Inorganica Chimica Acta, 100 (1985) 17–21

Mössbauer Spectroscopy of Tin Tetrachloride Solutions Trapped in the Pores of a 'Thirsty Glass' Carrier

K. BURGER

Department of Inorganic and Analytical Chemistry, A. József University, P.O. Box 440, H-6701 Szeged, Hungary

A. VÉRTES, M. SUBA

Laboratory of Nuclear Chemistry, L. Eötvös University, Budapest, Hungary

and I. DÉKÁNY

Department of Colloid Chemistry, A. József University, P.O. Box 440, H-6701 Szeged, Hungary

Received October 16, 1984

Abstract

The Mössbauer effect was achieved in liquid tin tetrachloride solutions trapped in the pores of a Corning Vycor 'thirsty glass' carrier at room temperature. It was shown that in aqueous solutions the $SnCl_4$ solute was not in direct contact with the glass surface in the carrier. The effect of the surface on the isomer shift value was hardly greater than the experimental error. Tin tetrachloride dissolved in DMSO showed a similar behaviour.

Introduction

It has been shown in our previous papers [1–3] that a recoil-less γ-ray resonance absorption (the Mössbauer effect) can be achieved in liquid samples trapped in the pores of a silicate glass carrier made of Corning Vycor 'thirsty glass'. The technique based on this recognition was called Capillary Mössbauer Spectroscopy (CMS). Liquid compounds and liquid solutions containing Mössbauer active isotopes served as model systems. The Mössbauer spectra reflected three types of behaviour depending on the properties of the models used.

(a) The Mössbauer active compound was adsorbed on the surface of the pores in the glass carrier. The Mössbauer spectrum showed only the presence of one type of species in strong interaction with the surface. In the case of $Fe(CO)_5$ *e.g.* the 2.52 mm/s quadrupole splitting value measured in the frozen liquid decreased to 0.79 mm/s due to this surface effect when measuring the $Fe(CO)_5$ liquid trapped in the pores of the carrier [3].

(b) The Mössbauer spectrum indicated the presence of two types of species, one adsorbed on the glass surface the other situated in the bulk. The Mössbauer parameters of the latter differed only by the temperature shift from those measured in frozen state. Tin(IV) chloride – a liquid at room temperature – showed this behaviour [2].

(c) In aqueous solutions the solvent covered the surface of the pores in the carrier, the Mössbauer spectra indicated the presence of only one type of species in the solution [1]. The Mössbauer parameters of a 0.5 mol dm^{-3} $FeSO_4$ solution trapped in the pores of the carrier were found to be identical with those of $FeSO_4 \cdot 7H_2O$ crystals at room temperature. (It is known that both aqueous $FeSO_4$ solution and $FeSO_4 \cdot 7H_2O$ crystals contain iron in the form of $Fe(H_2O)_6^{2+}$ species.) Thus, the Mössbauer data did not indicate any interaction between iron and the glass surface.

It is evident that Mössbauer active liquid compounds fixed by adsorption on the glass surface can undergo a recoil-less γ-ray resonance absorption because of the strong interaction with the surface, which is also reflected by dramatic changes in the Mössbauer parameters. The question, however, remained what made the recoil-less γ-ray resonance absorption possible for species which are not in direct contact and interaction with the solid surface in the carrier.

To answer the latter question a model calculation was performed [3] assuming that in the pores of the carrier (average pore size 4 nm) the recoil is hindered by the lack of space and by the rigidity of the walls of the pores. In this calculation no chemical or physical interactions between the Mössbauer active molecule and the carrier were taken into consideration. Since we could get Mössbauer parameters apparently free of the surface effect in aqueous solutions, and because of the well-known hydrogen bonded cluster structure [4] of such solutions, an interaction through

0020-1693/85/$3.30

TABLE I. Mössbauer Parameters of the $SnCl_4$ Solutions.

Composition of the solution[a]			Trapped in thirsty glass						Frozen solution		
$SnCl_4$ mol dm^{-3}	Reagent	mol dm^{-3}	293 K			80 K			80 K		
			IS[b] mm s^{-1}	Line width	Intensity	IS[b] mm s^{-1}	Line width	Intensity	IS[b] mm s^{-1}	Line width	Intensity
1.0	–	–	−0.13	1.18	0.00956	0.09	1.31	0.2249	0.16	1.34	0.2937
3.0	–	–	−0.02	1.22	0.00671	0.20	1.44	0.0911	0.24	1.54	0.3192
1.0	NaCl	4.0	+0.02	1.18	0.00460	0.22	1.24	0.2574	0.32	1.17	0.2277
1.0	NaF	0.77	−0.15	1.12	0.01347	0.04	1.34	0.3247	0.12	1.37	0.3041
1.0	NaOH	0.1	−0.09	1.18	0.00536	0.11	1.33	0.3188	0.15	1.43	0.3779
1.0	NaOH	3.0	−0.02	1.50	0.00675	0.04	1.20	0.3721	0.06	1.35	0.2970
1.0	HCl	30%	No absorption			0.49	0.96	0.1566	0.43	1.25	0.2943
3.0	HCl	30%	No absorption			0.50	1.18	0.2468	0.49	1.24	0.2409
1.0	HNO_3	30%	No absorption			0.26	1.14	0.1394	0.29	1.20	0.2977
1.0 in DMSO			−0.12	1.50	0.00374	0.19	1.24	0.2067	0.30	1.12	0.2290

