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Ultrasonic Absorption in Solutions of Propionic Acid

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The effect of a solvent on the ultrasonic relaxation of propionic acid has been studied. The relaxation frequency is affected a little in hydrophilic solvents, while in non-hydrophilic solvents it shifts to a higher-frequency side. The activation enthalpy in a reaction from open to cyclic dimers decreases with dilution in the non-hydrophilic solvents; the magnitude of the change in the hydrophilic solvents is less than in the non-hydrophilic solvents. This means that the open dimer is destabilized by non-hydrophilic solvents. The sequence of the magnitude of the solvent effect on the relaxation frequency is consistent not with that estimated from the magnitude of the dielectric constant of the solvent, but with that estimated from the magnitude of the non-hydrophilic strength of the solvent. The stability of an open dimer in a hydrophilic or polar solvent is attributed to the interaction of the free OH group on the open dimer with the solvent.

The present authors have previously reported that the mechanism of ultrasonic relaxation in solutions of propionic acid[1] and other carboxylic acids[2] is associated with the perturbation of the equilibrium between the cyclic and open dimers formed by intermolecular hydrogen bonding between carboxyl groups. It was reported there[1] that the relaxation frequency increased with the dilution for various solvents. A similar result has also been observed for acetic acid

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[1] N. Tatsumoto, *J. Chem. Phys.*, **47**, 4561 (1967).

[2] T. Sano, N. Tatsumoto, T. Niwa, and T. Yasunaga, This Bulletin, in press.

by Piercy and Lamb.[3] One purpose of this paper is to study in more detail the effect of solvents on the relaxation in solutions of propionic acid. The solvents used are dioxane, methyl propionate, benzene, chlorobenzene, cyclohexane, and xylene.

Experimental

The measurements of ultrasonic absorption in various solutions were made over the frequency range from 2.5 to 95 MHz, at various temperatures from 15 to 35°C, by the pulse method. The apparatus and experimental techniques have been fully described in a previous paper.[1] The velocity of sound at 1.92 MHz was measured with a sing-around system produced by Cho Onpa Kogyo Kaisha (Tachikawa, Tokyo, Japan), model UVM-2-1, and that at 3.00 MHz, with an ultrasonic interferometer. The experimental procedures have also been described in previous papers.[4] The dielectric constant was measured with the bridge method at 200 kHz. The chemical shift of the acid proton of propionic acid in NMR was measured at 34°C in various solvents, where tetramethylsilane was used as the reference. The chemicals used were all guaranteed reagents and were used without further purification except in the case of propionic acid. Propionic acid was purified by fractional distillation under reduced pressure.

Results and Discussion

As is shown in Fig. 1, the ultrasonic absorption in solutions of propionic acid in various solvents can be represented by a single relaxation equation:

$$\alpha/f^2 = \frac{A}{1+(f/f_m)^2} + B \qquad (1)$$

where α is the ultrasonic absorption coefficient; f, the frequency of sound; f_m, the relaxation frequency, and A, and B, the chemical and classical absorptions respectively. The values of f_m calculated from the experimental data are listed in the table. In Fig. 2, the relaxation frequencies are plotted against the concentrations. As can be seen in Fig. 2, the relaxation frequency, f_m, does not change with the concentration in methyl propionate, but it decreases in dioxane, chlorobenzene, benzene, cyclohexane, and xylene. The magnitude of its change with the concentration increases in the order noted. Since the relaxation frequency changes monotonously with the concentration, it is highly probable that the relaxation mechanism in those solutions is identical with that in liquid propionic acid itself. The relaxation mechanism may, therefore, be associated with an equilibrium:

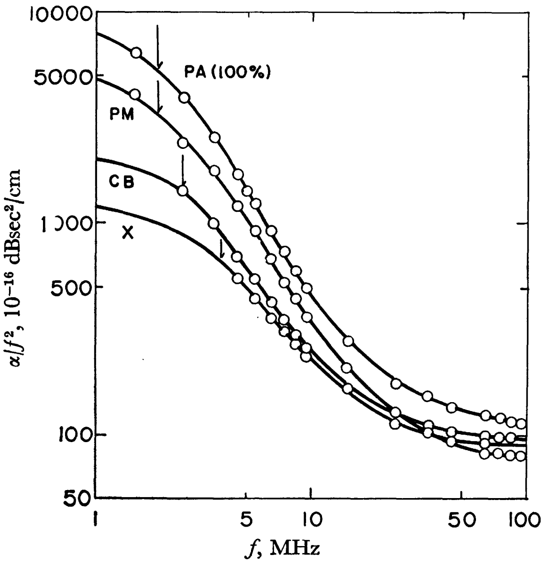


Fig. 1a. Ultrasonic absorption spectra in various solvents at 20°C: PA (100%), 100% propionic acid; PM, in methyl propionate; CB, 10M in chlorobenzene; X, 10M in xylene.

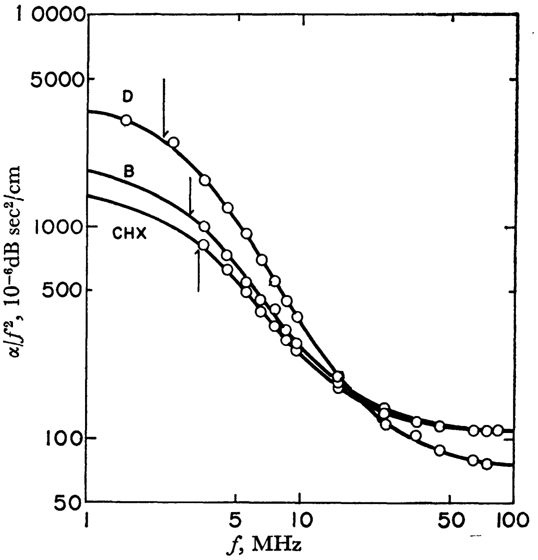
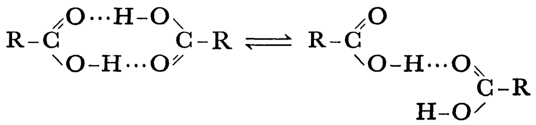


Fig. 1b. Ultrasonic absorption spectra at 20°C: D, 10M in dioxane; B, 10M in benzene; CHX, 10M in cyclohexane.



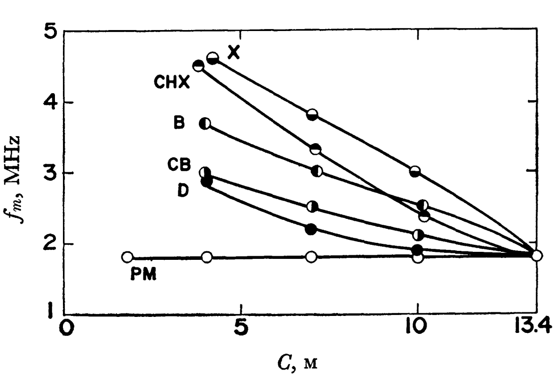


Fig. 2. Changes in relaxation frequencies at 20°C with concentration of propionic acid in various solvents:
○ PM, methyl propionate;
● D, dioxane;
◑ CB, chlorobenzene;
◐ B, benzene;
◓ CHX, cyclohexane;
◒ X, xylene.

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[3] J. E. Piercy and J. Lamb, *Trans. Faraday Soc.*, **52**, 930 (1956).

[4] T. Yasunaga, N. Tatsumoto, and M. Miura, This Bulletin, **37**, 1655 (1964). T. Yasunaga, M. Tanoura, and M. Miura, *J. Chem. Phys.*, **43**, 3512 (1965).

