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Abstract

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SOLUBILITY OF SILICON TETRAIODIDE IN NONAQUEOUS SOLVENTS

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Recrystallization of silicon tetraiodide in nonaqueous solvents is one of the important stages in its purification in the process of obtaining high-purity silicon. This stimulates interest in the study of the solubility of silicon tetraiodide in nonaqueous solvents.

The solubility data available in the literature ([1,2]) are limited in character; it therefore seemed of interest to study systematically the solubility of silicon tetraiodide in nonaqueous solvents. Benzene, toluene, xylene, cyclohexane, chloroform, carbon tetrachloride, normal octane, and silicon tetrachloride were chosen as such solvents.

Silicon tetraiodide was prepared by direct synthesis from technical silicon of 98% purity and iodine of analytical grade, then recrystallized from benzene and sublimed in vacuum. The silicon tetraiodide prepared in this way contained: Al $2 \cdot 10^{-4}$, Fe $5 \cdot 10^{-5}$, Ti $< 1 \cdot 10^{-4}$, Mg $< 1 \cdot 10^{-5}$, Ca $< 1 \cdot 10^{-5}$, Cu $< 1 \cdot 10^{-5}$, and Zn $< 1 \cdot 10^{-4}$ wt. %. Aluminum was determined polarographically; iron, titanium, copper, magnesium, calcium, and zinc—colorimetrically. The crystals of silicon tetraiodide were white with a faint greenish tint.

Solvents of the following grades were used in the work: benzene (thiophene-free), toluene, chloroform, carbon tetrachloride, and silicon tetrachloride, analytical grade; metaxylene and *n*-octane—pure. Cyclohexane (pure grade) was subjected to additional purification and had a melting point of 6.2°.

The solubility was determined by Alekseev' s method ([3]). To protect silicon tetraiodide from hydrolysis in the presence of atmospheric moisture, all preparative operations were carried out in a special airtight chamber purged with dry nitrogen.

Weighed portions of tetraiodide and solvent were placed in an ampoule with a constriction. A small glass-coated iron cylinder was placed in the same ampoule. The contents of the ampoule were frozen; the nitrogen atmosphere in which filling had been carried out was evacuated, and the ampoule was sealed.

Thermostating was carried out in an oil thermostat. The temperature was set with the aid of a contact thermometer with an accuracy of ±0.1°. To stir the

Fig. 1. Solubility of silicon tetraiodide in nonaqueous solvents. 1 —toluene, 2 —benzene, 3 —xylene, 4 —chloroform, 5 —carbon tetrachloride, 6 —cyclohexane, 7 —normal octane, 8 —silicon tetrachloride

Figure 1: Fig. 1. Solubility of silicon tetraiodide in nonaqueous solvents. 1 —toluene, 2 —benzene, 3 —xylene, 4 —chloroform, 5 —carbon tetrachloride, 6 —cyclohexane, 7 —normal octane, 8 —silicon tetrachloride

contents of the ampoule, the thermostat was equipped with a special magnetic device that ensured intensive reciprocating motion of the iron cylinder placed inside the ampoule. At temperatures close to the temperature at which the solid phase disappeared, stirring was carried out for 3-4 hours. As preliminary experiments showed, this time is quite sufficient for establishing equilibrium between the liquid and solid phases.

The solubility curves of silicon tetraiodide are presented in Fig. 1.

Our results for determining the solubility of silicon tetraiodide in toluene differ sharply from those given in (2). If, according to those data, the solubility of silicon tetraiodide in toluene is 3.2 wt.% at 20°, then according to our data the solubility at 25° is 33 wt.%. It may be asserted that

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the solubility values for silicon tetraiodide in toluene given in (2) are clearly erroneous.

The character of the curves permits one to suppose that the solutions studied are regular.

For regular solutions, Hildebrand (4) derived the equation

$$RT \ln \frac{a_2}{N_2} = v_2 \left(\frac{N_1 v_1}{N_1 v_1 + N_2 v_2} \right)^2 \left[\left(\frac{\Delta E_2}{v_2} \right)^{1/2} - \left(\frac{\Delta E_1}{v_1} \right)^{1/2} \right]^2, \qquad \text{(A)}$$

where a_2 is the activity, N_1 and N_2 are mole fractions, v_1 and v_2 are molar volumes, and ΔE_1 and ΔE_2 are molar energies of evaporation.

To calculate $(\Delta E_2/v_2)^{1/2}$ (Table 1) for silicon tetraiodide, it is necessary to substitute into equation (A) the experimental solubility values, and in place of a_2 the ideal solubility. The ideal solubility was calculated by the Schröder–Le Chatelier equation. The melting temperature of silicon tetraiodide determined by us is 123.5-123.8°. For the heat of fusion we adopted (5) 1200 cal/mole. The molar volume of silicon tetraiodide, calculated from the data of (6), is 157.1 cm^3. The values of $(\Delta E_1/v_1)^{1/2}$ were taken from the data of (7). The value of $(\Delta E_2/v_2)^{1/2}$, calculated from vapor-elasticity data (6), is 9.07, which is somewhat lower than the value calculated from solubility data.

The variations in the value of $(\Delta E_2/v_2)^{1/2}$, calculated for various solvents, are small; moreover, chloroform, toluene, and *m*-xylene do not fall outside the series of the other solvents, despite their polarity. Taking into account the approximate data required for the derivation of equation (A), the agreement

Table 1

Solutions of silicon tetraiodide at 25°

Solvent	Dipole moment $\times10^{18}$, esu units	Mole fraction of silicon tetraiodide	$(\Delta E_1/v_1)^{1/2}$, $(\mathrm{cal \cdot cm^{-3}})^{1/2}$	$(\Delta E_2/v_2)^{1/2}$, $(\mathrm{cal \cdot cm^{-3}})^{1/2}$
Toluene	0,4	0,0776	8,9	12,03
Benzene	0	0,0707	9,15	12,38
Metaxylene	0,3	0,0661	8,8	11,92
Chloroform	1,1	0,0525	9,3	12,66
Carbon tetrachloride	0	0,0467	8,6	11,97
Cyclohexane	0	0,0427	8,2	11,56
n-Octane	0	0,0146	7,55	11,21
Silicon tetrachloride	0	0,0126	7,6	11,49
Average . . .				11,90

values of $(\Delta E_2/v_2)^{1/2}$ is quite satisfactory. This shows that silicon tetraiodide indeed forms regular solutions with the solvents studied.

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