# Effect of hydration on the dynamics of polymeric cation exchangers and polymeric sorbent inferred from the Rayleigh scattering of Mössbauer radiation

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Dependences of the dynamics of hydrophilic polymeric nets of acrylate cation exchanger, sulfonated poly(styrenedivinylbenzene) cation exchanger, and hydrophobic poly(divinylbenzeneethylstyrene) sorbent on the degree of hydration were studied by the Rayleigh scattering of Mössbauer radiation (RSMR). Dependences of the integral elastic fraction of RSMR of the polymer—water systems on the water/polymer mass ratio were determined. In the case of the cation exchangers, a considerable decrease in the elastic fraction of RSMR of the polymer during hydration was established. A considerable increase in the mobility of the nets indicates their transition from a glassy state to an elastic state. It was established that the intramolecular mobility of the hydrophobic polymeric sorbent remains unchanged during its hydration, and it contains water clusters with the nonzero elastic fraction of RSMR in its finest pores.

**Key words:** Rayleigh scattering of Mössbauer radiation, dynamics of polymers, polymeric ion exchangers, polymeric sorbents, hydration.

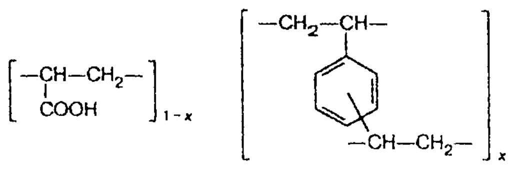
The study of the dynamics of polymers is motivated by the relation between their dynamics and important functional properties. This concerns completely a special class of reactive polymers, *viz.*, polymeric ion exchangers.

Previously,[1–4] it has been established by Mössbauer spectroscopy that the hydration of the three-dimensional polymeric net of an acrylate cation exchanger results in its transition from the glassy to the elastic state with very intense intramolecular motions. The frequency and amplitude parameters of these motions were studied quantitatively, and their strong dependence on the cross-linkage concentration of the polymeric net was established. In these works, the Mössbauer isotope $^{57}$Fe was introduced into the ion exchanger to form a strong complex with functional groups $(-\mathrm{RCOO}^-)_2\mathrm{Fe}^{3+}\mathrm{A}^-$. In this case, the dynamics of the Fe atom reflected the dynamics of the fragment of the polymeric net. The necessary presence of functional groups, which bind strongly the atom-label, is the natural restriction of this approach. In addition, the effect of a metal ion on the dynamics of the polymeric net and the dynamic heterogeneity of the net cannot be ambiguously separated in the strong dependence of the mobility on the number of metal ions introduced. When the Mössbauer probe is used, its mobility is mainly determined by the microstructure rather than the mobility of the net of the solvated ion exchanger.[5,6] Therefore, an alternative approach is very important: the study of the dynamics of a polymer—water (solvate) system by the Rayleigh scattering of Mössbauer radiation (RSMR). The possibility to study any substance in the absence of Mössbauer atoms is a great advantage of the method, although there is some uncertainty in separating the contributions of components of the two(multi)-component system to the integral spectrum of the scattered radiation.

In this work, we present the first results of the study of the dynamics of the polymeric ion exchanger—water and polymeric sorbent—water systems containing no metal atoms in a wide range of hydration degrees.

## Experimental

The following materials were used in the study: 1) two SGK-7 acrylate cation exchangers (VNIIKhT, Russia) based on polyacrylic acid cross-linked by divinylbenzene with cross-linkage concentrations of 2 and 30 wt.% (SGK-7-2% and SGK-7-30%)



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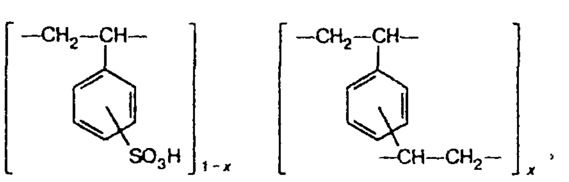
2) KRS-2p sulfonated cation exchanger (USSR) based on polystyrene cross-linked by divinylbenzene with a cross-linkage concentration of 2%



and 3) Porolas TM polymeric sorbent (VNIIKhT, Russia) based on the copolymer of divinylbenzene (70%) and ethylstyrene (30%)

Samples with different degrees of hydration were prepared from the entirely hydrated state by drying at room temperature in a desiccator over $H_2SO_4$ and $P_2O_5$ followed by storage (for 2 days) of the sample with a certain degree of hydration in a sealed measuring cell. Samples dried to a constant mass at 120 °C (SGK-7) and 140 °C (KRS-2p and Porolas TM) were accepted as maximum dehydrated samples.

