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ORIGINAL CONTRIBUTION

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Mössbauer study of the structure of liquid nanophases trapped in porous silicate and solid microemulsion matrix

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Abstract Mössbauer spectra of liquid solutions fixed as submicroscopic (nanosize) droplets in solid carriers were taken at room temperature and 77 K. A porous silicate ("thirsty glass") and microemulsions prepared with a paraffin/naphthalene mixture as dispersion medium served as carriers. Solutions of Mössbauer-active tin(IV) and iron(II) complexes were incorporated in these carriers as nanosize droplets. The Mössbauer effect was observed at temperatures above the freezing point of the solutions. For comparison, the systems were also studied in frozen state.

Depending on the nature of the system (carrier–solute–solvent) the presence of three types of species was shown in the droplets on the basis of the Mössbauer parameters: (a) situated in bulk position with no interaction with the walls; (b) adsorbed on the internal surface of the holes in the carrier and (c) in bulk position, but with Mössbauer parameters reflecting the influence of the carrier. In some cases surface-bound and bulk species were present together in the sample.

The appearance of the Mössbauer effect in liquid state reveals that the Mössbauer-active atoms are fixed in the nanosize pores by a network of hydrogen bonds which form between the solvent molecules, between solvent and solute molecules and between the solvent molecules and the walls of the pores in the carrier. The main parameters determining the rigidity of the network and the situation of the probe molecules are the hydrogen-bonding ability and the polarity of the components of the system.

On the basis of the above observations, a new procedure was elaborated for the Mössbauer study of solutions fixed as nanosize droplets in rigid carriers. The analysis of the Mössbauer parameters gives a qualitative picture regarding the solution structure in the interior of the pores, and the adsorption and wetting properties of the system.

Key words Liquid/solid interfaces – solution structure – in microemulsions

Introduction

Since the majority of chemical reactions and all life processes proceed in liquid solutions, techniques have been devised for the use of Mössbauer spectroscopy for the study of such systems. Recoilless γ-ray absorption was achieved in such media by quenching the liquids to be studied through quick freezing [1]. It was assumed that if a high freezing rate is used, resulting in the formation of a glass-like amorphous ice, the immediate surrounding of the Mössbauer-active solute in the frozen solution can be considered to be identical, or at least very similar, to that in the original liquid system [2]. Unfortunately, this assumption can only be valid in kinetically inert systems. Chemically labile equilibria may shift due to the temperature decrease during the quenching process, resulting in a change in the composition of the solution.

To achieve recoilless γ-ray absorption at temperatures above the freezing point of the solutions studied, we fixed them as nanosize droplets in suitable solid carriers [3–9]. Care has been taken to avoid systems which contain labile equilibria. We have compared the Mössbauer parameters recorded for solutions trapped in the pores of the carriers with those of the same solutions quenched by quick freezing at liquid nitrogen temperature. The presence or absence of the wall effect of the carrier in the spectra appears to be a suitable parameter to characterize the solid/liquid interactions at the inner pore surface in a direct way.

Experimental

To study solutions fixed as nanosize droplets the following model carriers were chosen:

a) Porous silicate carrier made of Corning Vycor "thirsty glass" plates (No. 7930) with average pore diameter of 4 nm and with a homogeneous size distribution of mainly cylindrical pores [3–6]. This type of carrier is characterized by strong hydrogen bonding ability and highly polar nature.

b) Rigid organic microemulsions prepared with hexadecylpyridinium chloride (HDPCl) cationic surfactant and *n*-pentanol as co-surfactant or HDPCl/Span 60 (cationic/nonionic) surfactant mixture and *n*-pentanol co-surfactant [7,8]. These carriers have hydrogen-bonding inner pore surfaces of low polarity.

c) Rigid organic microemulsions prepared with anionic surfactant Aerosol-OT and without a co-surfactant [9]. This carrier has no or low hydrogen bonding surface of low polarity.

