

Mössbauer Study of Brownian Motion in Liquids: Colloidal Cobaltous Hydroxy Stannate in Glycerol, Ethanol-Glycerol, and Aqueous-Glycerol Solutions*

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We have measured the resonant absorption of the 23.9-keV γ rays of Sn^{119m} in a colloidal suspension of $\text{CoSn}(\text{OH})_6$ in glycerol in the temperature range 110–323 °K. We measured the colloidal-particle radii with a scanning electron microscope, and found them to be $650 \pm 150 \text{ \AA}$. We have also studied the fixed-temperature Mössbauer line broadening of our glycerol-based colloid, as a function of ethanol and water dilution. We find that the diffusive broadening of the Mössbauer line is proportional to the absolute temperature divided by the viscosity. The constant of proportionality is the same within the experimental errors, whether the sample viscosity is changed by varying the sample temperature, or by diluting the sol with ethanol or water. These results are in good agreement with the Singwi-Sjölander theory and the Einstein-Stokes relation. For this system we observed a rapid falloff in the recoil-free fraction in the temperature region where diffusive broadening effects were observed, similar to other earlier observations of this effect. Attempts to prepare large-particle sols of $\text{FeSn}(\text{OH})_6$ in glycerol were made to try to see a breakdown in the Singwi-Sjölander theory. Some evidence for a failing in the theory was found for particle sizes of 1500 \AA , but these results were not conclusive, as the sols were always unstable for these large colloidal particles.

I. INTRODUCTION

The present study is intended to complement our study of dispersed ions in glycerol,¹ for a case where individual atomic jumps are precluded, because the ions studied are locked into microcrystals, whose diffusion depends purely on the interaction between the sol particles and the solution in which they are immersed. Since Singwi and Sjölander's prediction² that diffusion could be studied by measuring broadening of the Mössbauer line, several investigations have been carried out to study this effect, and much of the literature on this subject is reviewed in the preceding paper.

By combining the Einstein-Stokes relation³ with the predictions of the Singwi-Sjölander theory in the continuous diffusion limit, we find

$$\frac{\Delta\epsilon}{\Gamma_N} = \frac{\kappa^2 \tau_N k}{3\pi R} \frac{T}{\eta}, \quad (1)$$

where $\Delta\epsilon$ is the incremental broadening of the Mössbauer line, $\Gamma_N = \hbar/\tau_N$ is the linewidth of the nuclear level, κ is the wave vector of the Mössbauer γ ray, τ_N is the mean nuclear lifetime, k is Boltzmann's constant, R is the radius of the diffusing entity, or particle, T is the absolute temperature, and η is the viscosity of the medium in which the particle is diffusing. Thus, we would expect a plot of $\Delta\epsilon/\Gamma_N$ versus T/η to be linear, for cases where the Singwi-Sjölander and Einstein-Stokes theories apply.

Bonchev *et al.*⁴ have tested Eq. (1) for SnO_2 in glycerol and silicone oil. Their data indicate agreement with Eq. (1) for cases where they varied T/η by water dilution, but not for cases where T/η was

varied by temperature cycling. From these results and additional data, Bhide *et al.*⁵ have generalized the Singwi-Sjölander calculation, using a Langevin distribution to describe the motion of a colloidal particle in a liquid. They conclude that for sufficiently large particle undergoing Brownian motion, the line shape and diffusion broadening will be significantly altered from the Singwi-Sjölander predictions. The classical diffusion is described by the Langevin formula as

$$F_s(F, t) = [2\pi\rho(t)]^{-3/2} e^{-r^2/2\rho(t)},$$

where

$$\rho(t) = (2D/\beta)[\beta t - 1 + e^{-\beta t}]$$

and

$$\beta = \frac{kT}{MD} = \frac{6\pi R\eta}{M},$$

where M is the mass of the diffusing particle. Singwi and Sjölander treat the case where $\beta\tau_N \gg 1$ whence $\rho(t) = 2Dt$, and F_s is then the commonly used classical diffusion formula. Our studies focus on cases where the condition $\beta\tau_N \gg 1$ is satisfied, although we discuss some results where we attempted to violate this condition, using colloidal $\text{FeSn}(\text{OH})_6$ in glycerol. We found that all of the sols that we were able to prepare, which were stable, did satisfy the Singwi-Sjölander condition. Large-particle colloids that did not satisfy this condition always were unstable and gave undesirable particle settling effects.

