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Ultrasonic Relaxations in Aqueous Solutions of Propionic Acid in the Presence and Absence of *β*-Cyclodextrin

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Ultrasonic absorption coefficients in the frequency range 0.8−95 MHz were measured in aqueous solution of undissociated and dissociated propionic acid in the presence of *β*-cyclodextrin (*β*-CD) at 25 °C. A single relaxational absorption was found, although it was not observed in the absence of *β*-CD. The cause of the relaxation was attributed to a perturbation of a chemical equilibrium associated with an interaction between propionic acid and *β*-CD. The rate and thermodynamic constants for the association and dissociation reaction for the complex were determined from the concentration dependence of the relaxation frequency and the maximum absorption per wavelength. It was found that the complex formed by *β*-CD and propionic acid is more stable when the acid is in undissociated form. Further, the ultrasonic relaxation associated with a proton-transfer reaction was also observed when no additive exists in the solution. The rate and thermodynamic parameters were also determined precisely.

Introduction

Cyclodextrins (CD) (host) are doughnut-shape molecules with hydrophobic interior cavity, which can include various kinds of other compounds (guest) forming host-guest complexes. The ability is of highly interests in many application fields, such as solubilization agents and drug carries.[1−3]

Measurement of ultrasonic absorption is useful for probing the microscopic solution structure and may be used to study relaxation processes with characteristic time constant of $10^{-5}-10^{-10}$ sec. Dynamic association and dissociation processes between host and guest are of fundamental importance for certain functions of supra-molecular systems. The dynamic properties of the interaction between CD and nonelectrolytes or amino acid have been examined in our series of experimental study by the ultrasonic relaxation method.[4−7] These investigations have revealed that the stabilization of the complexes is sensitive to the size of cavity, and to the balance between hydrophobicity and the hydrophilicity of the guest. It is interesting and desirable to examine how the presence of charge on guest molecule affects the dynamical characteristics for host-guest complex formation process because the knowledge of these rate constants has direct applications when using CD to perform specific functions. To examine this charge effect, propionic acid has been chosen as a guest for *β*-CD in the present study. The results are compared with those for systems with nonelectrolytes. Another purpose of this present study is the clarification of a proton-transfer reaction of carboxylic acid in water. There are a few reports concerning the proton-transfer reaction in aqueous solutions of carboxylic acids in the restricted frequency range of the sound absorption.[8,9] A resonance method has proven to make it possible to measure the absorption coefficient down to 0.8 MHz. By this apparatus, a clear relaxational absorption may be observed.

Experimental Section

Chemicals. *β*-Cyclodextrin (*β*-CD) was purchased from Wako Pure Chemical Co. Ltd., and the purification procedure of *β*-CD was reported previously.[5] Propionic acid was also purchased from Wako Pure Chemical Co. Ltd. as the purest grade and was used without further purification. The sample solutions of *β*-CD and propionic acid were prepared from the stock solutions obtained by weighing. Distilled and filtered water from MilliQ SP-TOC system of Japan Millipore Ltd. was used as a solvent. The concentration of propionic acid in aqueous solution was determined by sodium hydrate solution titrated by oxalic acid dihydrate aqueous solution. Undissociated propionic acid (CH_3CH_2COOH) (over 99%) was prepared by adding concentrated hydrochloric acid solution at pH = about 1.8. Dissociated propionic acid solutions ($CH_3CH_2COO^-$) (about 70%) were obtained by sodium hydroxide solution at pH = about 5.2.

Apparatus. Ultrasonic absorption coefficients, α, were measured in the frequency range from about 0.8 to 9 MHz by a resonance method, which consists of three cells with 3, 5, and 7 MHz x-cut fundamental crystals. A pulse method was used in the frequency range from 25 to 95 MHz. More details about the absorption apparatus and the procedure for determining the absorption coefficient are described elsewhere.[10,11] Sound velocity value was obtained by the resonator at around 3 MHz and solution density was by a vibrating density meter (Anton Paar DMA 60/602). The temperature for the resonator cells was controlled within ±0.01 °C (Lauda RM20) and that for the pulse cell was maintained within ±0.1 °C (EYEYA UNI ACE BATH NCB-2200). All measurements were performed at 25 °C.

