Preparation and Surface Active Properties of Alcohol Ethoxylates with an Amide Oxime Terminal Group

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Amide oxime compounds have become of major interest because they can complex with uranium, gallium and various transition metal ions. In this work surface active amide oximes were prepared to make some functions of the amide oxime group exhibit as molecular aggregates in aqueous media. Amide oximes were obtained from nitriles which were prepared by the cyanoethylation of alcohol ethoxylates with a monodispersed oligo(oxyethylene) group. Surface active properties of these compounds were measured under various conditions and were compared with nonionics of the alcohol ethoxylate type. The pKa$_1$ values of these amide oximes were about five, and they acted as cationic surfactants under acidic conditions and nonionic ones under neutral and basic conditions. When they served as nonionics, the cloud point, CMC, γ_{CMC} and foaming properties of surface active amide oximes were similar to other alcohol ethoxylate nonionics.

It is known that amide oxime compounds can complex with various metal ions (1, 2), and many reports on the application of this property to practical uses are available. Especially the application of amide oximes to the separation, concentration or recovery process for valuable metals such as uranium or gallium and harmful metals such as mercury or cadmium has become of major interest recently. There are some reports on the recovery of uranium from seawater by amide oxime polymers (3, 4), the separation of various transition metals by telomer type surface active amide oximes such as the ion-flotation collectors (5, 6), or the concentration of gallium from the Bayer's solution by amide oximes (7, 8).

We have prepared novel surface active hydroxamic acids (9, 10), ketones and oximes (Masuyama, A., S. Komada and M. Okahara, unpublished work) by the modification of the terminal hydroxyl group of alcohol ethoxylates and clarified their surface active properties or the effect of the terminal functional groups on interfacial properties under various conditions.

In this work, a new type of surface active amide oximes [IIIa-f; $C_mE(n+1)AX$] was prepared from alcohol ethoxylates with monodispersed oligo(oxyethylene) group [Ia-g; $C_mE(n+1)$] to make some functions of the amide oxime group exhibit as molecular aggregations in aqueous media under various conditions. Surface active properties of these amide oximes were determined and compared with other alcohol ethoxylate functional surfactants developed by us. The synthetic route to amide oximes and abbreviations of compounds are shown in Figure 1.

EXPERIMENTAL PROCEDURES

Materials. Alcohol ethoxylates (Ia-g) were prepared from n-alkylbromides and monodispersed oligo(ethylene glycol)s (50–70%). 3-Alkyl[oligo(oxyethylene)]oxy-2-propionamide oximes (III) were obtained from nitriles [II; $C_mE(n+1)CN$)] which were prepared by the cyanoethylation of corresponding alcohol ethoxylates (11, 12). Amide oximes were purified by silica gel (metal free) column chromatography or recrystallization from hexane.

3-Alkyl[oligo(oxyethylene)]oxypropionenitrile (II): Typical procedure. After metallic potassium (0.2 g, 5 mmol) was dissolved in decyl tetra(oxyethylene) monoether (Id; $C_{10}E4$; 16.7 g, 50 mmol), acrylonitrile (3.0 g, 57 mmol) was dropped carefully at 30 C and the mixture was stirred at this temperature for 24 hr. After neutralization by hydrochloric acid, water (100 ml) was added and the reaction mixture was extracted with methylene chloride (100 ml, 4 times). After the extracts were combined and dried with $MgSO_4$, the evaporation of the solvent gave crude product (12.0 g; crude nitrile). The gas liquid chromatography (GLC)-pure 4,7,10,13,16-pentaoxahexacosanenitrile (IId; $C_{10}E4CN$) was obtained by the Kugelrohr distillation (b.p., 150 C/0.05 Torr; 10.9 g, 64% yield).

3-Alkyl[oligo(oxyethylene)]oxypropionamide oxime (III): Typical procedure. Hydroxylamine hydrochloride (3.50 g, 51 mmol) in methanol (30 ml) was added to sodium

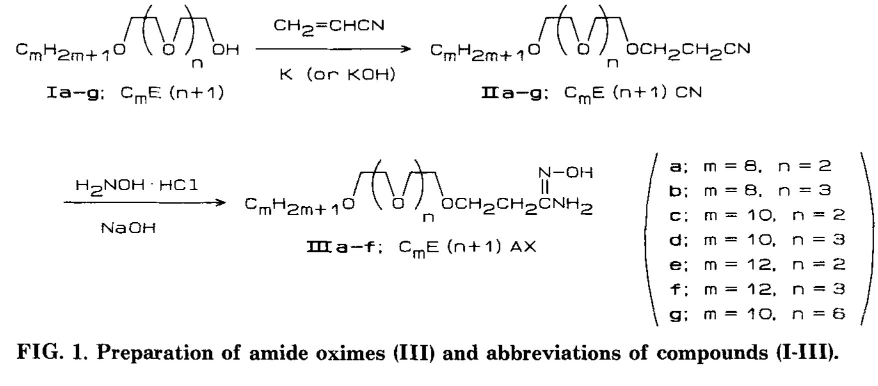

FIG. 1. Preparation of amide oximes (III) and abbreviations of compounds (I-III).

