

Influence of the Nature of the Solute and the Carrier Surface on the Mössbauer Effect in Aqueous Solutions Trapped in a Silicate Carrier

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Abstract

A comparison of the Mössbauer data recorded on aqueous solutions trapped in a porous glass ('thirsty glass') carrier of $\text{Na}_2\text{Sn}(\text{OH})_6$, $\text{SnCl}_4(\text{OH}_2)_2$, Na_2SnS_3 and hydrolysis products of the latter demonstrated the importance of the H-bonded cluster structure of the aqueous solution, and the connection of this cluster to the water layer adsorbed on the internal surface of the carrier pores, in the appearance of the Mössbauer effect in such systems. The Mössbauer data acquired in this way more or less reflect the structure of the original solution.

Introduction

Recoilless γ -ray resonance absorption has been achieved in liquids trapped in the pores of a special porous silicate carrier [1]. It has been shown that, when aqueous solutions are trapped in this carrier, the silicate surface of the pores is covered by a water layer which isolates the Mössbauer-active solute molecules from the surface. Thus, the Mössbauer parameters of the solution do not reflect the solution-surface interactions [2, 3].

It is evident that Mössbauer-active compounds in liquid solutions adsorbed on a surface can undergo recoilless γ -ray resonance absorption. Naturally, this strong interaction must be reflected in the Mössbauer parameters. The appearance of the Mössbauer effect for species which are formally in a liquid solution and not in direct contact with a solid surface is most surprising.

Model calculations have been performed of the Debye-Waller factors in liquids trapped in a carrier, in which only the lack of space and the rigidity of the

walls in the pores was assumed to hinder the recoil of the nucleus effectively, resulting in recoilless γ -ray absorption [4]. These calculations were rather simplistic, and the conclusion could be regarded only as indicative.

Room temperature Mössbauer investigations of aqueous tin tetrachloride solutions trapped in the pores of a 'thirsty glass' carrier have shown that recoilless γ -ray resonance absorption could be achieved only in (added) acid-free solutions. Hydrochloric or nitric acid-containing tin tetrachloride solutions did not display the Mössbauer effect at room temperature [2, 3].

It is known [5] that in aqueous solutions hydrated species are H-bonded to neighbouring water molecules, which are similarly connected to the bulk water, the latter consisting of H-bonded associations of water molecules. The whole system is connected by H-bonds to the water layer bound or simply adsorbed to the silicate surface in the pores of the carrier. This cluster-type structure is a dynamic one, the cleavage and formation of H-bonds occurring constantly. The hydrated solute is nevertheless effectively rigid relative to its close surroundings. Since this solution structure is partially or even completely destroyed by the addition of strong acids, as the oxygen atom of water favours hydrogen ions to the hydrogen atoms of the neighbouring water molecules, the disappearance of the Mössbauer effect in the presence of strong acids seemed to indicate that the H-bonded cluster structure of the liquid is needed if the Mössbauer effect is to be observed at room temperature for aqueous solutions trapped in the porous glass carrier.

To obtain additional support for the above suggestion, we have performed a Mössbauer study of aqueous solutions of compounds with different H-bonding abilities ($\text{Sn}(\text{OH})_6^{2-}$, $\text{SnCl}_4(\text{H}_2\text{O})_2$ and SnS_3^{2-} , and hydrolysis products of the latter) and

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also studied the effects of changes in the polarity and H-bonding ability of the carrier surface on the Debye–Waller factor of the system. The results are presented and discussed in this paper.

Experimental

The Mössbauer measurements were performed by the method given in our earlier paper [2] on capillary Mössbauer spectroscopy. The isomer shift (IS) values refer to SnO_2 at room temperature.

The porous glass carrier was made of Corning Vycor thirsty glass [6] plates (No. 7930), as reported in previous publications [2, 7].

SnCl_4 (Merck p.a.) served as the primary substance in the preparation processes. $\text{Na}_2\text{Sn}(\text{OH})_6$ was prepared by dissolving freshly precipitated $\text{Sn}(\text{OH})_4$ in an equivalent amount of NaOH in water [8]. Na_2SnS_3 and its hydrolysis products were prepared by dissolving freshly precipitated stoichiometric SnS_2 in saturated aqueous Na_2S solution or in an equivalent amount of Na_2S in water, respectively. Both precipitates, $\text{Sn}(\text{OH})_4$ and SnS_2 , were washed chloride-free with distilled water before the preparation process.