II. EXPERIMENTAL TECHNIQUES

To carry out the present study we sought an absorber with a linewidth as narrow as possible to the

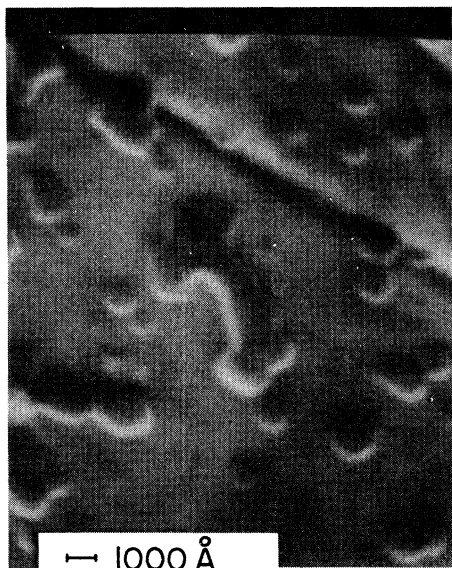


FIG. 1. Electron scanning micrograph of CoSn(OH)_6 particles used in the colloids studied.

minimum required by the uncertainty principle (0.6 mm/sec), which did not have a complicating hyperfine structure. Using a commercially available barium stannate source, we prepared several powder absorbers and measured the linewidth of each at room temperature. Typical values were 1.49 ± 0.03 mm/sec for SnO_2 and 1.31 ± 0.03 mm/sec for BaSnO_3 . Other tin compounds were also tried, but the best results were obtained for CoSn(OH)_6 , which gave a linewidth of 1.15 ± 0.02 mm/sec. Since this material could also be simply prepared as a stable sol with glycerol as a solvent, it was used for most of the measurements discussed in this paper.

We prepared CoSn(OH)_6 by the method of Strunz and Contag,⁶ and the structure was verified by a measurement of the x-ray powder pattern.

The colloidal suspension was prepared by the following technique. Equal quantities (molar) of $\text{CoCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{Na}_2\text{Sn(OH)}_6$ were prepared in aqueous solution and then mixed and agitated thoroughly. A pink precipitate formed and was filtered and washed with water two or three times to remove the undesirable electrolytic NaCl . The precipitated salt was dried as a powder and then dispersed in water as a colloidal suspension. The larger particles were removed by centrifuging, and the decant was added to pure dry glycerol. The large amount of water added to the glycerol in this process was removed by evaporation, achieved by heating the sample to 60–70 °C. To avoid coagulation it was necessary to repeat this process several times, being careful to remove the water after each addition of

the aqueous sol. The concentration of CoSn(OH)_6 in glycerol was determined empirically by making Mössbauer measurements at low temperatures (~ 110 °K). After reaching an adequate concentration of colloidal material, a final drying of the colloid was performed by heating to 70 °C in a vacuum for about two weeks. The viscosity of these samples was measured by a standard technique¹ and agreed with the viscosity values of 100% pure glycerol.

The absorbers were held in Lucite disc-shaped containers,^{1,7} and their temperature was monitored with copper-constantan thermocouples during Mössbauer runs. Mössbauer spectra were measured in the temperature range 113–323 °K with a commercial (Elron) spectrometer of the double-transducer type, used in the constant-acceleration mode. The method of temperature regulation is described elsewhere,⁷ and was good to within about 1 °K. A 30-mCi Sn^{119} in BaSnO_3 source was used throughout the experiments. A semiconducting detector capable of distinguishing the Mössbauer γ ray from the tin x ray was used in all experiments.