The microemulsions were prepared as described previously [10–12]. Solutions of tin(IV) or iron(II) complexes were incorporated in the solid dispersion medium consisting of a mixture of paraffin in naphthalene. The microemulsions were prepared at 75 °C, subsequently cooled in liquid nitrogen, and then left to equilibrate at room temperature. At room temperature the liquid droplets are incorporated into the solid organic medium.

Aqueous solutions of $SnCl_4$, $Na_2Sn(OH)_6$, Na_2SnS_3 and $FeSO_4$, methanolic solutions of $SnCl_4$ and iron(II)-chloride–ascorbic acid, and $SnCl_4$ dissolved in ethylene glycol were used as Mössbauer-active solutions. The Mössbauer spectra of the different solutions were measured both in the quick-frozen state and incorporated in the nanosize cavities of either thirsty glass or rigid organic microemulsion. For comparison, spectra of solid Fe(II)-sulphate crystals and quick-frozen anhydrous liquid $SnCl_4$ have also been measured.

For the Mössbauer measurements, a sample holder of thin glass was prepared. It contained the carrier with nanosize holes saturated with the solution of Mössbauer-active system to be studied.

The Mössbauer spectra have been recorded in absorption geometry using a "Ranger Electronics" Mössbauer spectrometer in conjunction with a multichannel analyzer [4,8]. 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 reproducibility of the IS and QS are ± 0.02 and ± 0.04 mm/s for crystalline and frozen samples, respectively, while the same values for measurements at 293 K are ± 0.03 and ± 0.06 mm/s.

Comparison of room temperature and liquid nitrogen temperature measurements in the carrier with those of solutions quenched by quick-freezing were carried out to achieve a distinction between surface bound and bulk species in the system.

Results and discussion

The Mössbauer parameters of the Fe(II) and Sn(IV) model solutions in the thirsty glass carrier are given in Tables 1 and 2. For the aqueous iron(II) solution trapped in the carrier (Table 1) the IS (isomer shift) and QS (quadrupole splitting) values are characteristic of fully hydrated $Fe(H_2O)_6^{2+}$ species present also in crystalline $FeSO_4 \cdot 7H_2O$. Decreasing the extent of hydration from $FeSO_4 \cdot 7H_2O$ to anhydrous $FeSO_4$ leads to variation of both IS and QS values. The methanolic solution of Fe(II)-chloride–ascorbate did not show recoilless γ-ray resonance absorption in the thirsty glass carrier at room temperature, but cooling to the temperature of liquid nitrogen led to spectra characteristic of the bulk species in the frozen state.

The appearance of only one, bulk-type solute species in both cases means that the hydrophilic silicate surface is solvated both with water and methanol and the solute is separated from the surface by solvent layers so that the pore surface has no effect on the electronic structure and the Mössbauer parameters of the iron nuclei (Fig. 1A). The

Table 1 Mössbauer spectra of Fe(II) species fixed in thirsty glass carrier

Species	State and temperature	IS [mm s^{-1}]	QS [mm s^{-1}]	Position
$FeSO_4 \cdot 7H_2O$	Crystalline, 293 K	1.25	3.20	
$FeSO_4 \cdot H_2O$	Crystalline, 293 K	1.23	2.70	
$FeSO_4$	Crystalline, 293 K	1.31	2.94	
$FeSO_4$	Aq. solution	1.25	3.17	Bulk
	Thirsty glass, 293 K			
$FeCl_2$–ascorbate	Methanolic solution	1.36	3.42	Bulk
	Quick-frozen			
	Thirsty glass, 293 K	No absorption	No absorption	
	Thirsty glass, 77 K	1.36	3.25	Bulk

