# Solvatochromism in Mössbauer spectroscopy. Effects of solvents on structure and electronic structure of iron and tin compounds

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## Abstract

The Mössbauer parameters of nine tin and iron compounds, measured in quick-frozen solutions in different solvents (altogether 59 systems), were used to describe the effects of the solvents on these parameters (i.e. solvatochromism in Mössbauer spectroscopy) by an empirical model. It was shown that the solvent dependence of the isomer shift could be described for all of the systems studied, while the solvent dependence of the quadrupole splitting could be described for most of the systems, as a linear function of two or three independent solvation parameters (the Gutmann donicity, the Dimroth-Reichardt $E_T$ value and the relative permittivity). The use of this model provided information on the natures and contributions of the different processes participating in the solvent effect.

## Introduction

It is known from Mössbauer studies on frozen solutions [1-8] that the Mössbauer parameters may depend strongly on the nature of the solvent. The solvent dependence of the Mössbauer spectrum has been explained for different systems in terms of various chemical or physical phenomena accompanying the solvation processes [1-10]. No general treatment is known, however, for a quantitative rationalization of the solvent-dependent changes in the Mössbauer parameters.

The Mössbauer isomer shift (*IS*) [9] is proportional to the electron density at the atomic nucleus for the Mössbauer-active isotopes. Only electrons in s orbitals have finite densities at the atomic nucleus, whereas electrons in p, d and f orbitals shield the s electrons and thereby strongly influence the electron density at the nucleus. Consequently, all processes accompanied by changes in the electron structure of Mössbauer-active compounds should result in changes in *IS*. Only in exceptional cases may the opposite effects of the s and shielding electrons compensate each other.

The dissolution of a molecule in a solvent is due to the solute-solvent interactions, i.e. to the solvation of the molecule to be dissolved. In the majority of systems investigated, these processes are considered to be Lewis-type donor-acceptor interactions. Both solute and solvent may act as donor or as acceptor. In complicated systems, each reaction partner may react at the same time in both ways [10-12]. Since these types of reactions change the electron densities in all orbitals involved, their effects must be reflected by changes in *IS*. Much smaller changes in the electron structure are caused by simple electrostatic solute-solvent interactions, or by solvation due to polarization or to London forces, etc. Nevertheless, solvation without changes in the electronic structures of the reactants is hardly conceivable.

The Mössbauer quadrupole splitting (*QS*) [9] is proportional to the electric field gradient at the Mössbauer-active nucleus, which is determined by the symmetry of the electronic shell of the Mössbauer-active atom. The latter is strongly influenced by the symmetry of the near surroundings (coordination sphere) of the atom in question.

Solvation may result in the direct coordination of the solvent to the Mössbauer-active atom, either by occupying free coordination sites, in this way changing the coordination number and symmetry of this atom, or by substituting molecules or ions bound to the Mössbauer-active atom without changes in the O-O coordination number, but changing the electron population in the orbitals involved. The latter change may also alter the symmetry of the electronic shell and consequently the electric field gradient around the Mössbauer-active nucleus, this being reflected in the change in *QS*.

The solvation of species (or moieties) in the near surroundings of the Mössbauer-active atom may affect

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the interactions between the latter atom and its surroundings leading to electron structure changes which may also be reflected by the Mössbauer spectrum.

Besides these direct effects of solvation on the Mössbauer parameters, secondary effects may also appear, e.g. dissociation–association equilibria due to the change caused in the polarity of the system by a solvent change, etc.

On the above basis, it may be stated that the effects of solvents on the Mössbauer parameters in frozen solutions are exerted in a complex way through several different processes. Some of them even lead to opposite results.

On the other hand, solvation phenomena have been shown to be controlled by only a few characteristic properties of the solvent, e.g. its electron pair donor and acceptor strength, its polarity and possibly its polarizability [10–15]. This allowed the use of simple empirical models to describe the effects of solvents on different experimentally determined physicochemical properties in solution [13–19].

Our present aim was to describe the effects of solvents on the Mössbauer parameters of frozen solutions as linear functions of independent complementary terms characteristic of the solvents in question.

## Models characterizing the solvent effect

The solvent dependence of various physicochemical parameters and properties, such as light absorption spectra, NMR chemical shifts, activity coefficients of ions, solvation enthalpies, redox potentials, reaction rates, equilibrium constants, etc., have been described as linear functions of parameters characterizing different properties of the solvent [10, 13–19]. These investigations have shown that the Lewis basicity (donor strength), Lewis acidity (acceptor strength or H-bonding ability), polarity and polarizability are the properties which probably predominate in the solvent effect. The sensitivities of the experimental parameters to the different solvent properties have been found to vary.