Results

Figures 1 and 2 show representative ultrasonic absorption spectra in aqueous solutions of undissociated (pH = about 1.8) and dissociated propionic acid (pH = about 5.2) in the presence and in the absence of *β*-CD, respectively. As can be seen, the

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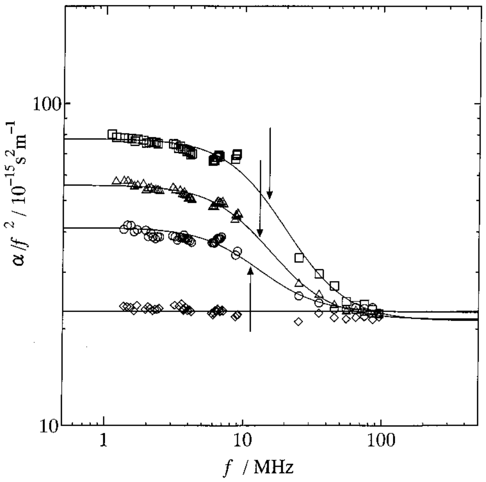

Figure 1. Representative ultrasonic absorption spectra in aqueous solution of propionic acid with 0.0087 mol dm^{-3} β-CD at 25 °C (pH = about 1.8). (○): 0.0090 mol dm^{-3} propionic acid, (△): 0.020 mol dm^{-3} propionic acid, (□): 0.070 mol dm^{-3} propionic acid, and the spectrum in the solution without β-CD. (◇): 0.100 mol dm^{-3} propionic acid.

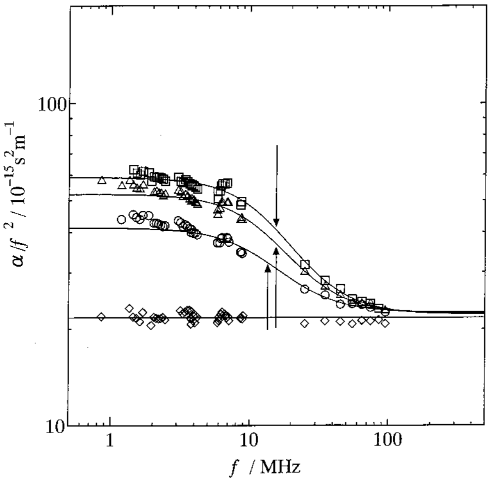

Figure 2. Representative ultrasonic absorption spectra in aqueous solutions of propionic acid with 0.0087 mol dm^{-3}β-CD (pH = about 5.2). (○): 0.030 mol dm^{-3} propionic acid, (△): 0.060 mol dm^{-3} propionic acid, (□): 0.080 mol dm^{-3} propionic acid, and the spectrum in the solution without β-CD. (◇): 0.100 mol dm^{-3} propionic acid.

frequency dependence of the absorption coefficient divided by the square of the frequency, α/f^2, was not observed in the solutions without β-CD. Also, the excess absorption is not found in solution of β-CD in our concentration range below 0.00870 mol dm^{-3},[4] although the relaxational absorption has been reported in the more concentrated solutions.[12,13]

When both of the two solutes, that is, β-CD and undissociated or dissociated propionic acid, coexist in the solution, the values of α/f^2 are dependent on the frequency. A Debye-type relaxational equation was used to test the frequency dependence of the absorption coefficient

$$\alpha/f^2 = A/[1 + (f/f_r)^2] + B \qquad (1)$$

where f_r is the relaxation frequency, A is the amplitude of excess absorption, and B is the background absorption. A slightly modified equation, $(\alpha/f^2)f = Af/[1 + (f/f_r)^2] + Bf$, was used to obtain the ultrasonic parameters, f_r, A, and B, by using a nonlinear least-mean-square method, because eq 1 is the monotonic decreasing function with the frequency. The solid curves in Figures 1 and 2 are the calculated ones, and it is seen that the experimental data fall on the theoretical curves. In Table 1, the ultrasonic relaxation parameters thus obtained are listed along with the pH value, and the sound velocity and density values. It is considered that the cause of the relaxation is due to the interaction between β-CD and propionic acid, because the relaxation appears only when both solutes are dissolved into water. Therefore, a perturbation of the similar chemical equilibrium to that for CD and nonelectrolytes interaction was taken into account

$$\mathrm{CD} + \mathrm{GST} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \mathrm{CDGST} \qquad (2)$$

where CD is β-CD as the host, GST is each propionic acid as the guest, CDGST is the complex, and k_f and k_b are the forward and backward rate constants, respectively. The equilibrium constant, K, is defined as $K = k_f/k_b = [\mathrm{CDGST}]/[\mathrm{CD}][\mathrm{GST}]$. The relationship between the relaxation time, τ, or the relaxation frequency, f_r, and the reactant concentrations is given by[7]

