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The use of rigid organic microemulsions to fix liquid solutions for Mössbauer studies*

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Abstract

Rigid organic microemulsions containing submicroscopic droplets of liquid solutions of tin(IV) chloride in methanol and in ethylene glycol were prepared. In those systems where the walls of the cavities in the microemulsion carried negative charges and the hydrophilic groups of the surfactants and cosurfactants had H-bonding ability, it was shown that the internal surface of the cavities in the microemulsion was covered by a solvent layer separating Mössbauer-active $SnCl_4$ from this surface. On the other hand, solvated $SnCl_4$ was bound through the H-bonded solvent cluster to this surface-bound solvent by H bonds, resulting in recoilless γ-ray resonance absorption (Mössbauer effect). Thus, the rigid organic dispersion medium of these microemulsions behaved as a carrier enhancing the Debye–Waller factor for the quasi-liquid phase of the system, resulting in Mössbauer spectra characteristic of $SnCl_4$ in the bulk solution.

Introduction

Recoilless γ-ray resonance absorption (Mössbauer-effect) has been achieved in liquid solutions fixed as submicroscopic droplets in suitable carriers. A special porous silicate ('thirsty glass') [1–4] or a rigid organic microemulsion [5] served as carriers, with aqueous solutions of $SnCl_4$ as model solutions. In these systems, the Mössbauer effect appeared at room temperature with parameters characteristic of the Mössbauer-active solute in the bulk solution.

It is known [6] that in aqueous solutions hydrated species such as tin(IV) chloride are H bonded to neighbouring water molecules, which are similarly linked to the bulk water, the latter consisting of H-bonded clusters of water molecules. The whole system may be connected by H bonds to the water layer on the surface in the pores of the carriers.

Systematic Mössbauer studies of liquid aqueous $SnCl_4$ solutions fixed in the mentioned carriers have shown that the prerequisites for the appearance of the Mössbauer effect characterising $SnCl_4$ in the bulk solution are; (i) the small size of the cavities in the carrier [7–9]; (ii) the above-mentioned H-bonded cluster structure of the solution [2, 3]; (iii) preferential binding of the solvent on the internal walls of the carrier [4].

The solute is in this way separated by a solvent layer from the wall, but bound to this layer through the H-bonded cluster structure of the system. Destruction of the latter H-bonded structure, e.g. with a strong mineral acid [2, 3], or prevention of the strong binding of the solvent on the walls of the carrier, e.g. by silylation of the SiOH groups on the silicate surface, i.e. decreasing its polarity and H-bonding ability [4], led to the disappearance or dramatic decrease of the Mössbauer effect. Similar behaviour could be achieved by substituting the $SnCl_4$ with tin(IV) compounds of lower H-bonding ability [4], or the silicate carrier with an organic carrier of lower polarity [5].

Since all these investigations indicated the importance of the strength of interaction between the solvent (or

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solution) and the wall surface in the submicroscopic pores of the carriers, the nature of the latter interaction must be studied.

To distinguish between the contributions of electrostatic forces and H bonding (i.e. coordinate forces), the polarity and H-bonding ability of both solution and carrier surface had to be changed.

In the first step, a microemulsion containing submicroscopic aqueous $SnCl_4$ droplets in a non-polar dispersion medium was prepared [5] from paraffin and naphthalene as dispersion medium, hexadecylpyridinium chloride (HDPCl) as surfactant and n-pentanol as cosurfactant. The system incorporated 8% aqueous 0.1 M $SnCl_4$ solution. The hydroxy groups of the pentanol and the pyridinium chloride moiety of the HDPCl on the internal surface in the cavities of the microemulsion served for the anchoring of water molecules by H bonds on the latter surface, more or less similarly to the H bonding between silicate Si–OH groups and water in the thirsty glass carrier. On the other hand, the much lower polarity of the walls in the holes of the microemulsion than that in the silicate carrier resulted in a much weaker electrostatic interaction between the high-polarity solvent water and the surface in the former than that in the latter carrier.

The above difference was well reflected in the Mössbauer spectra. Whereas the Mössbauer spectrum of an aqueous solution of $SnCl_4$ trapped in thirsty glass exhibited a single line characteristic of the $SnCl_4$ in the bulk of the solution, the spectrum of the same solution in the microemulsion reflected the presence of two types of tin(IV) species: $SnCl_4$ bound on the surfaces in the holes of the carrier, and $SnCl_4$ in the bulk of the solution. Thus, the high-polarity silicate surface in the thirsty glass showed a higher affinity towards the polar water molecules than towards low-polarity $SnCl_4$, resulting in a water layer separating the Mössbauer-active tin(IV) from the surface. On the other hand, because of the low polarity of the surfaces in the holes of the microemulsion, the water covering the latter surfaces did not dominate over the bound $SnCl_4$ on it (in spite of the H-bonding ability of the surface).