In most systems, two properties, the Lewis basicity and Lewis acidity, were sufficient for a quantitative characterization of the solvent effect [13–15]. Only in exceptional cases did one property alone, usually the Lewis basicity, allow a good description of the above phenomenon. In certain complex systems, not only the Lewis basicity and acidity, but also the polarity or polarizability of the solvent, and possibly both, had to be taken into consideration [18].

To represent the solvent dependence of experimental Mössbauer *IS* and *QS* values (denoted in eqn. (1) by $Q$) as linear functions of independent but complementary parameters, we used the following equation

$$Q = Q_0 + aA + bB + cC \tag{1}$$

where $Q_0$ is the $Q$ value for the solvent-free system, $A$ is the donor strength (Lewis basicity), $B$ is the acceptor strength (Lewis acidity), $C$ is the polarity of the solvent, and $a$, $b$ and $c$ are the sensitivities of $Q$ to these solvent properties.

To measure the Lewis basicity $A$, the Gutmann donor strength (*DN*) [12] or the Kamlet–Taft $\beta$ values [16] were chosen; to characterize the Lewis acidity $B$, the Mayer acceptor number (*AN*) [15], the Dimroth–Reichardt $E_T$ values [20, 21] or the Kosower $Z$ values [22] were used*. To measure polarity, the term $(\epsilon-1)(\epsilon+2)^{-1}$ was used, where $\epsilon$ is the relative permittivity of the solvent.

To establish which combination of these parameters gives the best fit between the calculated and experimental data, combinations of the Lewis basicity parameters *DN* and $\beta$ with each of the three Lewis acidity parameters *AN*, $E_T$ and $Z$ were used for the computation. The results of these two-parameter approaches were compared with those of the three-parameter methods using $(\epsilon-1)(\epsilon+2)^{-1}$ as the third parameter. Each model calculation was performed by keeping $Q_0$ constant, using experimental *IS* or *QS* values measured for the solvent-free compounds.

To obtain a quantitative measure of the relative importance of the Lewis basicity $A$, Lewis acidity $B$ and polarity $C$ of the solvent for the Mössbauer parameters, partial regression coefficients $a'$, $b'$ and $c'$ were calculated

$$a' = a\left(\frac{\sum_{i=1}^{n}(A_i-\bar{A})^2}{\sum_{i=1}^{n}(Q_i-\bar{Q})^2}\right)^{1/2} \tag{2}$$

$$b' = b\left(\frac{\sum_{i=1}^{n}(B_i-\bar{B})^2}{\sum_{i=1}^{n}(Q_i-\bar{Q})^2}\right)^{1/2} \tag{3}$$

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*DN: the heat of solvation (kcal $mol^{-1}$) of $SbCl_5$ determined calorimetrically in dilute solutions prepared in dichloro ethane [12]; $\beta$: hydrogen bond acceptor basicity reflected by the solvatochromic shift of *p*-nitroaniline referred to that of *N,N'*-diethyl-*p*-nitroaniline in different solvents [16]; *AN*: the solvent dependence of the $^{31}P$ NMR shift of triethylphosphine oxide in different solvents referred to that with $SbCl_5$ [15]. $E_T$: the solvent induced shift of the absorption maxima of pyridinium-*N*-phenolbetaine in different solvents in kcal $mol^{-1}$ [20, 21]; *Z*: the solvent induced shift of the charge transfer band of 1-ethyl-4-carbomethoxy-pyridinium iodide in different solvents in kcal $mol^{-1}$ [22].

$$c' = c\left(\frac{\sum_{i=1}^{n}(C_i-\bar{C})^2}{\sum_{i=1}^{n}(Q_i-\bar{Q})^2}\right)^{1/2} \qquad (4)$$

where $\bar{A}$, $\bar{B}$, $\bar{C}$ and $\bar{Q}$ denote the average values of parameters $A$, $B$, $C$ and $Q$, respectively, in the given data set containing $n$ points, $A_i$, $B_i$, $C_i$ and $Q_i$, the values for $A$, $B$, $C$ and $Q$.

Since $a'$, $b'$ and $c'$ are on the same scale, they permit calculation of the percentage contributions of $A$, $B$ and $C$ to the solvent dependence of *IS* and *QS* according to eqns. (5)–(7).

$$a\% = \frac{100a'}{a'+b'+c'} \qquad (5)$$

$$b\% = \frac{100b'}{a'+b'+c'} \qquad (6)$$

$$c\% = \frac{100c'}{a'+b'+c'} \qquad (7)$$

The signs of $a$, $b$ and $c$ indicate either direct (+) or inverse (−) proportionality between the solvent effect and parameters $A$, $B$ and $C$.

