[Contribution from the Department of Chemistry, University of California]

SOLUBILITY. XI. SOLUBILITIES OF LIQUID STANNIC IODIDE IN SEVERAL LIQUID PARAFFINS

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Received July 23, 1928 Published November 6, 1928

Stannic iodide has been shown by Dorfman and Hildebrand[1] to have a sufficiently high internal pressure to cause incomplete miscibility in the liquid state with paraffin hydrocarbons. Since cases of incomplete miscibility are not numerous among non-metallic liquids of low polarity, and accurate data concerning such systems are lacking, a study of this sort seemed very desirable. We wished, first, to determine the way in which internal pressure varies among the paraffin homologs; second, to study the relation between the solubility of stannic iodide in the liquid and in the solid state in the light of methods recently proposed by the senior author[2] for dealing with deviations from the ideal solution laws.

Purification of Materials

Chemically pure stannic iodide was distilled twice under reduced pressure and then crystallized several times from hot carbon tetrachloride. As a further check, another sample of stannic iodide was prepared according to the method of McDermott.[3] A solution of c. p. resublimed iodine in pure carbon tetrachloride and an excess of c. p. tin were heated together. The stannic iodide solution resulting was decanted through a folded filter and crystallized three times from hot carbon tetrachloride. After each crystallization, the crystals were rinsed free from mother liquor on a small-holed Büchner funnel without filter paper. The crystals were finally dried by heating them under reduced pressure to a temperature slightly above their melting point.

The melting point of each preparation was found to be 143.6°, which agrees well with the value of 143.5° found in the "International Critical Tables." The purity was further checked by analysis. The stannic iodide was converted into hydrated stannic oxide by hydrolysis with ammonium hydroxide in the presence of ammonium sulfate. After standing overnight, the solution was neutralized with dilute nitric acid, methyl orange being used as an indicator, and was filtered through a Gooch crucible which had previously been ignited to constant weight. The crucible was then placed on a nichrome triangle in a large nickel crucible and heated to a red heat to drive off the water of hydration. The ratios of stannic iodide to stannic oxide were found to be for preparation I, 4.156, 4.161; and for preparation II, 4.155, 4.149, 4.158. The averages are 4.159 and 4.154, agreeing well with the theoretical value of 4.157.

The tin used in the above preparation was obtained as analyzed sticks containing, as impurity, a very small percentage of lead. This tin was further purified by electrolysis, using the tin sticks as electrodes and a slightly acid solution of stannic chloride as the electrolyte. The current density used was such that the tin was deposited at the cathode in the form of long crystals, the lead remaining at the anode.

Ammonium hydroxide was prepared by passing ammonia gas into distilled water. Carbon tetrachloride was purified by shaking it with sodium hydroxide to remove all

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[1] Dorfman and Hildebrand, This Journal, **49,** 729 (1927).

[2] Hildebrand, *Proc. Nat. Acad. Sci.*, **13,** 267 (1927).

[3] McDermott, This Journal, **33,** 1963 (1911).

acidic constituents and then by distilling it from phosphorus pentoxide. The normal hexane used was from Kahlbaum, prepared from propyl iodide; the octane, from the same source, had been prepared from normal butyl iodide from butyl alcohol. The *iso*-octane, 2,2,4-trimethylpentane, was obtained from the Ethyl Gasoline Corporation. The preparation and properties of this substance were described by Edgar.[4] Dr. Lachman, of this Laboratory, had tested our sample for the presence of butyl alcohol and unsaturated bodies, finding them practically absent. The constancy of boiling point also showed the liquid to be sufficiently pure for all ordinary purposes. The heptane was from a supply of high purity prepared for a previous investigation in this Laboratory.[5] All of the liquids used were distilled using a fractionating column and the middle fractions only were taken. All gave boiling points in close agreement with the values in the "International Critical Tables."

Experimental Procedure

Pyrex glass tubes were closed at one end, drawn out into a capillary for subsequent sealing and opened into a funnel at the other end. A tube was weighed, an appropriate amount of stannic iodide was placed in the funnel, melted into the closed end of the tube and weighed. The liquid paraffin was then added so as nearly to fill the tube below the constriction; the tube was then cooled in liquid air, sealed off and the sealed tube weighed along with the rejected portion. From these weights the mole fractions of stannic iodide given in Table I were calculated.