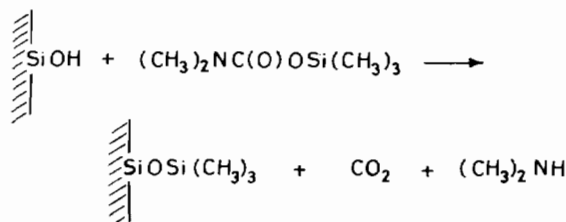
The dissolution of SnS_2 in saturated Na_2S solution resulted in quantitative formation of the stable SnS_3^{2-} species. The solution prepared by the interaction of stoichiometric amounts of SnS_2 and Na_2S underwent oxidative decomposition, catalysed by the surface of the carrier, resulting in the formation of hydrolysis products containing coordinated OH^- and S^{2-} ions and elemental sulphur.

Aqueous solutions of 1 mol dm^{-3} concentrations were used for the Mössbauer measurements. The compositions of the samples were checked through analytical determination of their tin content; for the sulphide compounds, the sulphur content too was determined.

For comparison, we also performed a Mössbauer study on a solid $\text{Na}_2\text{Sn}(\text{OH})_6$ sample.

To reduce the polarity and H-bonding ability of the silicate surface in the pores, the acidic OH groups on the surface were blocked by silylating the surface in the following way.

Before silylation, the thirsty glass carrier was dried by gradual heating (during 5 h) in vacuum to 200°C . It was kept at this temperature for 2 h, and then cooled to room temperature. A powerful silylating agent, *N,N*-dimethylcarbamic acid trimethylsilyl ester (DMCTMS [9]), was used, which reacts to form volatile by-products



The silylating reagent was added in vacuum to the dried sample (the glass body was covered by the reagent). After a reaction time of 30 min, the reagent excess and by-products were removed in vacuum. The treatment was completed by heating the sample at 120°C for one hour.

TABLE I. Mössbauer Parameters^a of Aqueous Solutions of Tin(IV) Compounds

Tin compound	Carrier surface	Trapped in thirsty glass						Frozen solution 80 K		
		293 K			80 K			IS	Γ	Intensity
		IS	Γ	Intensity	IS	Γ	Intensity			
$\text{Na}_2\text{Sn}(\text{OH})_6$	silicate	-0.06	1.36	0.025	0.00	1.42	0.197	-0.02	1.04	0.171
$\text{SnCl}_4(\text{OH}_2)_2$	silicate	-0.13	1.18	0.010	0.09	1.31	0.225	0.16	1.34	0.294
Na_2SnS_3 in saturated Na_2S	silicate	no absorption			1.25	1.20	0.2	1.26	1.26	0.3
Hydrolysis products of Na_2SnS_3	silicate	-0.22	1.26	0.2	0.18	0.99	0.2	1.28(QS 0.92)	0.3	
					1.29(QS 0.94)	0.4	0.4			
$\text{Na}_2\text{Sn}(\text{OH})_6$	silylated silicate	-0.08	1.14	0.0006	-0.01	1.03	0.020			
$\text{Na}_2\text{Sn}(\text{OH})_6$ crystalline		-0.01	1.34		0.06	1.82				

^a IS : isomer shift (mm s^{-1}) referred to SnO_2 ; reproducibility: $\pm 0.02 \text{ mm s}^{-1}$; Γ : line width (mm s^{-1}).

Results and Discussion

The results of the measurements are presented in Table I. Mössbauer parameters recorded at room temperature (formally in the liquid state of the aqueous solutions) and at liquid nitrogen temperature (solid state) for samples trapped in the pores of the carrier are compared with those measured for the same solutions after quenching by the quick-freezing technique used previously [10].