The deviations between the experimental (*IS* and *QS*) values and those calculated by using the different model combinations shown in Table 1 characterized the reliability of the models in question.

## Results and discussion

Several sets (altogether nine different solutes in 59 systems) of solvent-dependent Mössbauer *IS* and *QS* values were taken from the corresponding literature to study the applicability of the above models for their rationalization. A comparison of the computation results* for the combinations in Table 1 indicate that in most of the systems the *DN* and $\beta$ values are equally suitable for characterization of the Lewis basicity ($A$), as are the *AN*, $E_T$ and $Z$ values for characterization of the Lewis acidity ($B$). For practical reasons, we concluded that the combination containing *DN* and $E_T$ with $(\epsilon-1)\ (\epsilon+2)^{-1}$ as $A$, $B$ and $C$ was the best for further study of our systems, i.e. models III and IV in Table 1.

The $a\%$, $b\%$ and $c\%$ values for the solvent dependence of the *IS* and *QS* data showed that the contributions of the three parameters $A$, $B$ and C in the determination of the electron density at the nucleus (reflected by *IS*) differed significantly from their effects on the electric field gradient around this nucleus (shown by *QS*). This demonstrates that solvation of the Mössbauer-active central metal atom, which acts as an electron pair acceptor, and solvation of the electron pair donor ligand coordinated to this metal, influence the electron density at the Mössbauer nucleus and the electric field gradient around it in different ways.

### *Solvation of methyltin halides*

Several groups of workers [1–4] have studied the Mössbauer spectra of alkyltin halides in frozen solutions in different organic solvents. They explained the solvent-dependent changes in *QS* by changes in the tin–halide bond lengths (there are two such bonds with different lengths in these systems), due to the solvation of the molecules [2, 3]. They even introduced a coefficient calculable from *QS* to characterize the solvation strength of the solvent [4]. The solvent dependence of *IS* was

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*Especially the residual standard deviations of experimental and calculated values.

TABLE 1. Combination of solvation parameters in the equation $Q=Q_0+aA+bB+cC$ for characterizing the solvent effect and the residual standard deviations ($\Delta IS$ and $\Delta QS$) of experimental and calculated $Q$ values

| Model | $A$ | $B$ | $C$ | $Me_2SnCl_2$ | | $MeSnCl_3$ | | $SnI_4$[a] $\Delta IS$ | $FeCl_2$ $\Delta IS$ |
|---|---|---|---|---|---|---|---|---|---|
| | | | | $\Delta IS$ | $\Delta QS$ | $\Delta IS$ | $\Delta QS$ | | |
| I | *DN* | *AN* | | 0.05 | 0.12 | 0.02 | 0.28 | 0.06 | 0.04 |
| II | *DN* | *AN* | $(\epsilon-1)\ (\epsilon+2)^{-1}$ | 0.07 | 0.17 | 0.06 | 0.11 | 0.12 | 0.09 |
| III | *DN* | $E_T$ | | 0.05 | 0.14 | 0.02 | 0.19 | 0.06 | 0.05 |
| IV | *DN* | $E_T$ | $(\epsilon-1)\ (\epsilon+2)^{-1}$ | 0.03 | 0.14 | 0.06 | 0.21 | 0.11 | 0.10 |
| V | *DN* | $Z$ | | 0.02 | 0.10 | 0.02 | 0.20 | 0.01 | 0.03 |
| VI | *DN* | $Z$ | $(\epsilon-1)\ (\epsilon+2)^{-1}$ | 0.03 | 0.16 | 0.06 | 0.20 | 0.04 | 0.05 |
| VII | $\beta$ | *AN* | | 0.05 | 0.08 | 0.02 | 0.25 | 0.07 | 0.07 |
| VIII | $\beta$ | *AN* | $(\epsilon-1)\ (\epsilon+2)^{-1}$ | 0.05 | 0.10 | 0.02 | 0.13 | 0.12 | 0.03 |
| IX | $\beta$ | $E_T$ | | 0.006 | 0.08 | 0.02 | 0.24 | 0.09 | 0.12 |
| X | $\beta$ | $E_T$ | $(\epsilon-1)\ (\epsilon+2)^{-1}$ | 0.04 | 0.11 | 0.07 | 0.24 | 0.11 | 0.07 |
| XI | $\beta$ | $Z$ | | 0.005 | 0.05 | 0.02 | 0.24 | 0.01 | 0.11 |
| XII | $\beta$ | $Z$ | $(\epsilon-1)\ (\epsilon+2)^{-1}$ | 0.03 | 0.13 | 0.08 | 0.28 | 0.06 | 0.06 |

[a] In $CCl_4$ parent solvent.

explained [1–3] in terms of the differences in the donor strengths (Gutmann donicities) of the solvents used. The Mössbauer parameters also demonstrated that changes in the composition of the methyltin halides have great effects on the solvent dependence of these data.

