LETTERS TO THE EDITOR

THE NUCLEAR MAGNETIC RESONANCE OF WATER SORBED ON SODIUM POLYMETACRYLATE

In paper [1] we dealt with the nuclear magnetic resonance (NMR) of the influence of ultraviolet and thermal radiation on sodium polymetacrylate (SPM). We found inter alia that the recorded signal comes from the protons of water sorbed on SPM. The signal of the protons of SPM itself was not seen there because there was an unfavourably high percentage of water in the substance measured. In the present paper, by lowering the percentage of water content we create better conditions for the simultaneous observation of the signal of SPM and H₂O and we shall study the changes in width \( \Delta H \) and intensity \( J \) of the derivative of the absorption curve of NMR as a function of the water content.

Up to now water has been studied in silica gel, aluminium oxide, titanium dioxide, isinglass, cellulose, moulding powders, starch, in various fibres, plant materials and in polymers of different kinds. We consider the most important papers to be those of Zimmerman et al. [2, 3] on water sorbed on silica gel, of Bonera et al. [4] on silica gel and isinglass, Odajima et al. [5, 6] on cellulose and Abramova et al. [7] on viscose fibres. Hitherto measurements have not been performed on sodium polymetacrylate. They are the subject of the present paper.

Fig. 1. Dependence of line width \( \Delta H \) and relative intensity \( J \) of derivative of NMR absorption curve of water in sodium polymetacrylate on water content \( p \).

Fig. 2. Form of half derivative of NMR absorption curve of water in sodium polymetacrylate. a) 1 — at 9.775% H₂O, 2 — at 0.469% H₂O, 3 — at 0% H₂O (pure SPM), b) 1 — at 9.775% H₂O, 2 — part of curve corresponding to water, 3 — part of curve corresponding to pure SPM.
Letters to the Editor

Our equipment for NMR has already been described [8]. Figure 1 is a plot of the width and relative intensity of the derivative of the absorption curve of NMR as a function of the water content \( p \), characterized by the relation \( p = \frac{m}{M} \times 100 \) (\%) where \( m \) is the mass of the water, \( M \) the mass of the SPM. The plotted values of \( \Delta H \) and \( J \) are those for water, i.e. the recorded signal after subtracting the SPM signal. In Fig. 2 we see half the records of the derivatives of the absorption curves of NMR of \( \text{H}_2\text{O} \) protons in SPM, recorded at 20°C.

The courses of the dependences of \( \Delta H \) and \( J \) on the water content of SPM indicate that resonating protons of water molecules are no longer free in SPM but there exists a certain mutual effect between the protons of water and those of the adsorbent (i.e. the SPM) which lower the mobility of the water protons.

As regards the intensity of the SPM signal, this is proportional to the peak voltage produced by the autodyne NMR spectrometer during differential recording, for which the following relation was derived in [8]

\[
U = K \cdot f(U_1) \frac{N g^2 I (I + 1)}{2 \gamma H_0 T \tau^2} \frac{1}{3 k T}
\]

where \( f(U_1) \) is the sensitivity of the autodyne, which is a function of the h.f. voltage of its coil \( U_1 \), \( \gamma \) is the gyromagnetic ratio, \( H_0 \) the intensity of the resonance field, \( T \tau^2 \) the spin-spin relaxation time (the asterisk denotes the inclusion of the influence of field inhomogeneity), \( N \) the number of resonating protons per cm\(^3\), \( g_1 \) the nuclear g-factor, \( \mu_1 \) the nuclear magneton, \( I \) the absolute temperature, \( k \) the Boltzmann constant and \( K \) the conductivity factor of the oscillation circuit of the autodyne. When the set working conditions of the autodyne are maintained, all the factors in Eq. (1) are constant except for \( T \tau^2 \) and \( N \), which may vary. Therefore the intensity of the resonance curve, measured on two peaks of the derivative of the absorption curve, equals

\[
J = k_1 \cdot U = k_1 k_2 T \tau^2 N = AT \tau^2 N
\]

where \( k_1 \) is the proportionality constant of the whole measuring apparatus, \( k_2 \) the constant containing those terms in Eq. (1) that do not change, and \( A = k_1 k_2 \). It is seen from Eq. (2) that the intensity \( J \) of the curve would increase linearly with the number of resonating protons \( N \) if \( T \tau^2 \) were constant. Since the dependence \( J = f(N) \) is not a straight line throughout its course, the spin-spin relaxation time of the water protons \( T \tau^2 \) obviously varies. Because the slope of the dependence \( J = f(N) \) increases with concentration, \( T \tau^2 \) obviously grows, or \( \Delta H \) decreases, as is seen in Fig. 1. This can be explained as follows.

The water sorbed on SPM is substantially of three kinds as regards mobility. The least mobile is the monolayer of water dipoles bound so firmly to the hydrophil group of adsorbent that these molecules can be considered to be localized. Another part of the sorbed water is placed on the monolayer of such localized water molecules and is to a certain extent orientated, which partially prevents the motion of these molecules. The remainder of the sorbed water can move more freely, the more so the farther the molecule is from the adsorbent.

Then the macroscopically observable spin-spin relaxation time \( T \tau^2 \) and the line width \( \Delta H \) are defined by the relation

\[
\frac{1}{T \tau^2} = \frac{\gamma \cdot \Delta H}{2} = \frac{1}{T_2} + \sum_{i} \frac{p_i}{T_{2i}} + \frac{\gamma \cdot \Delta H}{\pi}
\]

where \( T \tau^2 \) is the transversal relaxation time of the localized water molecules in the monolayer, \( T_2 \) is the same quantity for the orientated molecules placed on the monolayer and \( T_{2i} \) are the individual relaxation times and \( p_i \) the quotients of the molecules with \( i \)-th relaxation time successively above the second layer. The times \( T_{2i} \) are larger, the farther the molecule is from the adsorbent. The expression \( \gamma \cdot \Delta H/\pi \) represents [9] the contribution of the field inhomogeneity to