Measurements were carried out on a setup for investigation of Rayleigh scattering of Mössbauer radiation with circular scattering geometry. A Mössbauer source of γ-quanta $^{57}$Co(Cr) with an activity of 110 mCi and active spot of 4 mm was the radiation source. The scattering angle $2\theta = 12 \pm 1.5°$ (wave vector $Q = 1.53$ Å$^{-1}$) and reception angle 5° made it possible to work in the so-called noncoherent variant when the divergence of a scattered γ-quantum beam covers tens of Bragg reflections.[7a] A close scattering angle was used in the study of the dynamics of polymers.[8] The combined absorber $[Li_3{}^{57}FeF_6+(NH_4F)_3({}^{57}FeF_3)_3]$, which gives a rectangular spectrum in the +1 to −1 mm s$^{-1}$ range, was used as the resonance RSMR analyzer ("black absorber"). The detector was a circular NaI(Tl) crystal with a thickness of 0.2 mm attached to a photomultiplier. The polymeric sample under study was the scattering material.

The elastic fraction of RSMR ($f_R$) was determined by the following procedure. Current pulses were detected by a detector with two counting channels $I_0$ and $I_\infty$, where $I_0$ corresponded to the counting rate when the radiation source was at rest relative to the scattering material and analyzer ($v = 0$), and $I_\infty$ corresponded to the counting rate when the source moved relative to the scattering material and absorber ($v = \infty$). The elastic fraction of RSMR was calculated by the formula

$$f_R = \left(\frac{I_x(2\theta) - I_0(2\theta)}{I_x(2\theta)}\right) \Bigg/ \left(\frac{I_\infty(0) - I_0(0)}{I_x(0)}\right), \quad (1)$$

where $I_x(2\theta)$, $I_0(2\theta)$, $I_x(0)$, and $I_0(0)$ are the radiation intensities behind (angle 2θ) and in front of the scattering material (θ = 0), respectively, in two regimes of operation ($v$ = 0 and ∞).

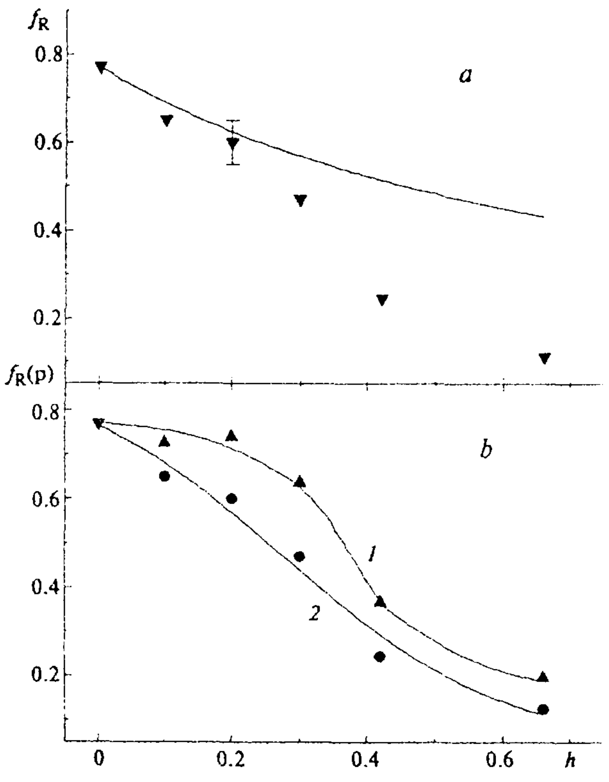


**Fig. 1.** Dependences of the dynamics of the acrylate cation exchanger SGK-7-2% on the water/polymer mass ratio ($h$). *a*, Dependence of the integral elastic fraction of RSMR ($f_R$) of the polymer—water system on $h$; points indicate experiment; line is the theoretical curve under the assumption that $f_R(H_2O) = 0$, $f_R(p) = 0.77$ = const; *b*, dependence of the elastic fraction of RSMR of the polymer $f_R(p)$ on h under the assumption that: *1*, $f_R(H_2O) = 0$; *2*, $f_R(H_2O) = f_R(p)$ at $0 < h < 0.493$, and $f_R(H_2O) = 0$ at $h > 0.493$; lines are approximations of calculated points.

