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Raman Spectroscopic Study of Hydrogen Bonding in Aqueous Carboxylic Acid Solutions. 3.[†] Polyacrylic Acid[‡]

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Introduction

The physical properties of aqueous polyacrylic acid solutions were studied by various methods.[1-7] The intrinsic viscosity of polyacrylic acid in alcohol/water mixtures[1] indicated that the hydrogen bond between carboxyl groups affected the conformation in alcohol/water mixtures. Miyamoto and Cantow[2] investigated the effect of solvents upon the conformation of meso and racemic 2,4-dimethylglutaric acids, model compounds of polyacrylic acid, by using high-resolution ^{1}H NMR spectroscopy. They concluded that interaction between nonadjacent segments due to intramolecular hydrogen bonding plays an important role in the intrinsic viscosity.

In the present study, dimerization constants, K_D's, of polyacryic acid and its monomer analogues in H_2O and D_2O were estimated at various concentrations by the band resolutions of the Raman spectra.

Previously infrared and Raman spectroscopic techniques were applied to aqueous solutions of polyacrylic acid.[3-7] Koenig et al. investigated the conformational transition of syndiotactic poly(methacrylic acid) in water by using Raman spectra.[4] They found that hydrogen bonding between carboxyl groups persisted in aqueous solutions of poly(methacrylic acid), but no quantitative analysis was done. In a recent paper, we investigated the dimerization of carboxylic acids in aqueous solutions[8] and that of deuterated carboxylic acids in heavy water[9] using Raman spectroscopy. The effects of alkyl chain length and the concentration of carboxylic acids on the dimerization constants in aqueous and heavy water solutions were investigated by the band resolution of the spectra.

Experimental Section

Materials. Glutaric acid (GA) and 1,3,5-pentanetricarboxylic acid (PTCA) were obtained from Tokyo Kasei (Tokyo, Japan) and used after recrystallization from water. Polyacrylic acids (M_w = 2000 (PAA2000) and 90 000 (PAA90000)) were purchased from Aldrich Chemical Co. (Milwaukee, WI) and purified by repeated ultrafiltration using an Amicon apparatus (Model 202, membrane; Diaflo YC 05, exclusion limit 500) and dialysis, respectively. Polyacrylic acid (M_w = 1000 (PAA1000)) was kindly offered by Kao, Co., Ltd. (Tokyo, Japan), and purified by ultrafiltration. All deuterated samples were prepared by the proton exchange with an excess amount of heavy water. A Milli-Q grade water and heavy water obtained from CEA (Gif-sur-Yvette, France) were used for preparation of sample solutions.

Spectroscopic Measurements. The Raman spectra of aqueous carboxylic acid solutions were recorded by an NR-1100 Raman spectrophotometer (Japan Spectroscopic Co., Tokyo, Japan) with a resolution of 5 cm^{-1}. The spectra were excited by the 488-nm line of an argon ion laser (GLG 3200, NEC, Tokyo) at powers of 300–500 mW. All measurements were carried out in a thermostated chamber controlled at 25 ± 0.5 °C by a Peltier device (Model RT-IC, Japan Spectroscopic Co.).

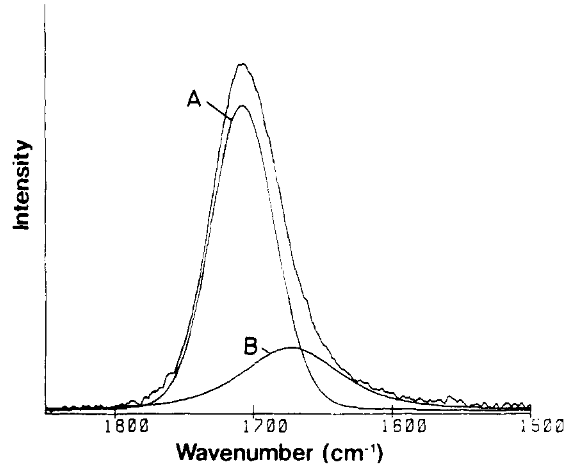

Figure 1. Computer-resolved Raman spectra of polyacrylic acid (M_w = 2000) in 50 wt % D_2O solution at 25 °C: (A) monomer, (B) dimer.

