Carrier Effect of Reversed Micelle on Imidazole Catalyst

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(Received May 10, 1978)

The reversed micelles of neither didodecyldimethyl ammonium bromide(DDAB) nor sodium 1,4-bis(2-ethylhexyl) 2-sulfonatosuccinate(AOT) catalyse the decomposition of *p*-nitrophenyl acetate(PNPA) by themselves. However, these reversed micelles increase the action of imidazole in the decomposition of PNPA by solubilizing it. This interesting carrier effect of the reversed micelle on imidazole was investigated in both anhydrous and hydrous systems. The carrier effect of DDAB was greater than that of AOT. This difference was related to the different interaction between imidazole and each of the surfactants. The existence of the different interaction was made clear from the investigation on the change of chemical shift of the H(1) proton of imidazole upon solubilization by the reversed micelle. The mechanism of the decomposition of PNPA was partially explained from NMR measurements. Aminolysis occurred in anhydrous systems and hydrolysis in hydrous systems. Water pooled in the reversed micelle was more effective than bulk water in enhancing the catalytic effect of imidazole.

It has been recently reported that oil-soluble surfactants such as alkylammonium carboxylate catalyse a variety of reactions in nonaqueous media.[1-4] It is thought that the reversed micelles formed by these oil-soluble surfactants play an important role in the catalysis. The reversed micelles can solubilize some oil-insoluble or oil-soluble ploar substances. Solubilized substances may affect the catalytic activity through their interaction with the surfactants. The effect of solubilized water on the catalytic activity of alkylammonium carboxylate has been previously published.[3-6] Also, the effect of methanol, propylamine or acetic acid solubilized by dodecylammonium propionate on the decomposition of PNPA has been reported by these authors.[7] Similarly, non-catalysing reversed micelles may change the catalytic properties of a solubilized catalyst through an interaction between the catalyst and micelle.

In this paper, the effects of the non-catalysing reversed micelle of cationic and anionic surfactants on the catalytic activity of imidazole for the decomposition of PNPA is studied in anhydrous and hydrous systems and these effects related to the interaction between the reversed micelle and imidazole. Because nonionic surfactants showed behavior differing from that of the ionic surfactants used here, studies on nonionic surfactants will be reported separately.

Experimental

Materials. Didodecyldimethyl ammonium bromide (DDAB) and sodium 1,4-bis(2-ethylhexyl) 2-sulfonatosuccinate(AOT) were used as typical oil-soluble cationic and anionic surfactants. Preparation and purification of the surfactants are described elsewhere.[8] The guranteed reagent grades of imidazole and *p*-nitrophenyl acetate(PNPA), the catalyst and the substrate, respectively, were utilized. Carbon tetrachloride (CCl_4) was used as the solvent for both UV and NMR measurements. The solvent was purified as usual and carefully dried with Molecular Sieve 4A. However, a small quantity of water in the reaction systems was inevitable because of the hydroscopicity of the surfactants. Water content measured with the Karl-Fischer method was approximately 2 mmol kg^{-1} for the DDAB system and 7 mmol kg^{-1} for the AOT system for the anhydrous systems.

Methods. The decomposition of PNPA was followed by measurement of the changes in UV absorption at 318 nm, the wavelength of maximum absorption for the *p*-nitrophenol produced by the reaction. The UV spectrometer was a Shimadzu Double Beam Spectrophotometer UV-200. The initial concentration of PNPA was always 6.45×10^{-4} mol kg^{-1}. The decomposition of PNPA was always observed to be a pseudo-first order for PNPA.

NMR spectra were taken with a Hitachi NMR Spectrometer R-21(60 MHz). Chemical shifts were obtained relatively to an external TMS standard.

UV and NMR spectra were taken at 30 and 35 °C, respectively. All of the concentrations were expressed in molality(m, mol kg^{-1}) except those in Fig. 1.