Table. The relaxation frequency and kinetic values for the reaction between cyclic and open dimers of propionic acid

t (°C)	f_m (MHz)	K (10^{-2})	H $\left(\frac{\text{kcal}}{\text{mol}}\right)$	k_f (10^5 sec^{-1})	k_b (10^7 sec^{-1})	$H_f^{\ddagger}$ $\left(\frac{\text{kcal}}{\text{mol}}\right)$	$H_b^{\ddagger}$ $\left(\frac{\text{kcal}}{\text{mol}}\right)$
	100% propionic acid						
15	—	—		—	—		
20	1.8	2.5		2.6	1.06		
25	2.2	2.8	4.3	3.6	1.29	~11	6.8
30	2.8	3.2		5.2	1.62		
35	3.8	3.6		7.0	1.96		
	10.0M in methyl propionate						
15	—	—		—	—		
20	1.8	2.7		2.9	1.06		
25	2.2	3.1	4.4	4.0	1.29	~11	6.8
30	2.8	3.5		5.7	1.63		
35	3.8	3.9		7.7	1.97		
	7.6M in methyl propionate						
15	—	—		—	—		
20	1.8	2.8		3.0	1.07		
25	2.2	3.1	4.3	4.0	1.30	~11	6.8
30	2.8	3.5		5.8	1.65		
35	3.8	3.9		7.7	1.99		
	4.1M in methyl propionate						
15	—	—		—	—		
20	1.8	3.7		4.0	1.07		
25	2.2	4.2	3.7	5.5	1.31	~11	6.8
30	2.8	4.6		7.6	1.65		
35	3.8	5.1		10.2	1.99		
	10.0M in dioxane						
15	—	—		—	—		
20	1.9	3.3		3.6	1.08		
25	2.4	3.7	4.1	5.1	1.37	~11	6.8
30	2.9	4.2		7.1	1.68		
35	3.6	4.6		9.4	2.03		
	7.2M in dioxane						
15	—	—		—	—		
20	2.2	3.8		4.9	1.29		
25	2.7	4.3	3.4	6.8	1.59	~11	6.8
30	3.3	4.7		9.1	1.94		
35	4.1	5.2		12.4	2.38		
	4.1M in dioxane						
15	—	—		—	—		
20	2.9	2.9		5.0	1.72		
25	3.6	3.2	3.7	7.0	2.19	~11	6.6
30	4.5	3.6		9.6	2.68		
35	5.5	4.0		13.0	3.25		
	10.0M in chlorobenzene						
15	1.7	1.0		1.0	1.04		
20	2.1	1.2		1.5	1.28		
25	2.6	1.4	5.1	2.2	1.57	~12	6.6
30	3.2	1.6		3.1	1.92		
35	3.9	1.8		4.2	2.33		
	7.0M in chlorobenzene						
15	2.0	0.52		0.64	1.24		
20	2.5	0.62		0.96	1.54		
25	3.0	0.73	5.8	1.3	1.85	~12	6.5
30	3.7	0.86		2.0	2.27		
35	4.5	1.0		2.8	2.75		
	4.0M in chlorobenzene						
15	2.5	0.30		0.47	1.56		
20	3.0	0.36		0.67	1.87		
25	3.7	0.43	5.8	0.99	2.30	~12	5.8
30	4.3	0.51		1.36	2.67		
35	5.2	0.58		1.87	3.23		
	10.1M in benzene						
15	2.0	1.1		1.3	1.22		
20	2.5	1.3		2.0	1.52		
25	3.0	1.5	4.8	2.7	1.81	~11	6.2
30	3.7	1.7		3.8	2.23		
35	4.4	1.9		5.0	2.64		
	7.1M in benzene						
15	2.5	0.48		0.74	1.55		
20	3.0	0.57		1.1	1.85		
25	3.5	0.67	5.8	1.4	2.16	~11	5.4
30	4.3	0.79		2.1	2.64		
35	5.0	0.92		2.8	3.06		
	4.1M in benzene						
15	3.1	0.30		0.58	1.93		
20	3.7	0.35		0.81	2.31		
25	4.3	0.42	5.7	1.1	2.68	~11	5.1
30	5.0	0.48		1.5	3.11		
35	5.9	0.56		2.1	3.66		
	10.1M in cyclohexane						
15	2.0	1.1		1.3	1.22		
20	2.4	1.2		1.8	1.46		
25	3.0	1.4	4.7	2.5	1.82	~11	5.4
30	3.6	1.6		3.5	2.17		
35	4.4	1.8		4.8	2.64		
	7.0M in cyclohexane						
15	2.7	0.55		0.92	1.67		
20	3.3	0.64		1.3	2.04		
25	4.0	0.73	4.7	1.8	2.47	~10	5.5
30	4.7	0.83		2.4	2.90		
35	5.5	0.94		3.2	3.39		
	3.9M in cyclohexane						
15	3.8	0.22		0.52	2.37		
20	4.5	0.26		0.73	2.81		
25	5.0	0.30	5.7	0.94	3.12	~10	4.1
30	5.7	0.36		1.3	3.55		
35	6.5	0.41		1.7	4.05		
	9.9M in xylene						
15	2.5	0.58		0.87	1.54		
20	3.0	0.68		1.3	1.84		
25	3.5	0.80	5.7	1.7	2.14	~11	5.4
30	4.2	0.94		2.4	2.56		
35	5.0	1.1		3.3	3.03		
	7.0M in xylene						
15	3.3	0.41		0.84	2.05		
20	3.8	0.48		1.1	2.36		
25	4.2	0.57	5.5	1.5	2.60	~9	3.9
30	4.9	0.66		2.0	3.03		
35	5.5	0.77		2.6	3.39		
	4.2M in xylene						
15	4.2	0.29		0.76	2.62		
20	4.6	0.34		0.98	2.87		
25	5.1	0.40	5.5	1.3	3.18	~8	2.5
30	5.5	0.46		1.6	3.42		
35	6.0	0.54		2.0	3.73		