Due to the use of the resonance Mössbauer filter, we provided a resolution ability by energy of up to $10^{-8}$ eV for Mössbauer spectroscopy on $^{57}$Fe in the scattering samples under study containing no Mössbauer nuclei.

## Results and Discussion

The dependences of the elastic fraction of RSMR ($f_R$) on the degree of hydration found in our experiments are shown in Figs. 1—4.

***Acrylate cation exchanger.*** For the dehydrated weakly linked acrylate cation exchanger (2% cross-linkage), the $f_R$ value is sufficiently high (0.77) and characteristic of the polymer in the glassy or crystalline state.

Hydration of this polymer results in a sharp decrease in the integral $f_R$ value (see Fig. 1). To determine the hydration dependence of the inherent polymeric net of the cation exchanger, one should take into account the contribution of scattering of the Mössbauer radiation on

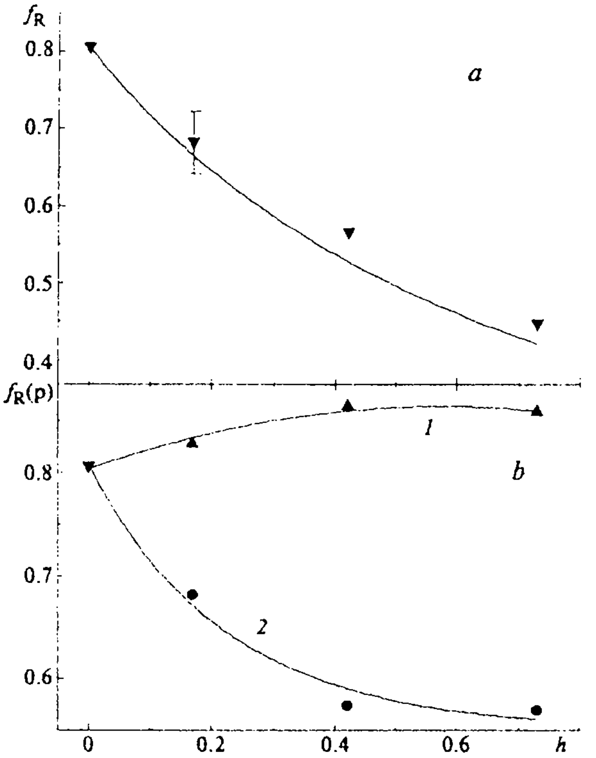


**Fig. 2.** Dependence of the dynamics of the acrylate cation exchanger SGK-7-30% on the water—polymer mass ratio (*h*). *a*, Dependence of the integral fraction of RSMS ($f_R$) of the polymer—water system on *h*; points are experiment; line is the theoretical curve under the assumption that $f_R(H_2O) = 0$, $f_R(p) = 0.806$ = const; *b*, dependence of the elastic fraction of RSMS of the polymer $f_R$(p) on h under the assumption that: *1*, $f_R(H_2O) = 0$; *2*, $f_R(H_2O) = f_R(p)$ at $0 < h < 0.403$, $f_R(H_2O) = 0$ at $h > 0.403$; lines are approximation of calculated points.