Results and Discussion

Anhydrous Systems. Changes in the observed rate constants (k_{obsd}) varying the concentration of imidazole and holding the surfactant concentration constant(0.1 m) were depicted in Fig. 1. Changes in the imidazole–dodecylammonium propionate(DAP) system were shown for comparison in the figure. Because the solubility of imidazole in CCl_4 is only 5 mmol $kg,^{-1}$ the increase of k_{obsd} with increased concentration of imidazole, as seen in Fig. 1, is due to solubilized imidazole. It is seen from Fig. 1 that

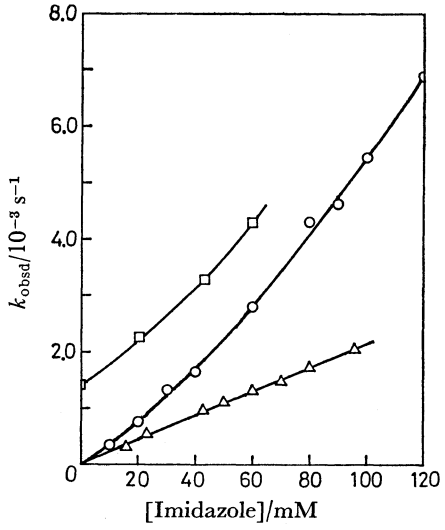


Fig. 1. Plots of k_{obsd} *versus* concentration of imidazole (mmol l^{-1}) at a fixed concentration of surfactants (0.1 m). —○—: DDAB, —△—: AOT, —□—: DAP.

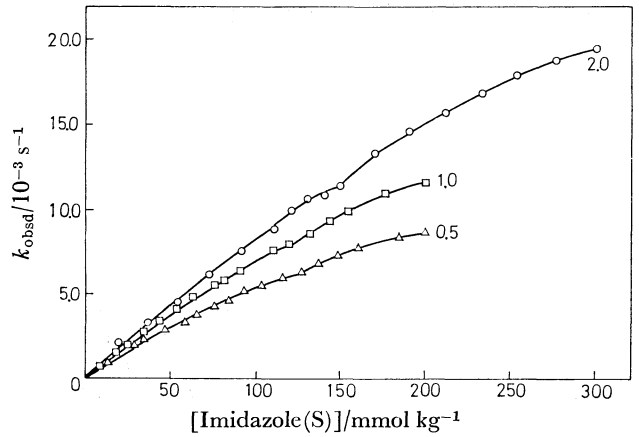


Fig. 2. Plots of k_{obsd} *versus* concentration of Imidazole-(S) in DDAB solutions. Figures show molar ratio of imidazole to DDAB.

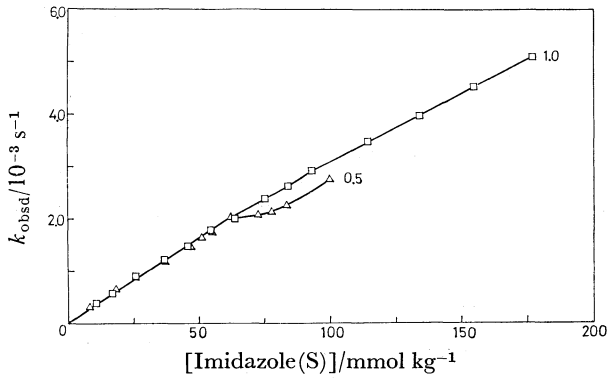


Fig. 3. Plots of k_{obsd} *versus* concentration of Imidazole-(S) in AOT solutions. Figures show molar ratio of imidazole to AOT.

DAP catalyzes the reaction in the absence of imidazole; however, neither DDAB nor AOT do so.

In order to investigate the effect of solubilization by non-catalsing micelle on the catalytic activity of imidazole, the systems solubilizing imidazole at a fixed ratio to a surfactnat were used and the change of reaction constant(k_{obsd}) with the concentration of solubilized imidazole was measured. The molar ratios of imidazole to the surfactant used were 0.5, 1.0, and 2.0. Imidazole solubilized at a fixed ratio is designated as "Imidazole(S)" or "Im(S)".

The relationship between k_{obsd} and the concentration of Im(S) for DDAB and AOT solutions is shown in Figs. 2 and 3. A linear relation can be seen at low concentration for both surfactant systems. The relation shows a curved line at higher concentration, some inflection appearing on the way. These changes may be due to changes in the size or shape of reversed micelles in this range. However, the present discussion forcuses on the lower concentration range.

