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Water ordering measurements in the aqueous polymer systems by waveguide dielectric resonance method

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The method of waveguide dielectric resonance, a variation of millimeter spectroscopic technique, was used for the monitoring of water ordering in the hydration shells of synthetic polymers.

The presence of solute molecules in water leads to a modification of the water structure in the hydration shells of these molecules as compared with bulk water. The hydrophobic hydration of solutes at low concentrations is useful for the prediction of hydrophobic interactions with these solutes in various processes of self-assembling, ligand binding, substrate–enzyme recognition *etc*.[1,2] The spectroscopic determination of the hydrophobic hydration of synthetic polymers by the quantification of a modified structure of water in hydration shells is of importance. Other methods, which engage the binding of polymers with probing molecules or two-phase partitioning, lead to conformational changes in labile polymers. The collapse transition of synthetic thermosensitive polymers is a well-known example of hydrophobic effects in non-living aqueous systems.[3] At ambient temperature, nonpolar groups of small solutes induce additional ordering of an H-bond network in the vicinity of these groups in accordance with the well-known 'iceberg' model.[4] In the light of recent theoretical studies of hydrophobicity, where hydrophobic effects were assumed to depend on solute size,[5,6] the applicability of the 'iceberg' model to the hydration of nonpolar groups of macromolecules, particularly, thermosensitive polymers, should be accurately verified. The method of waveguide dielectric resonance (WDR),[7,8] a variation of the millimeter spectroscopic technique,[9] was applied to hydration effects for various H_2O/polymer systems including poly(acryl amide) (PAA), poly(ethylene glycol) (PEG) and poly(*N*-isopropylacrylamide) (PNIPA).

Previously, absorption millimeter spectroscopy was engaged for the measurements of absorption coefficients for solutions and thereby for determinations of the hydration numbers of solutes.[9] Absorption millimeter spectroscopy is able to determine the fraction of free water molecules, which are involved in rotational motions (water dipole reorientational motions through significant angles) according to the wait-and-switch model.[10] These rotations are possible because of the reduction in an activation barrier for water dipole rotations owing to the interaction of a water molecule with an additional neighbouring water molecule (fifth neighbour H_2O in the random tetrahedral network of hydrogen bonds). Hydration parameters were estimated from the deficit of absorption, the difference in absorption between undisturbed water and water with solute, as it was attributed to a solute-induced reduction in water mobility.[9]

Table 1 Hydration number (*N*) for polymers at a concentration of 10 g dm^{-3}.

Polymer	30 °C	43 °C
PAA	1.9±0.1	1.9±0.1
PEG	2.4±0.1	2.3±0.1
PNIPA	4.6±0.2	1.8±0.2
PNIPA with SDS[a]	4.1±0.2	2.8±0.2

[a] 0.375 g SDS dm^{-3}.

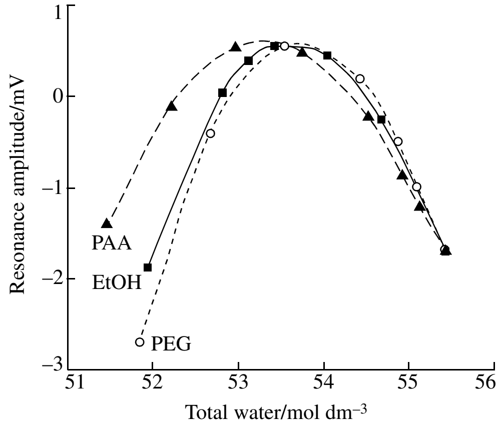

Figure 1 Resonance curves as functions of the total concentration of water C_1 for (■) EtOH, (▲) PAA and (○) PEG.

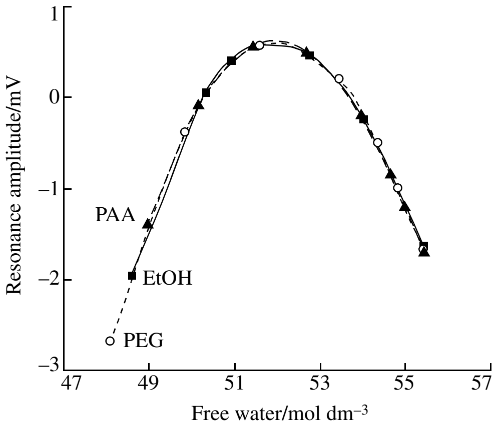

Figure 2 Coincidence of resonance curves as plotted on the concentration of free water $C_1 - NC_2$ for (■) EtOH, (▲) PAA and (○) PEG.

Hydration number, N, was introduced as the number of water molecules in a hydration shell, whose rotational mobility in a time scale of 10 ps has been lost owing to the presence of a solute.[9] The method of waveguide dielectric resonance allowed us to determine hydration parameters at low concentrations up to 2–5 g dm^{-3}.[7,8] Millimeter spectroscopy was used to measure the hydrophobic hydration of low-weight solutes by estimation of the quantity of water molecules, whose H-bonds were more stable comparatively to pure water.[7] Ordered water structures gave $N > 0$, while N was negative for the defects of a water network, which were generated by chaotropic solutes like urea.[7]

Electromagnetic radiation in the millimeter range (10 mm wavelength, 31 GHz) was generated by a stabilised high-frequency generator.[8] A waveguide was used for passing electromagnetic radiation into a measuring line with a waveguide resonator at the end. Aqueous solutions in the waveguide resonator led to a change of the dielectric resonance amplitude which was used for the measurements of hydration.

