Capillary Mössbauer Spectroscopy (CMS). The Study of Liquid Samples Trapped in the Pores of Thirsty Glass

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Introduction

Mössbauer spectroscopy is based on recoilless γ-ray resonance absorption which can be achieved only in cases when both source and absorber are incorporated tightly into a solid lattice. Thus Mössbauer spectroscopy is suitable for the study of solid samples only. Investigations of solutions could be performed in their frozen state [1].

Investigations of Turkevich and co-workers [2] have indicated that liquid solutions trapped in the capillaries of porous silicate glasses (*e.g.* Corning Vycor 'thirsty' glass) behave as if frozen at temperatures significantly higher than their freezing points.

This prompted the idea [3] to use porous glass plates as carriers in the study of liquids containing a Mössbauer active isotope to achieve the Mössbauer effect at temperatures higher than the freezing point of the liquid studied. The assumption was that in the liquid trapped in the pores of the glass, recoil of the Mössbauer compounds may be hindered. In an optimum case this may lead to the appearance of the Mössbauer effect, but naturally with lower intensity than in solid samples.

Experimental

For the Mössbauer measurements a sample holder of thin glass was prepared. It contained not only the porous glass carrier saturated with the liquid to be studied, but also a small excess of the liquid. In some experiments we also used sample holders made of thin rubber foil to decrease the γ-ray absorption which decreases the intensity of the Mössbauer lines.

To prevent (or to hinder as much as possible) the specific interactions of the internal surface of the capillary with the liquid containing the Mössbauer isotope which may lead to the formation of a solid layer on the glass surface, partners of low affinity towards each other had to be chosen. We used therefore in all experiments Corning Vycor 'thirsty' glass plates (No 7930) of pure silicate [4] (showing very low ionic exchange properties) as carrier with a mean pore diameter of 4 nm (*i.e.* mesopores) with homogenous size distribution of mainly cylindrical pores [5] and a void space of about 28% of its total volume.

The Mössbauer spectra have been recorded in absorption geometry using a 'Ranger Electronics' Mössbauer spectrometer in conjunction with a multichannel analyser. The Mössbauer sources were Co-57 in palladium and Sn-119 in $CaSnO_3$. The activity of both was 2×10^8 Bq. The linear combination of Lorentzian curves was used for the computer evaluation of the Mössbauer spectra. The isomer shift (IS) values of iron refer to α-iron, that of tin to SnO_2, both at room temperature.

The reagents used were of analytical purity. Tin tetraiodide has been prepared from Sn-119 isotope enriched tin, the iron(II)-dipyridil complex from Fe-57 isotope enriched iron. In the measurement of $SnCl_4$ and $FeSO_4$ compounds of natural isotope distributions were used.

Results and Discussion

Study of a Liquid Sample

Tin tetrachloride is a non-ionic tin(IV) complex which is a liquid at room temperature, and this served as our first model compound. The porous glass was saturated by the $SnCl_4$ liquid and the Mössbauer spectrum was recorded at room temperature (Fig. 1). The sample holder was immersed afterwards into liquid nitrogen, adapted to the cryostat, and the spectrum of the frozen sample was also recorded. This latter spectrum was compared with that of $SnCl_4$ solidified by our original rapid freezing technique [6].

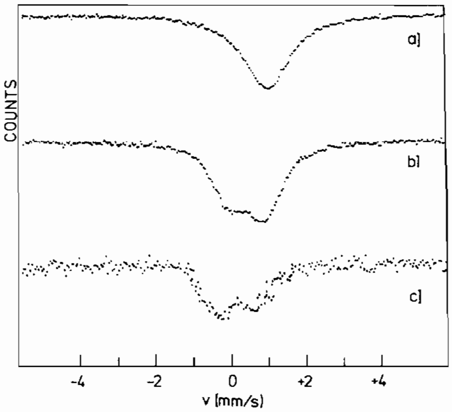

Fig. 1. The Mössbauer spectra of $SnCl_4$ samples: a) frozen and measured at 80 K; b) trapped in the pores of thirsty glass, measured at 80 K; c) trapped in the pores of thirsty glass, measured at room temperature.

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TABLE I. Mössbauer Parameters (mm/s) of the Systems Studied.

