Surface Active Hydroxamic Acids. I. Preparation and Properties of Long-Chain Alkyl[oligo(oxyethylene)] oxymethylenehydroxamic Acids

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For the development of surfactants having an ability to interact with metal ions, hydroxamic acids containing a long-chain alkyl[oligo(oxyethylene)] group were prepared. Any hydroxamic acid with an octyl, decyl or dodecyl group was made readily soluble in water by introducing four oxyethylene units into the molecule. These water-soluble hydroxamic acids had a micelle-forming ability and acted as polyoxyethylene-type nonionic surfactants under acidic and neutral conditions. Additionally, those compounds were found to form a water-soluble complex with ferric ion at pH 2, and these complexes also showed surface active properties.

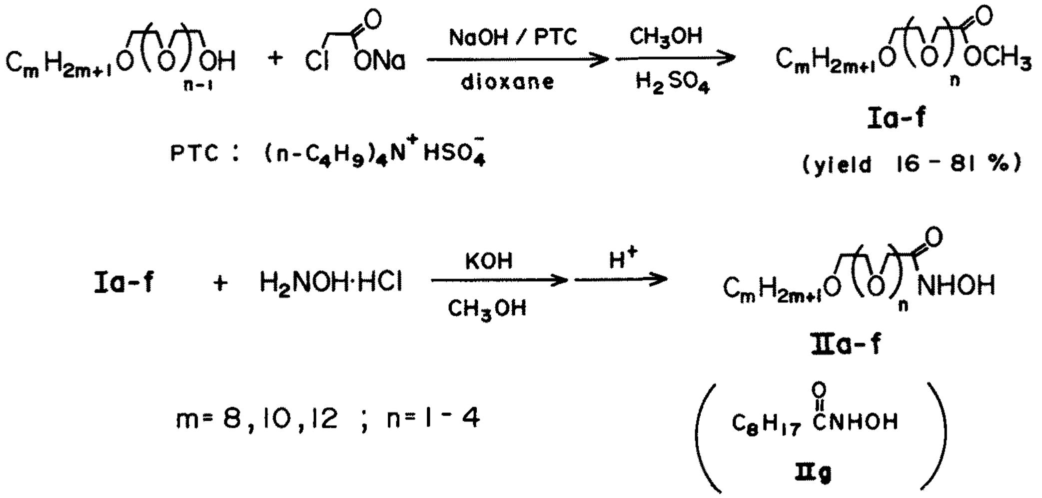
Recently, hydroxamic acids have been studied with respect to chelates with ferric ion for medical use and as siderophore models (1-8), the application to metal separation process (9,10), and so on. But most synthetic alkyl or aryl hydroxamic acids have poor water solubility, and their use in aqueous media is limited. Some trials have been undertaken to increase the water solubility of hydroxamic acids. For example, Katzhendler et al. reported the preparation of a hydroxamic acid type of micellar catalyst containing a quaternary ammonium group (11). Yamada et al. synthesized telomeric hydroxamic acids (12) and found some interesting properties in aqueous media (13,14).

For the purpose of both the development of water soluble long chain alkyl hydroxamic acids and the application to surfactants which can interact with metal cations and act as the micellar catalyst, we have prepared some compounds (II) with a hydroxamic acid group at the end of the hydrophilic part of oxyethylene type of nonionic surfactant. In this paper, the preparation of those hydroxamic acids and properties such as the water solubility, the pKa value, and the complexation with ferric ion are described. Furthermore, the possibility of micelle formation of II is mentioned from the results of the surface tension of aqueous solutions under various conditions.

EXPERIMENTAL PROCEDURES

Materials. Starting materials, alcohol ethoxylates, were synthesized from n-alkylbromides and oligo (ethylene glycol)s (50-65%). Long chain alkyl[oligo(oxyethylene)] oxymethylenehydroxamic acids (II) were prepared according to the equation given in Scheme 1. Their purity was confirmed by spectral (IR, Mass and NMR) and elemental analyses (±0.4%). The results of their preparations are summarized in Table 1 with their abbreviations.