Table 2 Mössbauer parameters of Sn(IV) species fixed in thirsty glass carrier

Species	State and temperature	IS [mm s^{-1}]	Intensity	Position
$SnCl_4$	Liquid			
	Quick-frozen	0.80	0.297	Bulk
	In thirsty glass 293 K	0.72	0.029	Bulk
		– 0.20	0.023	Surface bound
	In thirsty glass 77 K	0.82	0.15	Bulk
		– 0.20	0.11	Surface bound
$Na_2Sn(OH)_6$	Aqueous solution	– 0.02	0.171	Bulk
	Quick-frozen			
	In thirsty glass 293 K	– 0.06	0.025	Bulk
	In thirsty glass 77 K	0.00	0.197	Bulk
	Silylated th. glass 293 K	– 0.08	0.0006	Bulk
	Silylated th. glass 77 K	– 0.01	0.02	Bulk
$SnCl_4 \cdot 2H_2O$	Aqueous solution	0.16	0.294	Bulk
	Quick-frozen			
	In thirsty glass 293 K	– 0.13	0.01	Bulk
	In thirsty glass 77 K	0.09	0.225	Bulk
Na_2SnS_3	Aqueous solution	1.26	0.30	Bulk
	Quick-frozen			
	In thirsty glass 293 K	No absorption	No absorption	
	In thirsty glass 77 K	1.25	0.20	Bulk
$SnCl_4$	Aqueous solution 30% HCl	0.43	0.20	Bulk
	Quick-frozen			
	In thirsty glass 293 K	No absorption	No absorption	
	In thirsty glass 77 K	0.49	0.157	Bulk

difference in the temperature dependence of the spectra in aqueous and methanolic solutions can be understood on the basis of the following consideration. In methanol, the hydrogen bonded structure of the medium at room temperature is not anchored strongly enough to the highly polar silicate surface to achieve recoil-free absorption, while, in water, hydrogen bonding and electrostatic interaction of water dipoles with the surface leads to sufficiently effective anchoring.

For the aqueous solutions of tin(IV) complexes incorporated into the thirsty glass carrier (Table 2) one type of species, all situated in bulk position has been found (Fig. 1A). In the case of Na_2SnS_3, species with no hydrogen-bonding ability, the Mössbauer effect did not appear at room temperature. Adding a strong mineral acid (e.g. HCl) to the $SnCl_4$ solution also prevents recoilless γ-ray resonance absorption at room temperature, obviously as a result of destroying the H-bonds in the solution. Silylation of the hydrophilic silicate surface [13], i.e., decreasing the hydrogen-bonding ability of the wall, strongly decreased the Mössbauer effect (the intensity of the line dropped from 0.025, measured for the same $Na_2Sn(OH)_6$ solution in the hydrophilic thirsty glass carrier, to 0.0006) because of the weakening of anchoring of the solvated solute through the water cluster to the carrier surface.

Liquid anhydrous $SnCl_4$ (Table 2) trapped in thirsty glass shows two kinds of species, one with IS value characteristic of $SnCl_4$ in bulk position and the another with

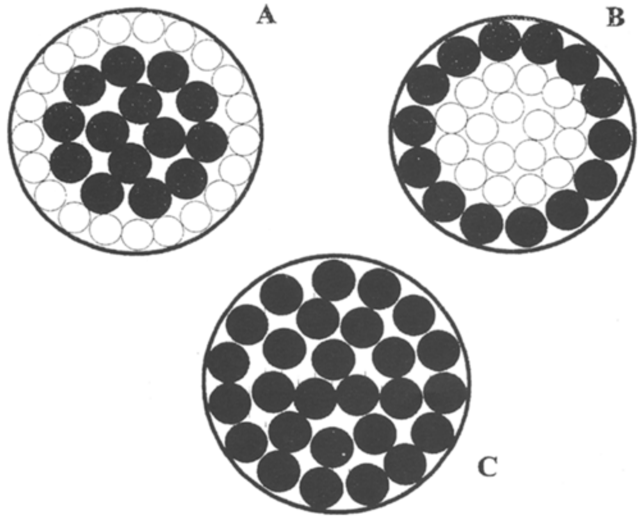

Fig. 1 The situations of solute (black) and solvent (white) molecules in the pores of the carrier