Sample	Trapped in thirsty glass						Frozen solution 80 K			Solid crystal 293 K	
	293 K			80 K							
	IS[a]	QS[b]	Γ_η[c]	IS[a]	QS[b]	Γ_η[c]	IS[a]	QS[b]	Γ_η[c]	IS[a]	QS[b]
$SnCl_4$	0.72	0	0.029	0.82	0	0.15	0.80	0	0.297		
	−0.20	0	0.023	−0.02	0	0.11					
SnI_4 in CCl_4	−0.04	0	0.011	0.13	0	0.138	1.60	0	0.087		
SnI_4 in DMF + CCl_4	−0.10	0	0.015	0.00	0	0.149	0.76	0	0.063		
SnI_4 in C_2H_5OH + CCl_4	−0.11	0	0.036	0.02	0	0.251					
$Fe(dip)_3^{2+}$ in H_2O	0.30	0.30	0.002	0.35	0.33	0.021	0.35	0.34	0.022	0.28	0.31
$Fe(H_2O)_6^{2+}$ in H_2O	1.25	3.17									
$FeSO_4 \cdot 7H_2O$ crystals										1.25	3.20
$FeSO_4 \cdot H_2O$ crystals										1.23	2.70
$FeSO_4$										1.31	2.94

[a] IS = isomer shift referred to SnO_2 and α-iron, respectively, reproducibility ±0.01 mm/s. [b] QS = quadrupole splitting. [c] Γ_η = integral intensity.

Frozen $SnCl_4$, having an electronic shell of spherical symmetry, shows a single line in the Mössbauer spectra. $SnCl_4$ in the pores of our glass carrier at room temperature (and at the temperature of liquid nitrogen) showed however two Mössbauer lines, one of them coinciding with the single line of frozen $SnCl_4$, the other indicating a lower electron density at the tin nucleus (Table I). The different intensities and temperature dependences of the two lines indicate the presence of two types of tin in the sample. One of them (higher IS value) can be assigned to the parent $SnCl_4$, the other to that on the glass surface in the pores.

The adsorption of $SnCl_4$ on the internal surface of the capillaries could be a simple explanation for the appearance of the second line. However physical adsorption alone does not seem to have an effect strong enough to cause as dramatic an decrease in the electron density at the nucleus of the tin central atom as that indicated by the IS difference of the two lines. This difference may be due either to the decreased *s* contribution in the tin orbitals or to the increased contribution of shielding *p* and *d* orbitals. The former explanation would suggest the formation of ionic Sn^{4+} species *i.e.* the substitution of the rather covalently bound chloride ligands by silicate oxygens, the latter coordination of these oxygens on the fifth and sixth coordination site of $SnCl_4$, resulting in a tetrahedral → pseudo octahedral transformation.

We do not yet have enough evidence to choose between these possibilities, but the latter explanation seems more convincing. The substitution of chlorides by silicate oxygens of the glass surface (a heterogenous reaction—considering also the higher affinity of chloride to Sn(IV) than that of most oxygen donor ligands) seems less likely. The coordination of silicate oxygens to the fifth and sixth coordination site of tin(IV) analogously to the well-known solvation reactions of tin(IV) halides by donor solvents resulting also in decreased IS values seem to be the reason of the change in the IS of tin(IV) in the glass carrier.

According to this explanation the ratio of the two types on $SnCl_4$ (adsorbed on the glass surface and bulk $SnCl_4$) is determined by the pore size of the glass and by the space requirement of the molecules in the pores. Since the pore size could not be easily changed the investigation has to be repeated with a model system of higher space requirement to prove or disprove the explanation given above. The symmetry and electronic structure of tin(IV) halides is analogous, their size increases however because of the increase of ionic radii of halides in the order $Cl^- < Br^- < I^-$. $SnBr_4$ and SnI_4 are solid at room temperature. Their solutions in CCl_4 seem to be suitable models in these investigations.

Study of Liquid Solutions

The appearance of the Mössbauer effect in the liquid $SnCl_4$ samples trapped in the pores of the thirsty glass carrier indicated the possibility of the application of this method for the study of liquid solutions containing Mössbauer active compounds as solutes.

Tin(IV) Iodide Solutions

SnI_4 dissolved in CCl_4 (a solvent of low polarity dissolving SnI_4 in undissociated form) served as our model for the study of the effect of the size of the Mössbauer active molecule on the Mössbauer spectra recorded in the glass carrier.