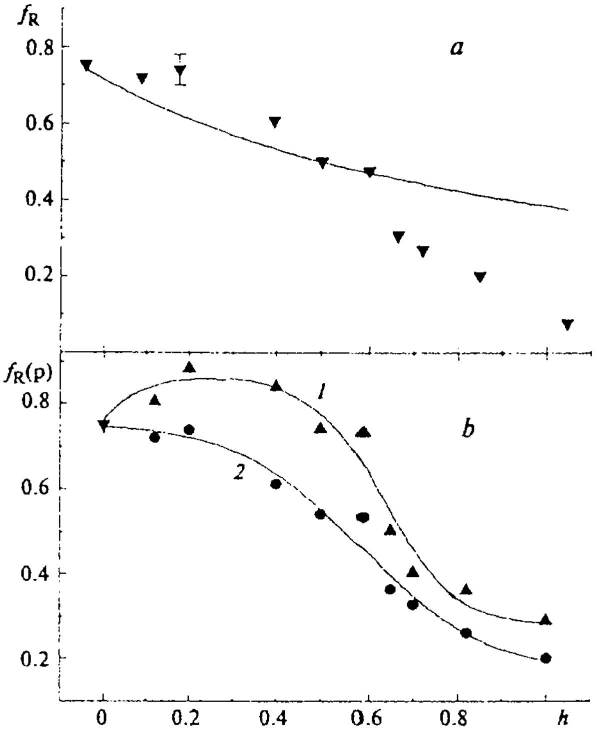


**Fig. 3.** Dependences of the dynamics of the sulfonated polystyrene cation exchanger KRS-2p on the water/polymer mass ratio (*h*). *a*, Dependence of the integral elastic fraction of RSMR ($f_R$) of the polymer—water system on *h*; points are experiment; line is the theoretical curve under the assumption that $f_R(H_2O) = 0$, $f_R(p) = 0.751$ = const; *b*, dependence of the elastic fraction of RSMR of the polymer $f_R$(p) on h under the assumption that: *1*, $f_R(H_2O) = 0$; *2*, $f_R(H_2O) = f_R(p)$ at $0 < h < 0.384$, $f_R(H_2O) = 0$ at $h > 0.384$, lines are approximations of calculated points.

the polymer and water atoms to the integral $f_R$ value. For the multicomponent system,

$$f_R = \sum_i \left\{ C_i \sum_j \frac{U_j}{A_i} f_{0j}^2 \right\} f_i \Big/ \sum_i \left\{ C_i \sum_j \frac{U_j}{A_j} \left( f_{0j}^2 + F_j \right) \right\}, \quad (2)$$

where $\sum$ denotes summation over all atoms of the *i*th component with atomic mass $A_j$, concentration $U_j$, atomic scattering factor $f_{0j}$, and Compton scattering amplitude $F_j$.

As can be seen in Fig. 1, the experimental points $f_R(h)$ lie considerably lower than the calculated integral curve found by Eq. (2) under the assumption that for the polymer, $f_R$(p) is independent of the degree of hydration, whereas for water in the polymer, $f_R(H_2O) = 0$, as for liquid water. A similar result has been observed previously in studying the hydration dependence of the dynamics of biopolymers by the RSMR method (see, *e.g.*, Ref. 7b). This implies that, in fact, the elastic fraction of RSMR of the inherent polymeric net decreases during hydration. The corresponding data of the hydration dependence of the elastic fraction of the polymer $f_R$(p) calculated by formula (2) in terms of the simplest physical model, which assumes that for all water in the polymer $f_R(H_2O) = 0$, are presented in Fig. 1, *b* (curve *1*).