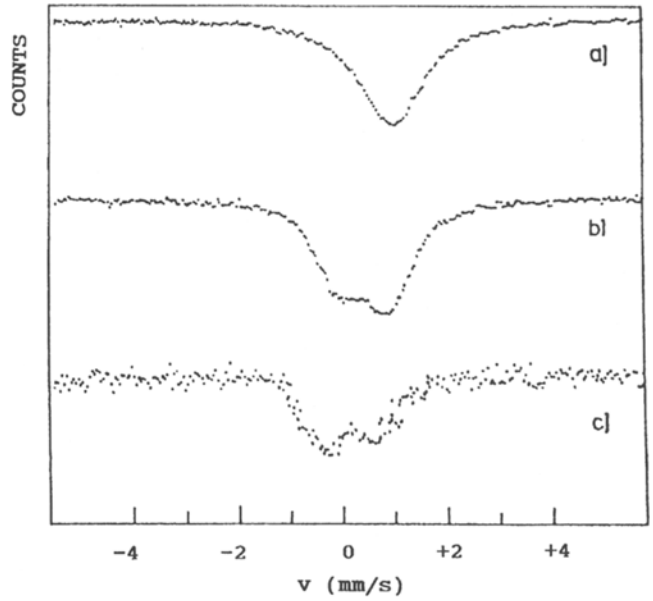

Fig. 2 The Mössbauer spectra of $SnCl_4$: (a) frozen and measured at 77 K, (b) trapped in the pores of "thirsty glass", measured at 77 K and (c) trapped in the pores of "thirsty glass", measured at 293 K

different IS which indicates significantly lower electron density at the tin nucleus (IS = $-$ 0.20 mm s^{-1} compared to 0.82 mm s^{-1}). Appearance of this second $SnCl_4$ species can be assigned to the influence of the wall of the carrier indicating a close contact of latter species with the wall [5]. The pores are completely filled with $SnCl_4$ so that the picture corresponds to the situation depicted in Fig. 1C. This result is a strong evidence of the fact that it is possible to distinguish between bulk and surface (or adsorbed) species in the nanopores of a solid carrier due to the changes in their Mössbauer parameters caused by the influence of the wall on the electronic structure. Since the direct interaction between the surface and the Mössbauer-active solute causes dramatic changes in the Mössbauer parameters, these can give direct information on the situation of the solute in the pores of the carrier and on the preference of the surface for the solute or solvent molecules.

The appearance of only bulk species (Fig. 1A) in Mössbauer spectra – recorded for solutions made with hydrogen bonding solvents – shows that the complex molecules are separated from the wall of the carrier by a solvent layer. The surface of the thirsty glass and the investigated solute species (except for Na_2SnS_3) have hydrogen-bonding ability. The hydrogen bonds between the complex and water fixes these species in the aqueous environment and hydrogen bonding between the water molecules and the surface seems to anchor the whole network to the solid carrier. In addition, electrostatic attraction of water dipoles by the polar silicate surface plays also an important role in anchoring. If the attractive interaction between solute and solvent or surface and solvent decreases, the bulk Mössbauer spectra do not appear at room temperature. An example for the former is the use of Na_2SnS_3 or the addition of HCl and for the latter silylation of the surface or the exchange of the solvent for ethanol. Conversely, surface-bound species always give a Mössbauer spectrum at room temperature.