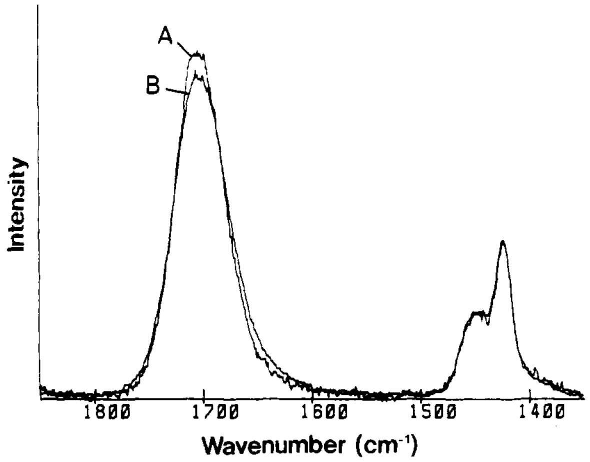

Figure 2. Raman spectra of glutaric acid-d_1 in D_2O at 25 °C: (A) 10 wt %, (B) 40 wt %.

Band Resolution. The spectra were resolved with the data decomposition program written by Drs. Hiroshi Kihara and Toru Ozeki, Hyogo University of Teacher Education, Hyogo Prefecture, Japan, using the Marquardt method. In the curve-fitting procedure, we occasionally got different but almost equally valid results when we changed the initial values for the curve fitting. In this case, we chose the result whose wavenumber of the peak top was reasonable compared with the result from the other concentrations or whose peak area was moderate.

Results and Discussion

Estimation of the K_D of Polyacrylic Acid. In the previous study,[8,9] we estimated the dimerization constants, K_D's, for carboxylic acids in aqueous solutions and their deuterated analogues in heavy water by the decomposition of their Raman spectra in the concentration range from 0.03 to 0.3 mole fraction. Using the same method (Figures 1 and 2), we estimated the K_D's of polyacrylic acid, GA (model for the dimer), and PTCA (model for the trimer) in H_2O and their deuterated analogues in D_2O in order to investigate the polymer effect on the dimerization constants.

In the previous studies, the C=O stretching peaks were normalized for exact comparison of the solutions of different concentrations by using an internal intensity standard.

The Raman intensity is directly related to the concentration of a species, and the integrated band area, *I*, is

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expressed as

$$I = JC \qquad (1)$$

where J is the molar intensity coefficient and C is the concentration (M) of the species.

When I_{mon} is the intensity of the monomer species and I_{stand} is that of the internal standard peak of the deconvoluted spectrum of carboxylic acid and its deuterated analogue, the normalized intensity of the monomer species, I'_{mon}, is derived as

$$I'_{\text{mon}} = \frac{I_{\text{mon}}}{I_{\text{stand}}} = \frac{C_{\text{mon}}J_{\text{mon}}}{C_{\text{nominal}}J_{\text{stand}}} = J'_{\text{mon}}F_{\text{mon}} \qquad (2)$$

where C_{nominal} is the total concentration of monomer that would be in the solution if there were no hydrogen bonding, C_{mon} is the concentration of the monomer species, and F_{mon} is the mole fraction of the monomer species to the "nominal" concentration of carboxylic acid. The ratio of the "normalized" molar intensity coefficient of the monomer (J'_{mon}) to that of the cyclic dimer (J'_{dim}) can be estimated from the ratio of the concentration dependence of I'_{mon} to that of I'_{dim}.

