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Mutual Solubilities of Hydrocarbons. III. Systems *cis*-Decahydronaphthalene–*trans*-Decahydronaphthalene, *cis*-Dehydronaphthalene–Tetracosane, *cis*-Decahydronaphthalene–Dotriacontane

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This paper comprises a continuation of the studies dealing with the mutual solubilities of hydrocarbons by the freezing point method. The following systems were examined; *cis–trans* decahydronaphthalene, *cis*-decahydronaphthalene-tetracosane ($C_{24}H_{50}$), *cis*-decahydronaphthalene–dotriacontane ($C_{32}H_{66}$).

Experimental.—The bulb method was used for most of the determinations for two reasons. First, the effect of air and moisture could be avoided and, second, relatively small amounts of the materials were required. All the hydrocarbons used had been synthesized and purified by methods described previously. The m. ps. were as follows: *cis*-d. 43.27°, *trans*-d. 30.65°, tetradecane, 50.6°, and dotriacontane, 69.5°.[1]

The cyclic isomers were dried over sodium and then allowed to run into the dried glass bulbs whose capacities were about 20 cc., by means of a small glass funnel. The composition was established by weighing the bulbs before and after each addition of hydrocarbon. Next the contents of the bulbs were frozen by means of Dry Ice evacuated to 0.1 mm. and sealed. This was done by allowing the tube to collapse about 5 cm. above the liquid level. Hence, there was only a very small amount of material in the vapor phase at any time. Also the tube was long enough to serve as a handle for manipulating the bulb in the cold-bath.

Before measuring the f. p. the mixtures were shaken intermittently for several hours and then allowed to stand for at least twenty-four hours at room temperature to insure complete mixing. The mixture whose f. p. was to be determined was then frozen in an acetone-bath, cooled with a stream of carbon dioxide escaping from a reservoir of Dry Ice. Solidification having taken place, the temperature of the bath was then allowed to rise slowly until one or two small crystals remained. The temperature was now adjusted so that the crystals showed no signs of growing or disappearing. After this temperature had been found, it was then held constant for ninety minutes and if no change in crystal size was noted, this was taken as the f. p. This performance was repeated twenty-four hours later to ensure complete mixing and to be able to observe whether there was any reaction between the components. This latter point was checked by removing the bulb contents and measuring the refractive index in a Pulfrich refractometer. Comparison of the readings with those of a previously constructed chart showed no change in composition had taken place. All attempts to get consistent temperature readings at the first appearance of crystals on cooling were unsuccessful. This seemed to be due to the large amount of undercooling required to bring about crystallization.

The freezing point operations involving the two paraffin hydrocarbons below 30° were identical with that described. Above temperatures of 30°, the capillary tube method was used, as it was the most convenient. In this case, the solutions were made up in a weighing bottle. A sample of the solution was drawn into a weighed, thin-walled capillary tube, about 1 mm. in diameter, by merely placing it in the molten solution. The upper end was then sealed and the capillary tube inverted until the contents had drained to the bottom. Upon solidification, the loaded tube was weighed. The length of solid in the tube was about 2 mm. The capillary tube was then immersed into the bath with the sample adjacent to the thermometer and the whole heated until melting occurred. The rate of heating was regulated so that the temperature rise was less than 0.2° per minute in the vicinity of the melting point. The temperature where all the crystals disappeared was noted. The bath was next cooled until the white crystals of diacetyl appeared, upon which the bath was heated again slowly until the last trace of crystals in the tube just disappeared. The temperature at this point was taken as the freezing point of the mixture. The procedure was repeated with two other capillaries of the same mixture until the readings agreed with one another. The point of disappearance of the crystals was fairly sharp.

All temperatures were measured by a L. & N. platinum resistance thermometer, calibrated at the U. S. Bureau of Standards. The freezing points and mole fractions are given in the following tables: *cis–trans*-decahydronaphthalene Table I, *cis*-d.–tetracosane Table II and *cis*-d.–dotriacontane Table III.

