Surface Active Hydroxamic Acids. II. Comparison of Surface Properties of Hydroxamic Acids with Ketones and Methyl Esters with Similar Hydrophilic and Lipophilic Structure

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Some surface properties of hydroxamic acids, ketones and methyl esters, which all contained long-chain alkyl[tetra(oxyethylene)] group, were measured and compared to clarify the influence of the terminal functional group on surface properties. From the results of cloud point (T_{cp}), CMC, γ_{CMC}, adsorption area per molecule at the surface (A) and foaming properties, it was proved that hydroxamic acids had better hydrophilicity and showed better surface properties than the corresponding ketones, methyl esters or typical monodisperse nonionic surfactants.

By the modification of the terminal OH-group of poly(oxyethylene) type of nonionics (alcohol ethoxylates), the improvement of surface properties compared with parent compounds and the appearance of new functions have been expected. There have been many reports on the introduction of additional functional groups into the end of the hydrophilic group of alcohol ethoxylates (1-3). Among them, surface properties of ether sulfates (4-6) and ether carboxylates (4,7) have been investigated in detail.

In the previous paper (8) we reported that (octyl, decyl or dodecyl)[tetra(oxyethylene)]oxymethylenehydroxamic acids (**Ia-c**; C_mE4HA, m = 8,10,12) could form micelles in water and acted as a kind of end-blocked nonionic under acidic and neutral conditions. Here, we report the comparison of surface properties of hydroxamic acids (**I**) with ketones (**II**; C_mE4KT) and methyl esters (**III**; C_mE4ME) containing the same hydrophilic and lipophilic structure, and typical monodisperse oligo(oxyethylene) nonionics (**IV**; C_mEn) under neutral conditions to investigate the effect of terminal hydroxamic acid group on surface properties when compounds **I** act as nonionic surface active agents (Fig. 1).

EXPERIMENTAL PROCEDURES

Materials. The preparation of long-chain alkyl[tetra(oxyethylene)]oxymethylenehydroxamic acids (**I**) and methyl long-chain alkyl[tetra(oxyethylene)]oxyacetates (**III**) was mentioned in the previous paper (8). The pKa values of **I** were as follows: **Ia**, 9.5; **Ib**, 9.6; **Ic**, 9.9 (in water at 20 C) (8). Long-chain alkyl [tetra(oxyethylene)]oxymethyl methyl ketones (**II**) were prepared by the acetonylation

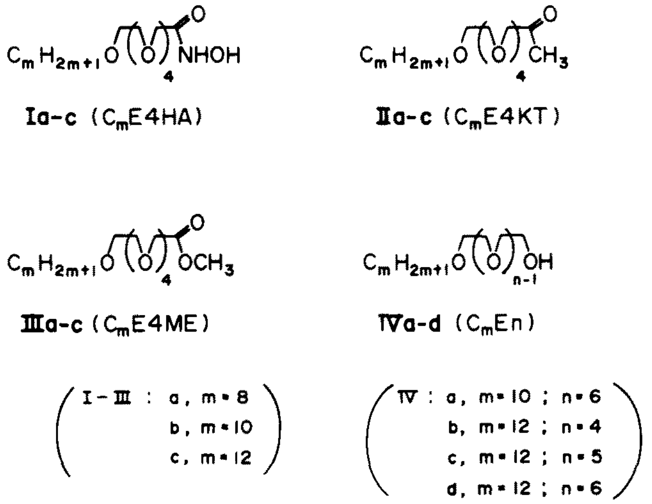
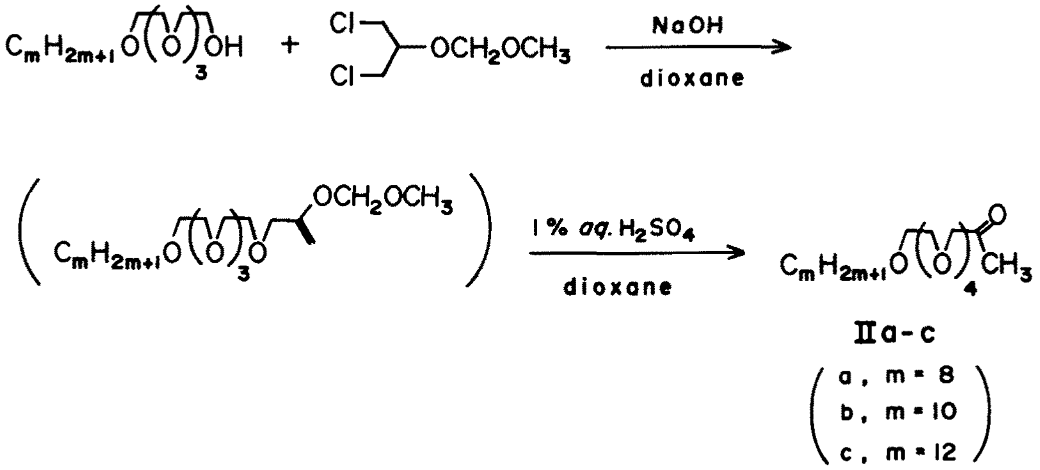


FIG. 1. Compounds I-IV.