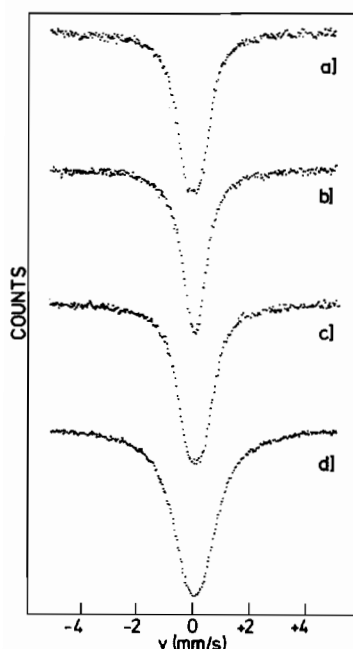


Fig. 1. Mössbauer spectra of $\text{Na}_2\text{Sn}(\text{OH})_6$: (a) 1 M aqueous solution, measured in thirsty glass at room temperature; (b) 1 M aqueous frozen solution measured at liquid nitrogen temperature; (c) 1 M aqueous solution, measured in thirsty glass at liquid nitrogen temperature; (d) solid (crystalline) $\text{Na}_2\text{Sn}(\text{OH})_6$, measured at liquid nitrogen temperature.

The Mössbauer spectra of the aqueous solutions of $\text{Na}_2\text{Sn}(\text{OH})_6$ (Fig. 1) and $\text{SnCl}_4(\text{OH}_2)_2$ exhibited only one line each. Comparison of the two IS values measured at liquid nitrogen temperature, *i.e.* that of the liquid trapped in the pores of the carrier and that of the material solidified by the quick-freezing technique, did not reveal any reflection at all of the effect of the carrier surface on the Mössbauer parameter for $\text{Na}_2\text{Sn}(\text{OH})_6$, and there was only a small surface effect (hardly larger than the experimental error) for $\text{SnCl}_4(\text{OH}_2)_2$. Thus, the room temperature spectra of the two systems trapped in the carrier reflected the structure and the electronic structure of the Mössbauer-active species in the bulk solution separated by water from the wall of the carrier.

The system containing SnS_2 dissolved in saturated aqueous Na_2S solution trapped in the porous glass carrier did not display recoilless γ -ray resonance

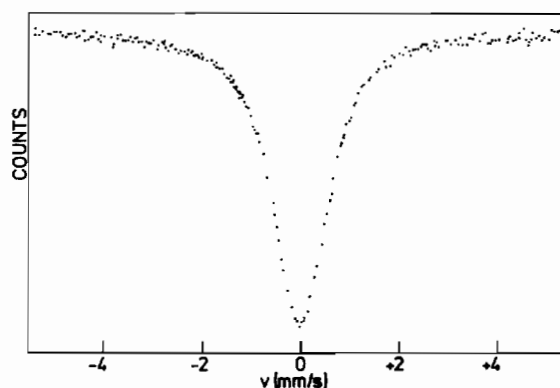


Fig. 2. Mössbauer spectrum of an aqueous solution of Na_2SnS_3 saturated with Na_2S trapped in thirsty glass, measured at liquid nitrogen temperature.

absorption at room temperature, but gave a single line in the Mössbauer spectrum at liquid nitrogen temperature (Fig. 2); this coincided with the line in the spectrum of the same solution after solidification by the quick-freezing technique [10]. Thus, the SnS_3^{2-} species are also situated in the bulk of the solution separated from the walls of the carrier by water, but the latter species do not give the Mössbauer effect at room temperature.

For the samples trapped in the carrier, the probability of recoilless γ -ray resonance absorption at room temperature decreased in the sequence $\text{Sn}(\text{OH})_6^{2-}$, $\text{SnCl}_4(\text{OH}_2)_2$ and SnS_3^{2-} (with disappearance of the Mössbauer effect for the latter sample). The fact that the H-bonding ability of these species decreased in the same sequence led us to conclude that mainly the H-bonded cluster structure of the aqueous solution is responsible for the appearance of the Mössbauer effect in a system trapped in the pores of the carrier.

In the Mössbauer spectrum of the sample solution prepared through the reaction of equivalent amounts of SnS_2 and Na_2S trapped in the thirsty glass carrier and recorded at liquid nitrogen temperature, one single (IS 0.18 mm s^{-1}) and one quadrupole split line appeared, the latter (IS 1.29 , QS 0.94 mm s^{-1}) practically coinciding with the quadrupole split line in the spectrum of the solution solidified by the quick-freezing technique [10] (Fig. 3). The IS value (0.18 mm s^{-1}) of the former line showed a much lower electron density at the tin nucleus than did that of the latter line. The ratio of the integral intensities of these two lines was 7:3. The spectrum recorded at room temperature for the solution trapped in the carrier exhibited a single line only, with an IS value of -0.22 mm s^{-1} .

