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The Solubility Parameter of Tetrasulfur Tetranitride

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Synopsis. The solubilities of tetrasulfur tetranitride in thirteen organic solvents were measured. The solubility parameter of tetrasulfur tetranitride was estimated from the solubilities and its deduced activity to be 13.$_7$ at 25 °C; we assumed it to be regular.

Only a few solubilities of tetrasulfur tetranitride, S_4N_4, have been reported — for example, those for carbon disulfide, ethanol, dioxane, and benzene.[1] Consequently, the solubility parameter of this compound has not been reported. In this work, the solubilities and the solubility parameter of tetrasulfur tetranitride were estimated.

Experimental

Materials. The tetrasulfur tetranitride was prepared by the method described by Jolly and Goehring[2] and was recrystallized repeatedly from the benzene solution. Thirteen solvents were used to estimate the solubilities, as is shown in Table 1. All the solvents were purified in the usual ways.

Procedure. Suitable amounts of the tetrasulfur tetranitride 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20 to 40 °C (from 10 to 30 °C for the dichloromethane) with a precision of ±0.03 °C. An aliquot of the solution was withdrawn through a fine Teflon tube with a glass filter by applying an excessive pressure in the flask. The concentration of the solution was estimated from its optical absorbance at 400 nm, after it has been diluted to a suitable concentration, by using the working curves for the respective solvents previously determined with 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 an average value was less than ±1.5%.

Results and Discussion

The X-ray powder diffractogram of the sample showed patterns attributable to tetrasulfur tetranitride only.[3] The melting point of the sample was determined microscopically to be 178—179 °C. This value agreed with that of the purified tetrasulfur tetranitride.[4,5]

The solubilities, X_2 (molar fraction), and the heats of solution, ΔH^d, of the tetrasulfur tetranitride in various solvents are shown in Table 1.

The absorption peak in the UV spectra of the tetrasulfur tetranitride was observed at approximately 250 nm in all the solvents except for those with themselves a strong absorption band near 250 nm. In the methanol and the ethanol solutions, a new absorption peak was observed at 420 nm, and the absorbance at 420 and 250 nm decreased with the lapse of time. When the alcoholic solutions were concentrated by heating, the tetrasulfur tetranitride decomposed into sulfate. Though the solubilities in the pyridine and the carbon disulfide at 25 °C (after 2 hr) were estimated to be 1.0×10^{-2} and 4.3×10^{-3} respectively, a black fine precipitate was deposited from the solutions on heating. Consequently, their data are not presented in Table 1.

Table 1. Solubilities, heats of solution, and solubility parameters of tetrasulfur tetranitride at 25 °C

Solvent	X_2 ($\times10^3$)	ΔH^d kcal/mol	δ_1[a]	δ_2
Methanol	0.23	9.9		
Ethanol	0.28	7.6		
Dichloromethane	5.3	4.8	9.7	14.$_0$
1,2-Dichloroethane	5.5	5.5	9.8	14.$_0$
1,1,2,2-Tetrachloroethane	11	4.9	9.7	13.$_3$
n-Hexane	0.32	7.7	7.30	13.$_4$
Cyclohexane	0.64	7.9	8.20	13.$_9$
Cyclooctane	1.2	7.6	8.55	13.$_9$
Benzene	4.9	5.5	9.15	13.$_5$
Chlorobenzene	5.7	5.8	9.5	13.$_7$
Dioxane	8.8	4.9	10.0	13.$_8$
Chloroform	5.7	5.2	9.3	13.$_5$
Carbon tetrachloride	1.7	6.5	8.6	13.$_7$

a) The solubility parameters of the solvents, δ_1, were those at 25 °C.[6]

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

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

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]

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

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

The molar heat of the fusion of the tetrasulfur tetranitride was deduced approximately as the difference between the molar heat of sublimation, ΔH^s, and that of vaporization, ΔH^v; it could not be estimated because the tetrasulfur tetranitride decomposed with fusion. Sato[9] pointed out that the molar entropy of vaporization of the normal liquids related to their vapor pressures, p (mmHg), at given temperatures as follows:

$$\frac{\Delta H^v}{T} = 23.61\left(\frac{p}{T}\right)^{-0.119} \quad (3)$$

The calculated values agreed with the actual values with a precision of 5%. This relation was derived from the Hildebrand general rule.[10]

The vapor pressure of the tetrasulfur tetranitride at its melting point (178 °C) was calculated to be 10.8 mmHg from the vapor pressure at 90 °C and the molar heat of sublimation (3.51×10^{-2} mmHg and 21.2 kcal/mol),[5] while the temperature change in the molar heat of sublimation was neglected. Assuming that the relation of Eq. (3) is possible on an imaginary liquid tetrasulfur tetranitride, its molar heat of vaporization, ΔH^v, at the melting point was calculated to be 16.6 kcal/mol. From the difference in the ΔH^s and the ΔH^v, the molar heat of fusion of the tetrasulfur tetranitride was obtained to be approximately 4.6 kcal/mol. The activity of the tetrasulfur tetranitride at 25 °C was calculated from Eq. (2) to be approximately 7.2×10^{-2}.

By using the values of the a_2, the X_2, the V_2, the ϕ_1, and the δ_1,[6] the solubility parameter, δ_2, of the tetrasulfur tetranitride at 25°C was calculated from Eq. (1); the results are shown in Table 1. The molar volume, V_2, of the tetrasulfur tetranitride in the supercooled liquid state was deduced from the partial molar volume (86 cm^3/mol), which was itself estimated from the benzene solutions at 25 °C with a precision of ±0.01 °C by using a modified Lipkin-Davison-type pycnometer. The solubility parameter of the tetrasulfur tetranitride at 25 °C was estimated to be 13.$_7$ as an average value.

References

1) A. A. Vosnesenskij, "Solubilities of Inorganic and Organic Compounds," Vol. I, Part 2, ed, by H. Stephen and T. Stephen, Pergamon Press, Oxford (1963), p. 981.
2) W. L. Jolly and M. Becke-Goehring, *Inorg. Chem.*, **1**, 76 (1962).
3) S. Hamada, A. Takanashi, and T. Shirai, This Bulletin, **44**, 1433 (1971).
4) W. L. Jolly, "The Synthesis and Characterization of Inorganic Compounds," Prentice-Hall, Englewood, N. J. (1970), p. 502.
5) S. Hamada, This Bulletin, **46**, 3598 (1973).
6) J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," Dover Publication, New York (1964), p. 435.
7) J. H. Hildebrand and R. L. Scott, *ibid.*, p. 66.
8) J. H. Hildebrand and R. L. Scott, *ibid.*, p. 270.
9) K. Sato, *Kagaku Kikai*, **14**, 270 (1950).
10) J. H. Hildebrand, *J. Amer. Chem. Soc.*, **37**, 970 (1915).