SCHEME 1. Synthesis of long-chain alkyl[tetra(oxyethylene)]oxymethyl methyl ketones (II).

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TABLE 1

Properties of Compounds II and III[a]

Compound (m)	Abbreviation symbol	Yield[b]	Bp[c]	¹H-NMR[d] ($CDCl_3$)	MS (70 eV)	Anal.
		%	C/Torr	δ	m/z (rel.intens.)	found(calcd)
IIa (8)	C_8E4KT	77	150/0.05	0.90(t,3H), 1.2-1.6(m,12H), 2.20(s,3H), 3.4-3.7(m,18H), 4.20(s,2H)	362(M⁺, 10), 101(97), 57(100)	C, 63.19(62.95) H, 10.29(10.57)
IIb (10)	C_{10}E4KT	83	160/0.05	0.90(t,3H), 1.2-1.6(m,16H), 2.20(s,3H), 3.4-3.7(m,18H), 4.20(s,2H)	390(M⁺, 8), 101(100), 57(87)	C, 64.19(64.58) H, 10.98(10.84)
IIc (12)	C_{12}E4KT	84	175/0.04	0.90(t,3H), 1.2-1.7(m,20H), 2.20(s,3H), 3.4-3.7(m,18H), 4.20(s,2H)	418(M⁺, 15), 101(100), 57(83)	C, 65.92(65.99) H, 11.22(11.08)
IIIa (8)	C_8E4ME	73	130/0.05	0.90(t,3H), 1.2-1.6(m,12H), 3.4-3.8(m,20H), 4.20(s,3H)	378(M⁺, Amp), 117(100), 59(45)	C, 60.00(60.29) H, 10.24(10.12)
IIIb (10)	C_{10}E4ME	81	165/0.05	0.90(t,3H), 1.2-1.6(m,16H), 3.4-3.8(m,20H), 4.20(s,3H)	406(M⁺, Amp), 117(100), 59(61)	C, 61.83(62.04) H, 10.48(10.41)
IIIc (12)	C_{12}E4ME	70	170/0.05	0.90(t,3H), 1.2-1.7(m,20H), 3.4-3.8(m,20H), 4.20(s,3H)	434(M⁺, Amp), 117(100), 59(48)	C, 63.59(63.56) H, 10.75(10.67)

[a] IR spectra: ketones; 2950, 2870, 1720, 1470, 1360, 1300, 1250, 1130, 940, and 870 cm^{-1} (neat), esters; 2950, 2870, 1760, 1460, 1440, 1350, 1290, 1220, 1130, 950, and 850 cm^{-1} (neat).

[b] Based on parent alcohol ethoxylates.

[c] Kugelrohr distillation.

[d] 100 MHz.

of corresponding alcohols according to the equation given in Scheme 1 (9). Purification of II and III was done by a Kugelrohr distillation. Their purity was ascertained by gas liquid chromatography (GLC), spectral (IR, mass and NMR) and elemental analyses (within ±0.4%). It also was assessed from the observed sharp break in surface tension-concentration curves. Their properties are summarized in Table 1 with their abbreviations. Dodecyl hexa(oxyethylene) monoether (**IVd**; C_{12}E6) as the typical monodisperse nonionic surfactant was the commercial product of guaranteed reagent grade (Nikko Chemicals Co., Tokyo, Japan).