Because of the complex nature of the latter investigations (four different solutes each in seven solvents), this system was chosen first to study the applicability of the above model for characterization of the solvent effect. The experimental and calculated *IS* and *QS* values are given in Tables 2–5. Models III and IV in Table 1 were used for these calculations. $IS_0$ and $QS_0$ are experimental values recorded for the solid (solvent-free) compounds. $IS_{\mathrm{calc,\ I}}$ and $QS_{\mathrm{calc,\ I}}$ refer to computations involving only two solvent parameters, *DN* and $E_{\mathrm{T}}$, whereas $IS_{\mathrm{calc,\ II}}$ and $QS_{\mathrm{calc,\ II}}$ refer to calculations with three solvent parameters, the third being $(\epsilon-1)(\epsilon+2)^{-1}$.

A comparison of the experimental and calculated parameters permits the following findings.

(a) The *IS* calculations led to values in good agreement with the experimental ones (within the error limit $\pm 0.03$–$0.04$ mm s$^{-1}$) without consideration of the third term, i.e. the polarity of the solvent.

(b) The contribution of the Lewis basicity (donor strength) to the solvent dependence of *IS* proved to be much higher in $CH_3SnX_3$ ($\sim 90\%$) than in $(CH_3)_2SnX_2$ ($\sim 70\%$), but the contribution of the Lewis acidity (acceptor strength) was not negligible either ($\sim 10\%$ and $\sim 30\%$, respectively, in these two groups).

(c) The signs of *a* and *b* indicated that, for all four solutes, a higher donor strength results in a decreased *IS*, and a higher acceptor strength in an increased *IS*. Thus, solvation of the electron pair acceptor tin decreased the electron density at the tin nucleus, but an increase in the solvation of the electron pair donor halide (bound to the tin) led to an increased electron density at the tin nucleus.

(d) As concerns the *QS* values, calculations involving the effect of the polarity of the solvent (three-parameter approach) led to a small but significantly better agreement between the experimental and calculated data than did the two-parameter approach.

(e) It is striking that the sign of *a* in systems containing $(CH_3)_2SnX_2$ as solute shows that a higher donor strength of the solvent results in an increased *QS* (an increased electric field gradient at the tin nucleus, i.e. a decreased symmetry of the electronic shell); in contrast, in $CH_3SnX_3$ a higher donor strength has the opposite effect. The different behaviours of these two types of systems is also reflected in the signs of *b* and *c*. In $(CH_3)_2SnX_2$, a higher acceptor strength of the solvent results in a decreased *QS*, while a higher polarity results in an increased *QS*. In $CH_3SnX_3$, just the opposite behaviour is observed.

(f) The contributions of the solvent parameters to the changes in *QS* also differed in the two groups of compounds. The contribution of the solvent donor strength to *QS* was $\sim 50\%$ in the $CH_3SnX_3$, and only 20–30% in $(CH_3)_2SnX_2$, while the contribution of the acceptor strength was 30–40% in the former systems and only $\sim 20\%$ in the latter.

(g) Analysis of the solvent dependence of both *IS* and *QS* (considering the signs of *a*, *b* and *c* and the values of *a*%, *b*% and *c*%) indicates that a higher halide content in the solute increases the electrophilic character of the tin favouring its solvation. In all four systems the latter process increases the population in shielding orbitals leading to decreased electron densities at the tin nucleus, but it decreases the symmetry of the electronic shell in $(CH_3)_2SnX_2$ systems and increases it in $CH_3SnX_3$. The effect of a higher halide content of the solute (resulting in its increased solvation) was shown to be greater on *QS* than on *IS*. Solvation of the negative centres (halides) in the $CH_3SnX_3$ systems has a stronger effect on the symmetry of the surroundings