First, the amount of liquid taken up by the carrier glass in the course of the saturation process was determined. We have found that the glass plate absorbed from the liquid 25% of its own volume. The amount of solute in the pores of the carrier saturated by the solution was determined experimentally and also calculated from the concentration of the model solution and its amount in the glass. A satisfactory agreement between the measured and calculated values indicated that neither solute nor solvent was enriched in the capillaries. The whole process proved to be reversible: the solute could be washed out completely from the glass carrier.

SnI_4 is known to coordinate donor molecules (*e.g.* donor solvents) on its fifth and sixth coordination site. To compare the effect of such coordination with that of the interaction with the glass surface, the Mössbauer parameters of 0.01 *M* SnI_4 solutions in pure carbon tetrachloride, in 1 *M* ethanol containing CCl_4 and in 1 *M* dimethylformamide containing CCl_4 measured in the glass carrier have been compared (Fig. 2 and Table I). According to our previous investigations [6, 7] this ethanol and DMF concentration, respectively, assures the quantitative formation of the solvated SnI_4 containing two solvent molecules in its coordination sphere, without increasing the relative permittivity of the system to such an extent which would cause the dissociation of iodie ions from the coordination sphere. For comparison the Mössbauer parameters recorded in samples prepared according to our original rapid freezing technique are also given in the Table.

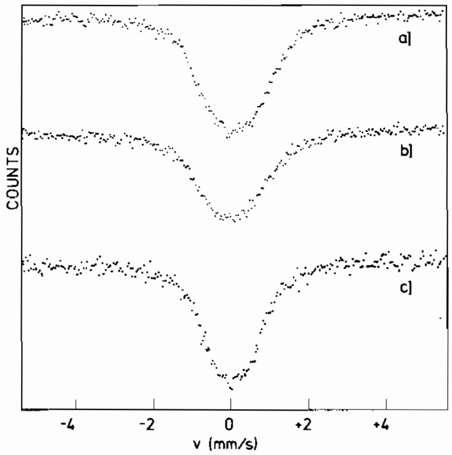

Fig. 2. The Mössbauer spectra of SnI_4 solutions trapped in the pores of thirsty glass, measured at room temperature: a) solvent: carbon tetrachloride; b) solvent: 1 *M* ethanol in CCl_4; c) solvent: 1 *M* dimethylformamide in CCl_4.

The SnI_4 solutions trapped in the pores of the glass have only one single line in the Mössbauer spectra, with a surprisingly low IS value. This seems to indicate that this line belongs to SnI_4 on the surface of the glass. The size of the molecule is large enough to occupy the pores completely, not leaving any space for free SnI_4 species.

This assignment is supported by the low (or no) solvent dependence of the IS of SnI_4 in the glass. The differences between the isomer shifts measured in pure CCl_4 and in its donor solvent containing mixtures are similar in size to the experimental error. The freezing of the solution in the pores of the glass carrier resulted in the expected temperature shift and in the increase of the Debye-Waller factor of the system. The solvent dependence did not change.

The coordination of a donor solvent by SnI_4 normally decreases the electron density at the place of the tin nucleus (reflected in a decrease of the isomer shift) due to the increased population in the shielding 5 *pd* orbitals. This effect did not appear in the thirsty glass since the isomer shift of SnI_4 was much lower even in CCl_4 than could be expected for in its strongly solvated form. This proved that the interaction of the SnI_4 solute with the internal surface of the pores was much stronger than that with the solvent in the pores. The space in the pores of thirsty glass are not large enough to house SnI_4 in its solvated form.

Iron(II) Solutions

To use thirsty glass as a neutral carrier not interacting with the solution, and in this way to get Mössbauer data referring to the species in the original solutions, model systems containing Mössbauer active solutes of small size have to be used in such a stable solvate or coordinate sphere which prevents its interaction with the glass surface. High spin iron(II) hexaaquo complexes and low spin tris(2,2′-dipyridil)iron(II) complexes have been used as model systems for these investigations (Fig. 3).