$$\tau^{-1} = 2\pi f_r = k_f\{[\mathrm{CD}] + [\mathrm{GST}]\} + k_b$$
$$= k_b[\{1 + K(C_{\mathrm{CD}}+C_{\mathrm{GST}})\}^2 - 4K^2C_{\mathrm{CD}}C_{\mathrm{GST}}]^{1/2} \qquad (3)$$

where C_{CD} and C_{GST} are the analytical concentrations of β-CD and propionic acid, respectively. At the fixed concentration of β-CD, 0.0087 mol dm^{-3}, the parameters, K and k_b, were obtainable by using a nonlinear least-mean-square method. Figure 3 shows the plots of $2\pi f_r$ vs the concentration term, $[\{1 + K(C_{\mathrm{CD}} + C_{\mathrm{GST}})\}^2 - 4K^2C_{\mathrm{CD}}C_{\mathrm{GST}}]^{1/2}$, in which the straight lines are the calculated ones and they go through the original point. These results show that the cause of the relaxational absorption is due to a perturbation of the equilibrium expressed by eq 2. The forward rate constant, k_f, was calculated from the definition of the equilibrium constant. Because the rate and equilibrium constants are determined, it is possible to estimate the relaxation frequency at different concentration of β-CD, using eq 3. The results are shown in Table 1 and Figure 3, and it can be seen that the experimental values are close to the calculated ones.

From the absorption data, the standard volume change, ΔV, of the reaction is also obtainable with the helps of the sound velocity and density. The maximum absorption per wavelength, $\mu_{\max}$, is widely used to calculate the volume change. It is given by the next equation

$$\mu_{\max} = 0.5\,Af_rv = \pi\,\rho\,v^2(1/[\mathrm{CD}] + 1/[\mathrm{GST}] +$$
$$1/[\mathrm{CDGST}])^{-1}(\Delta V)^2/2RT \qquad (4)$$

where ρ is the density of solution, v is the sound velocity, R and T are the gas constant and temperature, respectively. The equilibrium concentrations of the individual reactants and product can be calculated by using the determined equilibrium constant, K, and the analytical concentrations of β-CD and propionic acid. The solution density and velocity were measured independently. Therefore, the standard volume change, ΔV, was determined at the various concentrations of propionic acid, and the averaged value is shown in Table 2.

The absorption measurements were also performed in aqueous solutions of propionic acid without adding β-CD, below 0.100 mol dm^{-3}. In Figure 4, the representative absorption spectra are shown in the aqueous solution. Although the amplitude of the excess absorption is considerably small, the relaxation can be surely observed. The absorption data were again tested by

TABLE 1: Ultrasonic Relaxation Parameters, Sound Velocity and Density for Aqueous Solutions of Propionic Acid with β-Cyclodextrin at 25 °C