TABLE 2. Experimental and calculated Mössbauer parameters of $(CH_3)_2SnCl_2$ in frozen solutions in different solvents

| Solvent | $IS_{\mathrm{exp}}$ | $IS_{\mathrm{calc,I}}$ | $IS_{\mathrm{calc,II}}$ | $QS_{\mathrm{exp}}$ | $QS_{\mathrm{calc,I}}$ | $QS_{\mathrm{calc,II}}$ |
|---|---|---|---|---|---|---|
| Diethyl ether | 1.73 | 1.68 | 1.72 | 3.80 | 3.98 | 3.79 |
| THF | 1.66 | 1.69 | 1.70 | 4.04 | 3.99 | 3.94 |
| Acetone | 1.75 | 1.77 | 1.75 | 3.85 | 3.92 | 4.00 |
| DMF | 1.69 | 1.68 | 1.66 | 4.30 | 4.13 | 4.19 |
| DMSO | 1.64 | 1.65 | 1.64 | 4.33 | 4.19 | 4.24 |
| HMPT | 1.50 | 1.52 | 1.51 | 4.45 | 4.39 | 4.44 |
| Py | 1.60 | 1.58 | 1.59 | 4.05 | 4.27 | 4.21 |
|  | $IS_0$ |  |  | $QS_0$ |  |  |
|  | 1.59 |  |  | 3.60 |  |  |

$IS_{\mathrm{calc,I}}$ *a*: $-0.01067$ (74%), *b*: $+0.00847$ (26%).

$QS_{\mathrm{calc,II}}$ *a*: $+0.01589$ (32%), *b*: $-0.02191$ (20%), *c*: $+1.2248$ (47%).

THF: tetrahydrofuran; DMF: dimethyl formamide; DMSO: dimethyl sulfoxide; HMPT: hexamethylphosphortriamide; Py: pyridine.

TABLE 3. Experimental and calculated Mössbauer parameters of $(CH_3)_2SnBr_2$ in frozen solution in different solvents

| Solvent | $IS_{exp}$ | $IS_{calc,I}$ | $IS_{calc,II}$ | $QS_{exp}$ | $QS_{calc,I}$ | $QS_{calc,II}$ |
|---|---|---|---|---|---|---|
| Diethyl ether | 1.78 | 1.76 | 1.80 | 3.57 | 3.90 | 3.58 |
| THF | 1.82 | 1.78 | 1.79 | 3.98 | 3.92 | 3.84 |
| Acetone | 1.86 | 1.87 | 1.85 | 3.82 | 3.86 | 4.01 |
| DMF | 1.77 | 1.76 | 1.75 | 4.36 | 4.09 | 4.21 |
| DMSO | 1.64 | 1.73 | 1.72 | 4.32 | 4.17 | 4.25 |
| HMPT | 1.56 | 1.57 | 1.56 | 4.45 | 4.37 | 4.46 |
| Py | 1.70 | 1.64 | 1.66 | 3.98 | 4.24 | 4.13 |
| | $IS_0$ | | | $QS_0$ | | |
| | 1.62 | | | 3.40 | | |

$IS_{calc,I}$ $a$: −0.01282 (72%), $b$: +0.01105 (28%).
$QS_{calc,II}$ $a$: +0.01367 (20%), $b$: −0.03437 (22%), $c$: +2.1115 (58%).

TABLE 4. Experimental and calculated Mössbauer parameters of $CH_3SnCl_3$ in frozen solution in different solvents

| Solvent | $IS_{exp}$ | $IS_{calc,I}$ | $IS_{calc,II}$ | $QS_{exp}$ | $QS_{calc,I}$ | $QS_{calc,II}$ |
|---|---|---|---|---|---|---|
| Diethyl ether | 1.14 | 1.10 | 1.16 | 2.21 | 2.17 | 2.20 |
| THF | 1.12 | 1.09 | 1.11 | 2.34 | 2.19 | 2.28 |
| Acetone | 1.18 | 1.15 | 1.12 | 2.44 | 2.29 | 2.36 |
| DMF | 0.94 | 1.00 | 0.98 | 1.92 | 2.16 | 2.10 |
| DMSO | 0.88 | 0.96 | 0.94 | 1.96 | 2.13 | 1.91 |
| HMPT | 0.80 | 0.81 | 0.79 | 2.17 | 1.96 | 2.15 |
| Py | 0.97 | 0.89 | 0.91 | 1.94 | 2.03 | 1.89 |
| | $IS_0$ | | | $QS_0$ | | |
| | 1.32 | | | 2.07 | | |

$IS_{calc,I}$ $a$: −0.01574 (93%), $b$: +0.00237 (7%).
$QS_{calc,II}$ $a$: −0.01361 (56%), $b$: +0.01460 (27%), $c$: −0.2098 (17%).

