Physics of the Solid State, 2024, Vol. 66, No. 12

08

Probe Mössbauer diagnostics of dynamic properties of frozen water layers in montmorillonite pores

© A.A. Zalutskii, E.N. Shkolnikov

Yaroslavl State Technical University,
Russia, Yaroslavl

E-mail: zalutskii-2017@mail.ru

Received April 30, 2024
Revised October 28, 2024
Accepted October 30, 2024

A methodical approach has been developed and tested on the basis of Mössbauer spectroscopy, which allows one to effectively estimate the viscosity of a medium based on the measured diffusion coefficient of a probe in thin films of bound water in a clay mineral. The procedure for reconstructing a specific type of potential is based on the analysis of viscosity coefficients and ion mobility measurement data related to diffusion by the Einstein relation. The experimental results fill in the missing information relevant for constructing a theoretical model for the formation of natural nanotubes. Key words: Diffusion coefficient, microviscosity, Mössbauer probe, pores.

Keywords: Diffusion coefficient, microviscosity, Mössbauer probe, pores.

DOI: 10.61011/PSS.2024.12.60193.6478PA

Mixed porosity, mostly inherent in natural clays, is due to presence of various sources of pore origination therein: the primary mechanism is due to the damage of the crystalline structure of the mineral, and the secondary one — formation of gaps and cavities between the contacting clay particles (Figure 1).

The objective of the paper — to demonstrate the approaches developed specifically on the basis of proble Mössbauer spectroscopy (MS), which may apply the physics of viscoelastic and dynamic (energy) processes to films of water adsorbed in the pores of natural montmorillonite.

To solve the alloyed task, out of four shapes of the probe ^{57}Fe (Figure 1) two turned out to be most effective, as will be shown below. The spectrum of the first shape is specific for Fe^{3+}, consisting of dimers and amorphous polymer films (clusters) (*1* and *2* in Figure 2, *a*, accordingly). The experimental spectrum of the second shape is presented as a superposition of two partial spectra with parameters typical of cations Fe^{2+} located in a high-spin state in two nonequivalent positions. (shapes *1* and *2* on insert of Figure 2, *a*). Mathematical processing of experimental spectra (Table 1), obtained using a standard spectrometer in transmission geometry in the temperature range (90–330 K), was carried out using software complex MSTools, designed at the MSU faculty of physics by V.S. Rusakov. The number of partial spectra was defined by the results of imposition of „rigid“ and „non-rigid“ bonds on the variable Mössbauer parameters, at the same time the conditions of the type of inequalities and/or setting of the ignore areas (SPECTR software from MSTools complex) were used.

Since the water films are in supercooled liquid state, the diffuse and vibrational components of molecular movements are not statistically independent, opposite to what is usually assumed when simple fluids are described. In our case the reference point for the qualitative description of the simultaneous combination of the elasticity and fluidity (viscosity) properties could be the phenomenological relaxation Maxwell theory. If it is supplemented with a molecular

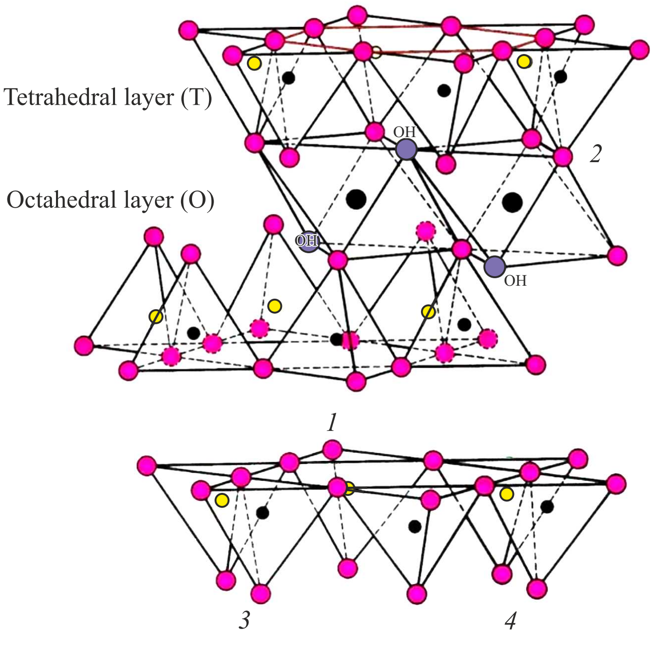

Figure 1. Schematic image of montmorillonite packet consisting of elemental structural layer of type 2 : 1 (octahedral (O) Al- or Mg-oxygen-hydroxyl lattice is enclosed between two lattices of silicon-oxygen tetrahedrons (T)) and interlayer gap. Additionally the areas of the Mössbauer probe localization are specified: *1* — interlayer space of mineral (clusters and dimers Fe^{3+}); *2* — dents of the packet and holes of mineral (compounds Fe^{2+}); *3, 4* — outer surface and interpacket space of mineral (ion form Fe^{3+} (*3*) and akaganeite (*4*)).