TABLE I

FREEZING POINTS OF MIXTURES OF *cis*- AND *trans*-DECAHYDRONAPHTHALENE

Mole fr. *trans*-D.	Temp., °C.
0.0000	−43.27
.0242	−44.22
.0536	−45.56
.0855	−47.04
.1752	- 51.25
.2525	−55.12
.3478	- 59.36
.382[a]	−61.1[a]
.4000	−57.71
.5023	−54.34
.5661	−50.07
.6199	−47.49
.6790	−45.29
.8000	−39.00
.8997	−34.05
.9688	−31.82
1.0000	−30.65

TABLE II

FREEZING POINTS OF SYSTEM TETRACONTANE ($C_{24}H_{50}$)-*cis*-DECAHYDRONAPHTHALENE

Mole fr. tetracontane	F. p., °C.
1.0000	50.65
.8704	48.87
.7767	47.20
.7408	46.20
.7085	46.03
.7048	45.91
.5648	43.35
.4173	39.80
.3743	39.11
.3016	36.17
.2236	32.82
.1587	29.45
.1374	27.80
.0958	24.26
.0666	21.00
.0404	15.80
.0162	8.65

TABLE III

FREEZING POINTS OF *cis*-DOTRIACONTANE ($C_{32}H_{66}$)

Mole fr. dotriacontane	F. p., °C.
1.0000	69.55
.9551	68.69
.8577	67.68
.7785	66.58
.7432	66.08
.6554	64.40
.5580	62.80
.5425	62.41
.4782	61.06
.3358	56.68
.2355	52.21
.1812	49.26
.1185	44.05
.0883	41.20
.0698	39.21
.0615	38.52
.0501	36.80
.0470	36.16

[a] Eutectic point from graph, Fig. 1.

Discussion of Results.—The results, when plotted, yielded Figs. 1, 2 and 3, indicating that all the systems approach the ideal state. Figure 1 gives a value of −61.2° for the eutectic temperature which agrees very closely with that calculated −61.55°, when the latent heats found by Parks and Hatton are used.[2]

A binary system such as is illustrated in Fig. 1 where there is a difference in the molecular volume

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[1] Wm. F. Seyer, Ralph F. Patterson and John L. Keays, THIS JOURNAL, **66**, 179 (1944).

[2] Geo. S. Parks and John A. Hatton, *ibid*, **71**, 2773 (1949).

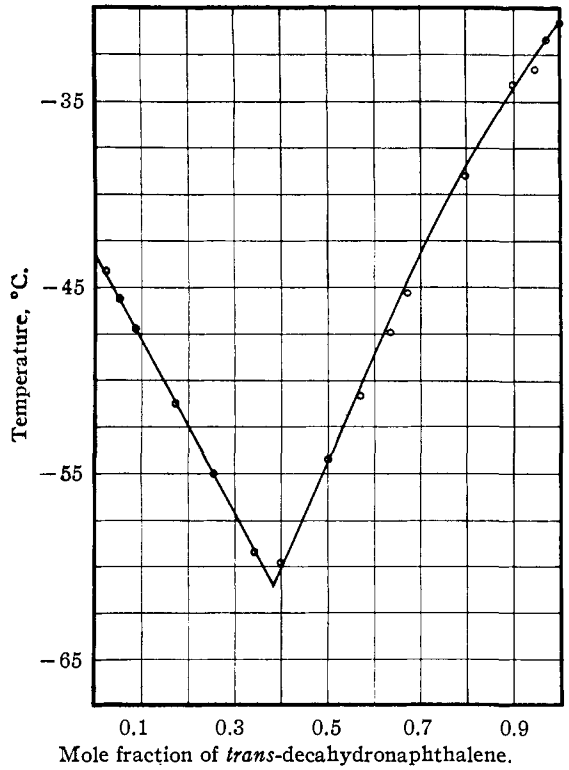

Fig. 1.—System *cis–trans*-decahydronaphthalene.

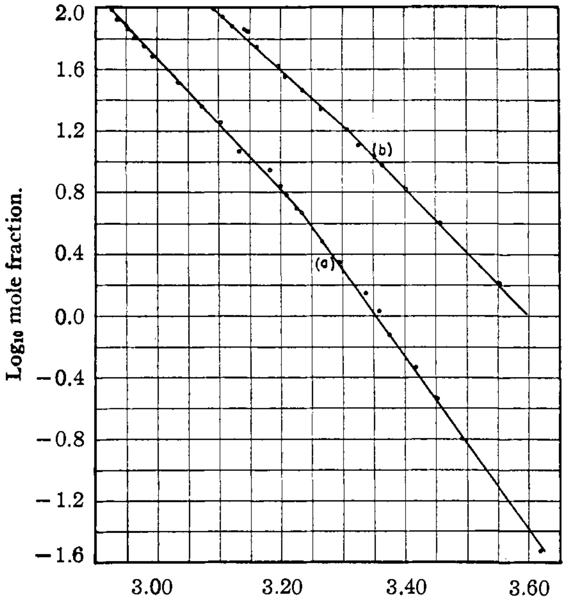

Fig. 2.—(a) Dotriacontane–*cis*-decahydronaphthalene; (b) tetracosane–*cis*-decahydronaphthalene.