Some glycerol-ethanol and glycerol-water samples were studied at room temperature. They were prepared by adding pure ethanol and pure water to the dry glycerol samples. The viscosity of these samples was determined by a direct measurement using standard laboratory apparatus.^{1,7}

The particle size for our sols was directly measured with a scanning electron microscope, model JSM-U3, manufactured by the Japan Electron Optics Laboratory Co., Ltd. Our sol was diluted with ethanol and dried on a platinum foil. A photograph of the dried colloid is given in Fig. 1. In cases where drying does not produce clustering, the particles are seen to be spherical in shape and of fairly uniform size. We determined the average particle radius from two photographs like the one shown in Fig. 1, and we found it to be 650 ± 150 Å. The error figure in this case represents the maximum range in particle size of the 14 cases measured. The standard deviation of the particle radius from the mean would be about one-half of this value, or 75 Å.

III. RESULTS AND DISCUSSION

Thirteen measurements of the Mössbauer spectra for the CoSn(OH)_6 colloidal suspension in glycerol were made and the temperature dependence of the linewidth is given in Table I. Seven representative spectra are shown in Fig. 2. The appearance and quality of the spectra were similar for the glycerol-ethanol and glycerol-water samples. The data all were fitted with a Lorentzian line shape, and it is apparent from Fig. 2 that this gave a very satisfactory fit to the experi-

TABLE I. T/η dependence to Mössbauer line broadening for $\text{CoSn}(\text{OH})_6$ in glycerol sol ($\Delta\epsilon = \Gamma - \Gamma_{\text{min}}$, $\Gamma_{\text{min}} = 1.13 \pm 0.02$ mm/sec, and $\Gamma_N = 0.31$ mm/sec).

T (°K)	Γ (mm/sec)	$\Delta\epsilon$ (mm/sec)	$\Delta\epsilon/\Gamma_N$	T/η (°K/P)
113 ± 2	1.12 ± 0.02			
123 ± 2	1.14 ± 0.03			
248 ± 2	1.10 ± 0.04			
265.5 ± 1.5	1.16 ± 0.04	0.04 ± 0.05	0.13 ± 0.16	
278.0 ± 1.5	1.29 ± 0.03	0.17 ± 0.04	0.55 ± 0.12	3.9 ± 0.2
284.0 ± 1.0	1.37 ± 0.04	0.25 ± 0.05	0.81 ± 0.16	8.0 ± 0.5
295.5 ± 0.5	1.88 ± 0.06	0.76 ± 0.07	2.45 ± 0.23	27.0 ± 2.1
303.0 ± 0.5	2.42 ± 0.08	1.30 ± 0.08	4.19 ± 0.26	49.5 ± 3.0
308.7 ± 0.5	3.39 ± 0.14	2.27 ± 0.14	7.32 ± 0.45	80.0 ± 4.8
310.5 ± 0.5	3.44 ± 0.36	2.32 ± 0.36	7.48 ± 1.16	99.0 ± 7.9
315.0 ± 0.5	3.93 ± 0.20	2.81 ± 0.20	9.06 ± 0.65	130.0 ± 9.1
319.0 ± 0.5	5.14 ± 0.32	4.02 ± 0.32	12.96 ± 1.03	170.0 ± 13.6
323.0 ± 0.5	6.44 ± 0.30	5.32 ± 0.30	17.16 ± 0.96	219.9 ± 15.5

mental results. Tables II and III give the temperature dependence to the Mössbauer line broadening for the glycerol-ethanol and glycerol-water samples, respectively. All of these data were taken at room temperature (295.5 °K) and the ratio T/η was effectively varied by changing the amount of dilution with either ethanol or glycerol. The values of T/η given in the last column of Tables II and III were determined from our directly measured values of viscosity.

In Fig. 3 we summarize the results of our measurements for all three sample types, where we have plotted $\Delta\epsilon/\Gamma_N$ versus T/η . The data are all consistent with a simple linear relation such as is expected from Eq. (1). The three lines shown are the best straight-line fits to the experimental data for the three sample types studied. The slope of the curves can be used to calculate the radius of the diffusing entity from Eq. (1), and the result of this calculation is $R = 741 \pm 96$, 680 ± 87 , and 582 ± 100 Å for the cases of pure glycerol, glycerol-ethanol, and glycerol-water, respectively. These values are the same as those measured directly with the electron scanning microscope (650 ± 150 Å)

TABLE II. T/η dependence of the Mössbauer line broadening for $\text{CoSn}(\text{OH})_6$ in (glycerol-ethanol) sol ($\Delta\epsilon = \Gamma - \Gamma_{\text{min}}$, $\Gamma_{\text{min}} = 1.12 \pm 0.02$ mm/sec, $\Gamma_N = 0.31$ mm/sec, and $T = 295.5$ °K for all data).