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TABLE 1

Properties of Nitrile (IIg) and Amide Oximes (IIIa-f)

Compound (m,n)	Abbreviation symbol	Yield[a] (%)	Bp[b] or Mp (C/Torr) or (C)	Anal. found (calcd)
IIg (10,6)	$C_{10}E7CN$	82	195/0.06	C, 61.86 (62.40) H, 10.37 (10.28) N, 2.86 (2.69)
IIIa (8,2)	C_8E3AX	89	oily	C, 58.12 (58.59) H, 10.53 (10.41) N, 7.83 (8.04)
IIIb (8,3)	C_8E4AX	92	oily	C, 58.15 (58.14) H, 10.31 (10.27) N, 7.14 (7.14)
IIIc (10,2)	$C_{10}E3AX$	90	oily	C, 60.52 (60.61) H, 10.78 (10.71) N, 7.29 (7.44)
IIId (10,3)	$C_{10}E4AX$	93	29.5–30.0	C, 59.98 (59.97) H, 10.62 (10.54) N, 6.62 (6.66)
IIIe (12,2)	$C_{12}E3AX$	89	30.5–31.0	C, 62.33 (62.34) H, 10.96 (10.96) N, 6.29 (6.92)
IIIf (12,3)	$C_{12}E4AX$	80	32.0–33.0	C, 62.13 (61.57) H, 10.73 (10.78) N, 5.70 (6.24)

[a] GLC- or IR-pure. Based on parent alcohol ethoxylate (in the case of nitrile) or nitriles (in the case of amide oximes).

[b] Kugelrohr distillation.

hydroxide (2.11 g, 50 mmol) in methanol (30 ml) at 0 C, and insoluble solids were separated off by filtration. To this filtrate 7.74 g of IId (20 mmol) in methanol (40 ml) was dropped and the mixture was stirred at room temperature for 24 hr (pH 5-7 under these conditions). After filtration and subsequent evaporation of the filtrate, methylene chloride (50 ml) was added to the residue. Insoluble solids were filtered off again, and 7.98 g of crude product was obtained by the evaporation of the filtrate. The pure 4,7,10,13,16-pentaoxahexacosanamide oxime (IIId; $C_{10}E4AX$), confirmed by its spectral data, was obtained by silica gel column chromatography with a hexane:2-propanol (4:1, v/v) eluent as colorless solids (m.p. 29.5–30.0 C, 7.82 g, 93% yield).

The structures of II and III were confirmed by their IR (Hitachi 260 spectrometer), ^{1}H NMR (JEOL JNM-PS-100), mass (Hitachi RMU-6E) spectra and elemental analyses. IR (neat): nitriles; 2950, 2870, 2250, 1480, 1350, 1120, 950 and 850 cm^{-1}, amide oximes; 3300, 2950, 2870, 1660, 1580, 1470, 1380, 1120, 940 and 860 cm^{-1}. ^{1}H NMR ($CDCl_3$): nitriles; $\delta = 0.88$ (t, 3H, CH_3-C-C), 1.2–1.8 (m, -CH_2 in alkyl chain), 2.55 (t, 2H, O-C-CH_2-CN), 3.39 (t, 2H, O-CH_2-C-CN) and 3.5–3.8 [m, O-CH_2CH_2-O and (alkyl chain)-CH_2O], amide oximes; $\delta = 0.88$ (t, 3H), 1.1–1.8 (m), 2.35 [t, 2H, O-C-CH_2C(=N-O)-N], 3.44 [t, 2H, O-CH_2-C-C(=N-O)], 3.5–3.8 (m) and 4.0–5.5 [br, 3H, C-C(=N-OH)-NH_2; disappeared by addition of D_2O]. The molecular ion peak of each compound was observed in its mass spectrum. The results of IIg and IIIa-f, the objects of this investigation about surface active properties, are summarized in Table 1 with the data of elemental analyses.

Methods. The pKa values were determined either in water ordinarily at 20 C or in a water-ethanol mixture (1:1, v/v) at 25 C under a nitrogen flow, according to the potentiometric method. The cloud point (T_{cp}) and other surface active properties of aqueous solutions of those compounds were measured by the previously reported methods (10). The T_{cp} and foaming properties were measured with a 1 wt% aqueous surfactant solution at 20 C, according to the usual procedure. The pH of aqueous solutions was adjusted by the addition of hydrochloric acid or sodium hydroxide.