Somewhat different result was obtained for the strongly cross-linked (30%) cation exchanger (see Fig. 2). In this case, the experimental points lie near the calculated model curve ($f_R$(p) = const, $f_R(H_2O) = 0$) and, moreover, somewhat higher. If we assume that for all water in the polymer $f_R(H_2O) = 0$, the experimental data of RSMR indicate only some increase in the elastic fraction of RSMR for the polymer $f_R$(p) during hydration (see Fig. 2, *b*, curve *1*). However, the Mössbauer data indicate an increase in the mobility of the strongly cross-linked polymer,[4] and it is difficult to explain the decrease in its mobility when a plasticizer (water) is added. Therefore, we believe that a model taking into account binding of water by functional groups of the cation exchanger is more appropriate. The fact of binding of water by hydrophilic groups is well known and should result in the appearance of elastic scattering. It has been shown recently by the RSMR method that water bound to the biopolymer possesses a considerable $f_R$ value.[9] In the case of the acrylate cation exchanger, based on the published data,[10,11] the quantity of bound water can be assumed to be equal to $2H_2O$/—COOH. The diffusion mobility of the bound water molecules can be estimated from the equation for the time during which the molecule is in the potential well with the depth $E$: $\tau = \tau_0\exp(E/RT)$. Taking for the estimation $\tau_0 \sim 10^{-13}$ s and equating $E$ to the differential heat of water adsorption ($\Delta H \approx 13$ kcal mol$^{-1}$ in a similar system[11]), we find $\tau \sim 10^{-4}$ s, *i.e.*, the residence time of the $H_2O$ molecule on the hydration center is much longer than the lifetime of the Mössbauer level of $^{57}$Fe. This implies that the diffusional broadening and the related decrease in the elastic peak intensity of the scattered radiation can be neglected in this case. If the high value $f_R(H_2O) \approx 0.9$ (determined by the low value of vibrational atomic displacements) in the molecular ice crystal at $T \approx 200$ K[12] is also taken into account, it is reasonable to accept, as a working hypothesis, that the elastic fractions of RSMR of the polymeric net and bound water are equal, *i.e.*, $f_R(H_2O) = f_R(p) = f_R(h)$ within degrees of hydration from 0 to the maximum content of the bound water $2H_2O$/—COOH, and for the rest of the water, $f_R(H_2O) = 0$ should be assumed. The $f_R(p)$ values of the polymeric net with 2 and 30% cross-linkage calculated in terms of this model are presented in Fig. 1, *b* (curve *2*) and Fig. 2, *b* (curve *2*).

It is impossible to determine unambiguously the $f_R$ values of the hydrated polymeric net from the results of our experiments without independent data. The pairs of dependences presented in Figs. 1, *b* and 2, *b* indicate limits that can contain, in principle, true values of $f_R(p)$. In the most appropriate (in our opinion) model taking into account the bound water, $f_R(p)$ of the polymer decreases upon hydration from 0.77 ($h = 0$) to 0.12 ($h = 0.66$) in the weakly cross-linked (2%) cation exchanger, and in the strongly cross-linked (30%) cation exchanger, it decreases from 0.81 ($h = 0$) to 0.57 ($h = 0.73$). Thus, first, at all cross-linkage concentrations (from minimum to maximum), the intramolecular mobility (IMM) of the polymeric net of the acrylate cation exchanger SGK-7 increases significantly upon hydration and, second, IMM of the hydrated cation exchanger depends strongly on the cross-linkage concentration.

Using the numerical $f_R(p)$ values found, we can determine the mean-square displacement of atoms by the known formula[7b]

$$f_R = a \cdot \exp(-Q^2\langle x^2\rangle), \qquad (3)$$

where $a = R/(R + C)$, $R$ and $C$ are the intensities of the Rayleigh and Compton radiations, and $\langle x^2\rangle$ is the mean-square displacement of atoms. The $\langle x^2\rangle$ values determined are the following: for the weakly cross-linked cation exchanger, 0.11 Å$^2$ ($h = 0$) and 0.91 Å$^2$ ($h = 0.66$), and for the strongly cross-linked cation exchanger, 0.09 Å$^2$ ($h = 0$) and 0.24 Å$^2$ ($h = 0.73$).