Our next goal was to prepare microemulsions with similar low polarity, but with different H-bonding ability, containing liquid $SnCl_4$ solutions of lower polarity than that of water, and to study their Mössbauer spectroscopic behaviour. The results of these investigations are presented below.

Experimental

Tin(IV) chloride was prepared by dissolving metallic tin (enriched in ^{119}Sn) in 6 M hydrochloric acid and afterwards oxidising the tin(II) with concentrated hydrogen peroxide. The resulting compound was dried *in vacuo* and dissolved in water-free methanol or ethylene glycol. The resulting two solutions (A: 0.1 M $SnCl_4$ in methanol, B: 0.1 M $SnCl_4$ in ethylene glycol) were dispersed as the liquid phase in the organic medium of the microemulsion at 75 °C.

Four microemulsions (I–IV) with the compositions given in Table 1 were prepared at 75 °C, according to the general procedure given in refs. 10 and 11. For comparison, the composition of the system studied in our previous paper [5] is also presented.

The components and their ratio in the above systems were chosen on the basis of a large series of trial and error experiments. Even small changes in composition prevented the formation of the microemulsion or, if such changes occurred during the experimental work (e.g. evaporation of n-pentanol *in vacuo*), this led to a break in the microemulsion.

All four microemulsions are liquid above 75 °C, but solidify below this temperature, then containing liquid submicroscopic droplets of the $SnCl_4$ solutions in the rigid organic carrier phase.

The cavities in the organic carrier are nearly spherical, with an average diameter of ~10 nm. Each cavity contains one submicroscopic droplet of the liquid phase.

In the walls of the cavities, the surfactant (HDPCl or AOT) and cosurfactant (n-pentanol) molecules are oriented so that their hydrophilic functional groups are on the wall surface, in direct contact with the liquid phase of the microemulsion, and the alkyl chains are

TABLE 1. Compositions of microemulsions I–IV

Components	I	II	III	IV	O[a]
Paraffin	9.4	7.5	13.1	12.5	12
Naphthalene	37.5	30.1	52.2	50.1	48
Hexadecylpyridinium chloride (HDPCl)	26.6	16.9			24
Di(2-ethylhexyl)-sulphosuccinate Na^+ (AOT)			19.6	26.6	
n-Pentanol	15.6	36.1			8
Solution A ($SnCl_4$ in CH_3OH)	10.9		15.1		
Solution B ($SnCl_4$ in $(CH_2OH)_2$)		9.4		10.8	

[a] O = composition of the microemulsion containing an 8% aqueous solution of 0.1 M $SnCl_4$ [5].

TABLE 2. Mössbauer isomer shift (*IS*) values for $SnCl_4$ measured in its solutions fixed in rigid organic microemulsions

No.	Surfactant	Solvent in the liquid phase	293 K		77 K			
			IS	Half-width	*IS*	Half-width	*IS*	Half-width
I	HDPCl + n-pentanol	methanol	0.30	1.16	0.53	1.07		
II	HDPCl + n-pentanol	ethylene glycol	0.27	1.05	0.52	1.09		
III	AOT	methanol	0.02	0.96	0.16	0.90(48%)	0.61	0.90 52%)
IV	AOT	ethylene glycol	0.02	0.99	0.06	0.94(51%)	0.50	0.94(49%)
O	HDPCl + n-pentanol	water	−0.27	1.40	−0.23	1.02	0.36	1.08
			0.30	1.30				

The isomer shift of anhydrous $SnCl_4$ at 77 K is 0.80 mm s^{-1} and that of $SnCl_4(H_2O)_2$ is 0.36 mm s^{-1}. The reproducibility of *IS* values recorded at 293 K is ± 0.15 mm s^{-1}, for those at 77 K ± 0.08 mm s^{-1}.