Table 1. Hyperfine parameters of partial Mössbauer spectra of proble atoms ^{57}Fe, adsorbed in montmorillonite, with the presence of regular and deuterated water in the adsorbent: chemical shift δ, quadrupolar splitting Δ, line width Γ, intensity I

T, K	Partial spectrum		δ^*, mm/s	Δ, mm/s	Γ, mm/s	I, %
Montmorillonite with H_2O						
150	Fe^{3+}	1	0.814(1)	1.650(2)	0.347(5)	57(1)
		2	0.742(2)	0.604(2)	0.526(7)	43(2)
100	Fe^{2+}	1	1.63(1)	3.43(1)	0.279(5)	44(4)
		2	1.63(2)	3.10(2)	0.458(5)	42(5)
Montmorillonite with D_2O^{**}						
149	Fe3+	1	0.797(1)	1.634(2)	0.369(5)	59(1)
		2	0.724(2)	0.636(1)	0.480(9)	41(1)
140	Fe^{2+}	1	1.66(1)	3.38(1)	0.252(4)	55(2)
		2	1.68(1)	3.08(1)	0.360(5)	45(3)

Note: * Chemical shift relative to sodium nitroprusside. ** Clay (after prior removal of „free“ H_2O from it) was soaked in vapours of D_2O with subsequent saturation of mineral with the solution made from $^{57}FeCl_3$ and D_2O.

mechanism, for example, using Frenckel's „hole“ theory of liquids [1], it is possible to describe data obtained from Mössbauer experiment (ME) from the universal positions. For convenience of the analysis the actual material experimental data of rather large volume was systematized using pore size r.

1. Use of MS to study water films localized in micropores ($r < 0.6$–0.7 nm) and supermicropores (0.6–$0.7 < r < 1.5$–1.6 nm) of montmorillonite. Mathematically the motion of the probe under the action of random hits from the side of the medium is described by stochastic differential Langevin equation, which in unidimensional form is as follows:

$$\ddot{x} + \gamma\dot{x} + \frac{1}{m}\frac{\partial U(x)}{\partial x} = \xi(t). \tag{1}$$

Here function $\xi(t)$ represents noise, the properties of which are described by an autocorrelator

$$\langle \xi(t)\xi(\tau)\rangle = 2D\gamma^2\delta(t-\tau),$$

$U(x)$ — potential energy, m — mass of Mössbauer probe, D — coefficient of particle diffusion in medium, and γ^{-1} — their mobility. At the same time the diffusion constant produced from ME, and the breaking force (particle mobility) are related by Einstein ratio ($\gamma D = kT/m$).

The nature of the probe movement and the specific nature of the process of Fe^{3+} ions interaction with the dense environment (the case of high friction) make it possible to model the potential $U(x)$ in the form of „railing“ from potential barriers, i. e. we have a peculiar imitation of the viscous medium by a potential „comb“. Then the abnormally sharp reduction in the area of Mössbauer spectrum $S(T)$ (non-typical for the solid body) without the widening of the spectral line (width of line Γ remains constant, which is not typical for liquid (Figure 3, a)) in the entire studied area of temperatures makes it possible to restore the temperature dependence of the dynamic viscosity $\eta(T)$. Within the model of limited diffusion proposed in [2], the temperature behavior $S(T)$ (Figure 2, b) is related not to the increase of the full amplitude of probe movement, but with the strong temperature dependence of the correlation time $\tau_c(T)$. The presence of the temporary parameter is the effect of solving the equation (1), and its change with temperature $\tau_c(T) = (\gamma(T))/\omega_0^2$ (here ω_0 is the frequency of harmonic oscillator used to model the movement of Mössbauer probe) makes it possible from the experimental behavior $S(T)$ to obtain dependence $\eta(T)$ with the possibiloty of subsequent assessment of the sought value of dynamic microviscosity. Then the received value of effective microviscosity of „frozen“ water in the presence of mineral indicates that the properties of the nearest environment of Mössbauer mark substantially differ from the properties of „free“ frozen water without mineral (Table 2).

