

Lattice dynamics of iron complexes embeddings in PMAA hydrogel Mössbauer study

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Abstract The interaction of cross-linked poly(methacrylic acid) (PMAA) hydrogel and ferroine(iron - phenantroline complex) resulted in gel collapse because additional cross-links have been formed. To find out the mechanism of metal-polymer bonding and defining parameters of these bonds the lattice dynamics of frozen samples was studied by means of Mössbauer spectroscopy. Lattice dynamics parameters, such as Mössbauer lattice temperature θ_M and effective mass M_{eff} were calculated for PMAA gel-ferroine system. These calculations allowed us to estimate the ferroine complexes embedded in the PMAA hydrogel bonds strength.

Keywords Poly(methacrylic acid) · PMAA · Ferroine · Lattice dynamics · Mössbauer spectroscopy

1 Introduction

PMAA can show specific ionic interactions with the opposite charges which can help in creating self-organized systems [1]. These systems are widely used in chemistry, biology, and physics. Numerous researched are devoted to interaction of PMAA with metal ions. Understanding the mechanism of these interactions can help to create 'intelligent' organic-inorganic hybrid materials. Ferroine as an iron complex can show the typical interaction of PMAA hydrogel and metal ion complex. The interaction of cross-linked PMAA gel with iron complexes results in their absorption and gel collapse. Polymer functional groups and

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iron ion bonds form additional cross-links in the gel structure which causes the collapse [2]. That is why it is important to study this system to reveal the properties of PMAA gel and iron bondings in the complex.

The aim of present work is study of molecular lattice dynamics and metal-polymer bond strength in PMAA gel-ferroine system by means of Mössbauer spectroscopy.

2 Experimental

In present study the PMAA hydrogel was incubated in ferroine aqueous solution for 7 days. The concentration of Fe^{2+} ions in the aqueous solution was 0,08 mol/l.

Temperature dependences of gel's and solution's Mössbauer spectra can be used to estimate the properties of bondings in such systems and reveal the bonding parameters [3]. Mössbauer spectroscopy data for the aqueous ferroine solution and incubated PMAA gel were obtained in the temperature range from 118 K up to the temperature of Mössbauer effect disappearing.

Mössbauer spectra were obtained in a standard transmission geometry using a $^{57}\text{Co}(\text{Rh})$ gamma source. The gamma radiation was detected with a $\text{Na}(\text{TI})$ scintillation detector. The spectrometer was calibrated with a standard $\alpha\text{-Fe}$ absorber. The spectra were analyzed with UNIVEM MS program, which ensures fitting by a combination of Lorentzians with adjustable Mössbauer parameters of isomer shift, quadrupole splitting and peak area under the curve.

3 Results and discussion

Mössbauer spectra of ferroine aqueous solution(A) and incubated PMA hydrogel(B) at the temperature $T = 118$ K are shown in Fig. 1

Mössbauer parameters of these spectra such as Isomer shift and quadrupole splitting remained the same for aqueous ferroine solution and incubated PMAA gel which means that the ferroine complex was not destructed during the PMAA gel and complex interaction. The embedding of iron ions in the structure of hydrogel occured as a whole complex.

Isomer shift's and recoilless fraction's (area under the curve) temperature dependences for ferroine aqueous solution and incubated PMAA gel are shown in Fig. 2. The dependence curves of recoilless fraction have contrary flexure point at the temperature near 200 K, which can be explained by diffusion motion of the iron complexes in the gel structure. Therefore the low temperature area of the temperature dependences was used for calculations.

Mössbauer lattice temperature θ_M and effective vibrating mass M_{eff} were estimated from the temperature dependences of recoilless fraction and second order Doppler shift δ_{SOD} . The normal vibration modes of molecule crystals usually consist of two parts [4]: the weaker intramolecular modes related to the vibration of molecular centre of mass and stronger modes with higher frequencies - vibrations within the molecule. Molecules are not entirely rigid in the molecular crystals due to some part of internal vibrations, that is why the mass of the molecule in the crystal should be replaced with the effective vibration mass parameter M_{eff} . The effectie mass' lower limit is the mass of Mössbauer iron isotope (57 Da) and the upper limit is the whole molecular weight. The first situation occurs when only iron ions

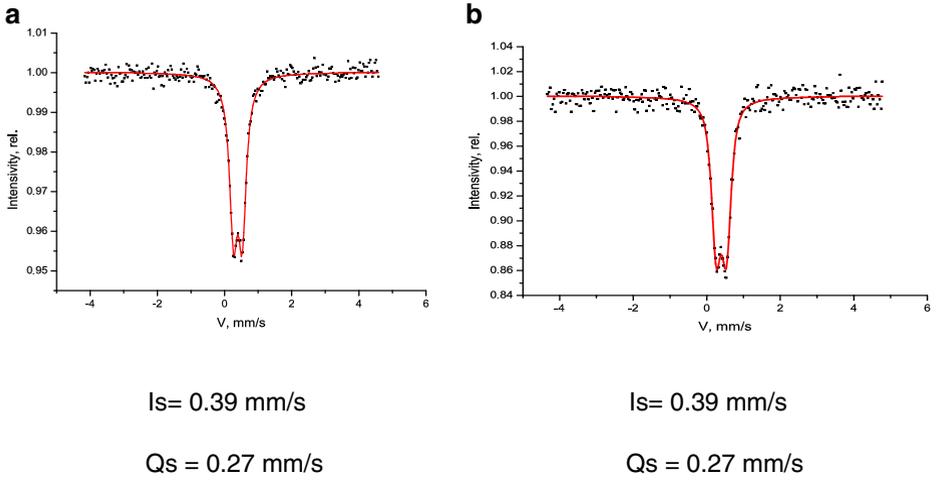


Fig. 1 Mössbauer spectra of aqueous solution of ferrioxine (a) and incubated PMAA gel (b) at the temperature $T = 118 \text{ K}$