[a] Solvent water, except the last system. [b] Referred to SnO_2. Reproducibility ± 0.02.

H-bridges between the water layer adsorbed on the glass surface and the water bound in the solvated species in the bulk can hardly be completely neglected [5].

For study of the latter interaction a series of Mössbauer measurements were performed using the aqueous solutions of tin(IV) chloride ($SnCl_4$) as models. In this system both solute and solvent are liquids at room temperature. For comparison the analogous investigation of $SnCl_4$ dissolved in DMSO was also performed.

In order to get independent informations on the interactions between the model solutions and the glass surface in the pores of the carrier a series of immersion wetting enthalpy measurements were made with the 'thirsty glass' samples.

The results are presented and discussed in the following.

Experimental

The Mössbauer measurements were made according to the methods given in our earlier paper on Capillary Mössbauer Spectroscopy [2]. The isomer shift values refer to SnO_2 at room temperature.

The porous glass carrier was made of Corning Vycor thirsty glass plates (No 7930) of 4.45 mm thickness with an average pore diameter of 4 nm (*i.e.* mesopores) and of homogeneous size distribution of mainly cylindrical pores [6], with a void space of about 28% of its total volume. This glass is made of pure silicate with no ion exchange properties.

The porous glass carrier after drying before each measurement *in vacuo* was immersed in the liquid to be investigated and kept there for a week to ensure complete saturation. The time needed for saturation was determined by independent measurements recording the weight increase and the tin content of the samples as a function of time. The amount of tin in the pores of the carrier was determined experimentally and also calculated from the concentration of the solution used and the weight increase of the sample. A satisfactory agreement between the measured and calculated values indicated that tin was not enriched in the capillaries.

The glass carrier saturated by the liquid to be investigated was covered by a thin layer of this liquid also in the sample holder during the measurements to prevent any deposition on the outer surface.

After recording the Mössbauer spectrum of the sample at room temperature, the carrier was immersed into liquid nitrogen, adapted to the cryostat and the Mössbauer spectrum of the frozen liquid in the carrier was also recorded. This latter spectrum compared with that of the same liquid solidified by the rapid freezing technique used in our earlier studies [7] gave us the most straightforward information on the effect of the glass carrier on the Mössbauer parameters, *i.e.* on the interaction between the Mössbauer active compound and the glass surface in the pores of the carrier. The Mössbauer parameters are presented in Table I. Characteristic spectra are shown in Fig. 1.

The immersion wetting enthalpy measurements were performed on an LKB Sorption Microcalorimeter Type 2107. The thirsty glass samples were dried at 120 °C at 10^{-2} mbar pressure for 24 hours before the measurements. In the course of the calorimetric measurements 50–80 mg of this glass was brought into immersion contact with 0.7 cm^3 of the investigated solution. The results are presented in Table II.

TABLE II. Immersion Wetting Enthalpy Values[a] of Thirsty Glass in $SnCl_4$ Solution (J g^{-1}).

$SnCl_4$ concentration mol dm^{-3}	Solvent		
	Water	20%HCl in water	Dimethylsulphoxide
0.125	–	–	35.9
0.25	–	34.8	35.9
0.5	34.8	35.7	34.4
1.0	–	33.8	35.8
1.5	34.7		
3.0	34.4		
Concentrated LiCl	26.4		

[a] Reproducibility: ±5%.