Methyl long chain alkyl[oligo(oxyethylene)] oxyacetate (I): Typical procedure. Sodium chloroacetate (35.0 g, 0.3 mol) and tetra(n-butyl)ammonium hydrogen



Scheme 1. Synthesis of long-chain alkyl[oligo(oxyethylene)] oxymethylenehydroxamic acids (II).

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TABLE 2

Physical Properties of Hydroxamic Acids (II)

Hydroxamic acid		Water solubility[a]	pKa[b]
C_8E1HA	(IIa)	not soluble	10.2
C_8E2HA	(IIb)	slightly soluble	10.2
C_8E3HA	(IIc)	partially soluble	10.3
C_8E4HA	(IId)	soluble	10.3 (9.5)
$C_{10}E4HA$	(IIe)	soluble	10.4 (9.6)
$C_{12}E4HA$	(IIf)	soluble	10.5 (9.9)
C_8HA	(IIg)	not soluble	10.2

[a] Measured at 25 C. Slightly soluble, ca. 0.01 mol/l; partially soluble, ca. 0.1 mol/l; soluble, freely soluble at least to 1.0 mol/l.

[b] Measured in ethanol-water (50:50, v/v) at 20 C. Values in parentheses were measured in water. Acetohydroxamic acid = pKa 9.4 in water (17).

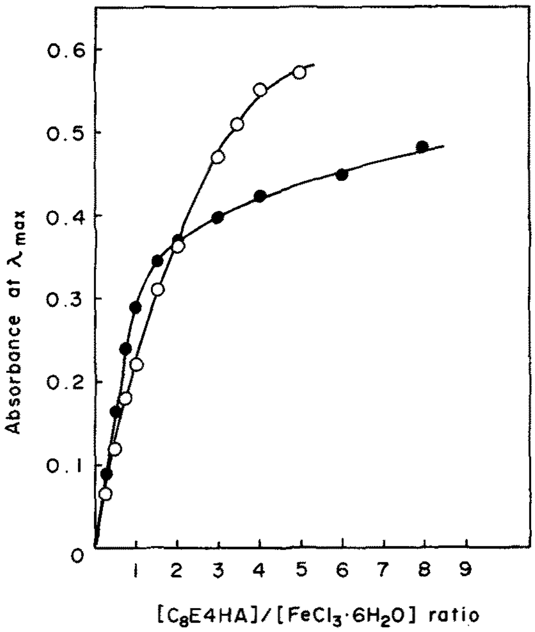

FIG. 1. Absorbance at λ_{max} vs. $[C_8E4HA]/[Fe^{3+}]$ ratio for hydroxamic acid (IId) solutions at 20 C. ○, in H_2O ($[FeCl_3 \cdot 6H_2O]$ = 6.0×10^{-3} mol/l); ●, in EtOH ($[FeCl_3 \cdot 6H_2O]$ = 2.5×10^{-4} mol/l).

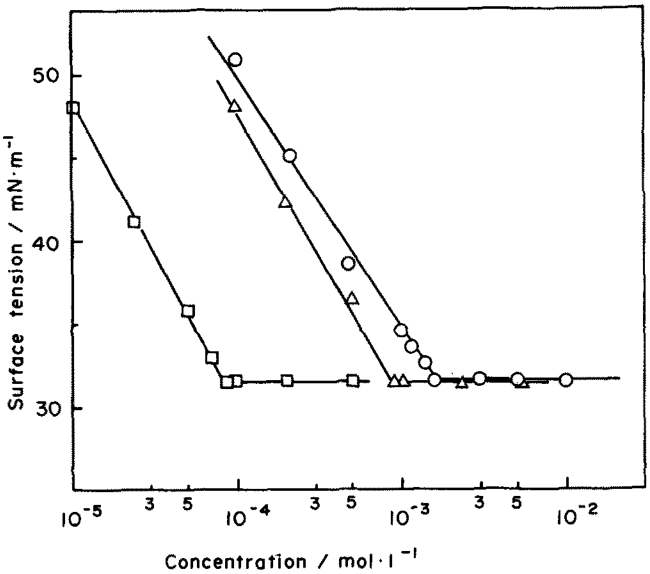

FIG. 2. Surface tension-concentration plots of aq. hydroxamic acid solutions at 20 C (pH 5.5). ○, C_8E4HA (IId); △, $C_{10}E4HA$ (IIe); □, $C_{12}E4HA$ (IIf).

hydroxamic acids could be readily soluble in water with the introduction of oxyethylene units into a molecule. In the range of this study, four oxyethlyene units were found to be enough to dissolve the hydroxamic acids with C_8-C_{12} alkyl groups in water. Little difference in pKa values was observed between IIa-d containing oxyethylene units and nonanohydroxamic acid (IIg), and the measured pKa values in water for IId-f were closer to that of acetohydroxamic acid [= pKa 9.4 (17)].