Γ (mm/sec)	$\Delta\epsilon$ (mm/sec)	$\Delta\epsilon/\Gamma_N$	T/η (°K/P)
1.79 ± 0.03	0.67 ± 0.03	2.16 ± 0.10	29.6 ± 1.8
1.95 ± 0.05	0.83 ± 0.06	2.68 ± 0.19	34.9 ± 2.4
2.08 ± 0.04	0.96 ± 0.05	3.10 ± 0.16	40.2 ± 3.2
2.35 ± 0.05	1.23 ± 0.06	3.97 ± 0.19	47.8 ± 3.5
2.64 ± 0.08	1.52 ± 0.08	4.90 ± 0.26	55.4 ± 4.4
3.32 ± 0.09	2.20 ± 0.09	7.10 ± 0.29	82.0 ± 6.7
3.83 ± 0.17	2.71 ± 0.17	8.74 ± 0.55	109.0 ± 8.7
6.00 ± 0.28	4.88 ± 0.28	15.70 ± 0.90	185.0 ± 16.6

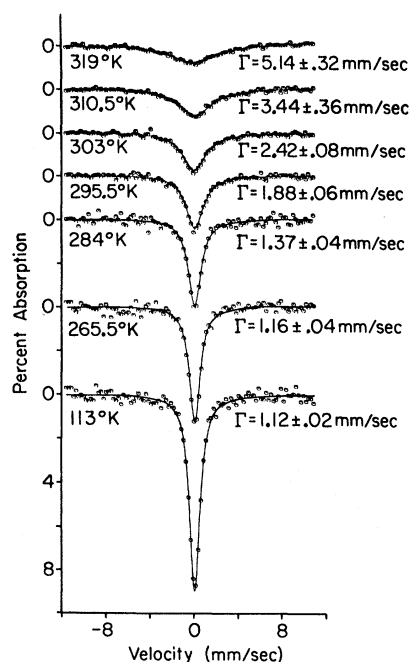


FIG. 2. Mössbauer spectra at various temperatures for $\text{CoSn}(\text{OH})_6$ in dry glycerol.

within the experimental errors. These results give a striking confirmation of the Singwi-Sjölander theory in the continuous diffusion limit.

Because numerous observations¹ of diffusion broadening have shown very rapid falloff in the recoil-free fraction in the temperature region where diffusion effects were observed, we also have looked for this effect. A plot of $\ln(\text{area})$ versus temperature is given in Fig. 4. The linear temperature dependence expected from the Debye model is observed, with a more rapid falloff in the region where diffusive broadening was observed. An attempt to plot $\Delta\epsilon/\Gamma_N$ versus $-\ln f$, as was suggested by Jensen,⁸ did not give a good linear curve, and the slope of the best straight line through the data was nearly vertical, which would suggest a very low effective relaxation time within Jensen's

TABLE III. T/η dependence to Mössbauer line broadening for $\text{CoSn}(\text{OH})_6$ in (glycerol-water) sol ($\Delta\epsilon = \Gamma - \Gamma_{\text{min}}$, $\Gamma_{\text{min}} = 1.12 \pm 0.02$ mm/sec, $\Gamma_N = 0.31$ mm/sec, and $T = 295.5$ °K for all data).

Γ (mm/sec)	$\Delta\epsilon$ (mm/sec)	$\Delta\epsilon/\Gamma_N$	T/η (°K/P)
1.84 ± 0.08	0.72 ± 0.08	2.39 ± 0.26	24.7 ± 1.6
2.06 ± 0.10	0.94 ± 0.10	3.03 ± 0.32	34.8 ± 2.4
2.40 ± 0.12	1.28 ± 0.12	4.13 ± 0.38	47.4 ± 3.3
3.15 ± 0.21	2.03 ± 0.21	6.55 ± 0.68	63.0 ± 5.1
3.61 ± 0.20	2.49 ± 0.20	8.03 ± 0.64	83.0 ± 4.9
4.67 ± 0.28	3.55 ± 0.28	11.45 ± 0.90	114.0 ± 9.1