For propionic acid

$$J'_{\text{mon}}/J'_{\text{dim}} = 1.8 \pm 0.1 \qquad (3)$$

For propionic acid-d_1

$$J'_{\text{mon}}/J'_{\text{dim}} = 1.15 \pm 0.1 \qquad (4)$$

The K_D's of the acids were calculated from these values as described in our previous reports.[8,9] The proportions of the concentrations of monomer and dimer can be calculated as

$$\frac{C_{\text{mon}}}{2C_{\text{dim}}} = \frac{J'_{\text{dim}}}{J'_{\text{mon}}}\frac{I'_{\text{mon}}}{I'_{\text{dim}}} \qquad (5)$$

Consequently, K_D is given by

$$C_{\text{mon}} = C_{\text{nominal}}\frac{C_{\text{mon}}}{C_{\text{mon}} + 2C_{\text{dim}}} = C_{\text{nominal}}\frac{C_{\text{mon}}/(2C_{\text{dim}})}{[C_{\text{mon}}/(2C_{\text{dim}})] + 1} \qquad (6)$$

$$C_{\text{dim}} = (C_{\text{nominal}} - C_{\text{mon}})/2 \qquad (7)$$

$$K_D = C_{\text{dim}}/(C_{\text{mon}})^2 \qquad (8)$$

When eq 3 and 4 were used, the K_D's of polyacrylic acid, GA, PTCA aqueous solutions, and their deuterated analogues in heavy water were calculated.

Association of the Carboxyl Group. The results in H_2O for acetic acid, propionic acid, GA, PTCA, and polyacrylic acid (M_w = 2000 and 90 000) are given in Figure 3. The K_D values obtained for acetic acid and propionic acid at the lowest concentration in this figure were in accord with the result by Martin and Rossotti.[14] In all cases, the value of K_D decreased with concentration, which can be attributed to the nature of carboxylic acids as structure breaker.[10] It is well-known that the K_D's of carboxylic acids in aqueous solution increase with the alkyl chain length.[11-14] The difference in K_D values between acetic acid and propionic acid is consistent with this observation.

The values of K_D of GA and PTCA were smaller than those of acetic acid and propionic acid. This is caused by the chemical structure of GA and PTCA; it is impossible for GA and PTCA molecules to form hydrogen bonding between neighboring carboxyl groups as can be confirmed by the CPK model. If GA and PTCA are compared at a given normality of carboxyl groups, it is easily seen that they may form hydrogen-bonded dimers more unfavorably than acetic acid and propionic acid.

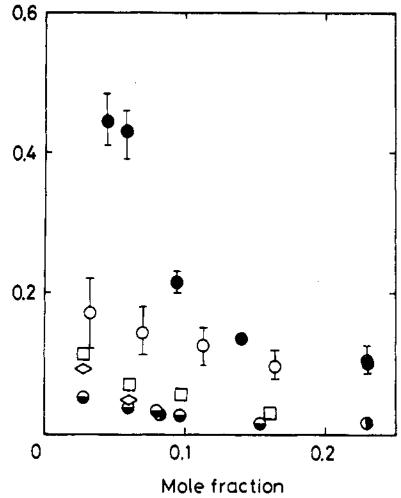

Figure 3. Concentration dependences of K_D of various carboxylic acids at 25 °C in H_2O: (○) acetic acid (data from ref 9), (●) propionic acid (data from ref 9), (⊖) glutaric acid, (◑) 1,3,5-pentanetricarboxylic acid, (□) polyacrylic acid (M_w = 2000), (◇) polyacrylic acid (M_w = 90 000). The abscissa shows the molar fraction of the carboxyl group of each acid and not that of the molecules.

The K_D values for PAA2000 and PAA90000 are almost the same, being slightly larger than those of GA and PTCA. The structure of polyacrylic acid should be more unfavorable than those of GA and PTCA for the dimerization because much more carboxyl groups are neighboring. Many investigations have been done on the complexation of polyacrylic acid with water-soluble polymers such as poly(ethylene glycol) and poly(vinylpyrrolidone).[15-18] It has been claimed that stable complexes of these polymers should be formed in water, though water can form a hydrogen bond of almost the same strength as that of the interpolymer hydrogen bond. To explain the preferential complexation between polymers, the "cooperative" hydrogen bonding between polymers has been proposed.[15,16] This cooperative hydrogen bonding may be formed in the polyacrylic acid aqueous solution and makes the K_D value greater than those of GA and PTCA.