2. Use of MS to study water films localized in mesopores or transition pores 1.5–$1.6 < r < 100$–200 nm) of montmorillonite. Use of the scale-invariant theory to analyze the parameters of Mössbauer spectra of probe Fe^{3+} near the phase transition (or critical point) showed that scaling of thermodynamic characteristics under temperature change correlates well with parameters of the effective potential of particle-to-particle interaction of (Lennard–Johnes type (L–J)). Then the scaling of parameters of local dynamics (τ or η) for 2D-ice with participation of intermolecular repulsive potential $U(r) \sim (\sigma/r)^{3\gamma_{LJ}}$, where constant σ has the sense of specific distance, where interaction disappears, makes it possible to determine the scaling parameter γ_{LJ}. It, in its turn, may be related to Gruneisen constant γ_G, which characterizes the variation in the frequency of lattice vibration depending on the change in the volume of system V; value γ_G may be taken from the data of ME we did previously [3–5]. In our case the assessment γ_G was carried out within Debye approximation ($\gamma_G = -d\ln\theta_D/d\ln V$, where θ_D is Debye temperature). But in case of probe Fe^{2+}, testing water behavior in mineral holes and dents, the nonconformity of parameters was established experimentally ($\gamma_{EOS} \gg \gamma_{LJ} \gg \gamma_G$). Here γ_{EOS} is the scale parameter under scaling of density of the maximum energy barrier, received when using the modified Avramov model [6]. Such behavior of scaled parameters is traditionally explained by transition from supercooled Van der Waals liquids to strongly H-bound materials. Please find below the alternative explanation, provided for by the change in the type of intermolecular potential in the studied system.

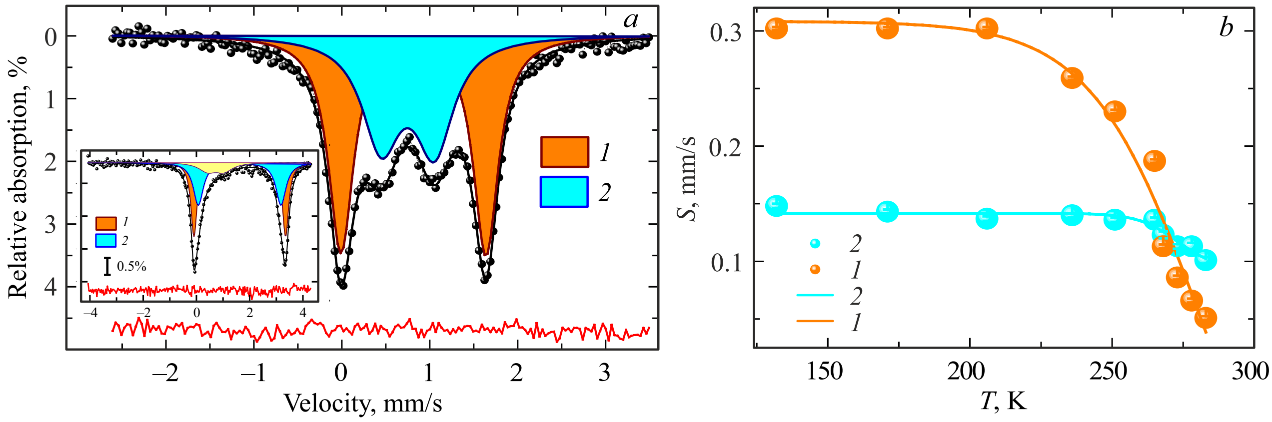

Figure 2. (*a*) Result of model decryption of Mössbauer spectra of probe atoms ^{57}Fe in the system of „montmorillonite–H_2O“: *1* — probe in the form of ions Fe^{3+}, forming together with groups OH^- the dimers of iron $[Fe_2^{3+}(OH)_2^-]^{4+}$, *2* — probe in the form of polymer film (clusters) with the structure similar to hydroxide Fe^{3+}, and having spatial geometry (*2D* or *3D*) depending on the areas of localization in the mineral. The insert presents the result of similar analysis of data for the same system, but for a probe in the form of bivalent iron compounds (yellow is the contribution of the probe Fe^{3+} in the form of polymer film). (*b*) Temperature dependence of normalized areas of Mössbauer spectra for dimers (*1*) and clusters (*2*) of iron in the film of frozen „bound“ water in clay (dots — experiment, lines — result of mathematical processing of spectra within the model of limited diffusion).