These tubes were rocked back and forth in an oil-bath in an electric oven

TABLE I

SOLUTION TEMPERATURES OF STANNIC IODIDE

SnI$_4$, mole fraction	Temp., °C.	SnI$_4$, mole fraction	Temp., °C.	SnI$_4$, mole fraction	Temp., °C.
n-Octane		0.4573	136.7	0.3225	146.4
		.4745	136.3	.3714	148.8
0.3602	127.3	.4776	136.9	.4526	148.7
.3824	129.4	.4861	136.7	.5344	145.4
.4454	131.1	.5142	136.4	.5916	138.2
.4541	131.2	.5209	136.3		
.5418	132.3	.5606	135.4	*iso*-Octane	
.5832	131.5	.5700	135.9		
.6297	130.2	.5847	134.8	.3029	183.4
.6430	129.4	.5945	134.7	.3146	185.4
		.6105	131.5	.3692	191.6
n-Heptane		.6240	132.0	.4592	194.9
		.6548	128.9	.4758	194.9
.2836	127.6	.6818	127.2	.5193	195.4
.3220	130.9			.5380	194.9
.3434	131.6	*n*-Hexane		.5920	193.6
.3595	134.1			.6253	188.1
.3720	134.8	.2531	138.1	.6256	191.6
.4340	136.4	.2887	143.4	.6604	187.5
				.6922	181.5

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[4] Edgar, *Ind. Eng. Chem.*, **19**, 145 (1927).

[5] Westwater, Frantz and Hildebrand, *Phys. Rev.*, **31**, 135 (1928).

equipped with small glass windows and illuminated from the rear. The rate of heating and cooling was regulated by varying the resistance in the circuit. A sufficiently slow rate was maintained so that the mean of the readings taken at the point where the two liquid phases disappeared and of those taken where they appeared agreed, in every case, within 0.2°. At least six observations were made upon each tube, the averages being recorded in Table I. These observations seldom differed from one another by more than 0.4°.

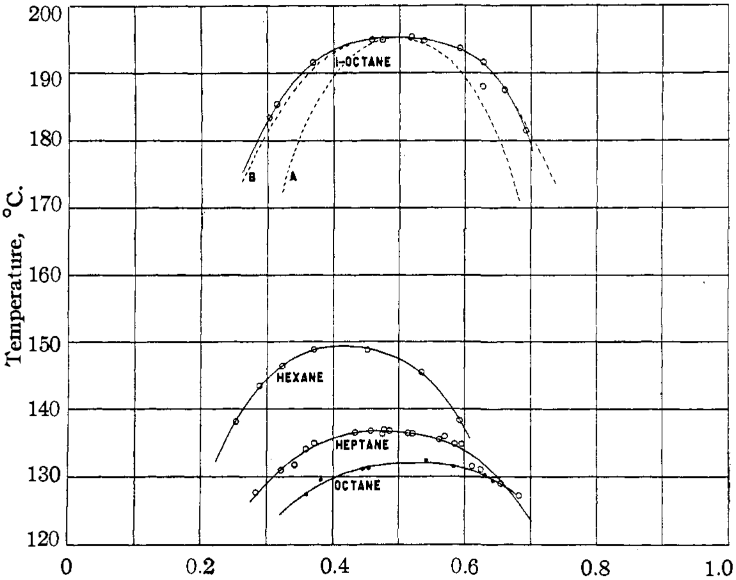

Fig. 1.—Mole fraction of stannic iodide.

From these values mole fraction–temperature curves were plotted, as shown in Fig. 1. It was impossible to determine the shape of the curves at much lower temperatures than those given, due to the crystallization of the stannic iodide. The maxima give the critical mixing temperatures recorded in Table II.

Table II

Critical Solution Temperatures of Stannic Iodide

Second liquid	*i*-Octane[a]	*n*-Hexane	*n*-Heptane	*n*-Octane
SnI_4, mole frac.	0.50	0.42	0.48	0.52
Crit. temp., °C.	195.3	149.4	136.8	132.0

[a] 2,2,4-Trimethylpentane.

