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Micellar Effect of Alkylammonium Propionates on Reaction Rate of Keto-Enol Tautomerism in Cyclohexane

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Synopsis. The rate of keto-enol transformation of acetylacetone or acetoethyl acetate was spectroscopically measured in the cyclohexane solutions in the presence of primary, secondary or tertiary alkylammonium propionate. The rate was enhanced by micelle formed. The order of effectiveness of the surfactants was that primary$\gg$secondary$>$tertiary. The order coincides with the number of protons in the ammonium ion of the surfactants and the aggregation number of micelle.

Reversed micelle of oil-soluble surfactants in apolar solvents which involves polar region or ion-pairs in the interior is expected to provide active sites for reactions. Because reversed micelle is more analogous to an enzymatic model than aqueous micelle as pointed out by Fendler *et al.*,[1] micellar catalysis in apolar media seems to be more interesting than that in water media. Furthermore, reversed micellar catalysis is possible to be modified by solubilization of polar substances such as water, acids, alcohols and amines and the solubilization has been considerably studied.[2]

Enhancement of the rate constant of mutarotation of 2,3,4,6-tetramethyl-α-D-glucose and decomposition of Meisenheimer complex in benzene in the presence of alkylammonium carboxylates has been recently reported by Fendler *et al.*[3,4] They have attributed the rate enhancement to the orientation of the reactants in the micelle and the transfer of proton from the ammonium ion of the surfactant to the reactant. However, such a system has little been studied.[5] The present authors have also studied the catalytic effect of alkylammonium carboxylates on hydrolysis of *p*-nitrophenyl esters.[6]

For the further investigation on the effect of proton of surfactant molecules of ammonium type, the rate of keto-enol transformation is now studied in the presence of a surfactant of primary, secondary or tertiary ammonium type in a nonpolar solvent.

Experimental

Materials: Dodecylammonium propionate (DAP), didodecylammonium propionate (DDAP) and cetyldimethylammonium propionate (CDAP) were used as oil-soluble surfactants. The preparation and purification were described in the previous paper.[6] They were further dried under reduced pressure at 50 °C immediately before use. Cyclohexane used as the solvent was purified by the process reported[7] and dried with Molecular Sieves 4A. Acetylacetone (AA) and acetoethyl acetate (EA) used as the substrates were of the chemical grade.

Methods: The rate was measured by following UV-absorption spectra of the keto-form with the Spectrophotometer UV-200 of the Shimadzu Manufacturing Co. The absorption peaks of the keto-form used for calculation of the rate constant were 275, 285 and 304 nm for EA in the DAP solution, EA in the DDAP solution and AA in the DAP solution, respectively.

All of the rates of transformation were the pseudo-first order and the apparent rate constants (k_ϕ) were obtained by the Guggenheim method.[8] In pure cyclohexane, 43% of EA or 88% of AA is present as the enol-form.[9] The initial concentration of the enol-form used throughout the present measurements was 2.5×10^{-5} M and 5.0×10^{-5} M for EA and AA, respectively. Temperature of the solutions in the cell was kept at 30 °C.

The measurement of aggregation number and critical micellar concentration (CMC) or critical aggregating concentration (CAC) were carried out with a vapor pressure osmometer, the Hitachi-Perkin-Elmer Molecular Weight Apparatus, as reported previously.[10]

Results and Discussion

The equilibrium concentration of the enol- or keto-form of EA or AA in cyclohexane is considerably different from that in water. Hence water present in the cyclohexane solution may affect the rate of the shift reaction. Hence, the reaction rate of EA was measured by varying the quantity of water in the DAP solution. The result was shown in Fig. 1. Further experiments were carried out below the 0.5 molar ratio.

Transformation reaction from enol-form to keto-form for EA and AA occurred in all of the surfactant solutions used, though the reaction did not appear in pure cyclohexane. The increasing rate constant (k_ϕ) of the keto-form of EA and AA was depicted as a function of surfactant concentration in Fig. 2, with the inserted small figure enlarging lower concentration range. The aggregating number (n) and CMC or CAC obtained experimentally were listed in Table 1.