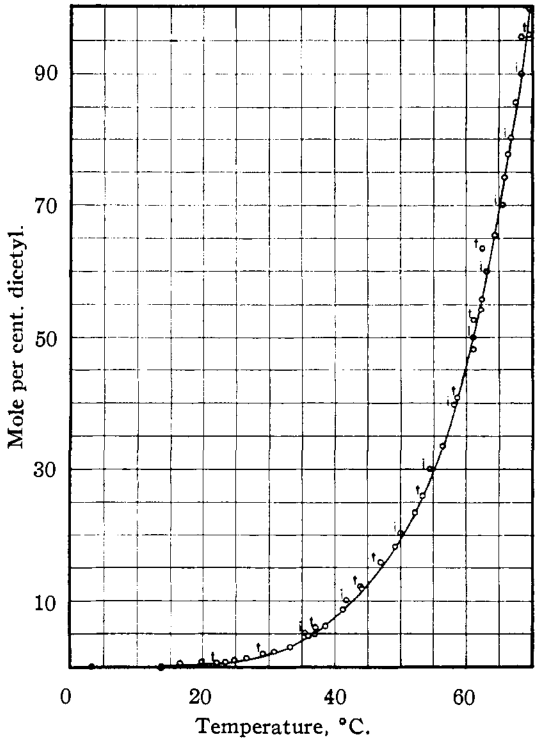

Fig. 3.—O, Mole per cent. dotriacontane; t_0, mole per cent. tetracosane; i_0, ideal system.

of only 2.9% should be expected to give rise to some solid solution formation. Thus, Smittenberg, Hoog and Henkes reported that in the case of the system octane–nonane, where the molecular volume differed by 6.3%, a considerable amount of solid solution formed upon freezing a mixture of the two substances. However, they also found that in the case of mixtures of iso-paraffins and *n*-paraffins the systems behaved in an ideal manner with no solid solution forming.[3] Hence, it would appear that in mixtures where the components have different spatial configurations such that one species cannot enter the crystal lattice of the other, solid solution does not take place even if there is only a slight difference in their molecular columns. The behavior of the *cis–trans*-decahydronaphthalene mixture is then what one would expect on the basis of Hassel and Viervoll's spatial models of these two isomers. Assuming that Mohr's model for the *trans* form is correct, they have shown that then his model for the *cis* form cannot be so, but must have one of the rings almost at right angles to the other. This can occur, they point out, if one of the ring connecting bonds is of the χ-type and the other of the ϵ type.[4] This difference in structure appears to be sufficient to prevent either from occupying the crystal lattice of the other.

The systems depicted in Fig. 2 show both the effect of molecular volume and shape on the form of the freezing point curves. A transition point is clearly apparent at point (a) but less so at (b). As would be expected from the work of Piper

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[3] J. Smittenberg, H. Hoog and R. A. Henkes, THIS JOURNAL, **60**, 17 (1938).

[4] O. Hassel and H. Viervoll, *Acta Chemica Scandinavia*, **1**, 194 (1947).

and his co-workers, the f.ps. of the solutions are depressed about 2.5° from that of the pure compounds.[5]

A comparison of the solubility of the cyclic hydrocarbon in the two *n*-paraffins as found, and as calculated on the basis of an ideal solution, is shown in Fig. 3. It also shows that the solubility of the cyclic hydrocarbon in the high molecular *n*-paraffins is very high, but the converse is not so.

Summary

1. The freezing points of the systems *cis*–*trans* decahydronaphthalene, dotriacontane–*cis*-decahydronaphthalene and tetracosane–*cis*-decahydronaphthalene have been examined and found to be very close to the ideal state.

2. The results indicate that the *cis* and *trans* isomers of decahydronaphthalene have different spacial configurations.

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[5] S. H. Piper, *et al.*, *Biochem. J.*, **25**, 2074 (1931).