Long-chain alkyl[tetra(oxyethylene)]oxymethyl methyl ketone (II): Typical procedure. A mixture of tetra(ethylene glycol) monodecyl ether (m = 10; 7.0 g, 21 mmol), 1,3-dichloroprop-2-yl methoxymethyl ether (6.7 g, 42 mmol) (10), and NaOH (pellet; 3.5 g, 84 mmol) in dioxane (20 ml) was stirred vigorously at 60 C. The reaction was continued until the GLC peak based on the alcohols disappeared (24 hr). After the insoluble solid was removed by a short column filtration (silica gel), evaporation of the eluent gave residue (8.3 g, intermediate olefin) as a liquid. A mixed solution of 1% aq H_2SO_4 (30 ml) and dioxane (30 ml) was added to the residue. After 2 hr of stirring at room temperature and subsequent extraction of the reaction mixture with ether (100 ml, 3 times), crude ketone (7.7 g) was obtained as a residue after the evaporation of the solvent. Distillation of the crude product under reduced pressure using a Kugelrohr apparatus (b.p. 160 C/0.05 Torr) gave pure **IIb** (6.8 g, 83%).

Methods. The cloud point (T_{cp}) was determined by the naked eye with a 1% aqueous solution of the surfactant. The surface tension of a surfactant solution below T_{cp} (20 C, ordinarily) was measured with a Wilhelmy tensiometer using a series of aqueous solutions at various

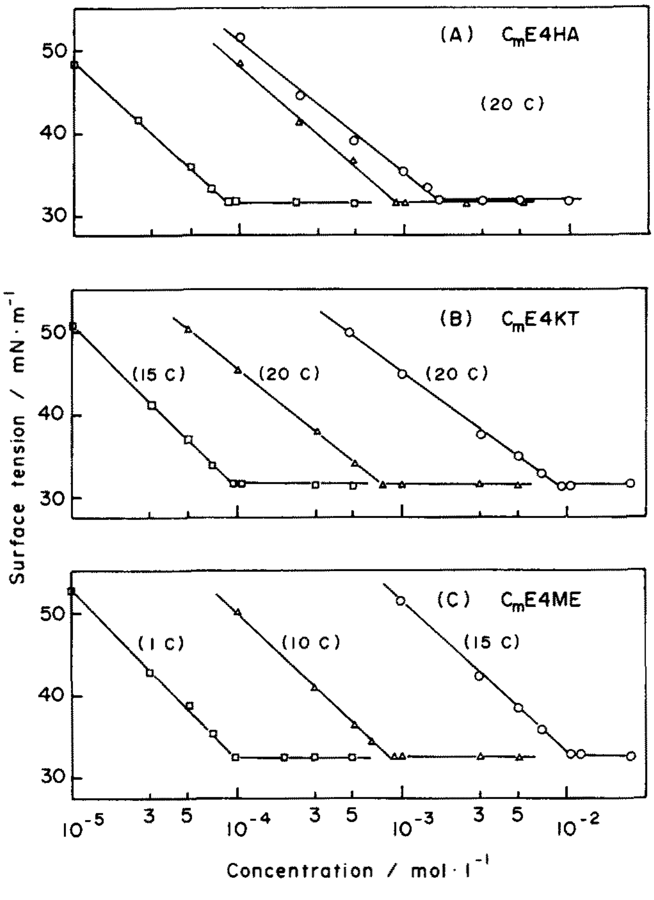

FIG. 2. Surface tension-concentration plots of aqueous surfactant solutions. (A), hydroxamic acid; (B), ketone; (C), methyl ester; ○, C_8; △, C_{10}; □, C_{12}.

TABLE 2

Surface Properties of Compounds I, II, III and IV (20 C)

Compound	T_{cp} C	10^4CMC mol.l^{-1}	γ_{CMC} mN.m^{-1}	10^2A nm^2
Hydroxamic acid				
C_8E4HA (**Ia**)	>75[a]	17	31.5	58
C_{10}E4HA (**Ib**)	72.0	8.7	31.5	48
C_{12}E4HA (**Ic**)	42.0	0.85	31.5	42
Ketone				
C_8E4KT (**IIa**)	38.5	91	31.5	64
C_{10}E4KT (**IIb**)	27.5	8.7	31.5	56
C_{12}E4KT (**IIc**)	18.5	0.94[b]	31.5[b]	47[b]
Methyl ester				
C_8E4ME (**IIIa**)	18.3	120[b]	32.5[b]	52[b]
C_{10}E4ME (**IIIb**)	11.7	7.8[c]	32.5[c]	49[c]
C_{12}E4ME (**IIIc**)	5.0	0.97[d]	32.5[d]	45[d]
Typical nonionic				
C_{10}E6[e] (**IVa**)	60.0	—	—	—
C_{12}E4[e] (**IVb**)	7.0	—	—	—
C_{12}E5[e] (**IVc**)	25.0	0.40	—	—
C_{12}E6 (**IVd**)	49.0	0.85	32.0	52

[a] Decomposition.

[b] At 15 C.