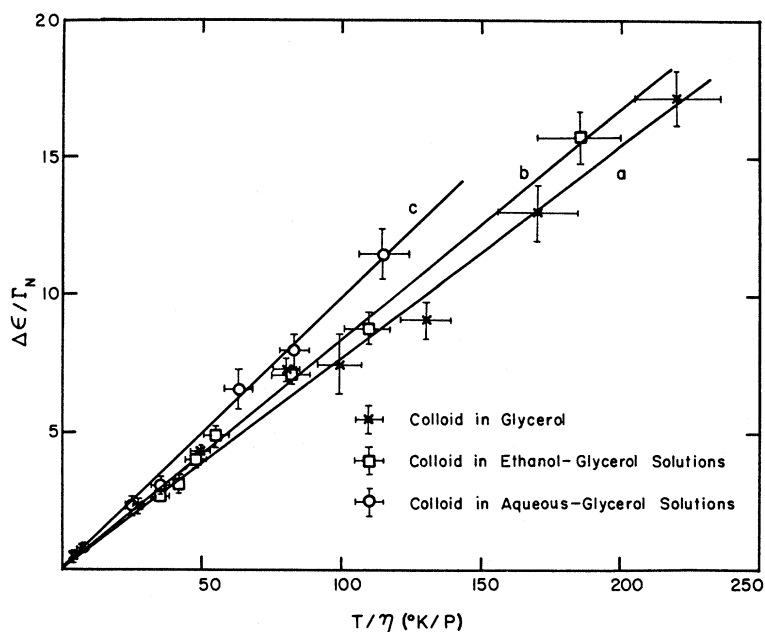


FIG. 3. Plot of $\Delta\epsilon/\Gamma_N$ versus T/η for (a) dry glycerol as temperature was varied, (b) glycerol-ethanol as dilution was varied, and (c) glycerol-water as water dilution was varied.

model. These results apparently indicate that this model does not apply well to this case.

Because of the curvature observed by Bonchev *et al.*⁴ and recent attempts^{5,9} to generalize the Singwi-Sjölander theory to account for these observations, we attempted to prepare colloids of larger size, comparable to those of Bonchev *et al.*⁴ (2000 Å). We were able to prepare larger particle colloids of $\text{FeSn}(\text{OH})_6$ with reasonably narrow lines at low temperatures, although these sols were never completely stable and settling effects were

always observed. A plot of $\Delta\epsilon/\Gamma_N$ versus T/η was made for our $\text{FeSn}(\text{OH})_6$ at room temperature by varying the viscosity by progressive water dilution of the glycerol host. The broadening was nearly linear up to $T/\eta \approx 240$ $^{\circ}\text{K}/\text{P}$ and showed a slight curvature at higher values of T/η , similar in shape to that of Bonchev *et al.*,⁴ but differing at most by only about 20% from linear at the highest T/η values. Bhide *et al.*⁵ suggest a broadening of the form $\Delta\epsilon/\Gamma_N \propto (T/\eta)^{1/2}$, and we were not able to confirm this relation even for this relatively large-

