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CATALYTICALLY ACTIVE COMICELLES OF HYDROXAMIC ACIDS AND SURFACTANTS FOR SELECTIVE HYDROLYSIS OF NONIONIC AND ANIONIC ESTERS

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The acylation activity of comicellar catalysts formed from hydroxamic acids and surfactants in the ester hydrolysis has recently received considerable attention[1-3]; a comicellar catalyst of N-dodecanoyl-N-methylhydroxamic acid and hexadecyltrimethylammonium bromide shows great activity as high as chymotrypsin for the hydrolysis of p-nitrophenyl esters, and its activity is ca. 500 times as high as that of the hydroxamic acid itself.[1,2]

In the present paper, we wish to report the acylation activities of comicellar catalysts (model of the Ser-195 part in chymotrypsin) formed from the following hydroxamic acids and surfactants in the selective hydrolysis of nonionic and anionic esters in an alkaline condition:

$H{-}(CH_2)_{m-1}{-}CONHOH$

C_m (m=10 and 12)[4]

$CH_3(CH_2)_{11}\overset{+}{N}(CH_3)_3\overset{-}{Cl}$

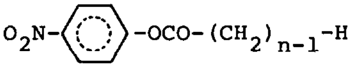
DTAC[5]

$CH_3(CH_2)_{15}\overset{+}{N}(CH_3)_3\overset{-}{Br}$

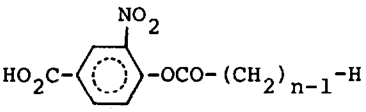
CTAB[5]

$CH_3(CH_2)_{17}\overset{+}{N}(CH_3)_3\overset{-}{Cl}$

OTAC[5]



S_n (n=2,4,6,10,12, and 16)[6]



S_n^- (n=2,4,6,10,12, and 16)[6]

The pseudo-first-order hydrolysis rates were followed spectrophotometrically by taking notice of the phenolate anion formation, and the second-order catalytic rate-constant, k_{cat}, obtained in a series of the present experiments are summarized in Table 1. The comicellar catalysts (C_m+ surfactants) , the activity of

Table 1. k_{cat} ($sec^{-1}M^{-1}$) Values for S_n (or S_n^-) Hydrolyses by Hydroxamic Acids at pH 9.06[a]

Catalyst	S_2	S_4	S_6	S_{10}	S_{12}	S_{16}
BHA [b]	25.0	9.7	9.1	0.90	0.72	-
C_{10}	40.1	20.2	20.0	5.8	4.7	4.4
	(31.3)	(12.2)	(13.8)	(20.3)	(14.8)	(9.7)
C_{12}	29.4	17.5	38.7	54.2	89.3	104
	(16.4)	(5.1)	(8.0)	(13.0)	(15.6)	(32.1)
BHA[b]+DTAC	58.8	34.0	40.1	38.8	41.0	25.8
BHA[b]+CTAB	56.8	44.9	68.9	70.8	67.5	18.3
BHA[b]+OTAC	68.1	51.1	90.0	91.2	86.7	53.5
C_{10} + DTAC	113	74.6	96.1	104	106	103
	(101)	(43.5)	(41.5)	(35.3)	(35.1)	(36.6)
C_{10} + CTAB	1032	1296	1554	2292	1382	451
	(413)	(480)	(497)	(298)	(346)	(313)
C_{10} + OTAC	1001	1053	1805	1960	1867	1364
	(280)	(178)	(209)	(169)	(141)	(145)
C_{12} + DTAC	132	91.0	123	140	146	101
	(117)	(48.3)	(47.4)	(35.3)	(38.3)	(47.8)
C_{12} + CTAB	664	694	1074	1680	1138	531
	(388)	(128)	(169)	(130)	(147)	(170)
C_{12} + OTAC	1396	1511	2110	2299	2017	1065
	(722)	(360)	(429)	(334)	(334)	(333)

Values in parentheses are those for the S_n^- hydrolysis catalyzed by the hydroxamic acids.

a. At 31 °C in 0.083 M tris(hydroxymethyl)aminomethane buffer (0.083 M KCl), 10 vol% CH_3CN-H_2O, 10^{-5} M of ester, 10^{-4} M of catalyst, 3.3×10^{-2} M of DTAC, and 5×10^{-3} M of CTAB and OTAC. k_{cat} values were evaluated from $(k_{obs}^{cat} - k_{obs}^{OH^-})/[cat]$, where $k_{obs}^{OH^-}$ denotes the rate constant in the absence of the catalyst. b. Benzohydroxamic acid.