The total molar concentration of water phase C_1 consists of the molar concentrations of free C_1^f and bound water C_1^b:

$$C_1 = C_1^f + C_1^b = \rho(1 - P_2)/M_1, \qquad (1)$$

where M_1 is the molecular mass of water, ρ is the density of solution, and P_2 is the solute mass fraction in the solution. For all studied aqueous solutions, C_1 was calculated according to equation (1) from ρ and P_2. Bound H_2O molecules with a concentration of C_1^b lose their rotational mobility in a time scale of 10 ps. Positive hydration as a surface phenomenon implies an increase in the hydration parameter with increasing accessible surface area of the solute molecule and, thereby, with increasing solute concentration.[7,8] Therefore, the concentration of bound water was assumed to be equal to NC_2, where N is the number of bound H_2O (hydration number) and C_2 is the molar solute concentration. C_1^f can be evaluated as follows:

$$C_1^f = C_1 - NC_2. \qquad (2)$$

The amplitudes of resonance as functions of C_1 for various solutes do not coincide, as shown in Figure 1 for PEG, PAA and EtOH. Previous studies of the absorption of millimeter radiation by aqueous solutions revealed that the absorption values were proportional to the concentration of free water.[9] Contributions to the absorptions by both the solute and bound water were significantly less than that for free water.[9] The amplitude of waveguide dielectric resonance was assumed to depend on the concentration of free water only. For example, resonance curves for PEG, PAA and EtOH coincide as plotted in the coordinate of free water, $C_1 - NC_2$ (Figure 2). This common resonance curve was accurately determined with ethanol solutions ($N = 3$). Using this calibration curve, C_1^f can be experimentally obtained from resonance amplitude for any solution with a given solute concentration. Values of C_1 as obtained from equation (1) and C_1^f were used to calculate N:

$$N = (C_1 - C_1^f)/C_2. \qquad (3)$$

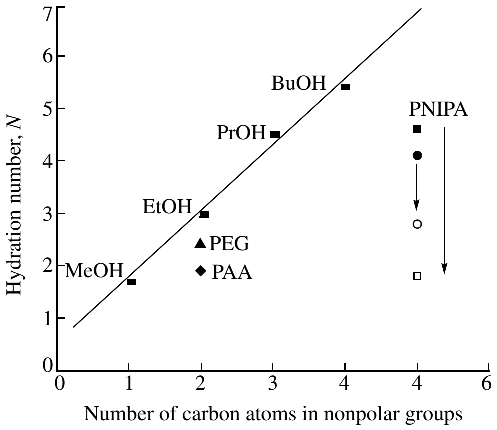

Figure 3 Dependence of the hydration number on the number of carbon atoms in nonpolar groups of (▲) PEG, (◆)PAA, PNIPA in pure water [(■) at 30 °C, (□) at 43 °C], and PNIPA with SDS [(●) at 30 °C, (○) at 43 °C]. Straight line corresponds to aliphatic alcohols. Asterisks indicate coil → globule transitions.

The values of N per monomer unit of polymers are presented in Table 1 for PAA ($M_w = 8\times10^5$), PEG ($M_w = 4.3\times10^4$) and thermosensitive PNIPA ($M_w = 7\times10^5$). The highest values of N were found for PNIPA, which includes the hydrophobic Pr^i group. Previously, it was revealed by millimeter spectroscopy that the contribution of CH_2 to N was one order of magnitude higher than that of uncharged polar groups.[7,8] Therefore, N was attributed to the hydration state of nonpolar groups. Measurements were made at temperatures below (30 °C) and above (43 °C) the temperature of a coil-globule transitions for PNIPA macromolecules (around 32 °C). For both coil and globular states, the hydration of PNIPA was found to be different in pure water and with the addition of sodium dodecyl sulfate (SDS) at a concentration below its cmc in water (Table 1). For globular state above transition temperature, N for PNIPA with SDS is higher than for PNIPA in pure water (Table 1). This is consistent with the fact that an increase in the surfactant concentration results in intra-molecular solubilization.[11]

Contribution to hydrophobic hydration of water-accessible Pr^i group against H group was estimated to be 3.6 as difference in N for Bu^{i}OH (5.3) and MeOH (1.7). For polymers, a smaller value of 2.7 was found as difference in N for PNIPA in pure water (4.6) and PAA (1.9). This is an indication that nonpolar groups in the coil state of the thermosensitive polymer are less accessible to water than nonpolar groups in low-weight solutes. The same conclusion was drawn from a consideration of N as a function of carbon number of nonpolar groups for studied polymers and aliphatic alcohols (Figure 3). Water ordering for polymers is smaller than a corresponding effect for aliphatic alcohols, because points for polymers are under the line corresponding to alcohols. Transitions of the PNIPA structure from a coil to a globule are accompanied by a decrease in N (asterisks in Figure 3) as a result of a decrease in contact with water of nonpolar groups upon chain folding.

The surface-relevant hydrophobicity of polymers, which are abundant in nonpolar groups, is not proportional function of the number of these groups because inter-chain hydrophobic interactions mask a part of nonpolar groups. Spectroscopic methods of the estimation of the water ordering (hydrophobic hydration) around non-polar groups are non-invasive allowing one to maintain polymer conformations. Raman spectroscopy was applied to assess the hydration of synthetic polymers by the estimation of intermolecular coupling of O–H oscillations of water.[12] However, Raman spectroscopy has failed in the determination of hydrophobic hydration in the presence of charged groups, as demonstrated for amino acids in zwitterionic form.[13] Contrary, a hydrophobicity scale for 20 natural amino acids was built using millimeter spectroscopy.[14] We hope that millimeter spectroscopy will allow us to compare hydrophobicities in a uniform scale of various classes of molecules from low-weight amphiphilic molecules to proteins and polymers.

The waveguide dielectric resonance method is able to assess the hydrophobic hydration of polymers which cause structured water to be in hydration shell in according to the traditional iceberg model.[15]

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