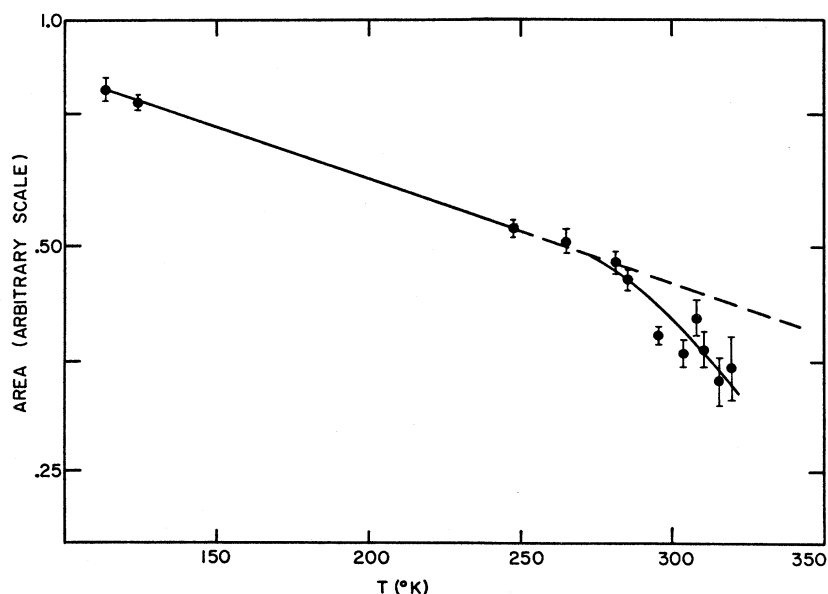


FIG. 4. Temperature dependence to the recoil-free fraction for $\text{CoSn}(\text{OH})_6$ in pure glycerol sol.

particle ($R = 1500 \text{ \AA}$) case. We would emphasize, however, that we were never able to prepare large-particle colloids that were stable enough to avoid particle settling and possible ambiguities in interpretation for these cases. Bonchev *et al.*⁴ apparently encountered similar difficulties.

In conclusion we find that, for the highly stable sol of cobaltous hydroxy stannate in glycerol, glycerol-ethanol, and glycerol-water, the Singwi-Sjölander theory gives a very satisfactory description of the diffusive broadening of the Mössbauer line. Rapid falloff in the recoil-free fraction in the temperature interval where diffusive effects are observed has not been satisfactorily explained, and more theoretical investigation of this point seems necessary.

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Decoupled-Mode Theory of Critical Viscosity and Diffusion in the Binary-Liquid Phase Transition*

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The fluctuation-dissipation formula for the viscosity in terms of the stress-tensor fluctuations reproduces the experimental logarithmic temperature dependence of the hydrodynamic viscosity. Using the theoretical wave-number- and frequency-dependent viscosity in the problem of critical diffusion, we find that the effects of nonlocality and retardation practically cancel, resulting in satisfactory agreement with a recent light scattering determination of the effective viscosity.

I. INTRODUCTION

It is well known that the binary liquid exhibits interesting critical behavior as the critical point is approached, just before it begins to separate into two distinct liquid phases. The most striking example is the critical opalescence or the scattering of light by the concentration fluctuations. A less-evident critical phenomenon which has been recently firmly established experimentally is the diverging behavior of the viscosity as the critical point is approached. It is customary¹ to separate the viscosity into a so-called "ideal" background component η_{id} and a critical component $\Delta\eta$. The

fraction by which the critical component accounts for the total viscosity is established experimentally^{2,3} to follow the temperature dependence as the temperature T approaches T_c ,

$$\Delta\eta/\eta = A_{\text{EXPT}} \ln q_D \xi, \quad (1.1)$$

where the correlation length is $\xi = 2.56 \text{ \AA} (T/T_c - 1)^{0.616}$, q_D is a Debye cutoff, and $A_{\text{EXPT}} = 0.051$. This relationship which gives a good fit to the experimental data is shown in Fig. 1 by the line labeled "HYD." (In this case the abscissa represents the inverse correlation length.) The purpose of the present paper is to give a theory of the viscosity not only in a hydrodynamic context, but also in its

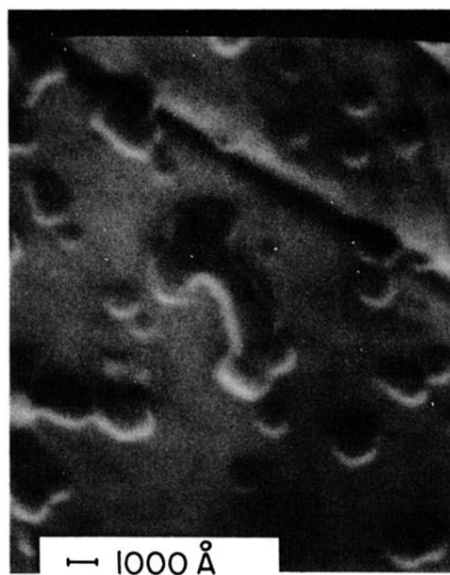


FIG. 1. Electron scanning micrograph of CoSn(OH)_6 particles used in the colloids studied.