Table 2. Values of coefficients of effective viscosity η of medium (nanofilms of frozen water), surrounding Mössbauer probe, by results of MS method

Object of study	η, P	Study method*	T, K	Physical model**
Glycerin ($C_3H_8O_3$)	121.0 39.5 14.8	Wide set	273 283 293	Wide set
Water (H_2O)	0.0175 0.0142 0.0082	Wide set	273 280 300	Wide set
Boundary layer on „the surface of volume“ ice	~ 0.80	Wide set	273	Wide set
Protein of methmyoglobin	$6 \cdot 10^4$ 570	MS	196 300	Brownian evanescent oscillator
Slides of reactive centers of photosynthetic membranes from *R.rubrum*.	10^4 10^2	MS	224 300	Brownian evanescent oscillator
Films of frozen water (probe in the form of dimers Fe^{3+}) $P/P_0 = 0.98$** $P/P_0 = 0.50$	67(3) 40(2)	MC	250 267	Brownian evanescent oscillator
Films of frozen water (probe in the form of clusters Fe^{3+}) $P/P_0 = 0.98$ $P/P_0 = 0.50$	1250(50) 840(40)	MS	250 267	Brownian evanescent oscillator
Films of frozen water (probe in the form of aquo ion Fe^{2+}) $P/P_0 = 0.50$	0.49(3)	MS	273	Of solid state (Debye) or free (weakly evanescent) oscillator

Note: * Information in the first three lines is not provided because of rather wide set of experimental methods of study. Information may be found in [2], and also see links in [3–5]. ** Same is true for physical models. *** Equilibrium relative pressure of water vapors, at which the specimens were soaked. Value $P/P_0 = 0.98$ corresponds to four, and $P/P_0 = 0.50$ — to two monolayers of water adsorbed on the surface of montmorillonite.

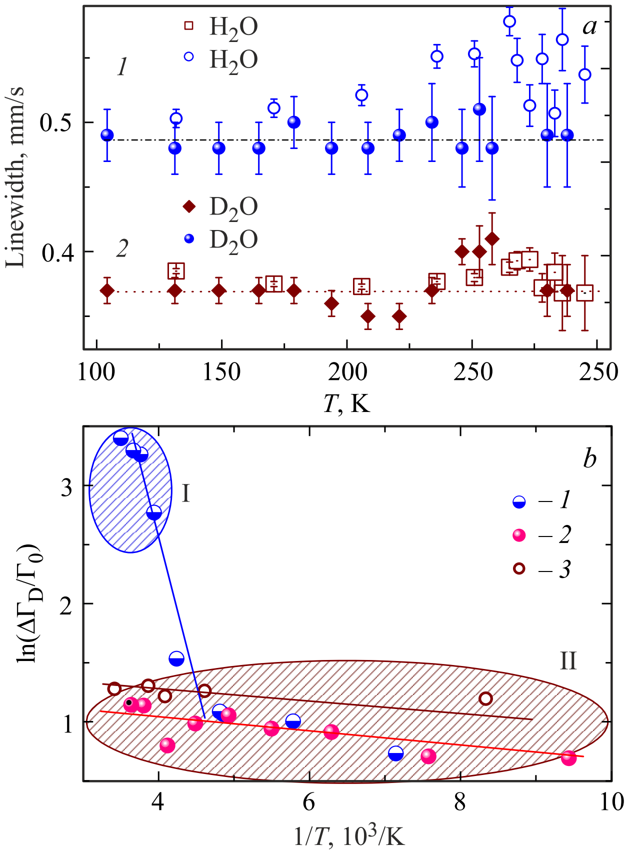

Figure 3. (a) Temperature dependences of width of Mössbauer line of spectra for trivalent iron compounds (in the form of clusters (1) and dimers (2)), present in the film of regular (H_2O) and deuterated (D_2O) bound water in natural clay (montmorillonite). (b) Dependence of diffusion component of Mössbauer line width $\ln(\Delta\Gamma_D/\Gamma_0)$ on $1/T$ for ions of bivalent iron in model and natural systems (1 — mineral with water, 2 — $FeCl_3$ without water, 3 — mineral without water); I — area of „pink“ noise, II — area of „white“ noise.

