Part II

PHYSICAL PROPERTIES

EVALUATION OF COMPOUNDS AND MATERIALS

Silicon Tetraiodide

Freezing Point and Solubility in Common Organic Solvents

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RECRYSTALLIZATION of silicon tetraiodide from solvents, for purification, has been used with considerable success (*3*, *5*), but there are few data on its solubility in the literature. According to Mellor (*4*) 100 parts of carbon disulfide will dissolve 220 parts of silicon tetraiodide at 27° C. or, stated slightly differently, this is a solution containing 24 mole % of solid. Rubin, Moates, and Weiner (*5*) report solubilities of 3.2 and 10.3 weight % in toluene at 20° and 110° C., respectively. The latter values correspond to 0.6 and 1.9 mole % solubility, which is considerably less than has been observed in this work.

EXPERIMENTAL

Materials. Silicon tetraiodide was prepared from 99.7% silicon (Electrometallurgical Co.) as described by Szekely (*8*). The samples were distilled in a 12-plate, all-quartz column to give a material of 99.9 + % purity as indicated by cryoscopic analyses.

Toluene, carbon tetrachloride, and benzene (reagent grade) and 99 + % *n*-heptane (Phillips Petroleum Co.) were used as solvents.

Techniques. Three methods of determining solubility were employed. The most elegant method utilized time-temperature studies in sealed tubes (0.75-inches outside diameter × 5.5 inches with a 2-inch internal thermocouple well) containing exactly weighed amounts of solvent and silicon tetraiodide. The tubes were warmed until a clear solution was obtained, and the sample was then cooled slowly with vigorous agitation within a Dewar flask. A Speedomax recorder (Leeds & Northrup) with variable 1-mv. full scale ranges was used to determine the freezing points of solutions in toluene, benzene, and *n*-heptane. Data thus obtained are reported in the tables under Freezing Temperature.

Dilute solutions in toluene and *n*-heptane were prone to extreme supercooling. In these cases the temperatures at which fine crystals were completely soluble is reported in the tables under Solution Temperature. The thermocouples for both kinds of determination were calibrated with benzoic acid thermometric standard cell No. 142 (National Bureau of Standards).

Perhaps the least accurate technique for determining solubilities depended on weighing samples of solution taken at various temperatures, evaporating the solvent in a vacuum, and weighing the remaining silicon tetraiodide. The technique is reasonably good for samples obtained near room temperature or lower, but it is not at all precise when applied to hot solutions that crystallize readily on cooling. Thermometers immersed to the proper depth were used to measure these temperatures.

RESULTS AND DISCUSSION

***n*-Heptane.** Table I records data from solubility measurements made on silicon tetraiodide in *n*-heptane in sealed tubes. The first six measurements were obtained by extrapolating the cooling curve after crystallization had started, through a small supercooled region, to the cooling curve for the liquid phase. In more dilute solutions supercooling became so much of a problem that the temperature at which very fine crystals completely dissolved seemed to be more reliable for the last two samples.

The less accurate technique of determining the composition of solutions in equilibrium with excess silicon tetraiodide was used for the determinations of Table II.

Another transition with a small latent heat occurs in solutions in which the freezing point is greater than 107° C. (Table III). In addition to the data acquired with the sealed tube containing 89.3 mole % of silicon tetraiodide, this transition was observed in an apparatus using a 1-liter flask which contained several hundred grams of silicon tetraiodide and an appropriate amount of solvent. This apparatus had the disadvantage that vaporization of the solvent altered the composition of the solution; but the large mass of material made the small thermal effect of the transition

Table I. Solubility of Silicon Tetraiodide in *n*-Heptane

Mole % SiI_4 in Soln.	Freezing Temp., ° C.	Solution Temp., ° C.
100.0	123.68 ± 0.06	
89.3	117.4	
78.0	112.9	
69.5	109.9	
57.5	106.7	
49.1	105.2	
19.6		92.2
8.0		68.2

Table II. Solubility of Silicon Tetraiodide in *n*-Heptane as Determined by Composition of Saturated Solutions

Mole % SiI_4 in Soln.	Temp., ° C.	Mole % SiI_4 in Soln.	Temp., ° C.
11.7	78	2.5	27
8.1	75	2.1	27
7.2	74	2.3	24
10.0	74	2.4	24
3.8	46	0.4	1.5
3.8	44.5	0.1	1.5
3.4	43	0.1	2
2.4	27		

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more easily observable. The determinations in the sealed tube are probably the most accurate, however.

The significance of the transition is not understood clearly at present, but one possibility is that it may be a peritectic temperature for a system consisting of silicon tetraiodide and a compound with an incongruent melting point, $(SiI_4)_x \cdot C_7H_{16}$. The ratio of silicon tetraiodide to *n*-heptane in such a compound is likely to be at least 2 and may be greater.

If this interpretation is correct, pure silicon tetraiodide is the solid first crystallizing when solutions containing more than 60 mole % of silicon tetraiodide are cooled. Pure silicon tetraiodide continues to separate out down to the peritectic temperature of 107° C., whereupon the remaining solution freezes as a mixture of silicon tetraiodide and $(SiI_4)_x \cdot C_7H_{16}$. The peritectic mixture should contain approximately 60 mole % silicon tetraiodide.