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Spectrophotometric Investigation of the Copper(II)-chloro Complexes in Aqueous Solutions of Unit Ionic Strength[1]

BY HARDEN McCONNELL AND NORMAN DAVIDSON

The marked influence of chloride ion on the formal extinction coefficient $\bar{\epsilon}$, of copper(II) in aqueous solutions, as illustrated in Fig. 1 for the 230–400 mμ wave length range, is generally attributed to strongly absorbing chloro-complexes of copper(II). One may therefore consider the equilibria represented in equation (1).

$$\left.\begin{array}{l} \mathrm{CuCl}_{n-1}^{3-n} + \mathrm{Cl}^- = \mathrm{CuCl}_n^{2-n} \\ (\mathrm{CuCl}_n^{2-n})/(\mathrm{CuCl}_{n-1}^{3-n})(\mathrm{Cl}^-) = K_n \end{array}\right\} n = 1,2,3,4 \qquad (1)$$

The quantities in parentheses in the equations are taken to be concentrations in units of moles/liter, so that the mass action constants, K_n, are functions of the activity coefficients of the various ions. Of the previous investigations of these equilibria,[2,3,4,5,6,6a] the most satisfactory is that by J. Bjerrum.[6] By using spectrophotometric measurements and rough activity approximations, Bjerrum found that only the copper(II)-chloro complexes for $1 \leq n \leq 4$ in (1) are of importance in aqueous solutions of cupric chloride and that the approximate values of the stability constants, K_n^0, at infinite dilution and at 22.5° are

$$K_1^0 \gtrless 1,\ K_2^0 = 0.1 - 0.4,\ K_3^0 = 0.02 - 0.06,\ K_4^0 = 0.003 - 0.01 \text{ liter/mole}$$

More accurate information about the equilibria of equations (1) was desired for studies of the non-additive light absorption in solutions containing the chloro-complexes of copper(I) and copper(II).[7] In this paper we describe a spectrophotometric study of the equilibria of equation (1) in solutions containing copper(II) perchlorate, hydrochloric acid and perchloric acid and at an ionic strength of unity. The ionic strength was fixed at this value in order to minimize the variation of the activity coefficients of the particular ions as the composition of the solution was varied. The interpretation of the results is based on the assumption that these variations are indeed negligible, so that one can deduce mass action equilibrium constants valid at the ionic strength of the measurements. (Actually the assumption is that the variations of the activity coefficient functions which relate the mass action equilibrium constants to the thermodynamic constants are negligibly small.) It may be said at this point that this assumption has been found to be in accord with the results of the present investigation. Such a simplifying assumption is not applicable for most of the previous investigations of the equilibria (1) which have been carried out at high and varying ionic strengths. On the other hand, because of the ready dissociation of the copper(II)-chlorocomplexes, they cannot readily be studied in much more dilute solutions. Indeed, in the solutions we have studied, only CuCl^+ and $\mathrm{CuCl_2}$ have been present in detectable concentrations.

[1] Presented at the Atlantic City Meeting of the American Chemical Society, September 20, 1949.

[2] E. Doehlemann and H. Fromherz, *Z. physik. Chem.*, **A171**, 353 (1934).

[3] G. Spacu and J. Murgulescu, *ibid.*, **A170**, 71 (1934).

[4] T. Moeller, *J. Phys. Chem.*, **48**, 111 (1944).

[5] V. Kohlschutter, *Ber.*, **37**, 1160 (1904).

[6] J. Bjerrum, *D. Kgl. Danske Vidensk. Selskab., Mat.-fys. Medd.*, **22**, no. 18 (1946).

[6a] NOTE ADDED IN PROOF.—R. Näsänen (*Acta Chem. Scand.*, **4**, 140 (1950)) has recently determined K_1 of equation (1) as a function of ionic strength in hydrochloric acid solutions. His values, ϵ_1 ($\lambda = 272$) = 1478, K_1 ($\mu = 1.0$) = 0.34, differ considerably from those reported by us, ϵ_1 ($\lambda = 272$) = 320, $K_1 = 1.30$. There are indications that most of this discrepancy is not due to differing experimental data: thus for the item in Näsänen's Table I for $\mu^{1/2} = 0.981$ where he obtains $D_{\mathrm{CuCl}^+} = 0.098$, our constants given 0.082. In Table II, for $\mu^{1/2} = 0.939$, our constants give $(\mathrm{CuCl}^+) = 0.00063$, $(\mathrm{CuCl_2}) = 0.00013$, $D_{\mathrm{CuCl}^+} = 0.199$, $D_{\mathrm{CuCl_2}} = 0.266$, $D_{\mathrm{total}} = 0.465$. Näsänen gives $D_{\mathrm{CuCl}^+} = 0.438$, $(\mathrm{CuCl}^+) = 0.00030$. We offer this criticism of his work. Only eleven items of data in Table II have been used to evaluate four constants (his α, B, ϵ, K_0). The formation of $\mathrm{CuCl_2}$ has been neglected, although he indicates that above $(\mathrm{Cl}^-) = 0.25$ (where there are five items of data) this assumption is not too good.

[7] H. McConnell and N. Davidson, THIS JOURNAL, **72**, 3168 (1950).