BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48(10), 2963—2964 (1975)

The Solubilities and the Solubility Parameter of Heptasulfur Imide

Shuichi HAMADA, Yoshiyuki KUDO, and Masako KAWANO
Department of Chemistry, Faculty of Science, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162

(Received March 31, 1975)

Synopsis. The solubilities of heptasulfur imide in eleven organic solvents were measured. The solubility parameter of heptasulfur imide was estimated to be $12._7$ at 25 °C from the solubilities and the activity deduced from the enthalpy of the fusion; we assumed the solutions to be regular.

The structure of heptasulfur imide, S_7NH, closely resembles that of cycloocta-sulfur; one of the sulfur atoms in it is, however, replaced by an NH group.[1] Only a few solubilities of heptasulfur imide have been reported—for example, those for carbon disulfide[2] and carbon tetrachloride.[3] In this work, the solubilities and the solubility parameter of this compound will be estimated.

Experimental

Materials. The heptasulfur imide was prepared by the method described by Heal;[4] the disulfur dichloride was reacted with an ammonia at −10 °C by passing the ammonia into its dimethylformamide sulution. A crude product was extracted with an ethyl ether, and then the heptasulfur imide was isolated chromatographically from the by-products by using a silica-gel column. The pure heptasulfur imide was obtained as pale yellow crystals by recrystallization from a benzene solution. Eleven organic solvents were used to estimate the solubilities, as Table 1 shows. All the solvents were purified in the usual ways.

Procedure. Suitable amounts of the heptasulfur imide and an organic solvent were put into a three-necked flask and were then stirred continuously for 2 hr at the temperature range from 20 to 40 °C (from 10 to 30 °C for the *n*-pentane), with a precision of ±0.03 °C. An aliquot of the solution was withdrawn through a fine Teflon tube with a glass filter by applying excessive pressure in the flask. The concentration of the solution was estimated from its optical absorbances at the range from 320 to 365 nm, after the solution has been diluted to a suitable concentration. The molalities of the solutions were estimated by using the working curves for the respective solvents previously determined by means of a double-beam spectrophotometer, model UV-200, from Shimadzu Seisakusho. The solubility was estimated repeatedly (at least three times) under the same conditions; its deviation from the average value was less than ±1.5%. The partial molar volume of the heptasulfur imide was estimated from the benzene solutions at 25 °C with a precision of ±0.01 °C by using a modified Lipkin-Davison-type pycnometer. The molar enthalpy of the fusion of the heptasulfur imide was estimated with a differential scanning calorimeter, model DSC-1B, from Perkin-Elmer. The enthalpy of the fusion was calibrated by using that of a metallic indium (0.781 kcal/mol at 156 °C).

Results and Discussion

The heptasulfur imide was isolated chromatographically three times because it could not be completely separated from the by-products by only one run. The X-ray powder diffractogram[1] and the IR spectrum[5] of the sample showed patterns attributable to heptasulfur imide only. The melting point of the sample was determined microscopically to be 113.5 °C; this value agreed with that of the purified heptasulfur imide.[6]

The solubilities, X_2 (mole fraction), at 25 °C of the heptasulfur imide in various solvents are shown in Table 1. The logarithms of the mole fractions in the saturated solutions for the respective solvents showed good linearities against the reciprocals of the absolute temperatures except for those in the acetone solution. The enthalpies of solution, ΔH^d, were estimated from the linear relationship between $\log X_2$ and $1/T$ with an accuracy of ±0.1 kcal/mol, as Table 1 shows. The solubility of the heptasulfur imide decreased abruptly with an increase in the enthalpy of solution except for that in the methanol. Though the solubilities for the acetone at 20 and 30 °C were estimated to be 1.3×10^{-2} and 1.8×10^{-2} respectively, the sulfur was detected as a decomposition product in the solution at 40 °C by means of thin-layer chromatography.