It was demonstrated by independent analytical measurements that part of the sulphide content of the system was oxidized by dissolved oxygen to elemental sulphur, forming Na_2S_2 . This reaction led

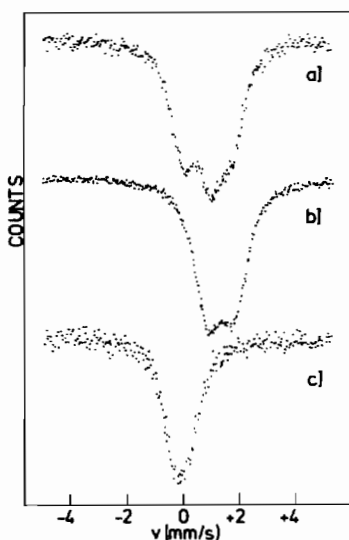


Fig. 3. Mössbauer spectra of the hydrolysis products of a 1 M aqueous solution of Na_2SnS_3 : (a) in thirsty glass, measured at liquid nitrogen temperature; (b) frozen solution, measured at liquid nitrogen temperature; (c) in thirsty glass, measured at room temperature.

to the hydrolysis products of SnS_3^{2-} containing coordinated OH^- ions besides coordinated S^{2-} ions. These species in the aqueous solution trapped in the pores of the carrier are situated partly (70%) in the bulk and partly (30%) on the surface of the pores in the carrier. At liquid nitrogen temperature, the former species give the quadrupole split line, indicating the electronic field gradient due to the asymmetry of the coordination sphere of tin containing sulphide and hydroxide. This quadrupole split line does not appear in the room temperature spectrum, however, indicating that the hydrolysis product of SnS_3^{2-} is not fixed strongly enough by the solution structure in the carrier to achieve recoilless γ -ray resonance absorption. The similarity of the IS value of the latter species (1.29 mm s^{-1}) to that of the parent compound SnS_3^{2-} (1.25 mm s^{-1}) indicates that S^{2-} is also the dominating ligand in the former system (S^{2-} has a much lower H-bonding ability than OH^- ; cf. for example the boiling points of H_2O and H_2S).

The single line (IS 0.18 mm s^{-1}) in the low temperature spectrum of the solution trapped in the carrier can be assigned to the species adsorbed on the silicate surface in the carrier. The surface effect caused a dramatic decrease in the IS (indicating a strong decrease in the electron density at the tin nucleus) and disappearance of the quadrupole splitting. A similar phenomenon was observed previously [7]. Naturally, the latter line appeared only in the spectra recorded for solutions trapped in the carrier.

To establish the influence of the polarity and H-bonding ability of the surface in the pores of the carrier on the appearance of the Mössbauer effect, we blocked the acidic OH groups on this surface by silylating them. In this way, the direct H-bonding connection between the carrier walls and the water cluster system was eliminated, or at least dramatically decreased. This led to a strong decrease in the probability of recoilless γ -ray resonance absorption (see Table I), indicating the importance of the connection between the solvated Mössbauer-active species and the rigid wall of the carrier through the H-bonded cluster structure of the solution for attainment of the Mössbauer effect in such systems.

The surprisingly great difference between the IS values of sulphide and hydroxide-containing tin(IV) complexes (1.2 versus 0.0 mm s^{-1}) reflects the π -acceptor ability of sulphide; this decreases the electron population in the shielding (p and d) orbitals of appropriate symmetry, resulting in an increased electron density at the site of the tin nucleus in its sulphide complexes.

Conclusions

These investigations seemed to prove the correctness of our earlier suggestion [3] that, to attain Mössbauer parameters for liquid aqueous solutions trapped in a suitable carrier which more or less reflect the structure of the original solution, the solvated Mössbauer-active solute must be separated by a water layer(s) from the wall of the carrier, but connected by H-bonds to the surrounding water molecules and through the water cluster to the water layer on the carrier surface.

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