The Mössbauer Spectroscopy of Frozen Solvent Extracts

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ALTHOUGH spectroscopic methods have been widely used to help identify the chemical species involved in solvent extraction processes, the possibilities of Mössbauer spectroscopy have hardly been explored. Few Papers, most of them dealing with Sn, have so far been published on the application of this technique to frozen solutions.[1] Yet it offers important advantages in the study of nonaqueous solutions, because the spectra are mainly determined by the immediate environment of the atoms whose nuclei show resonant absorption.

The isomer shift (δ) and the quadrupole splitting (Δ) are the most significant parameters that can be obtained from a Mössbauer spectrum. An interesting example is provided by the extraction of iron(III) into nitrobenzene, from chloride, bromide, and thiocyanate solutions. Conventional solvent-extraction work has established[2] that the chloro- and bromo-complexes present in this solvent are the anions FeX_4^-. Mössbauer experiments provide a straightforward confirmation of this conclusion. The spectrum of a frozen extract from 0·02M-iron (^{57}Fe enriched) and 8M-HBr is shown in Figure 1 as a direct computer plot[3] of a Lorentzian curve fitted to the experimental points. The

spectrum was obtained at liquid-nitrogen temperature, using a $^{57}Co/Pd$ source and a constant acceleration, 400-channel spectrometer.[4] The isomer shift is in this case 0·45 mm./sec. with respect to stainless steel; attempts to fit the data to two Lorentzians caused the fitting process to diverge. This is in agreement with the presence of a 4-co-ordinate, high-spin complex with the four ligands of the same kind ($\Delta = 0$). Similar spectra were obtained with anhydrous solutions of Me_4-$NFeCl_4$ ($\delta = 0·40$ mm./sec.), and extracts from 1M-Fe + 5M-HCl solutions ($\delta = 0·43$ mm./sec.). At lower iron concentrations, however, moderate line broadening occurred and the resonance peak became somewhat asymmetric.

The results obtained with thiocyanate extracts are more interesting. Distribution coefficient measurements show that sodium is co-extracted with iron from NaSCN solutions; if enough iron is forced into the organic phase (by adding $NaClO_4$) for accurate analysis to be feasible, a mole ratio Na : Fe : SCN = 1 : 1 : 4 is found in the extract. It might appear that the iron complex involved is simply the thiocyanate counterpart of $FeCl_4^-$ or $FeBr_4^-$. However, the Mössbauer spectrum

shows a quadrupole splitting ($\Delta = 0.56$ mm./sec.) and the isomer shift ($\delta = 0.61$ mm./sec.) indicates a 6-co-ordinate complex (Figure 1); the species
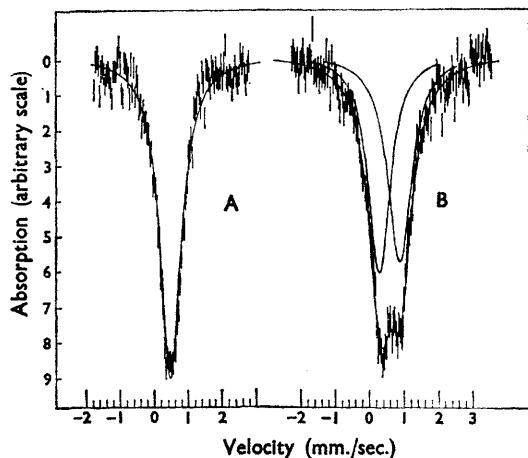

FIGURE 1. *Spectra of nitrobenzene extracts of* ^{57}Fe-*enriched iron, from* HBr (A) *and* NaSCN(B) *solutions.*

undergoing extraction must therefore be of the type $Fe(SCN)_4X_2^-$ where X stands for water or nitrobenzene. The implications of this fact, from the point of view of phase transfer, will be discussed elsewhere.

With Fe concentration in the range 0.01—1M, the spectra obtained after nitrobenzene extraction all looked much the same. The moderate line broadening and asymmetry mentioned above may be due to slight distortions of the FeX_4^- tetrahedra embedded in the nitrobenzene glass. There is of course no guarantee that on freezing a solution a true, uniform glass always forms; it is possible that "clusters" of the metal complex are segregated. Caution must therefore be used in deciding the relaxation mechanism on grounds of temperature- and concentration-dependence of the resonance patterns. However, it is tempting to suggest that in the nitrobenzene extracts fast (ionic) spin–lattice relaxation takes place.

With some solvent systems where apparently spin–spin relaxation predominates, both the simple quadrupole split spectra and well resolved magnetic patterns can be easily obtained by varying the iron concentration. An example is provided by ferric bromide extracted into trioctylphosphine oxide dissolved in benzene (Figure 2). At iron concentrations of the order of 0.1M the spectrum consists

of two lines but, as the concentration is decreased, at least six additional lines gradually appear.

In comparing magnetic spectra of complexes of unknown structure, it seems reasonable to assume that the six most intense lines (usually the only ones that can be seen clearly) arise from a pure Kramer's doublet $S_z = \pm 5/2$. There are indeed reasons why this state should relax more slowly than those with spin $\pm 3/2$ or $\pm 1/2$.[5] If a comparison of spectra on this basis is justified, it is interesting that the magnetic splitting may differ remarkably between species which would be expected to have similar structures. This is very clear for the chloride and bromide–tryoctylphosphine oxide extracts (Figure 2). A sharp non-magnetic spectrum of the chloride extract could not be recorded, but the broad single lines obtained at high concentrations of iron corresponded to δ values in the range 0.40—0.49 mm./sec., suggesting a different co-ordination number than for the bromide complex ($\delta = 0.60$ mm./sec., $\Delta = 0.48$ mm./sec.).
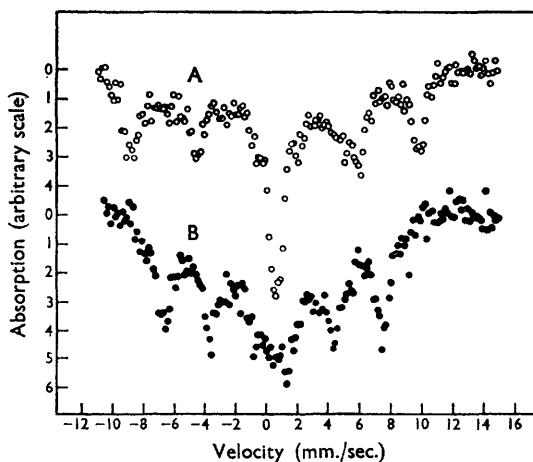

FIGURE 2. *Spectra of trioctylphosphine oxide extracts of* ^{57}Fe-*enriched iron, from* NaBr (A) *and* NaCl (B) *solutions.*

It thus seems that the only situation where little useful information can be derived from the Mössbauer spectra of frozen extracts is that of intermediate relaxation times, when several lines, or all of them, coalesce into one broad peak of non-Lorentzian shape. This commonly happens when spin–lattice relaxation is involved. The shape of the spectrum is hardly changed by changes in metal concentration, and an increase in temperature, which will reduce the relaxation time, generally

leads to too weak a Mössbauer absorption for satisfactory measurements.

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