which are substantially higher than C_m thereof (and than BHA and BHA + surfactants tested for sake of comparison), show their efficient activities in the S_n hydrolysis rather than in the S_n^- hydrolysis. The steric hindrance of the nitro and carboxyl groups on the benzene ring in S_n^- against the incorporation of S_n^- by the comicelles probably retards the rate of the S_n^- hydrolysis. Here, especially worthy to note is that the comicellar catalysts of C_m + CTAB and C_m + OTAC selectively hydrolyze S_{10} with the maximum k_{cat} value in the series of the S_n (n=2-16) hydrolyses, and the hydrolyzing activities of C_{10}+ CTAB and C_{12}+ OTAC are the greatest among the comicellar catalysts investigated. The contribution of hydrophobic forces to the incorporation of S_n by the comicellar catalysts increases with increasing the acyl chain length in S_n, but the hydrophobic approximation effect[7] of the surfactants (CTAB and OTAC) seems to be most effectively exhibited for the hydrolysis of S_{10} possessing an appropriate acyl chain length; BHA + CTAB or BHA + OTAC also shows its highest activity in the S_{10} hydrolysis. In this regard, the comicellar catalysts of C_{10}+ CTAB and C_{12}+ OTAC formed through the electrostatic charge attraction and hydrophobic interaction between the anionic C_m and the cationic surfactants seem to be fit most effectively for the S_n (especially, S_{10}) hydrolysis in terms of the hydrophobic approximation.

On the other hand, S_n^- possessing a relatively short acyl chain length (especially, S_2^-) tends to be more easily hydrolyzed by the comicellar catalysts than S_{10}^- having the same acyl chain length to S_{10}; hence, the electrostatic charge attraction between the anionic S_n^- and the cationic micelles contributes to the condensation of S_n^- having relatively short acyl chain lengths on the micelles so as to make the hydrolysis easy. At any rate, the magnitude of the micellar influence of the surfactants on the enhancement of the S_n hydrolysis, which can be measured by the ratio of the k_{cat} value in the presence of the surfactant to that in its absence, is fairly large in the S_n (n=10 or 12) hydrolysis by the C_{10}+ CTAB or C_{10}+ OTAC catalyst (Fig. 1); the hydrolyzing activity of C_{10} is enhanced by the surfactant to be ca. 400 times as high as that of C_{10} itself.

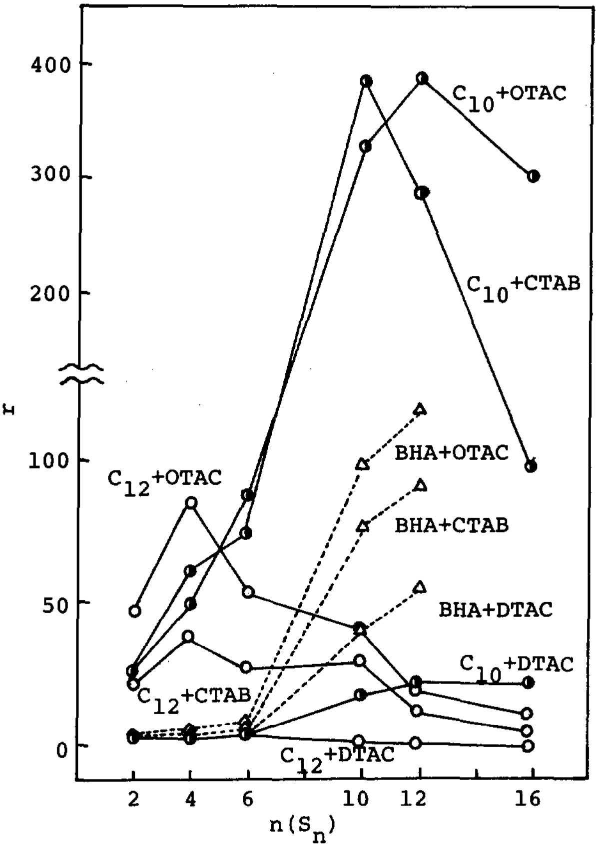


Fig. 1. The dependence of the r value on the acyl chain length (n) in S_n.

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4. They were prepared by the reaction of their ethyl esters with hydroxylamine and were recrystallized from methanol-water.
5. The commercially available surfactants were recrystallized from anhydrous ethanol-ether prior to use them in the present experiments.
6. S_n were prepared in accordance to M. Bodansky and V. du Vigneaud, J. Am. Chem. Soc., 81,5688 (1959), and S_n^- were supplied in accordance to C. G. Overberger, R. C. Glowaky, and P. -H. Vandewyer, J. Am. Chem. Soc., 95, 6008 (1973).
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