Discussion

We may note, first, that the order of critical temperatures is in rather good agreement with such data as we have regarding internal pressures. For estimating the latter, we have only the boiling points, t_b, using a relation previously given by the senior author[6] $(5200 + 30t_b)/\mathrm{v}$, where v is the molal volume of the liquid at 20°. For the liquids here employed, we have the data in Table III.

TABLE III

RELATIVE INTERNAL PRESSURES

	Density at 20°	Molal vol.	B. p., °C.	$(5200 + t_b)/\mathrm{v}$	t_c
i-Octane	0.690	165.5	99.3	49.4	195.3
n-Hexane	0.660	130.5	69.0	55.7	149.4
n-Heptane	0.683	146.5	98.4	55.6	136.8
n-Octane	0.701	162.8	124.6	59.4	132.0
Stannic iodide	4.16	150.7	340	102	...

The figures in the next to the last column for relative internal pressures agree with the order of critical solution temperatures repeated in the last column except for the minor difference between hexane and heptane. In view of the lack of accurate figures for the heats of vaporization, it is believed that the critical temperatures best represent the true order of the internal pressures. We may note, further, that heptane does not quite fall midway between hexane and octane, although the difference is so small that it may not be significant. It is especially striking that the *iso*-octane has an internal pressure much lower than *n*-octane. The generally lower boiling points of *iso*-paraffins indicate that their internal pressures will probably be found lower than those of the corresponding normal paraffins. These trends in internal pressure may be expected to determine rather accurately the general solubility relations of the paraffins.

In a paper by the senior author now in preparation, there is set forth a method for calculating mutual solubility curves for non-polar liquids. As a first approximation, the equation

$$\log \frac{1 - \mathrm{N}_1'}{\mathrm{N}_1'} = \frac{k}{T}(1 - 2\mathrm{N}_1') \qquad (1)$$

has been derived, where N_1' is the mole fraction of component 1 in one phase, T the absolute temperature and k a constant depending, in part, upon the difference in internal pressure of the two components. The mole fraction of component 2 in this phase is $1 - \mathrm{N}_1'$, while in the second phase the two mole fractions are interchanged. This equation applies to symmetrical systems only, that is, to those whose critical composition is 0.5. When the critical composition is not 0.5, an additional constant must be used and two simultaneous equations are obtained whose solution is mathematically very laborious. Consequently, we will illustrate the treatment by using the curve for *iso*-octane, which is practically symmetrical. The dotted curve in Fig. 1, marked A, represents Equation 1, using $k = 407$. In solving this equation arbitrary values are assigned to N_1', and the equation is solved for T, since the reverse procedure would

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[6] Hildebrand, "Solubility," Chemical Catalog Company, New York, **1924**, p. 108.

require a method of successive approximations. It is seen that Curve A is too steep; however, the equation is of such a nature that slight changes in k greatly affect the spread in N, and it is known from other systems as well as from theoretical considerations that k is likely to diminish with increasing temperature.

A determination of the solubility of solid stannic iodide in this *iso*-octane, to be presented in the paper now in preparation, has given a value of k of 503 at 25°. If we represent the variation of k with temperature by the equation $k = 671 - 0.565\ T$, we get the dotted curve, *B*, Fig. 1, which agrees excellently with the experimental points, although this makes k vary only 2% in 15°.

In the case of heptane, we have not carried through the troublesome calculations, since the curve is unsymmetrical, but it is evident from a few figures that the rate of change of k necessary to give the value obtained from the solubility of stannic iodide, 130° lower, also gives the proper spread to the liquid solubility curve.

Summary

1. Critical solution temperatures of stannic iodide have been obtained with liquid paraffins as follows: *n*-octane, 132.0°; *n*-heptane, 136.8°; *n*-hexane, 149.4°; *i*-octane (2,2,4-trimethylpentane), 195.3°.

2. The mole fractions of stannic iodide at the critical solution temperatures are, respectively, 0.52, 0.48, 0.42 and 0.50.

3. The internal pressures increase for the normal hydrocarbons in the order of increasing molecular weight.

4. The normal octane has a higher internal pressure than the *iso*-octane used; this difference between a normal and an *iso*-paraffin is probably general.

5. The form of the liquid-liquid solubility curve has been calculated.

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