The slope of the linear part gives the first order rate constant for Im(S), which was listed as k_1 in Table 1. To obtain the rate constant for imidazole dissolved in pure CCl_4, the rate constant for a small quantity of imidazole in the absence of any surfactant was measured. The rate constant obtained was designated as k_1°. The ratio, k_1/k_1° listed in Table 1 is a measure

Table 1. Rate constants for imidazole solubilized in anhydrous media

Surfactant	Molar ratio	k_1 (kg mol^{-1} s^{-1})	k_1/k_1° a)
DDAB	0.5	0.067	5.4
	1.0	0.077	6.2
	2.0	0.080	6.4
AOT	0.5	0.033	2.6
	1.0	0.033	2.6

a) k_1°: the first order rate constant for imidazole in pure CCl_4: the value is 0.0124 kg mol^{-1} s^{-1}.

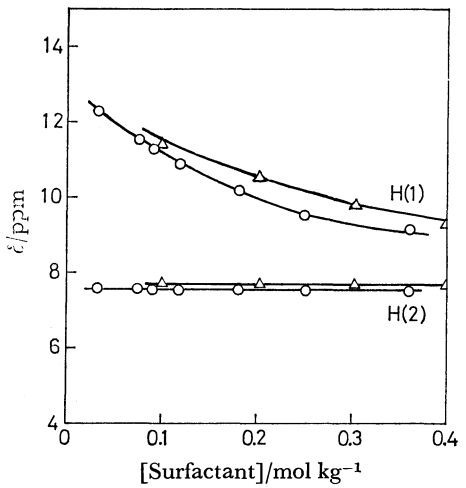


Fig. 4. Change of chemical shift of H(1) and H(2) protons of imidazole with concentration of surfactants. —○—: In DDAB solutions, —△—: in AOT solutions.

of the carrier effect of the surfactants. It is apparent that both surfactants show carrier effect for imidazole. DDAB shows a greater effect than AOT as seen in Table 1. Increase of the values of k_1/k_1° with increase of the molar ratios for DDAB as seen in Table 1 seems to show a concentrating effect of imidazole in the reversed micelle. It is considered that the difference in the observed rate constants of two surfactants is due to different interaction with imidazole.

The chemical shifts of the H(1) and H(2) protons of imidazole were measured in order to examine the interactions mentioned above. The result was shown in Fig. 4. It was observed that the chemical shift of the H(1) proton in both DDAB and AOT solutions shifts to higher field with increase of surfactant concentrations, though that of the H(2) proton does to minor extent. The high field shift shows the existence of the interaction of the H(1) proton with the polar part of the surfactant molecule in the reversed micelle. It is considered that the high field shift resulting from the interaction is due to electron-donation from bromide ion or sulfonate ion of each surfactant to the proton. Here bromide is more electron-donative(basic) than sulfonate, because the latter is partially hindered by neighboring sodium ion.

The interaction has been also discussed by NMR method on the solubilization of methanol and acetic acid by DDAB and other surfactants.[9] Higher field

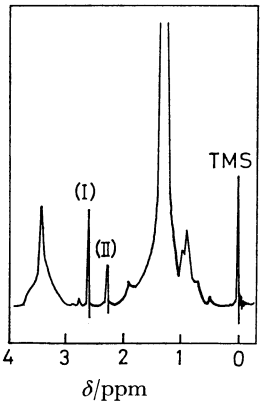
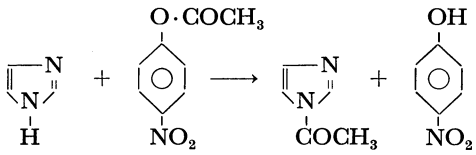


Fig. 5. NMR spectrum of DDAB–imidazole–PNPA solution in anhydrous CCl_4. Peak (I): $\underline{CH_3}CO$- of acetylimidazole, peak (II): $\underline{CH_3}CO$- of PNPA.

shifts correspond to higher interaction constants.[9] Therefore, the higher field shift of the H(1) proton in DDAB solution than that in AOT solution seen in Fig. 4 shows that the interaction of the H(1) proton with the reversed micelle is more intensive in the DDAB solution. This correlates with the higher values of k_1/k_1^0 for DDAB than AOT in Table 1. Minor change of the H(2) proton shows that the proton interacts with the surfactant in the micelle to minor extent.

NMR was further used to obtain some information on the reaction mechanism involved. Here, a higher concentration of PNPA was used in order to obtain a significant peak in the spectrum. A mixture of DDAB, imidazole and PNPA in CCl_4 (each component 0.1 m) was prepared and allowed to stand overnight. The NMR spectra of the mixture was shown in Fig. 5. The appearance of a peak corresponding to $\underline{CH_3}CO$– of 1-acetylimidazole(I) but none corresponding to acetic acid, shows that the reaction is a kind of aminolysis as shown in Eq. 1 and does not proceed to hydrolysis which may be expected from minor inevitable content of water.