TABLE 1. SOLUBILITIES, ENTHALPIES OF SOLUTION, AND SOLUBILITY PARAMETERS OF HEPTASULFUR IMIDE AT 25 °C

Solvent	X_2 ($\times10^3$)	ΔH^d kcal/mol	δ_1[a]	δ_2
Methanol	4.1	5.7		
n-Pentane	0.45	7.7	7.1	$12._4$
n-Hexane	0.67	7.9	7.3	$12._4$
n-Heptane	0.81	7.8	7.5	$12._5$
Cyclohexane	2.0	7.3	8.2	$12._8$
Cyclooctane	4.3	7.3	8.55	$12._7$
Benzene	14	6.4	9.15	$12._7$
Toluene	18	5.9	8.9	$12._3$
Chlorobenzene	14	6.3	9.5	$13._0$
Chloroform	9.6	6.4	9.3	$13._0$
Carbon tetrachloride	3.8	7.3	8.6	$12._9$

a) The solubility parameters of the solvents, δ_1, were those at 25 °C.[7]

Therefore, the data are not presented in Table 1. The absorption peaks in the UV spectra of the heptasulfur imide were observed at approximately 270 and 225 nm in all the solvents except for those with strong absorption bands near 270 and 225 nm. The UV spectra of the heptasulfur imide in all the solvents did not change over a period of three days, while the color of the acetone solution at 40 °C turned light yellow.

If it is assumed that these solutions are regular solutions,[7] the following equation can be obtained:[8]

$$RT \ln a_2 = RT \ln X_2 + V_2\phi_1^2(\delta_1-\delta_2)^2 \qquad (1)$$

where a_2 is the activity of the solute based on its supercooled liquid state at a given temperature; V_2, the molar volume of the solute in the liquid state; ϕ_1, the volume fraction of the solvent; δ_1 and δ_2, the solubility parameters of the solvent and the solute, and R, the gas constant. The activity of the solute can be calculated by means of the following equation:⁷⁾

$$\ln a_2 = -\frac{\Delta H^f}{R}\left(\frac{T_f - T}{T_f T}\right) \qquad (2)$$

where ΔH^f is the molar enthalpy of the fusion, and T_f, the melting point of the solute.

The molar enthalpy of the fusion of the heptasulfur imide was estimated to be 4.5 kcal/mol at its melting point by using the differential scanning calorimeter. The activity of the heptasulfur imide was calculated to be approximately 1.8×10^{-1} at 25 °C. The molar volume, V_2, of the heptasulfur imide in the supercooled liquid state was deduced from the partial molar volume (127 cm^3/mol), which was itself estimated from the benzene solutions at 25 °C.

By using the values of a_2, X_2, V_2, ϕ_1, and δ_1,⁷⁾ the solubility parameter, δ_2, of the heptasulfur imide at 25 °C was calculated from Eq. (1); the results are shown in Table 1.

The solubility parameter of the heptasulfur imide at 25 °C was estimated to be $12._7$ as an average value. This value agreed with that of cyclooctasulfur (12.7).⁹⁾

References

1) J. Weiss, *Z. Anorg. Allgem. Chem.*, **305**, 190 (1960).

2) H. G. Heal, *Nature*, **199**, 371 (1963).

3) M. Goehring, "Ergebnisse und Probleme der Chemie der Schwefelstickstoffverbindungen," Akademie-Verlag, Berlin (1957), p. 57.

4) H. G. Heal and J. Kane, "Inorganic Syntheses," Vol. XI, ed. by W. L. Jolly *et al.*, McGraw-Hill, New York (1968), p. 184.

5) J. Nelson, *Spectrochimica*, **27A**, 1105 (1971).

6) H. Tavs, J. Schultze-Steinen, and J. E. Colchester, *J. Chem. Soc.*, **1963**, 2555.

7) J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," Dover Publications, New York (1964), p. 66.

8) J. H. Hilderbrand and R. L. Scott, *ibid.*, p. 270.

9) J. H. Hildebrand and R. L. Scott, *ibid.*, p. 280.