[c] At 10 C.

[d] At 1 C.

[e] Ref. (12).

concentrations. The foaming properties were evaluated by the semi-micro TK method (11) with a 1% aqueous solution of surfactant below T_{cp} (20 C, ordinarily). All surface properties were measured at pH 5.5 (neutral condition). The water was purified according to the method described in the previous paper (8). The data of surface properties of general nonionics (**IVa-c**) were quoted from the literature (12).

RESULTS AND DISCUSSION

The surface tension-concentration curves of aqueous solutions of hydroxamic acids (**Ia-c**), ketones (**IIa-c**) and methyl esters (**IIIa-c**) are shown in Figure 2.

CMC was determined from the break point of each curve (Fig. 2). The adsorption area/molecule at the air-water interface (A) was calculated from the plot of the surface tension-logarithm concentration below CMC using the Gibbs adsorption isotherm (13). Those results and T_{cp} are summarized in Table 2 with data of some typical nonionics (IV). The results of foaming properties are given in Table 3.

The T_{cp} values of hydroxamic acids (**I**) were much higher than corresponding ketones (**II**) and methyl esters (**III**). Additionally, on comparing C_{12}E4HA (**Ic**) with nonionic surfactants **IVc,d** (Table 2), the T_{cp} value of **Ic** was 17 C higher than that of C_{12}E5 (**IVc**) having the same number of ether oxygens, and the contribution of the terminal $CH_2C(=O)NHOH$ group to the hydrophilicity was similar to that of one oxyethylene unit of nonionics **IV** in the rough estimation. The solution of C_8E4HA (**Ia**) and other hydroxamic acids (**Ib,c**) irreversibly turned pale yellow above 75 C, probably because of hydrolysis. It was found that the hydrophilicity of ketones (**II**) was better than that of methyl esters (**III**).

TABLE 3

Foaming Properties of Compounds I, II, III and IV

Compound	Temp. C	Foaming Volume/ml 0″	30″	1′	1′30″	2′	5′
Hydroxamic acid							
C_8E4HA (**Ia**)	20	40	0	—	—	—	—
C_{10}E4HA (**Ib**)	20	140	100	70	30	0	—
C_{12}E4HA (**Ic**)[a]	20	260	260	260	260	260	200
Ketone							
C_8E4KT (**IIa**)	20	80	10	0	—	—	—
C_{10}E4KT (**IIb**)	20	160	80	20	0	—	—
C_{12}E4KT (**IIc**)	15	260	260	160	80	20	0
Methyl ester							
C_8E4ME (**IIIa**)	10	30	0	—	—	—	—
C_{10}E4ME (**IIIb**)	10	100	20	0	—	—	—
C_{12}E4ME (**IIIc**)	1	180	100	60	20	0	—
Typical nonionic							
C_{12}E6 (**IVd**)	20	250	220	160	140	100	0

[a] 20′, 120 ml; 30′, 70 ml; 40′, 0 ml.

The CMC of three corresponding types of surfactants showed similar values except C_8E4HA (**Ia**). Although precise comparison was difficult because the measurement was carried out at different temperatures, a linear relation between the alkyl chain length (m) of both ketones (**II**) and methyl esters (**III**) and log CMC was observed. However, in this study a similar relation was not found in the case of hydroxamic acids (**I**).

γ_{CMC} values were almost the same among three types of compounds and were by no means inferior to the typical nonionic surfactant C_{12}E6 (**IVd**). The adsorption area/molecule at the surface (A) decreased with an increase in the number of carbon atoms in the lipophilic group in each type of compound. This tendency is similar to that of general nonionic surfactants (13).

The foaming ability and foam stability of surfactants with a dodecyl group are superior to those with an octyl or decyl group. A feature of end-blocked nonionics is low foaming or antifoaming properties (14), but C_{12}E4HA (**Ic**) especially showed good foaming ability and foam stability.

From the above facts, it might be concluded that long-chain alkyl[tetra(oxyethylene)]oxymethylenehydroxamic acids (**I**) had better hydrophilicity and showed better surface properties than the corresponding ketones (**II**), methyl esters (**III**) or typical nonionics (**IV**). Those hydroxamic acids seem to be applicable to new types of "functional" surface active agents because hydroxamic acids can foam chelates with transition metals and can be transformed into isocyanates by Lossen rearrangement. Additionally, those compounds can be used as the hydrolytic enzyme model compounds, as reported earlier (8). An investigation of the hydrolysis catalytic activity of these hydroxamic acids in the micellar system is now in progress.

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