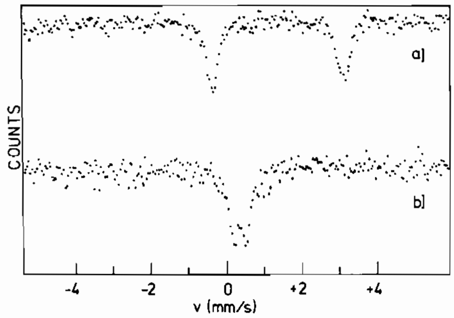

Fig. 3. The Mössbauer spectra of the aqueous iron(II) solutions trapped in the pores of the glass carrier: a) 0.5 *M* $FeSO_4$ solution; b) 0.01 *M* tris(2,2′-bipyridil)iron(II) solution.

The 0.5 *M* aqueous solution of iron(II) sulphate served as a model for the $Fe(H_2O)_6^{2+}$ measurements in the thirsty glass performed at room temperature. For comparison the Mössbauer parameters of $FeSO_4 \cdot 7H_2O$ crystals containing iron(II) in its hexaaquo complex have been determined at the same temperature (Table I). The isomer shift and quadrupole splitting values of the aqueous iron(II) sulphate solution trapped in the pores of the glass carrier agreed, within the experimental error, with that measured in the $FeSO_4 \cdot 7H_2O$ crystal, but differed from other solid iron(II) sulphates.

The Mössbauer spectra of the aqueous solution of the 0.01 *M* tris(2,2'-dipyridil)iron(II) complex recorded at room temperature in the glass carrier, in its frozen original solution, and in its frozen solution in the glass showed similar pictures (Fig. 4). The Mössbauer parameters measured at liquid nitrogen temperature in the original solution and in that trapped in the glass have been found to be completely identical. The data measured at room temperature in the glass reflected the expected temperature shift only. Thus the effect of the interaction between the glass surface in the pores and the Mössbauer active solute proved to be negligible in the latter two systems.

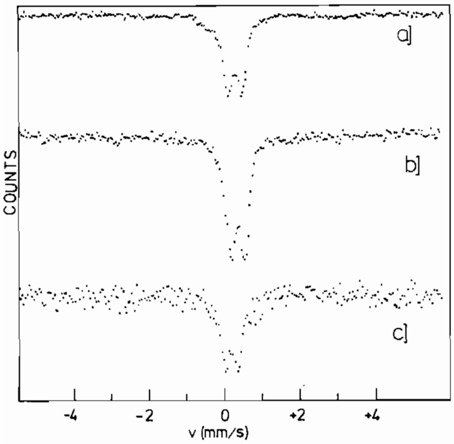

Fig. 4. The Mössbauer spectra of the aqueous solution of tris-(2,2'-bipyridil)iron(II), (0.01 *M*): a) frozen and measured at 80 K; b) trapped in the pores of thirsty glass, measured at 80 K; c) trapped in the pores of thirsty glass, measured at room temperature.

Conclusions

Recoilless γ-ray resonance absorption has been achieved in liquid samples (in liquid $SnCl_4$ and in solutions of SnI_4, $FeSO_4$ and tris(2,2'-dipyridil)iron(II)) trapped in the pores of a Corning Vycor thirsty glass carrier.

In the case of solutes of suitable size and closed coordination sphere (hexaaquo iron(II) and tris(2,2'-dipyridil)iron(II) complexes in aqueous solution) the Mössbauer spectra reflected the electronic structure of the Mössbauer active solute in the original liquid solution.

In the tin tetrahalide systems interaction with the glass surface in the pores of the carrier resulted in a significant decrease in the IS values due to the coordination of silicate oxygens of the glass on the fifth and sixth coordination site of tin, resulting in a tetrahedral → pseudo octahedral transformation. In the Mössbauer spectrum of $SnCl_4$ in the glass carrier a line characteristic for bulk $SnCl_4$ has been recorded beside the line of the species on the glass surface. In the spectrum of SnI_4 only the line belonging to the species on the glass surface could be seen. The larger size of SnI_4 prevented the presence of different species in the 4 nm pores of the glass carrier.

On the bases of these experiments Capillary Mössbauer Spectroscopy (CMS) seems to be a promising method for structural studies of liquid samples. The pore size of the carrier and the possibility of interactions with the glass surface may limit, however, its practical application. The study of further liquid systems by CMS is in progress.

References

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