TABLE 5. Experimental and calculated Mössbauer parameters of $CH_3SnBr_3$ in frozen solution in different solvents

| Solvent | $IS_{exp}$ | $IS_{calc,I}$ | $IS_{calc,II}$ | $QS_{exp}$ | $QS_{calc,I}$ | $QS_{calc,II}$ |
|---|---|---|---|---|---|---|
| Diethyl ether | 1.39 | 1.24 | 1.38 | 2.07 | 2.07 | 2.08 |
| THF | 1.27 | 1.24 | 1.28 | 2.37 | 2.10 | 2.21 |
| Acetone | 1.34 | 1.32 | 1.26 | 2.32 | 2.19 | 2.29 |
| DMF | 0.97 | 1.15 | 1.10 | 1.83 | 2.13 | 2.06 |
| DMSO | 1.06 | 1.09 | 1.06 | 2.00 | 2.12 | 2.12 |
| HMPT | 0.93 | 0.91 | 0.87 | 2.27 | 1.99 | 2.21 |
| Py | 1.05 | 1.01 | 1.05 | 1.83 | 2.03 | 1.86 |
| | $IS_0$ | | | $QS_0$ | | |
| | 1.44 | | | 1.75 | | |

$IS_{calc,I}$ $a$: −0.01849 (90%), $b$: +0.00458 (10%).
$QS_{calc,II}$ $a$: −0.00799 (49%), $b$: +0.01510 (42%), $c$: −0.0746 (9%).

of the tin than on the covalency of the tin–halide and tin–solvent donor atom bonds.

*Solvation of tin tetrahalides*

Vértes *et al.* [6, 7] utilized Mössbauer spectroscopy to examine the solvation of tin tetrahalides by organic solvents.

Measurements were made in frozen solutions in the solvents to be investigated for $SnCl_4$ and $SnI_4$, and with solvent mixtures containing a parent solvent of low polarity besides the studied solvent for $SnI_4$ and $SnBr_4$. Experimental *IS* values and those calculated according to models III and IV in Table 1 are compared in Tables 6 and 7.

It is to be seen that only for the study of $SnI_4$ in solutions in the individual solvents was the use of the three-parameter approach needed (with *DN*, $E_T$ and $\epsilon$ as the solvation parameters) to get a significantly

TABLE 6. Experimental and calculated isomer shift values of $SnI_4$: (a) in frozen solutions in different solvents; (b) in solvent mixture in the parent solvent $CCl_4$

| Solvent (a) | $IS_{exp}$ | $IS_{calc,I}$ | $IS_{calc,II}$ |
|---|---|---|---|
| Ethanol | 0.40 | 0.47 | 0.30 |
| DMSO | 0.48 | 0.51 | 0.49 |
| DMF | 0.51 | 0.60 | 0.67 |
| Tributyl phosphate | 1.09 | 0.86 | 1.01 |
| $CCL_4$ | 1.64 | 1.36 | 1.55 |
| | $IS_0$ | | |
| | 1.50 | | |

$IS_{calc,II}$ $a$: $-0.06200$ (56%), $b$: $-0.01068$ (16%), $c$: $+1.4026$ (28%).

| Solvent (b) | $IS_{exp}$ | $IS_{calc,I}$ | $IS_{calc,II}$ |
|---|---|---|---|
| $CCl_4$ | 1.64 | 1.51 | 1.63 |
| Nitrosobenzene | 1.40 | 1.39 | 1.30 |
| Acetonitrile | 1.04 | 1.11 | 1.07 |
| Acetone | 0.95 | 1.03 | 1.01 |
| Ethylacetate | 0.96 | 1.01 | 0.97 |
| DMF | 0.65 | 0.75 | 0.76 |
| HMPT | 0.56 | 0.41 | 0.45 |
| | $IS_0$ | | |
| | 1.50 | | |

$IS_{calc,I}$ $a$: $-0.02847$ (98%), $b$: $+0.0027$ (2%).

TABLE 7. Experimental and calculated isomer shift values of $SnCl_4$ (a) and $SnBr_4$ (b) in frozen solutions in different solvents

| Solvent (a) | $IS_{exp}$ | $IS_{calc,I}$ | $IS_{calc,II}$ |
|---|---|---|---|
| DMSO | 0.32 | 0.26 | 0.28 |
| DMF | 0.29 | 0.34 | 0.34 |
| Tributyl phosphate | 0.24 | 0.25 | 0.24 |
| Acetonitrile | 0.64 | 0.65 | 0.63 |
| | $IS_0$ | | |
| | 0.83 | | |

$IS_{calc,I}$ $a$: $-0.0244$ (67%), $b$: $+0.00357$ (33%).

| Solvent* (b) | $IS_{exp}$ | $IS_{calc,I}$ |
|---|---|---|
| Acetonitrile | 0.36 | 0.35 |
| Acetone | 0.25 | 0.27 |
| THF | 0.22 | 0.20 |
| | $IS_0$ | |
| | 1.26 | |

$IS_{calc,I}$ $a$: $-0.03624$ (74%), $b$: $-0.00874$ (26%).

