The Chemical Preparation of Tin Organosol

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Synopsis. A stable colloidal tin suspension in an organic solvent was prepared by the chemical reduction of tin(II) chloride with sodium tetrahydridoborate in the presence of a protective agent. The tin organosol was examined by means of the Mössbauer absorption spectra of ^{119}Sn in the frozen solution and by means of an electron microscope.

Vernon *et al.* have extensively studied the chemical preparation of colloidal metal suspensions in non-aqueous solvents.[1,2] They have reported the preparation of a stable tin organosol of a very dilute concentration by reducing tin(II) chloride with phosphorus-hydrazine. We have tried to obtain tin organosols in concentrations higher than 0.2% by Vernon's method. However, it was difficult because tin(II) chloride was not reduced sufficiently, even at the raised temperature of 70 °C.

In this study, we have tried to prepare a colloidal tin suspension in ethanol by chemical reduction with the reducing agent of $NaBH_4$ in the presence of a protective agent.

Experimental

Freshly prepared anhydrous stannous chloride (0.17—1.36 mmol) was dissolved in dry ethanol (20 ml). Three times as much poly(vinylpyrrolidone) (PVP) as $SnCl_2$ was added to the solution as a protective agent. Then three times as much $NaBH_4$ as $SnCl_2$ was added at 3 °C under a nitrogen atmosphere, while the solution was stirred by means of ultrasonic waves. The solution became red-brown immediately, and after a few minutes it gave a homogenous black solution forming a stable tin suspension.

The tin microcrystals in the suspension were examined by means of the Mössbauer absorption spectra of ^{119}Sn in the frozen solution and by means of an electron microscope.

Results and Discussion

Stannous chloride is reduced to tin by $NaBH_4$ in ethanol according to this reaction:

$$SnCl_2 + 2NaBH_4 \xrightarrow[3\,°C]{\text{ethanol}} Sn + B_2H_6 + H_2 + 2NaCl$$

In confirmation of this reaction, the fine powder filtered out of the suspension were identified by means of X-ray diffraction as a mixture of β-tin and NaCl. Observation of the electron micrograph of the microcrystals in a suspension with a tin concentration of 1 mg cm^{-3} revealed that the particle size of the microcrystals was about 300 Å and that the microcrystals aggregated to a size of 1000 Å or more.

The Mössbauer absorption spectra of ^{119}Sn in frozen solutions with various tin concentrations at 90 K are shown in Fig. 1. The values of the isomer shift (δ) and the total area under the absorption peak derived from the spectra are shown in Table 1. The values of the isomer shift at the higher concentrations coincide with the value of the bulk of β-tin, 2.56 mm s^{-1}. However, at the lower concentrations the values turned out to be more negative.

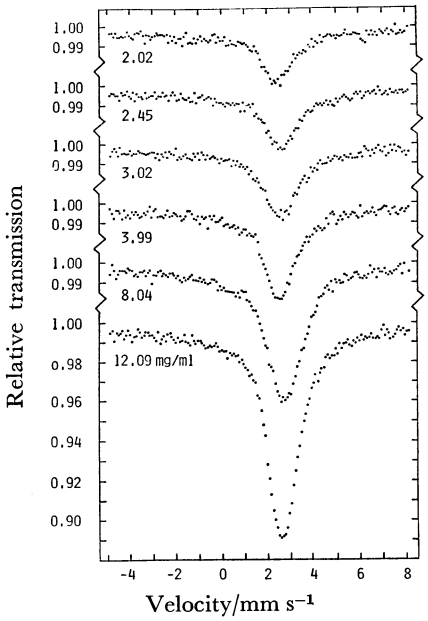

Fig. 1. Mössbuer absorption spectra of ^{119}Sn in the frozen solutions of tin suspension in ethanol at 90 K.

Table 1. ^{119}Sn Mössbauer data of tin organosol

Concentration / mg cm^{-3}	δ / mm s^{-1}	Area
1.01	2.22	0.035
2.02	2.42	0.056
2.45	2.59	0.075
3.02	2.53	0.049
3.99	2.47	0.114
8.04	2.69	0.186
12.09	2.60	0.258

The plots of the total area against the tin concentration are shown in Fig. 2. The area decreases linearly with the decreasing concentration, but it deviates from the line to the lower value at lower concentrations.

Suzdalev *et al.* have investigated, in an aerosol, tin particles with diameters of 250, 370, and 600 Å; they reported that the probability of the Mössbauer effect diminishes as the particle diameter decreases and that this result is associated with the influence of the surface.[3] With reference to their findings, it seems likely that the size of the mycrocrystals formed in the organic suspensions will be reduced with the decreasing tin concentration and that the surface effects will become manifest at concentrations lower than 3 mg cm^{-3}.

A few cases of isomer-shift differences between bulk and microcrystals have been reported and their origins

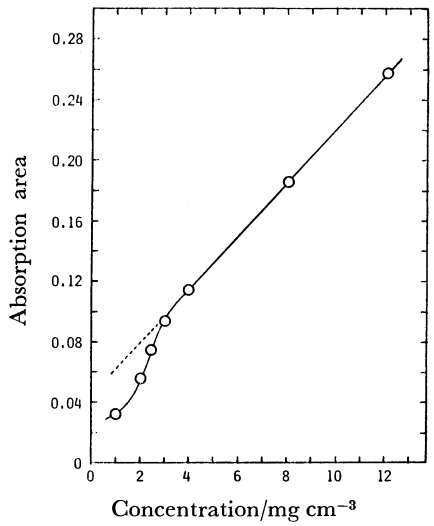

Fig. 2. Total area under the absorption peak *vs.* concentration of tin in suspension.

discussed by Schroeer.[4] The isomer-shift difference, *i.e.*, the decrease in the microcrystals formed at the lower concentration, is also observed in our study. In tin microcrystals, the negative isomer shift to a bulk value may occur through the second-order Doppler shift, surface bonding, and the conversion of β-tin to α-tin. However, it is difficult to make the origin clear.

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