SPECTROSCOPIC STUDIES OF THE STRUCTURAL VARIABILITY OF WATER CONTAINING LINEAR ANTITURBULENCE MACROMOLECULES

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Spectral studies are presented for aqueous solutions of WSR-301 polyethylene oxide at concentrations giving various levels of the Thomas effect.

There are many papers on the reduction in hydrodynamic resistance produced by polymer macromolecules in developed turbulence; there are various viewpoints [1-10] on the means whereby long polymer molecules damp high-frequency turbulent pulsations near a solid boundary.

It is usual [3, 4, 6, 8-10] to ascribe the reduction in turbulent resistance to the viscoelastic properties of the polymer solutions.

However, the Barenblatt–Kalashnikov [8] hypothesis indicates that small-scale turbulence is suppressed by the viscoelastic characteristics only if large clumps of macromolecules occur in the boundary layer, these clumps containing solvent molecules having an elasticity substantially higher than that of the three-dimensional spatially inhomogeneous net.

The association hypothesis [8] indicates that polyethylene oxide solutions are to be considered as suspensions of viscoelastic particles in a viscoelastic liquid, while solutions of guara resin are to be considered as suspensions of viscoelastic particles in a virtually Newtonian solvent; this theory, and some others [1, 2, 5, 7], does not give a satisfactory explanation of the relative resistance reduction when small amounts of linear polymers are introduced into the boundary layer.

As we are concerned with a detailed molecular mechanism, a purely empirical approach to the nature of the effect is valueless; for this reason, we need to use the latest physical methods to provide a detailed analysis of the molecular interactions between the reactive functional groups in the macromolecules and those in the solvent in each particular case.

For instance, aqueous solutions of antiturbulence macromolecules of the type of polyethylene oxide, polyacrylamide, or polysaccharide will produce associated forms, as well as a spatially inhomogeneous network at concentrations such that the spheres of action of the individual molecules do not overlap; this can occur only via hydrogen bonds, and molecular spectroscopy can provide information on this.

As yet there is no accepted view on the resistance reduction mechanism in the presence of a solid boundary, so we examined the concentration range in which the macromolecules substantially influence the structure of the water.

Structural changes in polymer solutions were examined from Raman spectra recorded with a DFS-12 grating spectrophotometer fitted with a standard illuminator and DRS-600 lamp; the 4358 Å line of mercury was used. A chart recorder operating at 720 mm/h was

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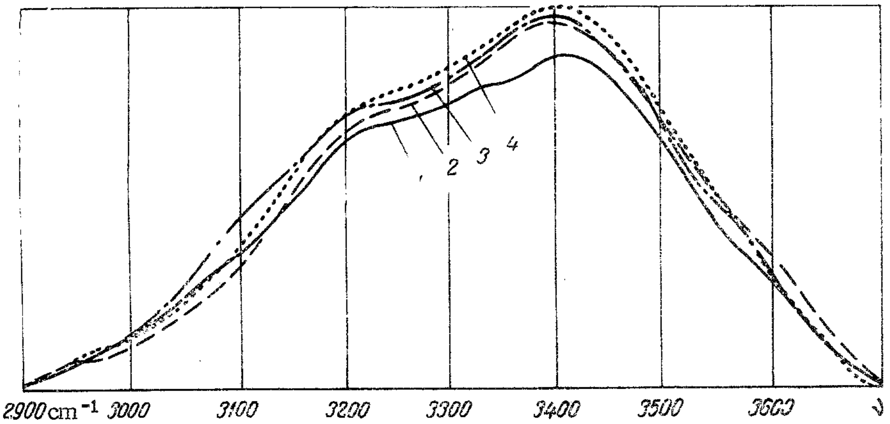

Fig. 1. Raman spectra of aqueous WSR-301 polyethylene oxide solutions: 1) Raman spectrum of pure water; 2-4) Raman spectra corresponding to poly-ox concentrations of 10, 30, and 1000 mg/liter, ν in cm^{-1}.

TABLE 1. Relative Integral Intensity of the ν_{OH} Band and Peak Frequency Shift

Integral relative intensity	Concentration	Shift $\Delta\nu$ (cm^{-1}) of ν_{OH} peak
1,00 RS *	Pure water	—
1,01 «	$1\cdot10^{-5}$	8
1,08 «	$3\cdot10^{-5}$	6
1,14 «	$1\cdot10^{-3}$	4
1,41 IR *	$1\cdot10^{-3}$	No shift
1,45 «	$2\cdot10^{-2}$	No shift

*RS, Raman spectrum; IR, infrared spectrum.

employed to record the spectrum; the scan rate was 6.1 Å/min. The widths of both slits were 95 μm.