The procedure to determine the specific type of potential will be carried out using the results of detailed analysis of temperature behavior of the parameters of Mössbauer spectrum of probe Fe^{2+}. Temperature broadening of the absorption line has a complex dependence with the clearly marked inflection point, which may separate various diffusion mechanisms (Figure 3, b). At low temperatures (or in region II) the diffusion occurs by a hop-like process, but approximation with a sudden hop inherent in the diffusion in solid state, does not describe the experimental data. It is suggested to interpret the obtained experimental data within Frenckel's hole theory [1]. Mathematical processing of Fe^{2+} spectrum absorption line broadening ($\Delta\Gamma = 2\hbar k^2 D$, where $\hbar$ — Planck constant, and k — wave vector of gamma-rays), including additionally other probes (Figure 3, b), made it possible to obtain values of diffusion coefficients D. Subsequent use of Arrhenius ratio ($\eta = C\exp(W/k_B T)$, where k_B — Boltzmann constant, and W — activation energy at diffusion movement) made it possible to assess the effective microviscosity of „frozen“ water in mesopores of montmorillonite (Table 2). Note that for adequent implementation of Frenckel's theory it is necessary to form a fluctuation „hole“ at the expense of collective dynamic effects in condensed medium. Then the estimate of the hole size obtained by us (directly using data of MS see [5]) once again speaks for the proper choice of the physical model.

The above diffusion nature of Mössbauer probe movement makes it possible to plan a reliable path to search for potential type. Indeed, the diffuse movement of the particle in the assumption of bistable potential $U(x)$ in the field of random forces $\xi(t)$ (the area of white noise diagnosed in [5]) may be described by equation (1). The obtained solution (Kramers problem [7]) or so called Kramers time τ_D, i.e. average time of particle diffusion from one well to another, isolated with a barrier of U_0 ($\tau_D = \tau_0\exp(U_0/\gamma mT)$) height, was satisfactorily matched with ME data.

The completed analysis of data for high-temperature region I (Figure 3, b) contrary to the results of paper [8], where such nature of behavior $\Delta\Gamma(T)$ was studied for glycerin, did not require a change in the diffusion mechanism. If we assume according to Frenckel [1] that the activation energy decreases by linear law ($W = W_0 - \alpha T$, where α — temperature coefficient of linear expansion), then the temperature dependence of viscosity $\eta(T)$ is well matched with ME data. Note that the expression for viscosity proposed in [8] and based without any physical substantiation on Litovitz empirical formula for activation energy ($W = W_0/T^2$), does not comply with our data. But due to the presence of „color“ noise [5] in region I, it was not quite correct to use the solution to Kramers problem for potential searching. Then the approach was implemented, which was based on using two methods. The first method was based on the model Lorentz system of equations (LS), which makes it possible to effectively track the stochastic resonance (SR) in the object. Our data are well-matched with the theoretical dependence proposed in [9] to explain SR phenomenon using SL. This, in its turn, presumes the availability of bistable potential $U(x)$, which quantitatively explains the SR presence in the object. The second method is more visual and consists in the fact that three SL equations may be converted to the type of bistable oscillator with inertial nonlinearity [10]. Then in case of high values of normalized Rayleigh number, the equation of bistable oscillator is obtained without a non-linear inertial member or Duffing oscillator. This does not only guarantee the presence of SR effect in the system, but also validly confirms the type of bistable potential $U(x)$.

Therefore, the approach tested above (dynamic parameters of MS → diffusion parameters → viscosity coefficients) demonstrated adequate results when studying the viscoelastic physical properties of the systems, the distinctive feature of which was unavailability of obtaining such information by the traditional method.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] J. Frenkel. Kinetic Theory of Liquids. Oxf. Univ. Press, Oxford (1946).
[2] K.V. Shaitan, A.B. Rubin. Molecular biology **14**, *6*, 1046 (1980).
[3] A.A. Zalutskii. Crystallogr. Rep. **65**, 371 (2020).
[4] A.A. Zalutskii. Izv. vuzov. Ser. khimiya i khim. tekhnologiya **57**, *12*, 41 (2014). (in Russian).
[5] A.A. Zalutskii, V.V. Morozov, A.Yu. Sokolov, E.N. Shkolnikov. Solid State Phys. **65**, *12*, 2052 (2023).
[6] I. Avramov. J. Non-Cryst. Solids **262**, 258 (2000).
[7] H.A. Kramers. Physica **7**, *4*, 284 (1940).
[8] A. Abras, J. G. Mullen. Phys. Rev. A, **6**, *6*, 2343 (1972).
[9] R. Benzi, A. Sutera, A. Vulpiani. J. Phys. A: Math. Gen. **14**, L453 (1981).
[10] Yu.I. Neimark, P.S. Landa. Stochastic and Chaotic Oscillations. Springer, Dordrecht (1992). 500 p.

Translated by M.Verenikina