CHEMISTRY LETTERS, pp. 733-736, 1983.

FUNCTIONAL FLUOROCARBON MICELLES. PHASE SEPARATION AND REACTIVITY CHANGE OF HYDROXAMATE NUCLEOPHILES IN MIXED MICELLES OF HYDROCARBON AND FLUOROCARBON SURFACTANTS [1)]

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The titration behavior of long-chain(hydrocarbon and fluorocarbon) hydroxamic acids in the presence and absence of micellar matrices is influenced by phase separation of hydrocarbon and fluorocarbon species. The same factors operate in the hydrolysis of phenyl esters.

Although the limited miscibility of hydrocarbon and fluorocarbon surfactants in mixed micelles has been reported by several research groups,[2-6)] these interesting physicochemical characteristics have never been exploited for the purpose of preparing novel classes of the functional micelle. We describe in this paper that hydroxamate-functionalized mixed micelles of hydrocarbon and fluorocarbon surfactants in fact show peculiar titration behavior attributable to the presence of separate domains of the two surfactants. This finding was used to explain peculiar reactivity changes in the reaction of hydroxamate nucleophiles and p-nitrophenyl esters. The structures of nucleophile, substrate and matrix molecules are given below, together with their abbreviations.

	R_1	R_2	Abbreviation
Nucleophile	$CF_3(CF_2)_7(CH_2)_2-$	$(CH_3)_3N^+(CH_2)_4-$ Br^-	C_{10}^F-HA-N^+
$R_1-\overset{\overset{O}{\|}}{C}-N(R_2)(OH)$	$CF_3(CF_2)_7(CH_2)_2-$	CH_3- Br^-	C_{10}^F-MHA
	$2(n\text{-}C_{18}H_{37})N\overset{\overset{O}{\|}}{C}(CH_2)_2-$	$(CH_3)_3N^+(CH_2)_4-$ Br^-	$2C_{18}$-HA-N^+
	$n\text{-}C_{17}H_{35}-$	CH_3- Br^-	C_{18}-MHA

	R	Abbreviation
Substrate	$CF_3(CF_2)_7(CH_2)_2-$	C_{10}^F-PNP
$R-\overset{\overset{O}{\|}}{C}O-C_6H_4-NO_2$	$CH_3(CH_2)_{10}-$	C_{12}-PNP
	CH_3-	PNPA

Matrix	$CH_3(CH_2)_{15}N^+(CH_3)_3$ Br^-	CTAB
	$CF_3(CF_2)_7CH_2CH_2-\overset{\overset{O}{\|}}{C}NH(CH_2)_3N^+(CH_3)_3$ Br^-	C_{10}^F-C_3-N^+

C_{10}^{F}-HA-N^{+}(waxy solid) and $2C_{18}$-HA-N^{+}(liquid crystalline from room temperature to 118°C) were prepared as follows: O-Benzylbenzohydroxamic acid[7] was allowed to react with 1,10-dibromobutane in KOH/acetone and the product hydrolyzed in hydrochloric acid to give N-(4-bromobutyl)benzyloxyamine hydrochloride, which was then condensed with the respective carboxylic acids(a Ugine Kuhlmann product and an unpublished product), quaternized and subjected to debenzylation(Pd/H_2). C_{10}^{F}-MHA (mp 72-73°C) and C_{18}-MHA(mp 60-62°C) were obtained by condensation of the same carboxylic acids with N-methylhydroxylamine. Substrates were prepared by reaction of carboxylic acids and p-nitrophenol: C_{10}^{F}-PNP, mp 69.5-70.5°C; C_{12}-PNP, mp 42-43°C; PNPA, mp 78-78.5°C. C_{F}^{10}-C_3-N^{+}(waxy solid) was obtained by condensation of 3-bromopropylamine with the perfluorocarboxylic acid, accompanied by quaternization. Commercial CTAB was purified by recrystallization. The final products were identified by NMR spectroscopy, thin-layer chromatography and elemental analysis.

