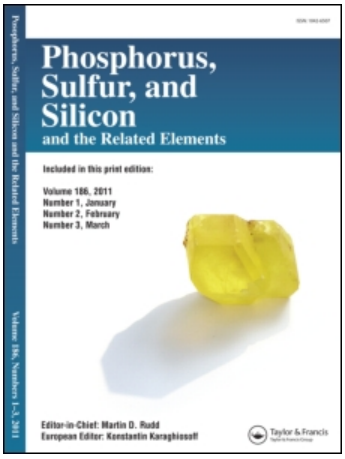

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Solubility of Elemental Sulfur in Water at 298 K

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SHORT COMMUNICATION

Solubility of Elemental Sulfur in Water at 298 K

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The solubility of elemental rhombic sulfur in water is $1.9(\pm 0.6) \times 10^{-8}$ mole $S_8 \cdot kg^{-1}$. This value is in agreement with thermodynamic considerations on the solubility of sulfur and experimental data on sulfur hydrosols.

INTRODUCTION

Elemental sulfur is known to be insoluble in water. However, in certain processes, such as geological processes, where time compensates for the very small concentration, the solubility of sulfur in water can be of interest. This paper deals with the measurement of the solubility of elemental rhombic sulfur in water at 298 K.

EXPERIMENTAL

One gram of very pure finely ground sulfur (Isotope Reference Sample no. 120, NBS) was put in a polyethylene container containing 25 liters of deionized water. The water was regularly degassed with N_2 (12 hours with N_2 purified by passage through a V^{2+} solution[1]) and stirred with a magnetic stirrer. The experiments were carried out in the dark at 298 K. Three experiments were done with different time intervals (1, 2 and 3 months). At the end of the equilibration, the water was filtered on 0.01 μ Millipore filters. Then dissolved sulfur was extracted with 50 ml of chloroform or trichloroethylene. The light absorption was measured at 264 nm in trichloroethylene ($\varepsilon = 1034$)[2] and at 280 nm in chloroform ($\varepsilon = 826$).[3] The measurements were compared to a "blank" which was treated as a sample except that no sulfur was in contact with water.

RESULTS

The results are given in Table I (results for 1 and 2 correspond to the mean of duplicated experiments) and characteristic spectra are given in Figure 1. It appears that the solubility of rhombic sulfur in water is $1.9(\pm 0.6) \times 10^{-8}$ mole $S_8 \cdot kg^{-1}$.

TABLE I

Results of the experiments of dissolution of elemental sulfur in water

Experiment	Duration (months)	Extraction Solvent	m_{S_8} (mole · kg^{-1})
1	1	$ClHC{=}CCl_2$	2.5×10^{-8}
2	2	$CHCl_3$	1.5×10^{-8}
3	3	$ClHC{=}CCl_2$	1.7×10^{-8}

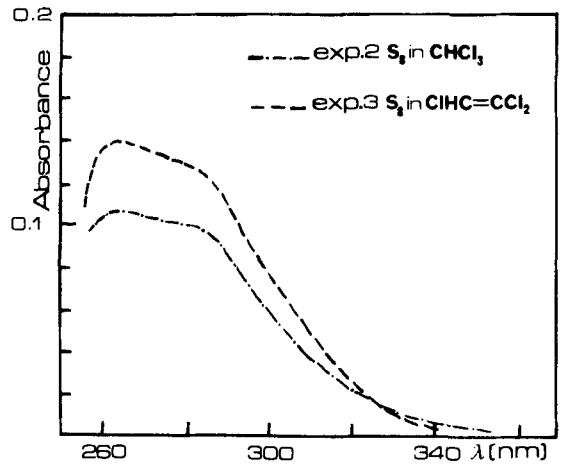

FIGURE 1 Uv absorption spectra of sulfur in chloroform (experiment 2) and in trichloroethylene (experiment 3) after extraction from 25 liters of water. Volume of extraction solvent = 50 ml. Quartz cells, 1 = 2 cm. The absorbance scale is linear.

DISCUSSION

The solubility of sulfur in water can be compared with the solubility calculated from the laws of the solubility of solids. The solubility of sulfur in a non-polar solvent should be:[4]

$$\ln(x_{S_8}) = (\Delta H_m^F/R \cdot T_m)(1 - T_m/T) - (V_S \cdot (\delta_S - \delta_0)^2 \cdot \phi_0^2)/R \cdot T \quad (1)$$

where x_{S_8} is the mole fraction of sulfur in water, ΔH_m^F is the molar heat of fusion of rhombic sulfur at its melting point T_m, V_S is the molar volume of S_8, δ_S and δ_0 are the "solubility parameter" of S_8 and H_2O, respectively, and ϕ_0 is the volume fraction of H_2O. If the change of heat capacity ΔC_P^F on melting is not neglected (1) becomes:

$$\ln(x_{S_8}) = (1/R)\{(\Delta H_m^F/T_m) \cdot (1 - T_m/T) + \Delta C_P^F(\ln(T/T_m) + T_m/T - 1)\} - (V_S \cdot (\delta_o - \delta_0)^2 \cdot \phi_o^2)/R \cdot T \quad (2)$$

To calculate x_{S_8} with (2), the necessary data are: $\Delta H_m^F = 4.02$ kcal · mole^{-1},[5] at $T_m = 384$ K, $\Delta C_P^F = 11.5$ cal · mole^{-1} · K^{-1},[5] $V_S = 135$ cm^3,[6] $\delta_0 = 23.4$ cal$^{1/2}$ · cm$^{-3/2}$.[7] In non polar solvent $\delta_S = 12.7$ cal$^{1/2}$ · cm$^{-3/2}$ for hypothetical supercooled sulfur.[4] Owing to the properties of water as a solvent of non-polar solute,[7] we have added 1 cal$^{1/2}$ · cm$^{-3/2}$ to the above value of δ_S. In this instance x_{S_8} calculated from (2) is 1.55×10^{-10}, which corresponds to the molality $m_{S_8} = 8.6 \times 10^{-9}$ mole · kg^{-1}. This value is in good agreement with the experimental solubility.

Another interesting comparison can be deduced from experimental data on sulfur hydrosols. The critical limiting supersaturation of dissolved sulfur c_{SS} before the appearance of sulfur hydrosols is approximately[8] 1.25×10^{-7} mole · kg^{-1}. The ratio c_{SS}/m_{S_8} is 1.19 in organic solvents and its value in water is larger, although unknown.[8] It corresponds to 1.05×10^{-7} mole · kg^{-1}, which is a maximum value for the molality of dissolved elemental sulfur in water. Although this last estimation is approximate, it is is agreement with our measurement of m_{S_8}.

In organic solvents the molecular form of dissolved sulfur is cyclooctasulfur.[9] In the above calculation of the solubility of sulfur we have employed only values referring to rhombic sulfur. Owing to the agreement of the calculations with the experimental results, it is highly probable that the molecular form of dissolved rhombic sulfur in water is also cyclooctasulfur.

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