*In benzene as parent solvent.

better agreement between the experimental and calculated values than with the two-parameter ($DN$ and $E_T$) approach.

The use of the models demonstrated that in all of the investigated systems the donor strength is the predominating factor in the solvent dependence of $IS$, but the effect of the acceptor strength can be neglected only in the $SnI_4$ solutions in the solvent mixtures containing $CCl_4$ to keep the relative permittivity of the system at a constant low value.

The signs of $a$ demonstrate that a higher donor strength of a solvent leads in all systems to a decreased $IS$, indicating that solvation increases the electron population in shielding orbitals, resulting in a decrease in electronic density at the tin nucleus. On the other hand, the signs of $b$ indicate that a higher acceptor strength of a solvent results in an increased $IS$ in the $SnCl_4$ system and in solutions of $SnI_4$ in the mixed solvents, and in a decreased $IS$ in the $SnBr_4$ and $SnI_4$ systems, indicating that solvation of the halide may change the electron density in both types (s and shielding) of tin orbitals. The latter effect should be due to the change caused in the covalency of the tin–halide bonds by solvation of the halide.

### *Solvation of bis(N,N-diethyldithiocarbamate)iron chloride*

De Vries *et al.* [5] studied the solvent effect in frozen solutions of bis(*N*,*N*-diethyldithiocarbamate)iron(III) chloride, $(Fe(dtc)_2Cl$, in different solvents. They demonstrated that $QS$ is significantly lower for a frozen solution than for the solid complex. This effect was explained by assuming that the pentacoordinated iron(III) in the solid substance is transformed to hexacoordinated iron(III) in the solution, due to coordination of the solvent.

To determine the contributions of the solvent parameters to the above transformation, models III and IV in Table 1 were used to calculate $QS$. The experimental and calculated $QS$ values are compared in Table 8.

It is to be seen that only the three-parameter approach ($QS_{calc,\ II}$) leads to results in good agreement with the

TABLE 8. Experimental and calculated Mössbauer quadrupole splitting values of bis(*N*,*N*-diethyl-dithiocarbamate)iron(III) chloride in frozen solutions in different solvents

| Solvent | $QS_{exp}$ | $QS_{calc,I}$ | $QS_{calc,II}$ |
|---|---|---|---|
| DMF | 0.70 | 0.87 | 0.70 |
| Acetonitrile | 0.77 | 0.89 | 0.77 |
| DMSO | 0.84 | 0.10 | 0.85 |
| 1,2-Dimethoxyethane | 0.85 | 0.37 | 0.85 |
| Py | 0.71 | 0.67 | 0.71 |
| | $QS_0$ | | |
| | 2.76 | | |

$QS_{calc,II}$ $a$: $+0.01579$ (12%), $b$: $+0.1278$ (43%), $c$: $-2.7774$ (45%).

experimental $QS$ values. Surprisingly, the effect of the donor strength (12%) on the symmetry around the iron is much smaller than the effects of the acceptor strength (43%) and the polarity (45%) of the solvent.

It may be concluded that the solvation of ligands acting as donors towards the solvent, and polarization of the molecule, are needed for the transformation, resulting in a decreased $QS$.

The signs of $a$, $b$ and $c$ indicate that an increase in either the donor or the acceptor strength acts against the $QS$ decrease, which is favoured by an increased polarity of the system. This seems to indicate that the decrease of $QS$ is accompanied by a heterolytic dissociation of the species in solution. The latter process was confirmed by conductometric measurements [23].

One may conclude, therefore, that the dramatic decrease of $QS$ (from 2.76 mm $s^{-1}$ in solid state to 0.7–0.8 mm $s^{-1}$ in solution) is due to the dissociation of chloride from $Fe(dtc)_2Cl$, resulting either in tetrahedral $Fe(dtc)_2$ or in octahedral $Fe(dtc)_2(solvent)_2$ but certainly not in $Fe(dtc)_2Cl(solvent)$. The unambiguous determination of the coordination sphere of iron(III) in the solvated species needs further investigations.

### *Solvation of iron(II) chloride*

Vértes *et al.* [8] determined the Mössbauer parameters of iron(II) chloride in quick-frozen solutions in solvents of different polarities ($\epsilon$ between 6.8 and 81.0). In such systems, the symmetry and electronic structure of the species in solution depends not only on the properties of the coordinated solvent molecules, but also on the dissociation of $FeCl_2$. In fact, this latter process could be the predominant factor in the determination of the solvent effect. The stepwise dissociation of $FeCl_2$ in solutions of medium polarity may even result in the presence of species of different compositions in the system.