Titration Behavior

Dissociation of the hydroxamic acid unit is estimated from the absorption of the hydroxamate anion at 240 nm. The extent of dissociateion, α, is obtained by

$$\alpha = \frac{Abs_{obsd} - Abs_{A}}{Abs_{A} - Abs_{HA}} \qquad (1)$$

where Abs_A and Abs_{HA} are absorbances of the dissociated and undissociated species obtained at pH 12(NaOH) and 2(HCl), respectively.

The titration curve of polyelectrolytes usually obeys the modified Henderson-Hasselbalch equation[8]

$$pH = pK_a - n'\log\frac{1-\alpha}{\alpha} \qquad (2)$$

The equation holds true in many micellar systems. The pk_a and n' values are influenced by microenvironmental factors. For example, pK_a of a long-chain hydroxamic acid is lowered in cationic micelles.[9] The n' value, if greater than unity, indicates suppression of the subsequent dissociation and is a measure of the coulombic repulsion among dissociable groups.[10,11]

Figure 1 shows examples of the titration data plotted according to Eq. 2. Satisfactorily linear relations(r=0.998) were obtained, and pK_a and n' were determined from intercept and slope, respectively. Table I summarizes the titration data. In the absence of the matrix, C_{10}^{F}-HA-N^{+} and $2C_{18}$-HA-N^{+} produce micellar and bilayer aggregates, respectively.[12] The n' values of these aggregates are much larger than unity, indicating significant coulombic repulsion among the hydroxamate species. The bilayer membrane of $2C_{18}$-HA-N^{+} is in the crystalline(gel) state at 30°C.[13] At 50°C where the membrane is fluid(liquid crystalline), n' becomes smaller. On the other hand, when C_{10}^{F}-HA-N^{+} is imbedded in micelles of the fluorocarbon surfactant(C_{10}^{F}-C_3-N^{+}), pK_a is lowered and n' becomes close to unity. Similar changes arise when $2C_{18}$-HA-N^{+} is mixed with the micellar CTAB. Therefore, the fluorocarbon(hydrocarbon) hydroxamate is supposedly dispersed well in the

fluorocarbon(hydrocarbon) matrix, experiencing less coulombic repulsion. Highly contrasting data are obtained, when the functional fluorocarbon is imbedded in the hydrocarbon aggregate or vice versa. The pK_a value of C_{10}^F-HA-N^+ in the CTAB matrix is somewhat enhanced compared with that without CTAB, and n' remains large. It is evident that C_{10}^F-HA-N^+ is not prone to disperse in the CTAB micelle and probably forms separate domains. The pK_a variation suggests that the coulombic repulsion among the hydroxamate group is greater in the presence of CTAB micelles than in their absence. The same conclusion is obtained for $2C_{18}$-HA-N^+ upon addition of the fluorocarbon micelle. These surprising results imply that C_{10}^F-HA-N^+(or $2C_{18}$-HA-N^+) produce domains of better molecular orientation in the matrix of the hydrocarbon (or fluorocarbon) micelle than without matrices.

The effect of the micellar matrix on the titration behavior of simpler hydroxamates, C_{10}^F-MHA and $2C_{18}$-MHA is the same: both of the pK_a and n' values of C_{10}^F-MHA are higher in the CTAB micelle than in the C_{10}^F-C_3-N^+ micelle, and those for $2C_{18}$-MHA are higher in the C_{10}^F-C_3-N^+ micelle than in the CTAB micelle.