***Sulfonated polystyrene cation exchanger.*** The validity of the aforementioned approach, which takes into account the low mobility of the bound water, is confirmed by the result of studying the KRS-2p cation exchanger in which this effect is more pronounced. The experimental points for the integral $f_R(h)$ values in the region of low degrees of hydration (below $h \approx 0.5$) lie considerably higher that the calculated curve, assuming $f_R(p) =$ const and $f_R(H_2O) = 0$ (see Fig. 3, *a*). This, as in the case of SGK-7-30%, implies that if $f_R(H_2O) = 0$ is accepted for all water, the $f_R(p)$ value during hydration first increases and then decreases (see Fig. 3, *b*, curve *1*). We cannot find a reasonable physical explanation for this $f_R(p)$ behavior. If the model presented above, which takes into account the bound water, is accepted (assuming its value to be equal to $4H_2O$/—$SO_3H$,[13,14] the value of the differential adsorption heat for it is $\Delta H \approx 13$ kcal mol$^{-1}$,[14] and correspondingly, $f_R(H_2O) = f_R(p) = f_R(h)$ within the degrees of hydration from 0 to $4H_2O$/—$SO_3H$ and $f_R(H_2O) = 0$ for the rest of water), the $f_R(p)(h)$ curve gains its standard monotonic form (see Fig. 3, *b*, curve *2*). In this case, the numerical $f_R(p)$ value decreases rather strongly: from $f_R(p) = 0.75$ ($h = 0$) to 0.20 ($h = 1.0$), which corresponds to an increase in $\langle x^2\rangle(p)$ from 0.12 to 0.69 Å$^2$. Thus, in the case of sulfonated poly(styrenedivinylbenzene) cation exchanger, the intramolecular mobility of the polymeric net increases considerably during hydration. This increase for KRS-2p is still lower than that for SGK-7-2% (at close cross-linkage concentrations), which agrees with the lower mobility of the aromatic chain as compared to that of the aliphatic one.

The question of the character of the spatial distribution of water in polymer is crucial for the interpretation of the results of studying two-component polymer—water systems. In this respect, the entirely hydrated hydrophilic polymeric nets of ion exchangers (at a water/polymer mass ratio from ~1 to several tens) can be considered as homogeneous: the nonuniform distribution of water molecules can be related only to the spatial heterogeneity in the arrangement of functional groups, hydration centers, and free elements of the net volume. However, in the case of partially hydrated ion exchangers, their heterogeneity cannot be ruled out *a priori*, *i.e.*, the co-existence of strongly and weakly hydrated regions in a macroscopic sample. Previously,[15] using the poly(styrenedivinylbenzene) cation exchanger with the gel structure, we demonstrated (by Mössbauer spectroscopy) the homogeneity of the ion exchanger—water system in the sense indicated above at intermediate degrees of hydration and fulfillment of conditions for achieving equilibrium. Therefore, this study is based on the prerequisite of homogeneity.

***Polymeric sorbent.*** For comparison, we studied the dynamics of the sorbent—water system. The Porolas TM sorbent is hydrophobic. Water can be introduced into it