(1)

The NMR spectra of the AOT–imidazole–PNPA solution in CCl_4 were similar to those of DDAB solution. Similar aminolysis of the ester by benzamidine and piperidine has also been observed.[10,11] The proposed mechanism was further supported by the UV spectra of the mixture of AOT(0.1 m), imidazole(0.1 m), and PNPA(6.4×10^{-4}m) in hexane, which showed a gradual decrease of the peak corresponding to PNPA (263 nm) and the simultaneous increase of the peaks corresponding to *p*-nitrophenol(313 nm), and 1-acetylimidazole(220 nm) during the successive mixing for 4 h.

Acceleration of Reaction 1 by the reversed micelle may be due to combined catalytic action by imidazole and the basic part of the micelle(Br^- in DDAB or SO_3^- in AOT). This action is well known in aqueous solutions, as in the action of imidazole and hydroxide

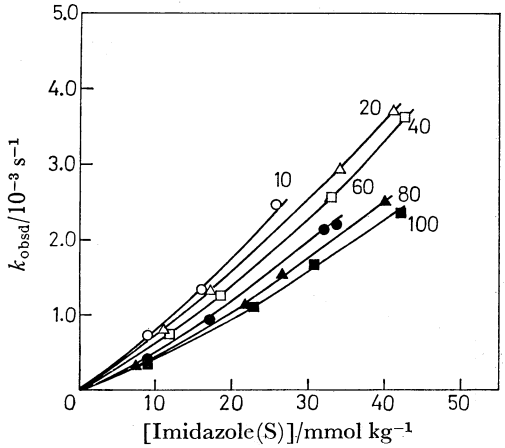


Fig. 6. Plots of k_{obsd} *versus* concentration of imidazole at a fixed concentration of water (0.020 m). Figures show concentration of DDAB (mmol kg^{-1}).

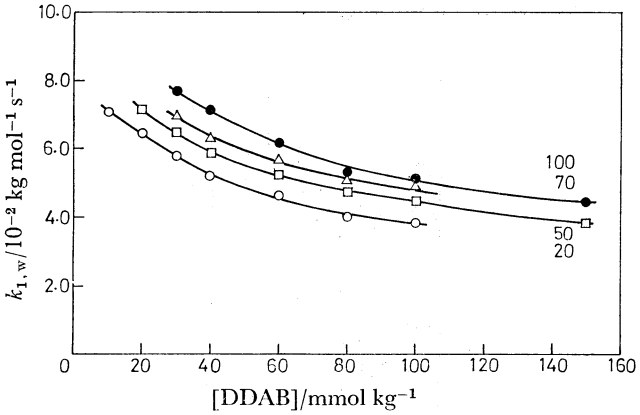


Fig. 7. Plots of $k_{1,w}$ *versus* concentration of DDAB. Figures show concentration of water(mmol kg^{-1}).

anion.[12] The existence of such an interaction between imidazole and the basic part of a reversed micelle can be seen from the remarkable shift of the H(1) proton in Fig. 4. Differences between DDAB and AOT with regards to interaction and acceleration of reaction may result from a difference in the structure of their reversed micelles. In the DDAB systems, the anion is exposed to the interior of the micelle, while in the AOT system, the anion is partially covered by Na^+. The effect of didodecyldimethyl ammonium chloride (DDAC) and iodide(DDAI) was compared with that of DDAB to check the basic activity. The order of the effects on both the rate and the chemical shift was DDAC>DDAB>DDAI. The order corresponds to that of the basicity of halogen ions.

Hydrous Systems. The quantity of water added to the reaction systems of imidazole–PNPA–surfactant in CCl_4 was of the same order as the surfactant. Because partition of water between the micelle and the solvent is of great advantage to the micelle, though the solubility of water in the solvent is 0.045 m at 30 °C, it was reasonably assumed that all of water added is solubilized in the reversed micelle and that water affects the imidazole catalyst under the state trapped in the interior of the micelle.