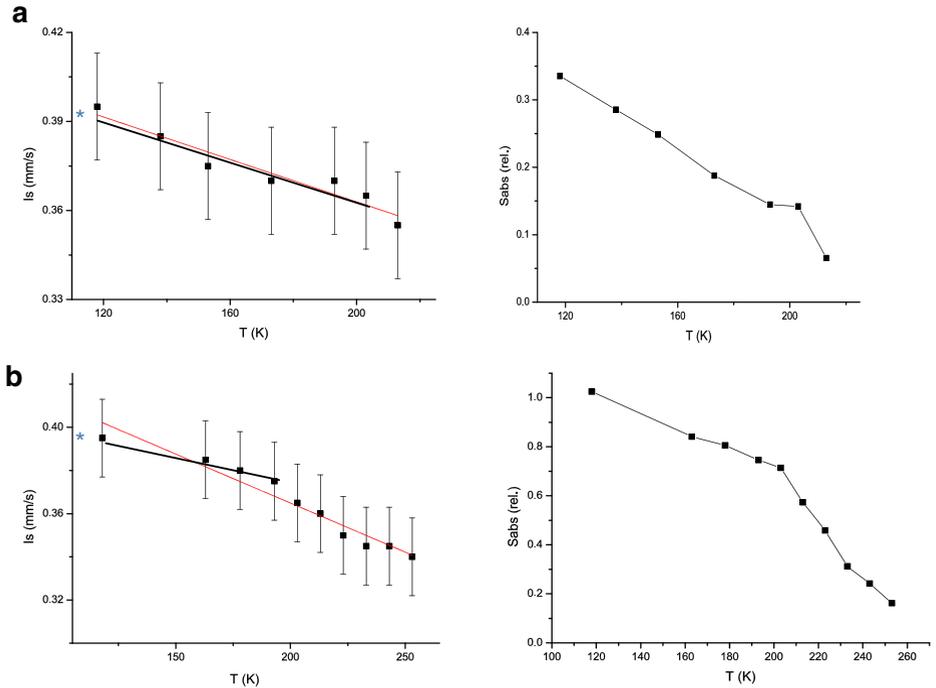


Fig. 2 Temperature dependences of isomer shift and recoilless fraction of ferrioxine aqueous solution (a) and incubated PMAA gel (b).(*) - LSM for points below 200 K

are vibrating, the second situation occurs when the molecule vibrates as a whole unit. If this situation occurs, the bonds in molecular crystal are covalent.

Table 1 Lattice temperatures and effective vibrating masses for ferroine aqueous solution and incubated PMAA gel

| Sample | M_{eff} , Dalton | Θ_M , K | M_{eff}^* , Dalton | Θ_M^* , K |
|---------------------------|---------------------------|----------------|-----------------------------|------------------|
| Ferroine aqueous solution | 194 ± 11 | 62 ± 7 | 203 ± 12 | 63 ± 7 |
| Incubated PMAA gel | 208 ± 14 | 94 ± 7 | 432 ± 26 | 135 ± 11 |

For the lower temperature area δ_{SOD} and recoilless fraction can be calculated [4, 5] as:

$$\delta_{\text{SOD}} = -\frac{3}{2} \frac{kT}{M_{\text{eff}}c} + \text{const} \quad (1)$$

$$\ln f = -\frac{3E_\gamma^2}{M_{\text{eff}}c^2k\theta_M^2}T = \ln A(T) + \text{const} \quad (2)$$

where A is the area under the resonance curve, k - Boltzmann's constant, c - velocity of light, E_γ - energy of the emitted photon.

Approximating the temperature dependences of the isomer shift and $\ln A(T)$ with a linear function we can obtain the values of M_{eff} and θ_M . The lattice temperatures and effective masses for ferroine aqueous solution and incubated PMAA gel were calculated.

We use only experimental points below 200 K For $\ln A(T)$ because formula (2) is correct only for low-temperature area, where diffusive motion does not affect the Mössbauer parametra of the spectra significantly. There are two ways to calculate M_{eff} value from $I_s(T)$: the first one is calculating M_{eff} value using all the points of the temperature dependence, the second one is to use only points below 200 K (point of diffusive motion beginning). Though there is no obvious way for diffusive motion to affect on $I_s(T)$ dependence, we can't say that it does not affect the dependence at all. That is why two ways of calculations were performed.

The results are exposed in Table 1. Upper indexes are for two ways of calculating M_{eff} : no index for using all the points, (*) for using points only below 200 K.

The deviation of M_{eff} from the value of unbound iron atom (57 Da) reflects the covalence degree of Iron and it's neighbours bonds [6]. As the M_{eff} changed after the incubation, we can say, that additional bonds appear between iron complexes and COO^- groups of the polymer gel during the incubation. θ_M can be used as a quantative measure of such bonds. Thus, stable metal-polymer bonds are formed and the metal embeds in a polymer gel structure as a whole complex.

4 Conclusion

Mössbauer spectroscopy's high sensitivity to the nearest neighborhood and state of iron ions allowed us to conclude that iron embedded in PMAA gel structure during the incubation not as an ion [2], but as a whole ferroine complex. The temperature dependences of spectral recoilless fraction and isomer shift gave opportunity to estimate embedding parameters. At the first time this method was applied to such samples. The data obtained allow us to conclude that ferroine complex embed in the PMAA gel structure without destruction and form additional cross-links in the gel network due to strong covalent bonds of iron with COO^- groups of PMAA .

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