conc. mol dm^{-3} β-CD	conc. mol dm^{-3} propionic acid	f_r MHz	A 10^{-15} s^2 m^{-1}	B 10^{-15} s^2 m^{-1}	v m s^{-1}	ρ kg dm^{-3}	pH
		undissociated propionic acid solution					
0.0087	0.0090	11.2 ± 0.6	18.8 ± 0.6	22.54 ± 0.06	1501.0 ± 0.8	1.0013	1.939
0.0087	0.020	12.4 ± 0.2	34.5 ± 0.3	21.46 ± 0.04	1501.5 ± 0.6	1.0014	1.846
0.0087	0.040	13.4 ± 0.3	51.1 ± 0.6	20.58 ± 0.08	1502.2 ± 0.7	1.0015	1.875
0.0087	0.050	14.8 ± 0.4	51.9 ± 0.8	21.4 ± 0.1	1502.6 ± 0.8	1.0015	1.830
0.0087	0.070	14.6 ± 0.4	56.5 ± 0.8	21.2 ± 0.1	1502.8 ± 0.7	1.0016	1.825
0.0087	0.080	15.3 ± 0.3	58.4 ± 0.5	19.8 ± 0.1	1503.3 ± 0.8	1.0017	1.840
0.0087	0.100	16.5 ± 0.2	55.8 ± 0.4	21.75 ± 0.08	1503.7 ± 0.7	1.0017	1.844
0.0050	0.030	11.8 ± 0.4	26.0 ± 0.5	21.52 ± 0.06	1501.1 ± 0.8	0.9997	1.869
		(12.9)^b					
		dissociated propionic acid solution					
0.0087	0.030	13.9 ± 0.6	18.7 ± 0.4	22.49 ± 0.07	1503.1 ± 0.8	1.0021	5.195
0.0087	0.040	15.0 ± 0.4	22.5 ± 0.4	22.26 ± 0.07	1504.1 ± 0.6	1.0023	5.207
0.0087	0.060	14.9 ± 0.4	30.1 ± 0.4	22.29 ± 0.07	1505.8 ± 0.8	1.0029	5.210
0.0087	0.070	15.4 ± 0.4	33.1 ± 0.5	22.29 ± 0.08	1506.4 ± 0.9	1.0032	5.201
0.0087	0.080	15.5 ± 0.3	36.9 ± 0.4	22.17 ± 0.07	1507.6 ± 0.7	1.0035	5.207
0.0087	0.090	16.1 ± 0.3	38.6 ± 0.5	22.5 ± 0.1	1508.3 ± 0.7	1.0039	5.203
0.0050	0.050	15.0 ± 0.5	15.1 ± 0.3	22.09 ± 0.06	1504.3 ± 0.9	1.0010	5.215
		(14.7)^b					
		propionic acid solution					
	0.005	3.5 ± 1.2	8.1 ± 3.1	22.26 ± 0.06	1498.8 ± 0.7	0.9971	3.662
	0.010	6.4 ± 0.9	9.8 ± 1.1	20.64 ± 0.05	1499.5 ± 0.8	0.9971	3.483
	0.030	9.4 ± 0.6	10.3 ± 0.4	20.70 ± 0.03	1500.3 ± 0.8	0.9972	3.206
	0.050	10.9 ± 0.5	10.0 ± 0.3	20.68 ± 0.03	1501.0 ± 0.7	0.9974	3.109
	0.080	12.0 ± 0.8	11.4 ± 0.4	20.65 ± 0.05	1502.0 ± 0.7	0.9975	3.056
	0.100	11.3 ± 0.8	9.8 ± 0.4	21.59 ± 0.04	1502.7 ± 0.7	0.9977	2.918

[a] The errors of density values are within ±0.0001 kg dm^{-3}. [b] Those values are calculated from eq 3.

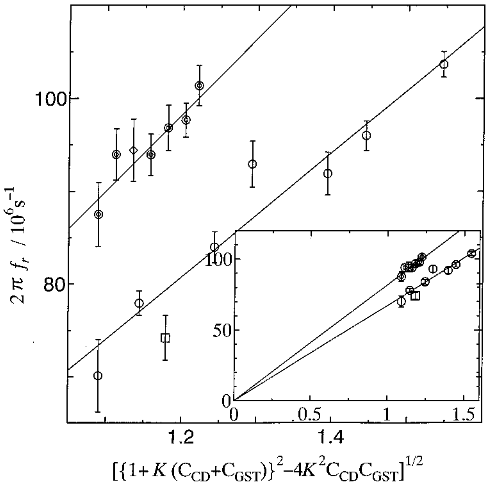

Figure 3. Plots of 2 πf_r vs the concentration term in eq 3. (○): at pH = about 1.8, (□): calculated value at different β-CD concentration at pH = 1.869, (◎): pH = about 5.2, (◇): the calculated value at different β-CD concentration at pH = 5.215.

TABLE 2: Rate and Thermodynamic Parameters for Complexation Reaction of Several Guests with β-Cyclodextrin at 25 °C

	k_f 10^8 mol^{-1} dm^3 s^{-1}	k_b 10^7 s^{-1}	K mol^{-1} dm^3	$\Delta\bar{V}$ 10^{-6} m^3 mol^{-1}
dissociated propionic acid $CH_3CH_2COO^-$	1.9 ± 0.1	8.19 ± 0.04	2.4 ± 0.1	16.2 ± 0.1
undissociated propionic acid CH_3CH_2COOH	3.6 ± 0.1	6.7 ± 0.1	5.3 ± 0.2	17.8 ± 0.7
1-Propanol $CH_3CH_2CH_2OH$	5.1 ± 0.7	12.1 ± 0.7	4.2 ± 0.6	12.5 ± 0.3
Methyl propionate $CH_3CH_2COOCH_3$	1.3 ± 0.1	8.7 ± 0.1	1.5 ± 0.1	24 ± 3
Methyl butyrate $CH_3CH_2CH_2COOCH_3$	3.7 ± 0.3	1.28 ± 0.03	29 ± 1	16 ± 2
1-Butyramide $CH_3CH_2CH_2CONH_2$	2.7 ± 0.3	9.8 ± 0.7	2.7 ± 0.3	12 ± 2
1-Butanol $CH_3CH_2CH_2CH_2OH$	2.8 ± 0.8	3.8 ± 0.6	7 ± 2	11.1 ± 1