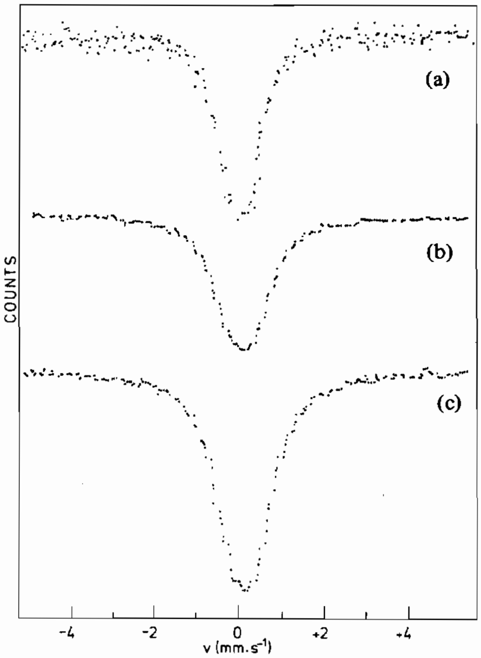

Fig. 1. The Mössbauer spectra of an aqueous $SnCl_4$ solution of 1.0 mol dm^{-3} concentration containing 0.77 mol dm^{-3} NaF: (a) trapped in the thirsty glass carrier, measured at room temperature, (b) trapped in the carrier, measured at liquid nitrogen temperature, (c) frozen solution at liquid nitrogen temperature.

Tin tetrachloride and all the other reagents used were of analytical purity.

Results and Discussion

Comparing the two isomer shift (IS) values measured for each system at liquid nitrogen temperature, *i.e.* that of the liquid trapped in the pores of the carrier and of that solidified by our previously used rapid freezing technique [7], the IS values of the liquid in the glass carrier were found to be lower than the other ones. The differences between the two corresponding IS values (0.04–0.10 mm/s) were hardly greater than the experimental error (±0.02 mm/s), but they do reflect a weak interaction between the glass surface and tin(IV) in the solute. Since the direct contact between $SnCl_4$ and the glass surface caused a much bigger difference (0.82 mm/s), as was shown in our previous paper [2], the data measured for aqueous solution clearly indicate that the solute is linked only by weak forces (*e.g.* through bridges of H-bonded water molecules) to the glass surface.

It is known from solution structure investigations [4, 5, 8] that in aqueous solution the hydrated species are bound by hydrogen bonds to the neighbouring water molecules which are connected by similar bonds to the bulk water consisting of H-bonded associations of water molecules. This cluster type structure is in dynamic motion and transformation with the cleavage of some H-bonds and the formation of others. The solute in such solutions is fixed in its near surroundings. The small IS value difference (0.04–0.10 mm/s) discussed above reflects naturally not the overall strength of this interaction, only the small increase due to the effect of the wall in the small pores of the carrier.

In the knowledge that the oxygen atom of water favours hydrogen ions to the protons of the neighbouring water molecules and therefore in aqueous solutions of strong acids the H-bonded cluster structure of water is partially or completely destroyed [4], the Mössbauer investigation of acid free, hydrochloric and nitric acid containing aqueous $SnCl_4$ solutions, respectively, was performed. The Mössbauer effect appeared at room temperature in the case of the acid free solutions only. When the glass carrier was saturated with hydrochloric or nitric acid containing $SnCl_4$ solutions, at room temperature no recoil-less γ-ray resonance absorption could be achieved. Solidifying the latter samples by freezing them resulted in the appearance of the Mössbauer effect.

These experiments showed that the H-bonded structure of the aqueous solution is needed for achieving the Mössbauer effect in the liquid trapped in the pores of our glass carrier at room temperature. The mobile H_3O^+ species formed in the interaction of acidic protons with water molecules take over the recoil energy preventing the recoil-less γ-ray resonance absorption.

Since the structure of aqueous solutions is concentration-dependent, the Mössbauer measurement performed first on $SnCl_4$ solutions of 1 mol dm^{-3} concentration has been repeated using solutions of 3 mol dm^{-3} concentration. This change caused only slight changes in the probability of recoil-less γ-ray absorption (in the Debye–Walker factor). Surprisingly, the isomer shift values measured for the frozen solution, however, increased with increasing $SnCl_4$ concentration. The addition of chloride ions (hydrochloric acid or sodium chloride) resulted in even greater IS increase and the solutions containing a great chloride excess (measurements in concentrated hydrochloric acid) did not show the $SnCl_4$ concentration-dependence of the IS values.

On the basis of these results one may assume that the $SnCl_4$ concentration-dependence of the Mössbauer parameters in the frozen solutions is due to the change of n in the $SnCl_n(H_2O)_{6-n}$ complex species present in the aqueous solutions. The increase in the half width of the Mössbauer lines with increasing $SnCl_4$ concentration supports the above idea.

Since the H-bonded connections between bulk and surface-bound water molecules depend on the strength of the interaction between the glass surface and the adsorbed water layer on it, the wetting enthalpy on the glass surface in the pores of the carrier was determined by microcalorimetric measurements with aqueous and hydrochloric acid containing aqueous $SnCl_4$ solutions and, for comparison, with saturated lithium chloride (at 25.0 °C) solution.