The change of k_{obsd} with concentration of imidazole

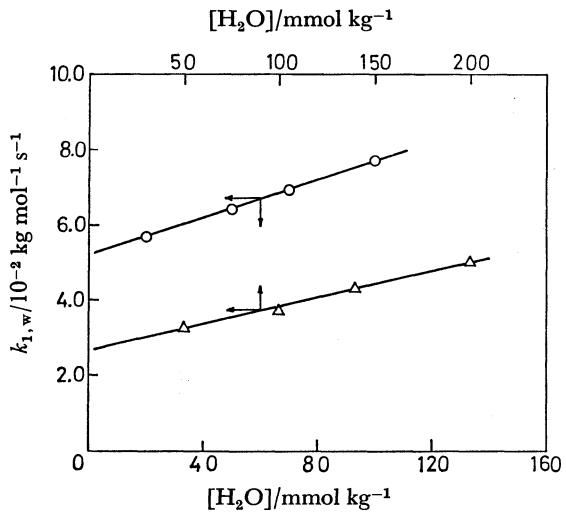


Fig. 8. Plots of $k_{1,w}$ *versus* concentration of water. —O—: solution of 30 mmol kg^{-1} of DDAB, —△—: solution of 20 mmol kg^{-1} of AOT.

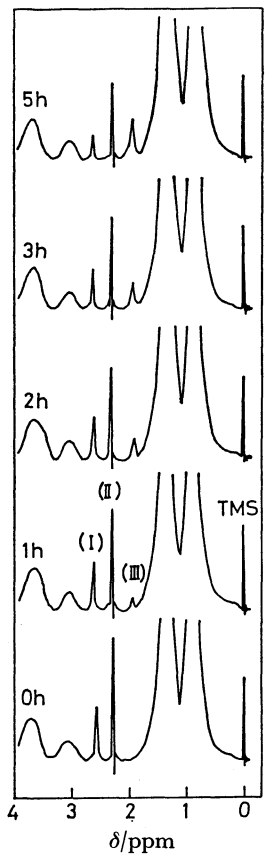


Fig. 9. NMR spectra of solution of DDAB-imidazole-PNPA-H_2O in CCl_4. Peak (I): $C\underline{H}_3CO$- of acetylimidazole, peak (II): $C\underline{H}_3CO$- of PNPA, peak (III): $C\underline{H}_3CO$- of acetic acid.

was measured by selecting the concentration of surfactant or water as a parameter. An example using the DDAB system(the concentration of water: 0.020 m) is given in Fig. 6. Similar plots were also obtained for 0.050, 0.070, and 0.100 m of H_2O. The initial slope of these plots is considered to be the first order rate constant for imidazole($k_{1,w}$), though the linearity is not complete. The values of $k_{1,w}$ were plotted against the concentration of DDAB,[DDAB], for various choices of the concentration of water, [H_2O], in Fig. 7. Relations quite similar to those shown in Figs. 6 and 7 were obtained for AOT system. The decrease of $k_{1,w}$ with increasing [DDAB] apparent in Fig. 7 shows the effect of dilution of the imidazole by the surfactant.

TABLE 2. RATE CONSTANT PARAMETERS FOR IMIDAZOLE IN HYDROUS MEDIA

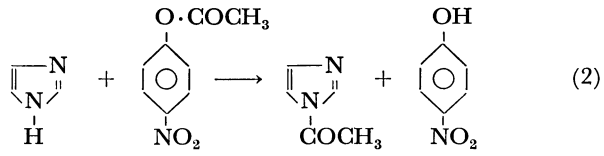
Surfactant	Concentration of surfactant (mmol kg^{-1})	$k^r_{1,w}$ [a] (kg mol^{-1} s^{-1})	$k^r_{1,w}/k^\circ_{1,w}$ [b]
DDAB	30	13.9	21.5
	40	13.9	21.5
	60	10.9	16.9
	80	8.6	13.3
	100	8.4	13.0
AOT	20	4.1	6.3
	40	3.1	4.9
	60	1.9	2.9
	100	0.7	1.1

a) $k^r_{1,w}$: rate constant calculated for 1 kg of water solubilized. b) $k^\circ_{1,w}$: rate constant for imidazole in pure water (the value is 0.645 kg mol^{-1} s^{-1}).

In Fig. 8 were rearranged the relation of Fig. 7 as plots between $k_{1,w}$ and [H_2O]. The slope of the resulting lines in Fig. 8 shows the increment of $k_{1,w}$ relative to [H_2O] of 1 mmol kg^{-1} in the reversed micelles. Therefore, the reduced rate constant, $k^r_{1,w}$, could be calculated by multiplying the slope by the molar concentration of pure water, 55.5 mol kg.$^{-1}$ The values obtained are listed in Table 2.