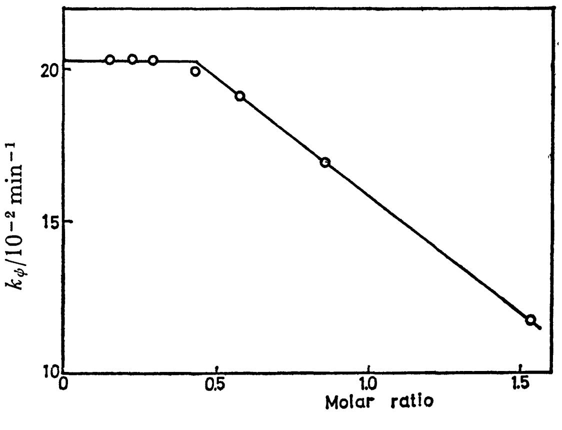


Fig. 1. Rate constant (k_ϕ) of transformation to the keto-form of EA *vs.* the amount of water (molar ratio of water to the surfactant) added in the DAP solution (50 mM).

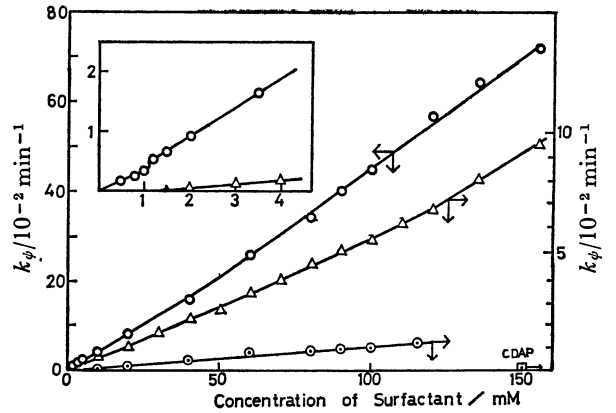


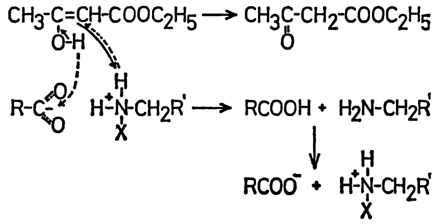
Fig. 2. Rate constant (k_ψ) of transformation to the keto-form *vs.* concentration of surfactants.
—○—: EA in the DAP solution, —△—: AA in the DAP solution, —⊙—: EA in the DDAP solution, ⊡: EA in the CDAP solution.

Table 1. The values of CMC or CAC and aggregation number (n) of surfactants (Dry systems, 30 °C)

Surfactants	CMC or CAC (mM)	n	Number of protons in ammonium ion
DAP	1.8	3.8	3
DDAP	4.4	1.2	2
CDAP	0.78	1.2	1

Combination of Fig. 2 and Table 1 elucidates the following effect of micelle on the reaction rate. Below CMC or CAC, transformation to the keto-form was too slow to calculate k_ψ for AA in the DAP solution and EA in the DDAP solutions, though k_ψ was obtained for EA in the DAP solution. That is, it can be seen that transformation to the keto-form is more enhanced by micelle than monomer, except for EA in the CDAP solution in which k_ψ was too small to be depicted in the Fig. 2 over the whole range of concentration measured. This may be due to concentration of polar groups by micelle formation which increases interaction with the substrate. It is also evident from Fig. 2 that effectiveness of the surfactant micelle on the k_ψ-values is the order of DAP≫DDAP>CDAP. The order coincides with the number of protons or hydrogen atoms in the ammonium ion and the aggregation number shown in Table 1, though the difference of n between DDAP and CDAP is ambiguous. Hence it is concluded that the surfactant having more protons and aggregation number shows the more effectiveness on the reaction rate.

It is considered from the above facts that keto-enol transformation is induced by proton transfer from the ammonium ion to the substrate. The consideration may propose a following scheme for the reaction mechanism similar to the proposition by Fendler *et al.*[3] As an example, for EA:



R: $CH_3(CH_2)_2$
R': $CH_3(CH_2)_{10}$
X: $CH_3(CH_2)_{11}$ or H

The inhibition effect of water shown in Fig. 1 may be due to hydration to ammonium and/or carboxylate.

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