The effect of changes in the polar nature and hydrogen-bonding ability of the pore surface on the Mössbauer parameters of tin(IV) and iron(II) complexes can be observed in the series of experiments where the solutions are incorporated into rigid organic microemulsions of varying composition (Table 3). In the microemulsions prepared with HDPCl, the *n*-pentanol content is high (between 10 and 36 wt%). Bulk $SnCl_4$ has been found in these microemulsions at room temperature indicating that water, ethanol and ethylene glycol forms hydrogen bonds with the OH-groups of *n*-pentanol at the solid surface anchoring the hydrogen-bonded bulk network to the wall. The surface has a higher affinity for ethanol and ethylene glycol than for water and, consequently, surface-bound $SnCl_4$ species appeared in the aqueous solution but not in solutions made with ethanol or ethylene glycol. In addition to the hydrogen-bonding ability, the preferential adsorption of methanol and ethylene glycol at the low polarity surface is a consequence of their lower relative permittivity compared to that of water. The isomer shifts for the solutions

Table 3 The IS values [mm s^{-1}] of Fe(II) and Sn(IV) species fixed in rigid organic microemulsion

Composition	293 K		77 K	
	Bulk	Surface	Bulk	Surface
$SnCl_4$/et. glycol/HDPCl/pentanol (36%)	0.27	—	0.52	—
$SnCl_4$/methanol/HDPCl/pentanol (15.6%)	0.30	—	0.23	—
$SnCl_4$/water/HDPCl/pentanol (10%)	0.30	0.27	0.36	− 0.23
$FeCl_2$/ascorbate methanol/HDPCl/Span60/pentanol (5%)	—	1.18 (QS = 1.71)	1.34 (QS = 3.2)	1.39 (QS = 2.0)
$SnCl_4$/methanol/AOT	—	0.02	0.61	0.16
$SnCl_4$/et. glycol/AOT	—	0.02	0.50	0.06

in ethanol and ethylene glycol coincide within experimental error. This indicates that the solvation shells in the two solvents are very similar.

The methanolic solution of Fe(II)-chloride–ascorbate was incorporated into a microemulsion prepared with HDPCl/Span 60 surfactant mixture (Table 3). In this system, the concentration of *n*-pentanol necessary for the formulation was only 5%. In this system only surface-bound species were observed at room temperature, but in the frozen state bulk species also appeared. A possible explanation for this behavior is that the decreased *n*-pentanol content decreases the possibility of hydrogen bonding of methanol to the surface, so that bulk species are not anchored to the wall through the solvent at room temperature. The Mössbauer parameters of the species in direct contact with the internal wall of the cavities closely resemble those of iron(II) ammonium sulfate [$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$], iron(II) oxalate [$FeC_2O_4 \cdot 2H_2O$) or iron(II) carbonate ($FeCO_3$) in all of which iron(II) atoms are surrounded by slightly distorted octahedra of oxygen atoms [14, 15].

In the microemulsions containing AOT (Table 3), the bulk species are Mössbauer-active only at the liquid nitrogen temperatre and surface-bound species are observed. Using Aerosol-OT as surfactant makes it unnecessary to add a co-surfactant to the system. The hydrogen-bonding ability of the internal wall surface in the absence of *n*-pentanol is very low, and the situation is similar to that in the HDPCl/Span 60 microemulsion.

Conclusions

It was shown that it is possible to fix liquid solutions of Mössbauer-active solutes in hydrogen-bonding solvents in silicate ("thirsty glass") carriers and in solid microemulsion carriers which impose a rigid structure on the liquids in their nanosize holes.

The prerequisite of obtaining Mössbauer spectra characteristic of the solute, situated in the bulk of the solution (i.e. free of the "surface effect") is – according to our investigations – the strong interaction of the solvent with the surface in the small pores of the carrier, leading to a solvent layer which prevents direct contact between the Mössbauer-active solute and this surface, but also acts as an anchoring place for the hydrogen-bonded solvent cluster fixing the solvated solute in the bulk solution. Solute species in close contact with the wall can be clearly distinguished from bulk solutes on the basis of the different temperature dependences of their Mössbauer spectra. The Mössbauer study of porous systems in the nanosize range using Mössbauer-active solute as probe molecule, beyond its invaluable contribution to the study of electronic structure and symmetry of complex molecules in solutions, proved to be a very useful tool in the investigation of solid/liquid interactions and solution structure inside the nanopores.

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