The effect of water pooled in the reversed micelle on the catalytic activity of imidazole was estimated by comparing these reduced rate constants($k^r_{1,w}$) with the first order rate constants of the catalytic reaction of imidazole in pure water ($k^\circ_{1,w}$) which was measured separately. The values of the ratio, $k^r_{1,w}/k^\circ_{1,w}$ in Table 2 show that water pooled in the reversed micelle accelerates the catalytic effect of imidazole more markedly than free water. It is also seen in Table 2 that DDAB has a greater acceleration effect than AOT and that $k^r_{1,w}$ and $k^r_{1,w}/k^\circ_{1,w}$ decrease with increasing concentration of surfactants, showing the effects of the dilution of imidazole by the surfactants.

Again, to obtain some information on the reaction mechanism in hydrous systems, changes in the NMR spectra with time for the mixture of DDAB, imidazole, PNPA, and water in CCl_4, each component being 0.1 m, were measured. The result was shown in Fig. 9. Immediately after mixing, a peak corresponding to $C\underline{H}_3CO$- of 1-acetylimidazole appeared. As time elapsed, this peak(I) decreased and a peak corresponding to $C\underline{H}_3CO$- of acetic acid(III) appeared and gradually increased. Hence we can safely assign the following well known hydrolysis mechanism(Eqs. 2 and 3) to the systems solubilizing imidazole and considerable amount of water.



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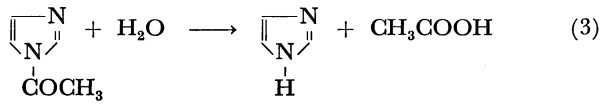

(3)

The rate of Eq. 2 was very fast due to the large quantity of PNPA used(0.1 m). Similar time dependence was observed in the NMR spectra of the AOT–imidazole–PNPA–H_2O system in CCl_4. However, it has not yet been determined how much water is necessary for Reaction 3 to proceed.

References

1) E. J. Fendler, J. H. Fendler, and R. T. Medary, *Chem. Commun.*, **1971**, 1497; J. H. Fendler, E. J. Fendler, and S. A. Chang, *J. Am. Chem. Soc.*, **95**, 3273 (1973); J. H. Fendler, R. T. Medary, and V. A. Woods, *J. Am. Chem. Soc.*, **94**, 7288 (1972).

2) K. Kon-no, K. Miyazawa, and A. Kitahara, *Bull. Chem. Soc. Jpn.*, **48**, 2955 (1975); K. Kon-no, T. Matsuyama, and A. Kitahara, *Nippon Kagaku Kaishi*, **1975**, 1857.

3) M. Seno, K. Araki, and S. Shiraishi, *Bull. Chem. Soc. Jpn.*, **49**, 899 (1976).

4) O. A. El Seoud, A. Martins, L. P. Barbur, M. J. da Silva, and V. Aldrigue, *J. Chem. Soc., Perkin Trans. 2*, **13**, 1674 (1977).

5) F. M. Menger, J. H. Donohue, and R. E. Williams, *J. Am. Chem. Soc.*, **95**, 286 (1973).

6) C. J. O'Conner, E. J. Fendler, and J. H. Fendler, *J. Am. Chem. Soc.*, **95**, 600(1973); **96**, 370 (1974).

7) A. Kitahara and K. Kon-no, "Micellization, Solubilization, and Microemulsion," ed by K. L. Mittal, Plenum Press, New York (1977), Vol. II, p. 675.

8) A. Kitahara and K. Kon-no, *J. Colloid Interface Sci.*, **29**, 1 (1969); **35**, 409 (1971).

9) A. Kitahara, K. Kon-no, and S. Fujiwara, *J. Colloid Interface Sci.*, **57**, 391 (1976); K. Kon-no and A. Kitahara, *J. Colloid Interface Sci.* in press.

10) F. M. Menger, *J. Am. Chem. Soc.*, **88**, 3081 (1966).

11) F. M. Menger and A. C. Vitale, *J. Am. Chem. Soc.*, **95**, 4931 (1973).

12) M. L. Bender and L. J. Brubacher, "Catalysis and Enzyme Action," McGraw-Hill, New York (1973), Chap. 3, Sec. 9.