The immersion wetting enthalpy data measured for both type of $SnCl_4$ solutions did not show a significant concentration-dependence (Table II) indicating that the $SnCl_4$ solutions contained enough 'free' water to cover the surface in the pores of the glass carrier. The similar behaviour of the acid-free and hydrochloric and acid-containing solutions showed that the disappearance of the Mössbauer effect in the acidic solutions is not accompanied by changes on the surface in the pores of the glass carrier. The wetting enthalpy data measured with saturated lithium chloride solutions were found to be significantly lower than those in the $SnCl_4$ systems, indicating in the former case competition of the solute with the glass surface for the water molecules.

The immersion wetting enthalpy values (Table II) proved to be small ($\sim$30–40 J g^{-1}) compared to that of zeolites (250–300 J g^{-1}), indicating the lower polarity of the glass surface in our carrier in good agreement with the negligibly low ionic exchange properties determined previously [2]. This is probably the reason why the change caused by the effect of the surface in the IS values measured for aqueous solutions trapped in the glass pores was hardly greater than the experimental error, so the Mössbauer parameters may be used to get information on the original solution.

In order to study the effect of mixed ligand complex formation or ligand substitution on the Mössbauer parameters recorded in the liquid trapped in the pores of the glass carrier, $SnCl_4$ solutions containing sodium fluoride and sodium hydroxide, respectively, have been investigated. The solubility of sodium fluoride in the $SnCl_4$ solutions limited its concentration to 0.77 mol dm^{-3}. This is less than 20% of the total chloride content of the solution. The Mössbauer parameters did not reflect significant changes due to the presence of fluoride under such circumstances. The effect of a 0.1 mol dm^{-3} sodium hydroxide concentration in 1.0 mol dm^{-3} $SnCl_4$ was similarly negligible. The Mössbauer parameters recorded for solutions containing 3.0 mol dm^{-3} sodium hydroxide, however, reflected the effect of the formation of mixed chloro–hydroxo complexes. The IS values of the frozen solutions (of both types) showed a small but significant decrease in the electron density on the tin nucleus due to the increased population in the shielding orbitals of tin caused by its increased coordination number in the mixed complex. According to these measurements the effect of the glass surface in the pores of the carrier on the Mössbauer parameters proved to be smaller than the experimental error of this system.

To get information on the effect of the solvent in the investigated system the analogous Mössbauer and microcalorimetric study has been performed for solutions using dimethylsulphoxide (DMSO) as solvent. DMSO is a strong donor (DN* = 29.8) of medium polarity (ϵ** = 48.9).

The isomer shift value measured in DMSO at room temperature was equal (within the experimental error) to that recorded for the aqueous solution. Only the significant increase of the line width and decrease in the line intensity indicated the difference between the two systems. The low temperature IS values showed a somewhat larger surface effect in

---

*Guttmann's donicity [9].

**Relative permittivity.

DMSO than in water. This difference is, however, negligibly small.

The microcalorimetric measurements reflected a similar picture. The wetting enthalpies of the aqueous and dimethylsulphoxide solutions proved to have similar values and showed no significant concentration dependence.

On the basis of both type of mesurements one may conclude that DMSO behaves similarly to water, covering the glass surface in the pores of our carrier and separating the solvated $SnCl_4$ from the surface. The Mössbauer parameters recorded for the liquid trapped in the carrier reflect more or less the structure of the original solution. Because of the two donor atoms (O and S), polarity and size of DMSO, solutions made with this solvent have an ordered structure [8] which seems to support the appearance of the Mössbauer effect in our system.

References

1 K. Burger and A. Vértes, *Nature (London), 306,* 353 (1983).

2 K. Burger, A. Vértes and I. Zay, *Inorg. Chim. Acta, 76,* L247 (1983).

3 A. Vértes, K. Burger, L. Takács and I. Horváth, *J. Radioanal. Nucl. Chem. Lett., 86,* 195 (1984).

4 R. A. Horne, 'Water and Aqueous Solutions', Wiley–Interscience, New York, 1972.

5 I. M. Strauss and M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 1, 74,* 2146, 2518 (1978).

6 W. Espe, 'Materials of High Vacuum Technology', Pergamon, Oxford, 1968, p. 414.

7 A. Vértes, L. Korecz and K. Burger, 'Mössbauer Spectroscopy', Elsevier, Amsterdam, New York, 1979, p. 230.

8 K. Burger, 'Solvation, Ionic and Complex Formation Reactions in Non-Aqueous Solvents', Elsevier, Amsterdam, New York, 1983.

9 Gutmann, 'Coordination Chemistry in Non-Aqueous Solutions', Springer, Vienna, New York, 1968.