RESULTS AND DISCUSSION

While the cyanoethylation of Ia-f was carried out in the presence of a catalytic amount of potassium without solvent, the reaction medium became solid in the case of Ig. Thus, potassium hydroxide and dioxane were used as base and solvent, respectively, for the preparation of nitrile (IIg). The preparation of amide oximes was very easy, and they were obtained in good yield.

The pKa values of III were measured by the general acid-base titration method. Amide oximes generally have two dissociation constants (Ka_1 and Ka_2) (1), but only pKa_1 was found in each amide oxime (III) by this method (Table 2). From the pKa_1 values, compounds (III) were expected to act as both cationic surfactants under acidic conditions and nonionic ones under neutral and basic conditions.

TABLE 2

pKa_1 Values[a] of Amide Oximes (IIIa-f)

Compound	pKa_1	Compound	pKa_1
C_8E3AX (IIIa)	4.9	$C_{10}E4AX$ (IIId)	5.1 (5.5)
C_8E4AX (IIIb)	5.1	$C_{12}E3AX$ (IIIe)	4.9[b] (5.3)
$C_{10}E3AX$ (IIIc)	4.8	$C_{12}E4AX$ (IIIf)	4.9 (5.3)

[a] Measured in water at 20 C. Values in parentheses were measured in ethanol-water (1:1, v/v) at 25 C.

$$R\text{-}C(=N\text{-}OH)\text{-}NH_3^+ \overset{Ka_1}{\rightleftharpoons} R\text{-}C(=N\text{-}OH)\text{-}NH_2 \overset{Ka_2}{\rightleftharpoons} R\text{-}C(=N\text{-}O^-)\text{-}NH_2$$

[b] At 5 C.

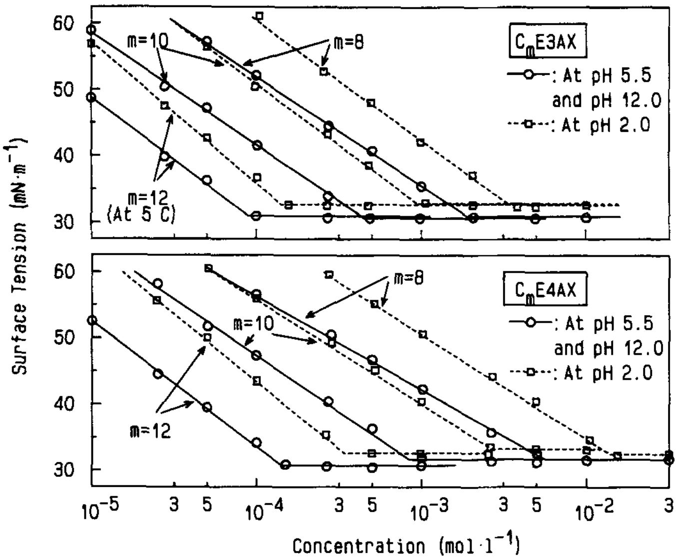

FIG. 2. Surface tension-concentration plots of aqueous amide oxime solutions under various pH conditions at 20 C.

TABLE 3

Surface Active Properties of Nitrile (IIg) and Amide Oximes (IIIa-f)

Compound	T_{cp}[a] (C)	10^4CMC[b] (mol•l^{-1})	γ_{CMC}[b] (mN•m^{-1})	10^2A (nm^2)
$C_{10}E7CN$ (IIg)	41.0	9.6	34.0	76
C_8E3AX (IIIa)	43.0	18 (36)	31.0 (33.0)	58
C_8E4AX (IIIb)	65.0	60 (120)	32.0 (33.0)	66
$C_{10}E3AX$ (IIIc)	24.5	4.4 (9.2)	31.0 (33.0)	56
$C_{10}E4AX$ (IIId)	45.0	8.5 (24)	32.0 (33.5)	58
$C_{12}E3AX$ (IIIe)	6.0	0.85[c] (1.6)[c]	31.0[c] (33.0)[c]	47[c]
$C_{12}E4AX$ (IIIf)	22.5	1.4 (3.5)	31.0 (33.0)	50

[a] At 1 wt%.

[b] Amide oximes were measured under acidic (pH 2.0), neutral (pH 5.5) and basic (pH 12.0) conditions, and the same values were obtained at pH 5.5 and 12.0. Data in parentheses were values at pH 2.0.

[c] At 5 C.