eq 1 and the calculated curves are fitted to the experimental data. The ultrasonic parameters are also listed in Table.1. This relaxation is very dependent on the solution pH. As can be seen in Figures 1 and 2, the relaxational absorption disappears when the pH values decrease or increase. Therefore, the cause of the relaxational absorption is considered to be associated with a protolysis expressed as[14]

$$CH_3CH_2COO^- + H^+ \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} CH_3CH_2COO^- \cdots H^+ \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} CH_3CH_2COOH \quad (5)$$

where k_{ij} is the rate constants at the individual step. The relationship between the relaxation frequency and concentration of reactant is given by the next equation on the assumption that the first equilibrium perturbation is the cause of the observed relaxation

$$2\pi f_r = \gamma^2\{[H^+] + [CH_3CH_2COO^-]\}k_{12} + k_{21} = 2\gamma^2[H^+]k_{12} + k_{21} \quad (6)$$

where γ is the mean activity coefficient calculated by Davis's empirical equation. The data accumulation in the concentrations less than 0.100 mol dm^{-3} was carried out in order to rule out the effect of the dimerization process in carboxylic acids. We assume that the values from pH meter provide the proton concentration because the individual activity coefficients of the ions are not obtained and the ion concentration is not high.

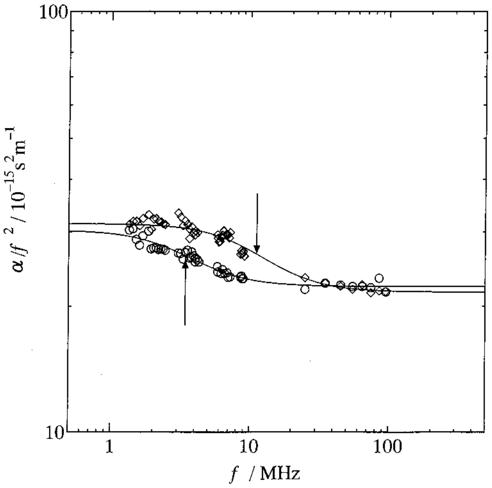

Figure 4. Representative ultrasonic absorption spectra in aqueous solution of proponic acid at 25 °C. (○): 0.0050 mol dm^{-3} at pH = 3.662, (◇): 0.100 mol dm^{-3} at pH = 2.918.

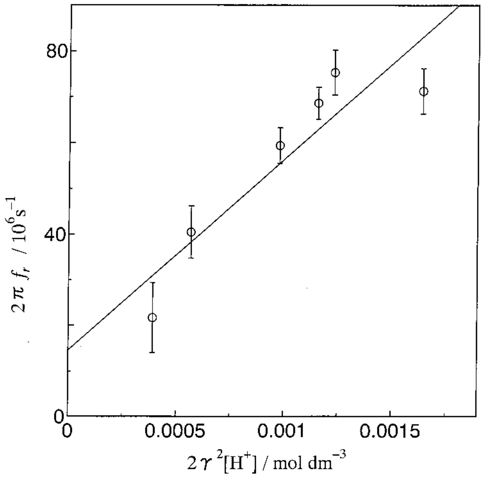

Figure 5. Plots of $2\pi f_r$ vs $2\gamma^2[H^+]$ for aqueous solution of propionic acid.

Figure 5 shows the plots of $2\pi f_r$ vs $2\gamma^2[H^+]$, of which the slope and intercept with a linear-least-mean square method provide the forward and backward rate constant, k_{12} and k_{21}, respectively. These values are listed in Table 3.

The conventional dissociation constant, K_a, can be obtained from the analytical concentration and hydrogen ion concentration as follows

$$K_a = \gamma^2[H^+]^2/(C_0\text{-}[H^+]) \tag{7}$$

The maximum absorption per wavelength for this reaction is given by

$$\mu_{max} = \pi\,\rho\,v^2(1/[CH_3CH_2COO^-] + 1/[H^+] + 1/[CH_3CH_2COO\cdots H])^{-1}(\Delta V)^2/2RT \tag{8}$$

The averaged standard volume change is also shown in Table 3.