Solutions containing less than 60 mole % silicon tetraiodide should yield crystals of the compound $(SiI_4)_x \cdot C_7H_{16}$ upon cooling. There is no difficulty in removing the *n*-heptane from this compound simply by pumping it out at room temperature, if the assumed material actually was obtained in these experiments.

Toluene. Table IV records data from the solubility measurements made on silicon tetraiodide in toluene in sealed tubes. The first six measurements were made directly from cooling curves. Below 49 mole % of silicon tetraiodide, supercooling of the solutions was so serious that it became necessary to observe the temperatures at which fine crystals are completely soluble. An example of the discrepancy that may occur is indicated by the data for 36.6 mole % of silicon tetraiodide in Table IV.

The shape of the upper part of a plot of this data is similar to that obtained for *n*-heptane, whcih suggests the possibility of a compound $(SiI_4)_x \cdot C_7H_8$. The sample containing 84.9 mole % of silicon tetraiodide was investigated at some length to try to identify an additional phase transition, but no reliable thermal evidence for a second arrest in the cooling curve was recorded.

Benzene. Table V records data for the solubility measurements made on silicon tetraiodide in benzene in sealed tubes and for the analyses of saturated solutions. An interesting feature of these data is that they fall on the same curve as the data for toluene.

Carbon Tetrachloride. The only measurements made on this solvent are analyses of the saturated solution which are recorded in Table VI. The saturated solution boils at 83° C., and there is a discontinuity between this point and some higher concentration of tetraiodide that undoubtedly exists at atmospheric pressure. The curve might be extended by studies in sealed tubes. The shape of the portion of the curve that has been established indicates that the system carbon tetrachloride–silicon tetraiodide may not be a simple one.

Table III. Transitions below Freezing Point of Some Solutions in System Silicon Tetraiodide–*n*-Heptane

Mole % SiI_4	Transition Temp., ° C.	Apparatus for Determination
89.3	107.1	Sealed tube
	106.7	
86 (approx.)	111	1-liter flask
	109	
	108	
76 (approx.)	107	1-liter flask
68 (approx.)	108	1-liter flask

Table IV. Solubility of Silicon Tetraiodide in Toluene

Mole % SiI_4 in Soln.	Freezing Temp., ° C.	Solution Temp., ° C.
100.0	123.68 ± 0.06	
84.9	113.2, 113.6	
68.0	100.1	
64.4	97.7	
56.9	92.1	
49.1	87.2	
36.6	(75.0)	77.4
23.1		61.7
14.8		46.9
8.7		(26) [a]
8.7		(26) [a]

[a] From analyses of saturated solutions.

Table V. Solubility of Silicon Tetraiodide in Benzene

Mole % SiI_4 in Soln.	Freezing Temp., ° C.	Mole % SiI_4 in Soln.	Freezing Temp., ° C.
100.0	123.68	14.1	45.0
68.7	100.9	7.51	(25.5)[a]
53.5	90.0	7.75	(25.5)[a]
39.9	79.1	7.79	(25.5)[a]
30.3	69.1	4.6	. . . [b]
21.5	58.3		

[a] From analyses of saturated solutions.

[b] Benzene-SiI_4 eutectic found at 2.06° C.

Table VI. Solubility of Silicon Tetraiodide in Carbon Tetrachloride as Determined by Composition of Saturated Solutions

Mole % SiI_4 in Soln.	Temp., ° C.	Mole % SiI_4 in Soln.	Temp., ° C.
22.4	83	4.6	26
20.7	83	2.5	3
16.1	56	2.5	3
4.9	26		

Freezing Point of Silicon Tetraiodide and Estimate of Purity. The freezing points were determined in sealed tubes with copper-Copnic thermocouples calibrated against reagent grade benzoic acid in sealed tubes. In all cases the tubes were vigorously agitated while cooling. The reagent grade benzoic acid used melted 0.002 mv. higher than the National Bureau of Standards sample, cell 142, for which a freezing point of 122.361° ± 0.003° C. is given. The difference is probably due to experimental error, because it is very unlikely that the authors' sample is purer than that of the National Bureau of Standards. If an experimental precision of ± 0.002 mv. is assumed the freezing point of silicon tetraiodide has been determined as 123.69° ± 0.06° and 123.67 ± 0.06° C. in two observations on the same sample. The average value, 123.68° ± 0.06° C., may be compared with 120.5° C. reported by Schwarz and Pflugmacher (*6*), and 122.0° to 122.5° C. reported by Litton and Andersen (*2*).

The impurity content of the silicon tetraiodide sample used in the determination of the freezing point was estimated by the cryoscopic method described by Stull (*7*). The heat of fusion required for this determination, 1200 calories per mole, is an estimate by Brewer (*1*). Two determinations gave 1.5×10^{-5} and 2.3×10^{-5} mole fraction of impurity, or the sample was 99.998 mole % silicon tetraiodide.

LITERATURE CITED

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