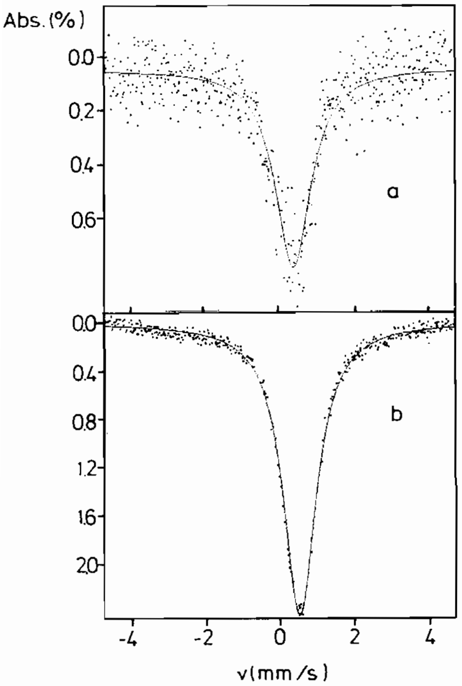

Fig. 1. Mössbauer spectra of $SnCl_4$ in microemulsion I at room temperature (a) and at liquid nitrogen temperature (b).

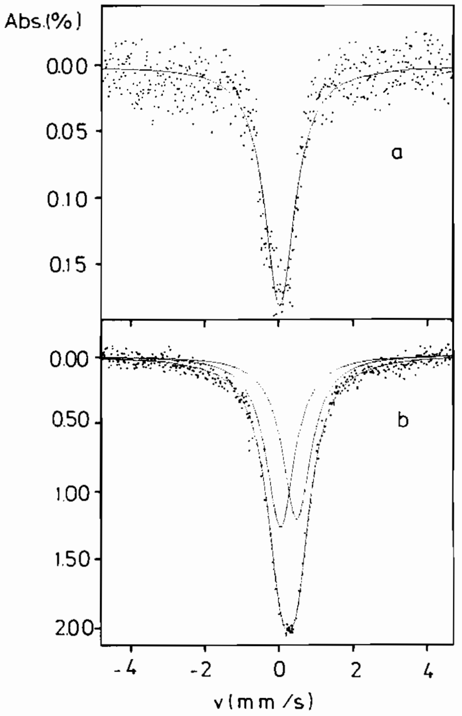

Fig. 2. Mössbauer spectra of $SnCl_4$ in microemulsion IV at room temperature (a) and at liquid nitrogen temperature (b).

incorporated in the bulk of the solid non-polar dispersion medium consisting of paraffin and naphthalene. Consequently, in systems I and II the pyridinium-nitrogens and chloride ions of HDPCl and the hydroxy groups of n-pentanol interact with the liquid phase, while in systems III and IV the succinate–carboxylate groups and sodium ions of AOT are in direct contact with the trapped solutions in the rigid microemulsion.

The Mössbauer study of the systems was performed as given in ref. 5. The results of measurements at room temperature (at which the samples contained the $SnCl_4$ solutions in liquid droplets) were compared with those at liquid nitrogen temperature on the completely frozen systems.

The Mössbauer spectra were evaluated by computer fitting to single Lorentzians. The isomer shift (*IS*) values are referred to that of SnO_2. The Mössbauer parameters are presented in Table 2. Typical spectra are shown in Figs. 1 and 2.

Results and discussion

(1) The Mössbauer spectra of microemulsions I and II, containing HDPCl as surfactant and n-pentanol as cosurfactant, each exhibited one line, indicating the presence of only one type of tin(IV) in the system. The corresponding *IS* values were comparable with those of $SnCl_4D_2$ (where D is a donor ion or molecule) in the bulk of its solution in a donor solvent. The reaction $SnCl_4 + 2D \rightleftarrows SnCl_4D_2$ results in an increased

population in the shielding orbitals, resulting in decreased *IS* values (see data in Table 2). A similar microemulsion, but containing $SnCl_4$ in aqueous solution as liquid phase instead of in methanol or ethylene glycol, gave a broadened line that could be evaluated only by assuming the presence of two types of tin(IV) species in the system: one of them had an *IS* value characteristic of $SnCl_4$ in the bulk of its aqueous solution, while the other had an *IS* value characteristic of $SnCl_4$ bound on the carrier surface [5].

Consequently, substitution of the water in the liquid phase with methanol or ethylene glycol resulted in the preferential solvation of the surface of the cavities in the microemulsion, leading to a solvent layer separating the Mössbauer-active solute from the carrier surface and acting at the same time as an anchoring layer for the H-bonded solution cluster containing the solvated solute ($SnCl_4$). In this way, during the Mössbauer measurement the system undergoes collective excitation, making possible the appearance of the Mössbauer effect, and the spectra give information on the solvated tin(IV) compound in the bulk of the solution.