Complexation of hydroxamic acids (II) with ferric ion. The interaction of hydroxamic acids (IIa-e, g) with ferric ion in ethanol (pH 1.5-2.0) was evaluated by the molar ratio-method using the UV spectrum ($FeCl_3 \cdot 6H_2O$ = 2.5×10^{-4} mol/l constant). The absorption maximum due to the complex formation was found at 490-510 nm, and a similar relation between absorbance at λ_{max} and molar ratio of hydroxamic acid to ferric ion was obtained in each case. Additionally, the measurement of water-soluble C_8E4HA (IId) in dilute hydrochloric acid (pH 2.0) was carried out in the same manner, changing the molar ratio of IId to ferric ion. Precipitations were formed at the ratio above five; however, the absorption maximum of the water soluble complex was observed at 470 nm until the ratio reached five. These results are shown in Figure 1. Since both the clear break point and the plateau part were not recognized in each curve, the equilibrium between some kinds of complexes which had different compositions might exist both in ethanol and in water (18). Each complex of $C_{10}E4HA$ and $C_{12}E4HA$ with ferric ion, however, was only partially soluble in water under those concentration conditions.

Surface tension of aqueous solution of water soluble hydroxamic acids (IId-f) under various conditions. Since it was observed that C_8E4HA, $C_{10}E4HA$ and $C_{12}E4HA$ could be freely miscible with water, these types of compounds were expected to be useful as surfactants. The surface tension-concentration plots of these hydroxamic acids are shown in Figure 2. It was proved that these three hydroxamic acids could form micelles in water because the break point was clearly noticed in each case.

Furthermore, to investigate the effect of the terminal hydroxamic acid group on surface properties, the surface tension of C_8E4HA solutions was measured under various pH conditions; pH 2.20, 3.82 (adjustment by HCl), 5.50 (neutral aqueous solution), 7.10, 8.95 (tris buffer), and 11.50 ($NaHCO_3$-NaOH buffer). Two types of surface tension-concentration curves were found (Fig. 3). One was obtained under acidic and neutral conditions, while the other was in a basic solution. In the basic region, the hydrophilicity of the molecule might increase by the dissociation of hydroxamic acid

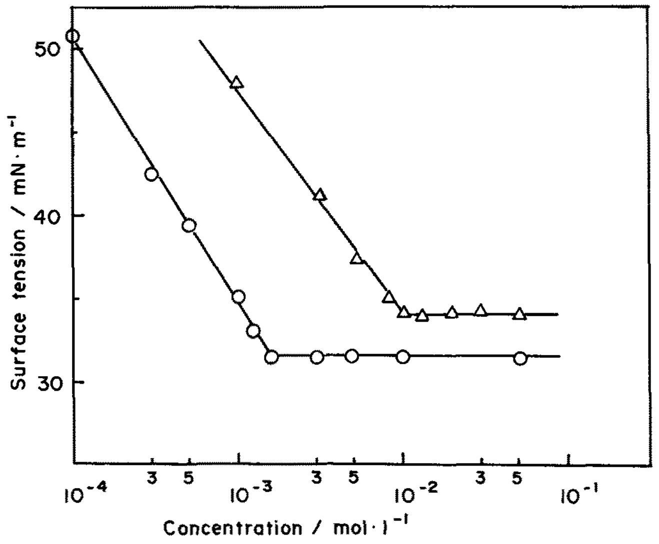

FIG. 3. Surface tension-concentration plots of aq. C_8E4HA (IId) solutions under various pH conditons at 20 C. ○, pH 2.20, 3.82, 5.50, and 7.10 (acidic and neutral conditions); △, pH 8.95 and 11.50 (basic conditions).