The relaxation time, τ, in this reaction is represented by this equation:

$$\tau^{-1}=2\pi f_{inf}\ (C_V^{\infty}/C_V^{0})=k_f+k_b\simeq 2\pi f_m \qquad (2)$$

where f_{inf} is the frequency of the inflection point in the curve of the dispersion of the sound velocity; C_V^0, the heat capacity at a constant volume and at zero frequency; C_V^{∞}, the heat capacity at an infinite frequency, and k_f and k_b, the forward and backward rate constants respectively.

When the reaction in this solution is principally one involving enthalpy rather than volume change, the temperature change in the heat capacity resulting from the chemical reaction at a constant pressure, C_p^r, is expressed as:

$$C_p^r=\frac{H^2}{RT^2}\cdot\frac{K}{(1+K)^2} \qquad (3)$$

$$K=k_f/k_b \qquad (4)$$

The equilibrium constants, K_1 and K_2, at the temperatures of T_1 and T_2 respectively are represented as:

$$K_1/K_2=exp\left\{\frac{H}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)\right\} \qquad (5)$$

where H is the enthalpy of reaction. Equations (3)—(5) are used to calculate H and K from the change in C_p^r with the temperature ascertained by using experimental data for the velocity of sound, density, thermal expansion coefficient, and heat capacity at a constant pressure and zero frequency, C_p^0. The C_p^0 values for the solutions at various concentrations are determined by the interpolation using those values found in the literature and our experimental data for the solute and solvents.[1,5] The reaction rate constants, k_f and k_b, are calculated by means of Eq. (2). As can be seen in the table, k_b is much greater than k_f, and the tendencies of the changes in k_b with the concentration are similar to those in f_m, as can be seen in Fig. 3. The enthalpy of activation is given by the temperature dependence of the rate constant:

$$k/T=C\exp(-H^{\neq}/RT)\exp(S^{\neq}/R) \qquad (6)$$

where C is a constant and where $H^{\neq}$ and $S^{\neq}$ are the enthalpy and the entropy of activation respectively. As can be seen in Figs. 2, 3, and 5, f_m and k_b increase with the concentration, while $H_b^{\neq}$ decreases with it. This shows that $H_b^{\neq}$ is one of the factors changing f_m and k_b. The magnitude of the change in f_m with the concentration stands in the order of the non-hydrophilic strength rather than in that of the dielectric constants of the solvents. This means that the open dimer is stabilized by the hydrophilic solvent; this increase in the stability is probably to be ascribed to the interaction of hydrophilic groups in the solvent with the free OH groups in the open dimer. In xylene, the change in f_m with the concentration is greater than that in other non-hydrophilic and non-polar solvents, benzene and cyclohexane. This seems to be attributable to the interaction of hydrophobic groups in propionic acid with two methyl groups in the benzene ring.

