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ROTATION OF A SPIN PROBE IN HYDRATED POLYETHYLENE GLYCOL BELOW FREEZING TEMPERATURE

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The ESR spectra of a spin probe, 2,2,6,6-tetramethyl-4-piperidone N-oxide, in water-polyethylene glycol (PEG) systems were measured below freezing temperature. The activation energy of the rotation of the probe in the hydrated PEG was considerably large. It was explained in terms of the breaking of the hydrogen bonds of the hydration water.

Interaction between polymers and water or the property of hydration water of polymers has been extensively studied using various techniques, such as dilatometry, NMR, dielectric relaxation etc. On the other hand, spin probe or label method became an important technique in recent years for studying the property of polymers$^{1)}$. Here, one of the interesting applications of the method was newly proposed as a tool to study hydration of polymers.

The ESR spectra of the spin probe dissolved in water (10^{-4}M) consisted of a sharp triplet separated by 16G above 0°C. The line shape did not change remarkably when cooled below 0°C. However, the sharp triplet turned suddenly into a broad singlet near at -17°C, and the singlet continued while the sample was heated from − 30°C to 0°C and changed into the triplet at 0°C. The singlet is generally observed in the spectra of conc. solutions of nitroxides and is taken as a result of strong spin-spin and exchange interaction. Therefore, the singlet measured at low temperature must be due to aggregation of the probe expelled from water because of formation of ice. Appearance of the singlet near at -17°C in the course of cooling means that the solution was supercooled to such a low temperature because the sample was placed in a capillary tube$^{2)}$. From these results, it was proved that the probe was not occluded in the lattice of ice.

Next, the spectra of PEG (M.W.≒1000)-H_2O systems were measured and the results were analysed in terms of the correlation time calculated according to ref.3. The plots of logarithm of the correlation times vs. the reciprocal of absolute temperature give nearly straight lines in all cases shown in Fig.1. The activation energies of the rotation of the probe were calculated from the slopes of the line, (A), (B), (C), (D) giving 12.7, 19.3, 5.5 and 7.1 Kcal/mol, respectively. The lines for the 100% PEG in the courses of cooling and heating are perfectly identical (A). In the case of the 10% aqueous solution, however, the values in the course of cooling are on the line (C), and suddenly jumped on another line (B) near at -20°C. The values in the course of heating are on the line (B). The line (C) is adjacent to the line (D) of supercooled water. Therefore, the 10% aqueous solution was actually supercooled until it was frozen at -20°C. The probe was segregated from ice also in this case, but the aggregation did not occur because the singlet did not appear.

The correlation time is proportional to the viscosity of the medium as described by Debye's

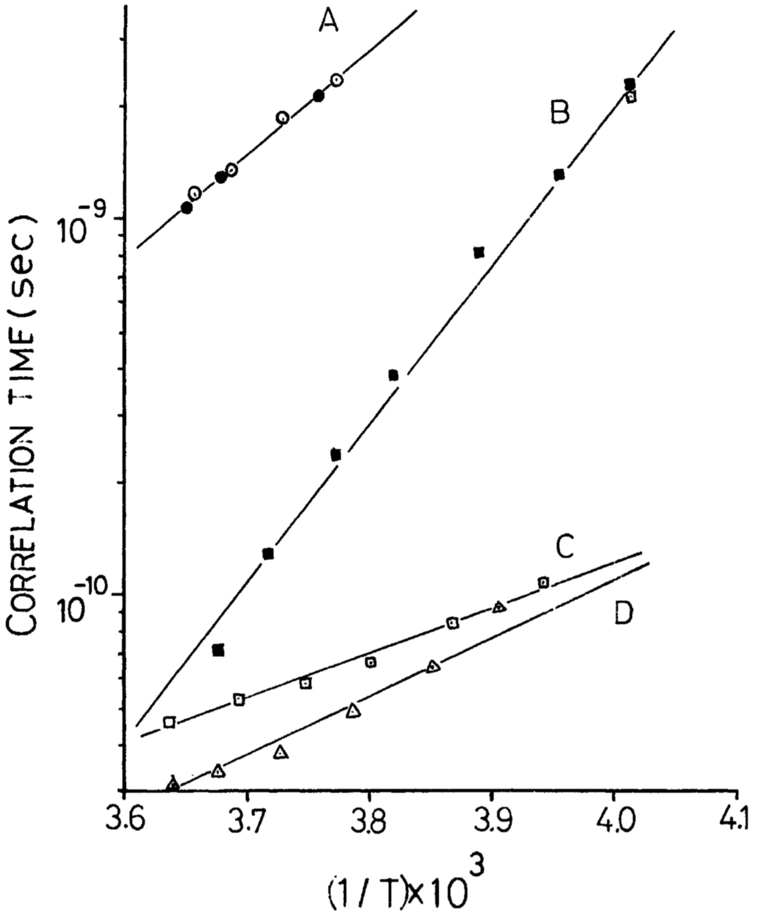

Fig.1 Correlation times vs. $(1/T)\times10^3$. A; 100% PEG. B and c; 10% aqueous solution of PEG. D; 100% H_2O. Open and closed symbols were experimental points measured in the courses of cooling and heating, respectively.

expression. Therefore, the activation energy ($\Delta H^{\ddagger}$) of the rotation of the probe correlates importantly with that of viscosity[4]. The $\Delta H^{\ddagger}$ value for the line (C) is comparable to that anticipated by the extraporation of the activation energy of the viscosity of water above 0°C[4]. The fact that the $\Delta H^{\ddagger}$ value for the line (C) is somewhat smaller than that for the line (D) means that the PEG molecule acts as a structure breaker and breaks hydrogen bonds of water. The probe must be dissolved in water and was not trapped in the PEG molecules in this case.

However, the $\Delta H^{\ddagger}$ value became large after freezing had occured, which was considerably larger than that of 100% PEG. This difference correlates evidently with the unfrozen hydration water of PEG as the probe is not dispersed in ice. That is to say, the probe must be occluded in hydration water, which is tightly packing, and large activation energy is necessary for breaking the hydrogen bonds and for providing with "free volume" for the rotation of the probe.

From these results and discussion, it was indicated that this method could give some important information about hydration water in water-soluble polymers.

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