Catalytic Hydrolysis

The hydrolysis of p-nitrophenyl esters by the micellar hydroxamates was subsequently examined under the pseudo first-order conditions. The reaction was followed by formation of p-nitrophenolate, and the catalytic rate was obtained by subtracting the spontaneous rate from the overall rate. The observed rate constant was converted to the rate constant for the hydroxamate anion by deviding by α. The results are summarized in Table 2. In general, combinations of hydrocarbon and fluorocarbon reagents lower the catalytic efficiency. These results are interpretable in terms of limited miscibility. The presence of the micellar matrices renders the situation more complex. Two features are worthy of emphasis. One is the fact that the reaction rate between C_{10}^F-HA-N^+ and C_{10}^F-PNP is virtually unchanged, regardless of whether the CTAB matrix is present or not. This catalyst-substrate combination(both fluorocarbons) appears to form separated domains in the CTAB matrix. Addition of the fluorocarbon surfactant matrix lowers the rate due to reagent dilution. The second feature is that the reactivities of hydrocarbon substrates, C_{12}-PNP and PNPA, are greater in the CTAB matrix than in the C_{10}^F-C_3-N^+ matrix, again regardless of whether the nucleophile is fluorocarbon or hydrocarbon derivatives. The difference in the binding efficiency of substrate molecules in the micellar phase may be responsible for this effect.

In conclusion, it is established that the dissociation and esterolytic behaviors of the hydroxamate function can be modified by taking advantage of limited miscibility of the hydrocarbon and fluorocarbon species.

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13) The crystal-to-liquid crystal phase transition temperature was determined by differential scanning calorimetry to be 42°C(peak top temperature).

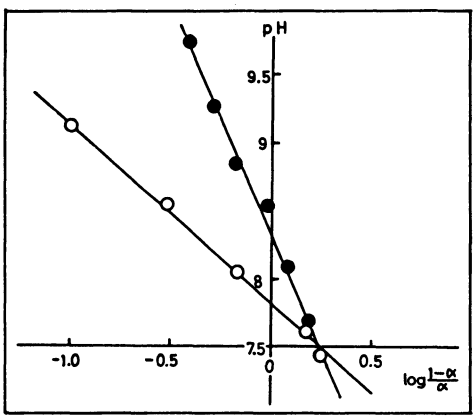

Fig. 1. Examples of titration data.
30°C, 0.01 M borate buffer,
μ = 0.01(KCl),
[hydroxamic acid] = 1.0×10^{-4} M,
[surfactant] = 1.0×10^{-3} M.
○: $2C_{18}$-HA-C_4-N^+/CTAB
●: $2C_{18}$-HA-C_4-N^+/C^F_{10}-C_3-N^+

Table 1. Titration data of hydroxamic acids[a].

Matrix	C^F_{10}-HA-N^+		$2C_{18}$-HA-N^+		C^F_{10}-MHA		C_{18}-MHA	
	pK_a	n'	pK_a	n'	pK_a	n'	pK_a	n'
none	8.14	1.52	8.08 (7.89	3.25 2.11)[b]	—	—	—	—
C^F_{10}-C_3-N^+	8.05	1.13	8.36	3.31	8.17	1.58	9.02	2.04
CTAB	8.23	1.5[c]	7.84	1.30	8.26	2.18	8.64	1.29

a: 30°C, 0.01 M borate buffer, μ = 0.01(KCl), [hydroxamic acid] = 1.0×10^{-4} M [surfactant] = 1.0×10^{-3}M. b: 50°C, other conditions are unchanged.
c: The plots of Eq. 2 are not linear.

Table 2. First-order rate constant of the reaction of hydroxamate anions with phenyl esters[a], s^{-1}

Catalyst		C^F_{10}-HA-N^+			C^F_{10}-MHA		C_{18}-MHA	
Matrix		none	C^F_{10}-C_3-N^+	CTAB	C^F_{10}-C_3-N^+	CTAB	C^F_{10}-C_3-N^+	CTAB
Substrate	C^F_{10}-PNP	1.85	0.71	1.99	0.59	0.56	0.39	0.035
	C_{12}-PNP	0.084	0.091	0.39	0.15	0.67	0.28	0.86
	PNPA	0.005	0.014	0.076	0.022	0.087	0.013	0.12

a: 30°C, pH 7.5, 0.02 M borate buffer, μ = 0.01(KCl), [nucleophile] = 1.0×10^{-4} M, [matrix] = 1.0×10^{-3} M. [substrate] = 1.0×10^{-5} M.

(Received March 7, 1983)