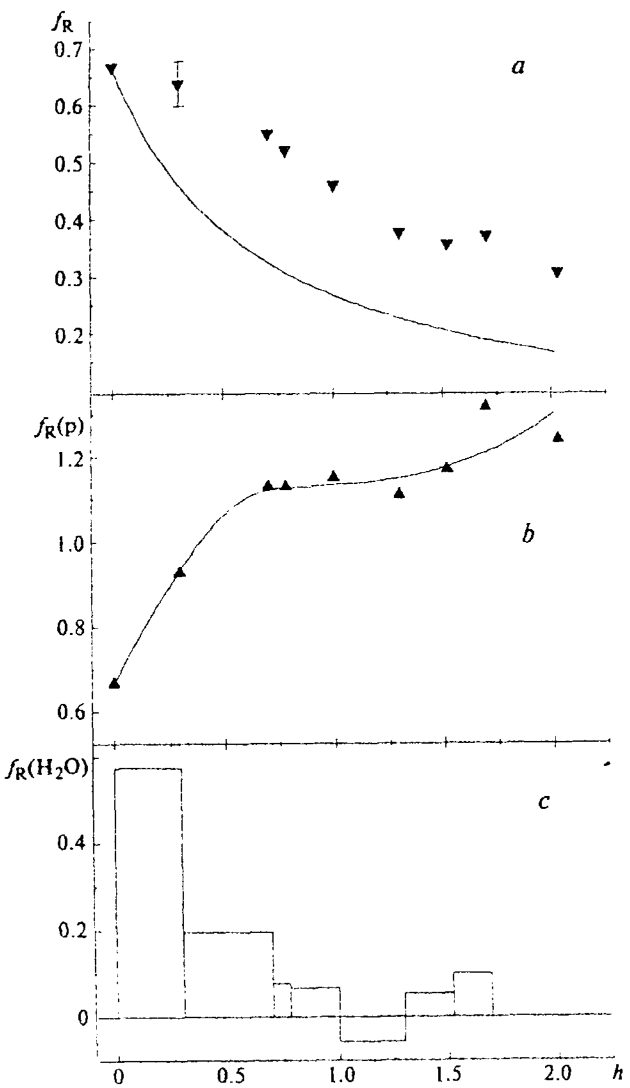


**Fig. 4.** Dependences of the dynamics of the polymeric sorbent Porolas TM on the water/polymer mass ratio (*h*). *a*, Dependence of the integral elastic fraction of RSMR ($f_R$) of the polymer—water system on *h*; points are experiment; line is the theoretical curve under the assumption that $f_R(H_2O) = 0$, $f_R(p) = 0.67 = \mathrm{const}$; *b*, dependence of the elastic fraction of RSMR of the polymer $f_R(p)$ on h under the assumption that $f_R(H_2O) = 0$; *c*, diagram of partial values of the elastic fraction of RSMR of water $f_R(H_2O)$ in the polymer—water system under the assumption that the elastic fraction of RSMR of the polymer $f_R(p)$ is independent of *h* ($f_R(p) = 0.67 = \mathrm{const}$).

only by the replacement of the primarily introduced organic solvent (we used isopropanol). The supermolecular structure of this sorbent is a system of rigidly linked mutually penetrating chains of polymeric globules with a size of ~1000 Å, which possess some internal porosity. We expected that the simplest model would take place: a rigid carcass, whose intramolecular mobility is independent of hydration due to its initial rigidity and weak interaction with water ($f_R(p) = \mathrm{const}$), and free liquid water with $f_R(H_2O) = 0$ with nonrestricted mobility due to the absence of a strong interaction with the pore surface. The results of measurements (see Fig. 4, *a*) are in marked contradiction with the situation expected: all experimental points lie considerably higher than the model curve. If the initial assumption $f_R(p) = \mathrm{const}$ is rejected, but $f_R(H_2O) = 0$ is accepted for all water (which seemingly is quite evident), the calculation shows that in this case, $f_R(p)$ increases as h increases and, moreover, considerably exceeds unity at high h values (see Fig. 4, *b*), which has no physical sense. This situation forces us to accept an alternative variant: the presence of a fraction of water with $f_R(p) > 0$ in the hydrated polymer. The diagram of the partial $f_R(H_2O)$ value under the assumption that $f_R(p)(2 \geq h \geq 0) = \mathrm{const}$ is presented in Fig. 4, *c*. According to this, a considerable fraction of water in the polymer (up to $h = 0.7$) possesses a high value $f_R \approx 0.6$—$0.2$, which is characteristic of a solid, and the $f_R$ value of the remaining water is close to zero within the experimental error.

It is well known that the Mössbauer effect is absent in liquids with a low viscosity due to high (as compared to those in solids) displacements of atoms (molecules) and high diffusional broadening of the Mössbauer line. This is also related to RSMR; therefore, for these systems, $f_R = 0$. Nevertheless, the Mössbauer effect was observed in liquids that are present in small pores of solids[16,17] and in "rigid emulsions." [18] The authors of these works explained this result by the small size of the liquid regions in the systems considered. In these cases, however, it is difficult to rule out completely a strong interaction of, at least, some fraction of the molecules of the liquid with the solid matrix, which, in particular, is evident from the change in isomer shift for this fraction of molecules.[17] Therefore, our observation of low-mobility water in the system with a very weak water—solid interaction is of special interest.

According to the data of mercury porosimetry, Porolas TM possesses a broad size distribution of pores within 10000—30 Å with a maximum at 200 Å, volume ~1 cm$^3$ g$^{-1}$, and specific surface 250 m$^2$ g$^{-1}$. However, the differential curve of the dependence of the pore volume on the diameter breaks at $d = 30$ Å (resolution of the method) and does not achieve zero. The specific surface found by the BET method reaches 700 m$^2$ g$^{-1}$, and the complete pore volume in the swollen state is ~2 cm$^3$ g$^{-1}$. Therefore, in this sorbent, a considerable part of pores has a size <30 Å, *i.e.*, substantially less than that in the porous Vycor glass in which the Mössbauer effect for liquid was observed.[17] We ascribe the nonzero elastic fraction of RSMR (see Fig. 4, *c*) precisely to very small water clusters in the smallest pores (amounting 0.7 g g$^{-1}$ of sorbent).