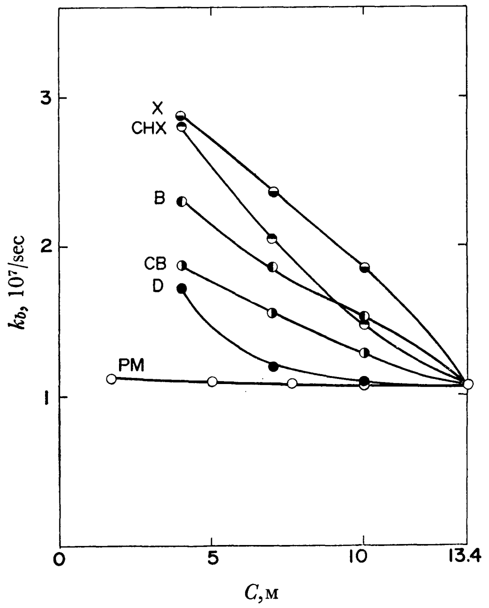

Fig. 3. Changes in backward reaction rates at 20°C with concentration of propionic acid in various solvents:
○ PM, methyl propionate;
● D, dioxane;
◑ CB, chlorobenzene;
◐ B, benzene;
◓ CHX, cyclohexane;
◒ X, xylene.

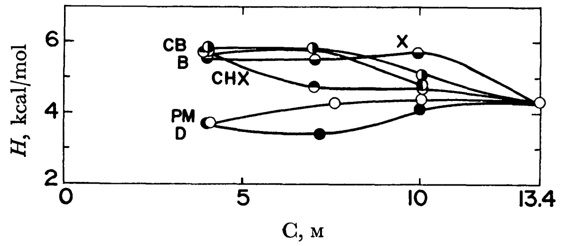

Fig. 4. Changes in reaction enthalpies with concentration of propionic acid in various solvents:
○ PM, methyl propionate; ● D, dioxane; ◑ CB, chlorobenzene; ◐ B, benzene; ◓ CHX, cyclohexane; ◒ X, xylene.

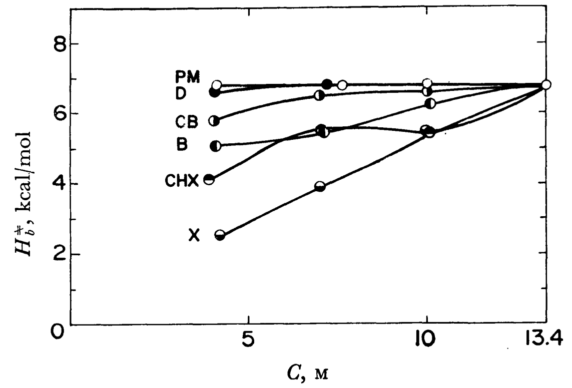

Fig. 5. Changes in activation enthalpies for backward reaction with concentration of propionic acid in various solvents
○ PM, methyl propionate; ● D, dioxane; ◑ CB, chlorobenzene; ◐ B, benzene; ◓ CHX, cyclohexane; ◒ X, xylene.

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5) H. H. Landolt and R. Börnstein, Physikalische Chemische Tabellen (Springer-Verlag, Berlin, 1931) part 2, p. 1203. International Critical Tables, **5**, 108.

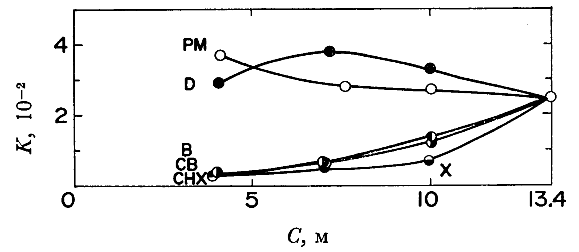

Fig. 6. Changes in equilibrium constants at 20°C with concentration of propionic acid in various solvents:
○ PM, methyl propionate; ● D, dioxane; ◑ CB, chlorobenzene; ◐ B, benzene; ◓ CHX, cyclohexane; ◒ X, xylene.

