter: the influence of the sulfur heteroatoms, which differ in size and force fields from the CH group in the molecules of the components of the solid solution.

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REFERENCES

1. H. G. Frank, Brennst. Chem., **34**, 3/4 (1953).

2. W. Swietoslawski, *Fizykochemia smoly weglowej*, 1956.

3. V. M. Kravchenko, ZhFKh, **13**, 133 (1939).

4. I. F. Shreder, Gorn. zhurn., No. 12, 272 (1890).

5. G. S. Parks, H. P. Huffman, Ind. and Eng. Chem., **23**, 1138 (1931).

6. H. L. Finke, M. E. Gross, J. F. Messerly, G. Waddington, J. Am. Chem. Soc., **76**, No. 3, 854 (1954).

7. V. M. Kravchenko, DAN, **79**, No. 3, 443 (1951).

8. L. Pauling, *The Nature of the Chemical Bond*, Moscow–Leningrad, 1947.

9. S. C. Abrahams, J. M. Robertson, J. G. White, Acta Cryst., **2**, 238 (1949) (cited according to A. I. Kitaigorodsky, *Organic Crystallography*, 1955, p. 419).

10. V. M. Kravchenko, Ukr. khim. zhurn., **19**, 599 (1953).

11. V. M. Kravchenko, ZhFKh, **24**, 1033 (1950).

12. V. C. Sinclair, J. M. Robertson, L. McMathieson, Acta Cryst., **3** (4), 245, 251 (1950).

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