The surface tension-concentration plots (by the Wilhelmy method) of aqueous solutions of amide oximes (C_mE3AX and C_mE4AX) are shown in Figure 2. The T_{cp}, CMC, the lowering ability of surface tension (γ_{CMC}) and the adsorption area/molecule at the surface (A) of IIg and IIIa-f are summarized in Table 3.

Nitriles (IIa-f) with three or four oxyethylene units were insoluble in water. Because the T_{cp} of $C_{10}E7CN$ (IIg) containing seven oxyethylene units is about 20 C lower than that of decyl hexa(oxyethylene) monoether [$C_{10}E6$; T_{cp} = 60 C (13)] with only six oxyethylene units, the terminal cyanoethyl group seemed to behave like a hydrophobic part. On the other hand, the T_{cp} values of amide oximes (III) were similar to those of alcohol ethoxylates with one more oxyethylene unit than corresponding amide oximes [for example: C_8E5, T_{cp} = 55 C; $C_{10}E5$, T_{cp} = 36 C; $C_{12}E5$; T_{cp} = 25 C (13)]. The terminal amide oxime group seemed to contribute to the hydrophilic property. The satisfactory results will be attained in the practical applications if compounds III have tetra(oxyethylene) units.

The surface tension of aqueous amide oxime (III) solutions was measured under acidic (pH 2.0), neutral (pH 5.5) and basic (pH 12.0) conditions, and two types of surface tension-concentration curves were found for each compound III. One was obtained under neutral and basic conditions, while the other was in an acidic solution. Under acidic conditions, the hydrophilicity of the molecule might increase by the protonation of the amide oxime group, so that the break in the curve (CMC) shifted to a higher concentration than that under neutral conditions. On the other hand, because similar curves were found under neutral and basic conditions, III could act as nonionic surfactants as discussed above about pKa values.

The γ_{CMC} values of neutral and basic aqueous amide oxime solutions were good as nonionic surfactants. The γ_{CMC} values of III under acidic conditions were higher than those under other conditions. This tendency caused by ionization of surfactants was also found in the case of hydroxamic acids and oximes, as previously reported (9, Masuyama, A., S. Komada and M. Okahara, unpublished work). The adsorption area/molecule (A) of III decreased with both an increase in the number of carbon atoms in the lipophilic group and a decrease in the number of oxyethylene units. This trend is generally evident in nonionic surfactants (14).

The foaming properties determined by the semimicro TK method (15) are given in Table 4.

For amide oximes (III) the measurement was carried out under various pH conditions, and similar results were obtained at pH 5.5 and 12.0. The foaming ability and foam stability of III with the cationic character were superior to those of III with the nonionic character. Though similar oximes showed excellent antifoaming properties (Masuyama, A., S. Komada and M. Okahara, unpublished work) these amide oximes did not have as much antifoaming character as expected. The foam stability of III seemed medium compared with corresponding alcohol ethoxylates (Masuyama, A., S. Komada and M. Okahara, unpublished work).

An investigation of the separation and concentration of gallium from aqueous solution by these amide oximes as the ion-flotation collectors is now in progress.

TABLE 4

Foaming Properties of Nitrile (IIg) and Amide Oximes (IIIa-f)

		Foam Volume[b] (ml)					
Compound	Condition[a]	0′	30″	1′	1′30″	2′	5′
C_{10}E7CN (IIg)	N	90	15	0			
C_8E3AX (IIIa)	N,B	30	0				
C_8E3AX (IIIa)	A	60	10	0			
C_8E4AX (IIIb)	N,B	20	0				
C_8E4AX (IIIb)	A	30	0				
C_{10}E3AX (IIIc)	N,B	130	50	30	10	0	
C_{10}E3AX (IIIc)	A	220	180	150	100	60	0
C_{10}E4AX (IIId)	N,B	80	10	0			
C_{10}E4AX (IIId)	A	100	40	20	10	0	
C_{12}E3AX (IIIe)	N,B[c]	180	120	90	70	50	0
C_{12}E3AX (IIIe)	A[c]	260	260	260	260	260	240[d]
C_{12}E4AX (IIIf)	N,B	140	90	60	20	0	
C_{12}E4AX (IIIf)	A	240	120	60	30	20	0

[a] N, neutral condition (pH 5.5); B, basic condition (pH 12.0); A, acidic condition (pH 2.0).

[b] By semi-micro TK method (6) at 1 wt% and 20 C.

[c] At 5 C.

[d] 10′, 200 ml; 30′, 100 ml; 50′, 10 ml; 80′, 0 ml.

The surface active properties mentioned above afford much information to the application of amide oximes to ion-flotation systems because, it is said, the HLB and interfacial properties of surfactant collector types are very important factors for such objects (5, 6).

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