The Raman spectra of Fig. 1 were recorded for concentrations between 10^{-5} and 10^{-3}, which correspond to different scales of the Thomas effect. Errors of fluctuation origin were eliminated by recording the spectrum of each specimen not less than three times, with subsequent averaging.

We use macromolecular polyethylene oxide type WSR-301; we chose this firstly because the νCH_2 frequency only slightly overlaps the ν_{OH} band of water; secondly, one expects that the variations in the integral Raman line strength and in the infrared absorption strength for this system will be similar to those for the water–dioxane system.

Consequently, the viscoelastic association and spatially inhomogeneous networks will make themselves felt by shifting the frequencies of the symmetrical stretching vibrations ν_1 and the antisymmetrical ones ν_3 toward larger wave numbers, which is characteristic of the water–dioxane bond, or else via the integral intensity of the lines in the ν_{OH} band, which are associated with the structure of water.

The relative integral intensity was calculated from

$$I = \frac{1}{1-C^*}\,\frac{\int_{\nu_1}^{\nu_2} I(\nu)\,d\nu}{\int_{\nu_1}^{\nu_2} I_0(\nu)\,d\nu}\,. \qquad (1)$$

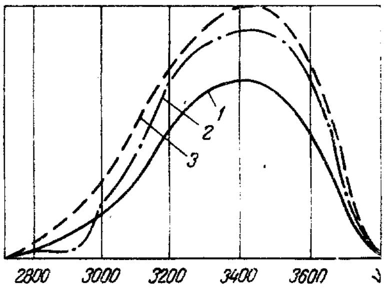

Fig. 2. Infrared spectra of aqueous WSR-301 poly-ox solutions: 1) infrared spectrum of pure water; 2,3) infrared spectra corresponding to polyethylene oxide concentrations of 1000 and 20,000 mg/liter; ν in cm^{-1}.

Table 1 gives results from this formula, which indicate that this intensity increases appreciably with the concentration for the Raman spectra (Fig. 1) and for the IR spectra (Fig. 2).

A hydrogen bond produces an electron density redistribution, which increases the dipole moment along the relevant coordinate and reduces the bond polarizability [11]. In that case, the IR spectrum should show an increase in the integral absorption:

$$A_i^2 = \frac{\pi}{3C}\left\{\left[\{e\}\left|\frac{\partial\vec{\mu}}{\partial g},\ \frac{\partial\vec{\mu}}{\partial\gamma}\right| + \{\vec{\mu}\}\left|\frac{\partial\vec{e}}{\partial g},\ \frac{\partial\vec{e}}{d\gamma}\right|\right]\left\|\begin{matrix} g \\ \gamma \end{matrix}\right\|_i\right\}^2. \tag{2}$$

The reverse relationship occurs in the Raman spectrum, where the intensity is a function of the bond polarizability:

$$I = C\,(5b_l'^2 + 13g_l). \tag{3}$$

We found that the integral intensity of ν_{OH} in Raman scattering increased at the same time as the IR absorption, so freshly prepared polyethylene oxide solutions do not contain elastic associated forms and spatially inhomogeneous networks. These would result in an electron density redistribution in the molecules involved in the hydrogen bonding. A consequence of this would be a difference in the sense of change in the integral intensities in the two forms of spectra (Figs. 1 and 2), with a shift in the frequency of the normal stretching modes of OH toward smaller wave numbers. As this does not occur, we conclude that the polyethylene oxide macromolecules do not form strong hydrogen bonds to the structured water lattice but fill the holes in the ice-type framework without disrupting the structure.

An analogous effect on the integral Raman and IR intensities occurs in the water–dioxane system [12, 13].

Our results on aqueous solutions of polyethylene oxide thus do not confirm the Barenblatt–Kalashnikov hypothesis.

We consider that the Thomas effect in its maximal occurrence is due primarily to a spiral conformation of the macromolecules (if these are stable) without overlap between the spheres of influence of the individual spirals. The damping of high-frequency turbulent pulsations is much reduced when there is substantial overlap between the spheres of influence of the spiral macromolecules [5, 14].

NOTATION

I is the relative integral intensity of spectral lines; $I(\nu)$ and $I_0(\nu)$ are the differential intensities in aqueous poly-ox solution and water, respectively; ν_1 and ν_2 are the boundary frequencies of ν_{OH} band; C^* is the poly-ox concentration in water; A_i^2 is the absolute intensity of i-th vibration; $\vec{\mu}$ is the dipole moment; e is the bond vector; g and γ are natural coordinates; C is the velocity of light (m/sec); b_l is the trace of the tensor for the derivatives of the polarizability with respect to normal coordinate; g_l is the anisotropy of the above.

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