It can be assumed as a hypothesis that when a water cluster is contained in a rigid pore with a very small size (<30 Å), the density fluctuations or number of vacancies are insufficient to provide the same rate of selfdiffusion of molecules within the cluster as in a large volume.

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## References

1. A. S. Plachinda, B. N. Laskorin, D. B. Poblinkov, E. F. Makarov, N. G. Zhukova, V. V. Krylova, I. A. Logvinenko, A. Yu. Permogorov, and V. I. Khromov, *Dokl. Akad. Nauk SSSR*, 1985, **280**, 938 [*Dokl. Chem.*, 1985 (Engl. Transl.)].
2. A. S. Plachinda, D. B. Poblinkov, B. N. Laskorin, E. F. Makarov, N. G. Zhukova, V. V. Krylova, I. A. Logvinenko, A. Yu. Permogorov, and V. I. Khromov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 1740 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1985, **34**, (Engl. Transl.)].
3. V. I. Khromov, A. S. Plachinda, A. Akashat, B. N. Laskorin, N. G. Zhukova, V. V. Krylova, S. I. Kamyshanskii, and S. I. Alexeeva, *Hyperfine Interact.*, 1990, **55**, 1133.
4. A. S. Plachinda, V. I. Khromov, A. Akashat, D. B. Poblinkov, B. N. Laskorin, N. G. Zhukova, and E. F. Makarov, *Hyperfine Interact.*, 1990, **55**, 1151
5. A. S. Plachinda, V. E. Sedov, V. I. Khromov, L. V. Bashkeev, and I. P. Suzdalev, *Chem. Phys. Lett.*, 1990, **175**, 101.
6. A. S. Plachinda, V. E. Sedov, V. I. Khromov, I. P. Suzdalev, V. I. Goldanskii, G. U. Nienhaus, and F. Parak, *Phys. Rev. B*, 1992, **B45**, 7716.
7. a) I. P. Suzdalev, *Gamma-rezonansnaya spektroskopiya belkov i model'nykh soedinenii* [*γ-Resonance Spectroscopy of Proteins and Model Compounds*], Nauka, Moscow, 1988, 207 (in Russian); b) 1988, 211.
8. D. C. Champeney and G. W. Dean, *J. Phys.*, 1975, **C8**, 1276.
9. G. Albaneze, A. Deriu, and F. Cavatorta, *Hyperfine Interact.*, 1995, **95**, 97.
10. F. Franks, *Phys. Trans. R. Soc. Lnd.*, 1977, **B278**, 89.
11. M. Escoubes and M. Pineri, in *Ion Exchange: Science and Technology*, Ed. A. E. Rodrigues, NATO ASI Series E, No. 107, Martinus Nijhoff Publishers, Dordrecht, 1986, p. 341.
12. Yu. F. Krupyanskii, D. Bade, I. V. Sharkevich, N. Ya. Uspenskaya, A. A. Kononenko, I. P. Suzdalev, F. Parak, V. I. Goldanskii, R. L. Mossbauer, and A. B. Rubin, *Eur. Biophys. J.*, 1985, **12**, 107.
13. G. Zundel, *Hydration and Intermolecular Interaction*, Academic Press, New York—London, 1969, 142, 176.
14. R. Duplessix, M. Escoubes, B. Rodmacq, F. Volino, E. Roche, A. Eisenberg, and M. Pineri, in *Water in Polymers*, Ed. S. P. Rowland, ACS Symposium Series 127, Washington, 1980.
15. A. S. Plachinda, V. I. Goldanskii, I. P. Suzdalev, and V. P. Korneev, *Dokl. Akad. Nauk SSSR*, 1969, **185**, 629 [*Dokl. Chem.*, 1969 (Engl. Transl.)].
16. K. Burger and A. Vertes, *Nature*, 1983, **306**, 353.
17. J. Hietaniemi, E. Ikonen, and T. Katila, *Eur. Lett.*, 1992, **18**, 373.
18. K. Burger, A. Vertes, I. Dekany, and Zs. Nemes-Velessy, *Struct. Chem.*, 1991, **2**, 277.

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