Figure 4 shows the K_D's of deuterated polyacrylic acid, acetic acid-d_1, propionic acid-d_1, glutaric acid-d_2 (GAD), and 1,3,5-pentanetricarboxylic acid-d_3 (PTCAD). The K_D of carboxylic acid-d_1 is greater than that of carboxylic acid. This is caused by the difference in strength of the hydrophobic interaction in water and heavy water. Oakenfull and Fenwick[19] estimated the free energy of the hydrophobic interaction between hydrocarbon chains in heavy water by the conductance measurements of micellar D_2O solutions. Using their results, we previously confirmed the validity of our results for the K_D's of carboxylic acids[9] by using the equations of Schrier et al.[20] It should be mentioned here that the isotope effects on hydrogen bonding are usually quite small, probably because of the compensation of lowering stretching frequencies on formation of hydrogen bonds by an increase in resistance to bending motion, leading to a near equivalence of binding at the hydrogenic site between hydrogen-bonded and free species.[21,22]

Similar to the results in Figure 3, K_D values of GAD and PTCAD in D_2O were smaller than those of acetic acid-d_1 and propionic acid-d_1, and K_D values for polymers did not depend much on molecular weights (M_w = 1000, 2000,

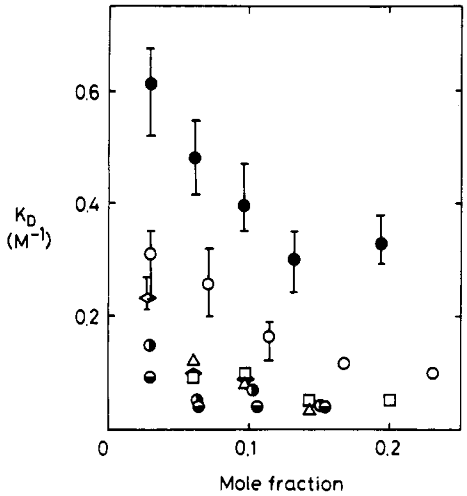

Figure 4. Concentration dependences of K_D of various carboxylic acids at 25 °C in D_2O: (○) acetic acid-d_1 (data from ref 9), (●) propionic acid-d_1 (data from ref 9), (⊖) glutaric acid-d_2, (◑) 1,3,5-pentanetricarboxylic acid, (△) polyacrylic acid (M_w = 1000), (□) polyacrylic acid (M_w = 2000), (◇) polyacrylic acid (M_w = 90 000). The abscissa shows the molar fraction of the carboxylic group of each acid and not that of the molecules.

90 000) and were slightly larger than those of GAD and PTCAD. This would be due to the same reason as that for aqueous solutions. Further, the differences between the K_D values of polyacrylic acid in H_2O and D_2O (10 wt % of PAA90000; 0.095 M^{-1} in H_2O and 0.230 M^{-1} in D_2O) suggest that hydrophobic interaction facilitated the hydrogen bonding between carboxyl groups in polyacrylic acid aqueous solution.

Conclusions

The dimerization constants, K_D, between carboxyl groups in polyacrylic acid and its monomer analogue in H_2O and D_2O were estimated from their Raman spectra. The K_D value of the polymer was smaller than those of acetic acid and propionic acid, while it was slightly larger than the K_D values of GA and PTCA. It is highly probable that cooperative hydrogen bonds are formed in the polyacrylic acid aqueous solution. The K_D values for polyacrylic acid and its monomer analogues in D_2O were larger than those in H_2O, which suggests the cooperativity between the hydrophobic interaction and the hydrogen bond on the dimerization phenomena of polyacrylic acid.

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