Discussion

First, the results for the interaction between β-CD and propionic acid are considered. In our kinetic studies concerning the dynamic interaction between CD and nonelectrolytes or amino acid by the ultrasonic absorption method,[4-7] we have concluded that the rate constants for the association and dissociation reaction rates for α-CD and β-CD with several guests are dependent on the structures of the CD and guest molecules. More precisely, when the same size of the cavity is used (β-CD), the backward rate constant, k_b, is considerably dependent on the hydrophobic group and also on the polarity of the functional group of guests. However, the forward rate constants, k_f, fall on the similar values at around 3×10^8 mol^{-1} dm^3 s^{-1}. This may be because the size of the cavity is much greater than those of the guest molecules.[7] For propionic acid which exists as the dissociated or undissociated form, the forward rate constants seem to be close to that expected from the results in nonelectrolytes and amino acid systems. We had considered that the effect of dissociated form on the backward rate constant were more striking because the hydrophilic group would interact with the hydroxyl groups locating at the rim of the β-CD molecules. Unfortunately, the results shows the small effect when the rate constant for dissociated and propionic acid is compared with those for undissociated propionic acid or methyl propionate as are shown in Table 2. This means that the main cause of the interaction is the hydrophobic interaction in the cavity with the host and guest. Therefore, the hydrophobicity of the guest molecules plays mostly the important role for the interaction. It should be noticed, however, that the equilibrium constant, K, for the dissociated form of propionic acid is smaller than that for the undissociated form.

Next, we discuss the results for the proton-transfer reaction in aqueous solution of propionic acid. The amplitude of the excess absorption, A, in carboxylic acid solutions is considerably small when compared with those observed in amine solutions.[15] Jackopin and Yeager[8] have reported the relaxation in aqueous solution of acetic acid, of which the relaxation frequency locates at around 13 MHz at 0.1 mol dm^{-3}. However, the concentrations range has been limited. For propionic acid solution,[9] the examination has been carried out at 1.0 mol dm^{-3}, changing the solution pH. These investigations have been performed using the pulse method and the measurement frequency has been above 15 MHz. The resonance method used in this study is very powerful in the range less than 10 MHz even if the relaxation amplitude is small. As can be seen in Figure 4, the clear relaxational absorption is observed. The relaxation associated with the proton-transfer reaction is usually analyzed by Eigen mechanism as is shown in eq 5.[14] If the second step affects the first step, the relaxation frequency is given by $2\pi f_r = 2\gamma^2[H^+]k_{12} + k_{21}/(1 + k_{23}/k_{32})$. Then, the plots in Figure 5 gives the k_{12} value as the slope and the $k_{21}/(1 + k_{23}/k_{32})$ one as the intercept. The ratio, $\{k_{21}/(1 + k_{23}/k_{32})\}/k_{12}$ should be close to the dissociation constant, K_a, but it is far from the literature value[14] or determined one using eq 7. The similar situations are also observed in aqueous solutions of various amines.[15] Therefore, we have considered that the cause of the ultrasonic

TABLE 3: Rate and Thermodynamic Constants of Proton-Transfer Reaction in Aqueous Solutions of Propionic Acid at 25 °C

k_{12}	k_{21}	K_{21}	K_{32}	K_a[a]	K_a[b]	$\Delta\bar{V}$
10^{10} mol^{-1} dm^3 s^{-1}	10^7 s^{-1}	10^{-4} mol dm^{-3}	10^{-2}	10^{-5} mol dm^{-3}	10^{-5} mol dm^{-3}	10^{-6} m^3 mol^{-1}
4.2 ± 0.6	1.5 ± 0.7	3.5 ± 2.2	2.6 ± 0.8	0.98 ± 0.08	1.334	15 ± 2

[a] From eq 7. [b] From ref 16.

relaxation is due to the perturbation of the first equilibrium in eq 5. The slope and the intercept of the plots in Figure 5 provide the forward and backward rate constant. The k_{12} value is reasonable as a diffusion controlled process in water. The equilibrium constant, K_{32}, was calculated following the same procedure described elsewhere.[15]

Finally, it should be considered how the proton-transfer reaction affects the association and dissociation reaction between β-CD and propionic acid. As are seen in Figures 1 and 2, the ultrasonic relaxation is not observed in propionic acid solutions at pH = about 1.8 and 5.2. This is because the amplitude of the relaxation due to the proton-transfer reaction decreases and the relaxation frequency increases drastically when the solution pH is changed by the addition of the acid or base, which are recognized from eqs 6 and 7. That is, the equilibria expressed by eq 5 shift to the right-hand side or the left-hand side sufficiently and therefore the proton-transfer reaction may not give any significant effect on the dynamic interaction between the host and guest.

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