to its anion form, so that the break in the curve (CMC) shifted to a higher concentration than that in neutral conditions. On the other hand, because similar curves were found in acidic and neutral conditions, it was considered that this compound could act as a kind of end-blocked nonionic surfactant. Additionally, to clarify the structural change of hydroxamic acid molecules between pH 7 and pH 9 in detail, the surface tension of this hydroxamic acid at a fixed concentration (2×10^{-3} mol/l) was measured under some pH conditions (adjustment by tris buffer). The relation between the surface tension and pH value is shown in Figure 4. The surface tension changed linearly from pH 7 to pH 9. It was considered that the dissociation of this hydroxamic acid to its anion form could occur above pH 7 from the calculation of the degree of dissociation using the pKa value. So those experimental facts seemed to agree with the calculation results.

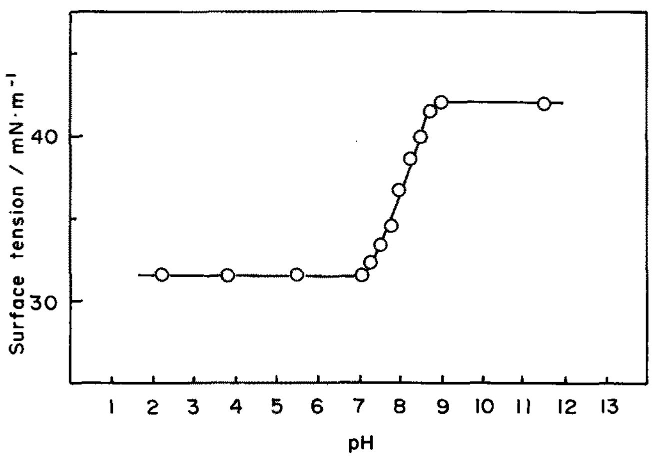

FIG. 4. Surface tension vs. pH for aq. C_8E4HA (IId) solutions (2×10^{-3} mol/l) at 20 C.

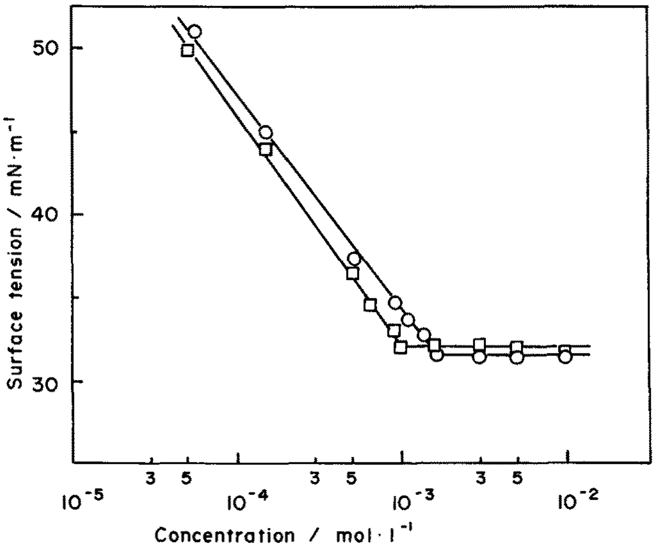

FIG. 5. Surface tension-concentration plots of aq. C_8E4HA (IId) solutions in the presence of (□) and in the absence of (○) ferric ion at 20 C (pH 2.0, [C_8E4HA]:[Fe^{3+}] = 1:1, 2:1, and 3:1).

The surface tension of some alkyl ethylenediamine-chelates has been reported (19) as one of the important surface properties of metal chelate surfactants. So the surface tension of solutions of C_8E4HA, which could form the water soluble complex with ferric ion, was measured in the presence of ferric ion. Similar surface tension-concentration curves were obtained for the three solution systems in which the molar ratio of hydroxamic acid to ferric ion was constantly kept at one, two and three, respectively (Fig. 5). CMC shifted to a lower concentration as compared to C_8E4HA only, and no precipitation was observed in the range of this measurement.

The investigation of the effect of terminal hydroxamic acid group on surface properties, by comparing compounds II with other nonionic surfactants, will be studied in detail in a future paper.

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[Received June 26, 1986]