It was questionable whether the model shown to be suitable for the characterization of the systems discussed so far is of any use in the rationalization of the solvent effect in such systems. To answer this question, the Mössbauer parameters were treated according to models III and IV in Table 1. Calculated and experimental $IS$ and $QS$ values are presented in Table 9. A comparison of the data demonstrates that the solvent dependence of $IS$ is well simulated by the model used, the three-parameter approach giving a somewhat better agreement between the calculated and experimental values than the two-parameter approach.

Both models indicate that the donor strength cannot be the only or the predominant factor in the determination of the solvent effect. The sign of $a$ shows that increasing donor strength of the solvent results in a decreased $IS$, i.e. an increased electron density at the iron(II) nucleus. Consequently, increased solvation of the electron pair acceptor iron(III) ion increases the population of the s orbitals more than that of the shielding orbitals. The similar effect of the solvation of chloride is reflected by the sign of $b$.

It is known from conductometric studies that iron(II) chloride is completely dissociated in aqueous solution, and is partially dissociated in several donor and acceptor solvents of medium polarity. In the three-parameter model the positive sign of $c$ reveals that the increase in the polarity of the system, i.e. the dissociation of $FeCl_2$ results in an increase in $IS$, indicating a decreased electron density at the iron(II) nucleus. The latter may be due to the decreased electron population in the s orbitals. Dissociation of $FeCl_2$ results in a decreased electron pair donation from chloride to iron(III).

A comparison of the calculated and experimental $QS$ values demonstrates that the models provide acceptable results for less than half of the $FeCl_2$ systems studied. This seems to indicate that the three-solvent parameters used in the model discussed are not good enough or not adequate for the characterization of the solvent dependence of $QS$. Because of the limited solubility of anhydrous $FeCl_2$ the limited number of systems which could be studied did not permit the introduction of further parameters into the model.

TABLE 9. Experimental and calculated Mössbauer parameters of $FeCl_2$ in frozen solutions in different solvents

| Solvent | $IS_{exp}$ | $IS_{calc,I}$ | $IS_{calc,II}$ | $QS_{exp}$ | $QS_{calc,I}$ | $QS_{calc,II}$ |
|---|---|---|---|---|---|---|
| Methanol | 1.41 | 1.30 | 1.37 | 3.50 | 2.88 | 3.02 |
| Py | 1.26 | 1.29 | 1.26 | 3.48 | 2.83 | 3.03 |
| DMF | 1.21 | 1.28 | 1.29 | 2.12 | 2.90 | 2.80 |
| DMSO | 1.34 | 1.29 | 1.29 | 2.36 | 2.87 | 2.83 |
| HMPT | 1.16 | 1.30 | 1.27 | 2.77 | 2.78 | 2.95 |
| Tributyl phosphate | 1.35 | 1.23 | 1.29 | 2.77 | 2.88 | 2.52 |
| Acetonitrile | 1.29 | 1.26 | 1.32 | 2.95 | 3.01 | 2.64 |
|  | $IS_0$ |  |  | $QS_0$ |  |  |
|  | 1.20 |  |  | 3.10 |  |  |

$IS_{calc,II}$ $a$: $-0.00233$ (30%), $b$: $-0.00107$ (31%), $c$: $+0.2228$ (38%).

The main reason for the inadequacy of this model is probably the presence of solvated species of different compositions (chloride-free, or containing one or two chlorides) in some of the systems. Since the *IS* values of such species are usually similar, their effect does not distort the calculated *IS*. *QS*, however, is more sensitive to such changes. Models which cannot take into consideration the presence of successively formed solvated species in the solution do not seem to be suitable for calculation of the *QS* values for such systems.

## Conclusions

The solvent dependence of Mössbauer *IS* and *QS* values measured in quick-frozen solutions could be described quantitatively as a linear function of two or three independent solvation parameters.

In the two-parameter approach, the donor strength (characterized by Gutmann donicities) and the acceptor strength (Dimroth–Reichardt $E_T$) were taken into consideration. In the three-parameter approach, the polarity of the solvent (characterized by $(\epsilon-1)(\epsilon+2)^{-1}$, where $\epsilon$ is the relative permittivity) was the third parameter used.

The application of this method could give valuable information on the natures and contributions of the different processes participating in the solvent effect.

The presence of successively formed solvation products in a system hinders the application of the above model for the characterization of *QS*.

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