The change caused in the behaviour of the system by the solvent exchange may be due to several reasons. Methanol and ethylene glycol are H-bonding solvents, as is water, but with much lower relative permittivities: ϵ for methanol is 32.6, that for ethylene glycol is 37.7 and that for water is 81. Liquids with low polarities have higher affinities towards apolar surfaces than do polar liquids.

The solvent change also influences the H bonding in the system. In the case of HDPCl, the chloride of the pyridinium chloride on the surface in the pores participates in H bonding. (The positively charged pyridinium and negative chloride ions form a compact electric double layer on the cavity walls.) Increasing relative permittivity favours the dissociation of chloride (which goes into solution), thereby decreasing the H bonding to the surface. Consequently, the substitution of water by other H-bonding solvents, but with lower relative permittivities, favours the binding of the latter to the surface in the carrier.

The latter two effects operate in the same direction. Their influence may be strengthened further by changes in the composition of the organic carrier due to the solvent exchange.

The substitution of water by methanol or ethylene glycol permitted and even necessitated the increase of the n-pentanol content (from 8 to 15.6 and 36.1%, respectively), and the increase in the number of alcoholic hydroxy groups favours H-bond formation on the surface. Besides the chloride of HDPCl, the n-pentanol hydroxy groups participate in H bonding.

(2) The room-temperature Mössbauer spectra of microemulsions III and IV containing AOT as surfactant each exhibited one line, with *IS* values characteristic of $SnCl_4$ bound to the carrier surface. The Mössbauer spectra of the frozen samples (at liquid nitrogen temperature) revealed the presence of both surface-bound and bulk $SnCl_4$.

Consequently, the use of AOT as surfactant instead of HDPCl with n-pentanol leads to a rigid microemulsion incorporating the liquid solution of $SnCl_4$, but in these systems the Mössbauer-active solute is not fixed strongly enough in the bulk of the solution in the submicroscopic cavities to achieve recoilless γ-ray resonance absorption at room temperature. Only surface-bound $SnCl_4$ proved to be Mössbauer-active.

This behaviour is due to the lack of strong H-bonding sites on the surface of the cavities in the microemulsion containing AOT as surfactant. In this system, the sodium carboxylate moiety of AOT is on the surface in the pores. This participates in H bonding only in its dissociated form, since the free carboxylate oxygen is the pillar atom of the H bond. In its undissociated sodium salt form, H-bond formation is hindered by the shielding effect of sodium ions on these oxygens. Under such circumstances, the positive charge of the double layer on the cavity wall stems from the sodium ions and is situated on the liquid surface, preventing H-bond formation with the carboxylate oxygen. Since this microemulsion could be prepared only with solutions of medium relative permittivity (methanol, ethylene glycol), the liquid phase in the pores does not favour ionic dissociation of the latter salt and hence H bonding.

(3) The Mössbauer *IS* values of the corresponding methanol and ethylene glycol-containing systems proved to be equal within experimental error. This indicates the similar solvation spheres of the tin(IV) in these systems. Chelate formation does not seem to occur in the case of ethylene glycol, the solvation sphere in the latter solvent therefore being similar to that for methanol solvates.

On the other hand, the composition of the microemulsion strongly depends on the nature of the solvent in the liquid phase. The ethylene glycol-containing systems needed a higher concentration of surfactant (26.6% AOT instead of 19.6%) or cosurfactant (36.1% n-pentanol instead of 15.6%) than in the methanol-containing microemulsions. This shows that the fixation of different liquid solvents for Mössbauer studies requires microemulsion of different compositions.

Conclusions

It is possible to prepare rigid organic microemulsions in which liquid solutions of Mössbauer-active solutes in H-bonding solvents are fixed as submicroscopic droplets. Because of its collective excitation, the Mössbauer study of such a system leads to recoilless γ-ray resonance absorption.

On the basis of previous [1–5] and the present investigations, it is concluded that in such systems 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 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 H-bonded solvent cluster fixing the solvated solute in the bulk solution.

Microemulsions containing surfactants and cosurfactants possessing hydrophilic groups with H-bonding ability and a liquid phase made up of H-bonding solvents with medium or low polarity are suitable for the above purpose. For the similar study of aqueous solutions (having high polarity) the polar thirsty glass carrier could be used with success.

All these investigations suggest that several different carriers might be prepared, whereby liquid solutions of Mössbauer-active compounds could be fixed without freezing, and hence information could be obtained from Mössbauer measurements on their electronic structure and symmetry in solution.

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