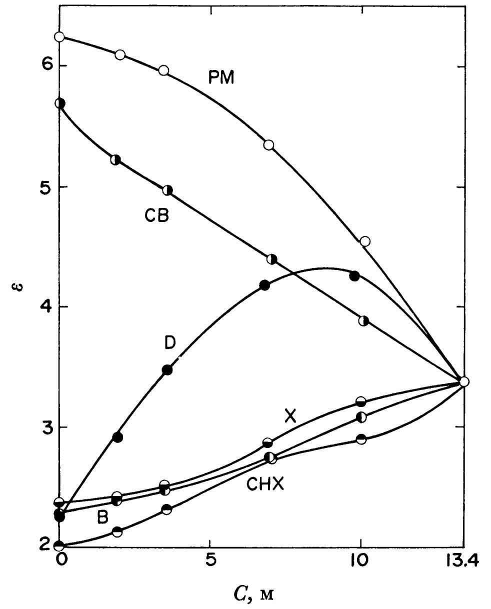

Fig. 7. Changes in dielectric constants at 20°C with concentration of propionic acid in various solvents:
○ PM, methyl propionate; ● D, dioxane; ◑ CB, chlorobenzene; ◐ B, benzene; ◓ CHX, cyclohexane; ◒ X, xylene.

Since the accuracy in H_f^* is rather poor, the change in it with the concentration will not be fully discussed here.

The energy and equilibrium constant of the reaction are listed in the table, while the changes in H and K with the concentration are shown in Figs.4 and 6. With dilution, the enthalpy of reaction, H, decreases in dioxane and methyl propionate and increases in the other solvents. From the changes in H and K with the concentration, it can be concluded that H can be regarded as a measure of the destabilization of the open dimer and K, as a measure of the stabilization. Figure 7 shows the changes in the dielectric constant with the concentration. As can be seen in the figure, they are concavo or complex curves, deviating little from the corresponding ideal straight line, for the benzene, cyclohexane, xylene, and chlorobenzene solutions, and clearly convex curves for the dioxane and methyl propionate solutions. The changes in the dielectric constants of hydrophilic solvents with the concentration, therefore, seem to be different from those of the other solvents. This is probably due to the fact that the open dimer, the dipole moment of which is greater than that of the cyclic dimer, is more abundant in the hydrophilic solvents than in the other solvents, as may be found from the changes in H and K with the concentration, as shown in Figs. 5 and 6. This conclusion is also confirmed by the NMR spectra. As can be seen in Fig. 8, the absorption of NMR shifts with dilution to the side of a higher magnetic field in the hydrophilic solvents and to the lower-side field in the non-hydrophilic solvents.

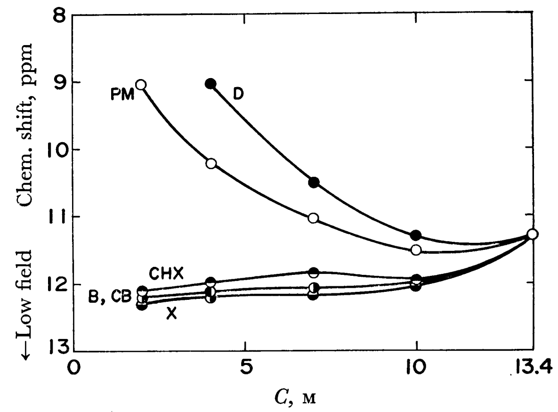

Fig. 8. Chemical shift of carboxylic acid proton in propionic acid in various solvents:
○ PM, methyl propionate; ● D, dioxane; ◑ CB, chlorobenzene; ◐ B, benzene; ◓ CHX, cyclohexane; ◒ X, xylene.

As was stated above, H increases with dilution in the non-hydrophilic solvent. This shows that the solvent effect on the open dimer decreases, until finally the value of H reaches that of the standard energy of the breakage of one hydrogen bond. The open dimer does not exist in an extremely dilute solution because of the decreases in H_b^* and K with dilution. In an extremely dilute solution, the equilibrium between the dimer and the monomer is similar to that in the gas state of propionic acid.[6] Further studies are in progress in a dilute solution of propionic acid; they will be reported in due course.

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[6] R. C. Herman and R. Hofstadter, *J. Chem. Phys.*, **7**, 460 (1939).