Preparation and Surface Active Properties of Terminal Amide Type of Alcohol Ethoxylates

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Three kinds of title amide compounds with different terminal structures (N-unsubstituted amide, N,N-dimethylamide and acylmorpholine) were prepared from alkyl tetra(oxyethylene) monoethers (alkyl: decyl or dodecyl). The cloud points of the N,N-dimethylamides and acylmorpholines were higher than the other corresponding alcohol ethoxylate derivatives previously developed by us, and all these amides inclusive of N-unsubstituted amides had sufficient hydrophilicity. Surface active properties (CMC, γ_{CMC} and foaming properties) of these amides in pure water and in hard water (1000 ppm of total hardness as $CaCO_3$) were almost the same and considered excellent as nonionic surfactants. Furthermore, they showed good lime-soap dispersing ability.

FIG. 1. Preparation of amides (III) from alcohol ethoxylates (I).

The investigation of surfactants with a sequestering ability for calcium and magnesium ions is still continuing to develop new types of phosphate-free detergents, builders and lime-soap dispersing agents (LSDA) (1-3). Amide groups have attracted interest in this field because this group is known to have a strong affinity for calcium ions (4,5). Linfield et al. have already reported that oxyethylated fatty amides can be applied to LSDA (6) and soil wetting agents (7) with excellent ability. They also have clarified that an oxyethylene group can make a significant contribution to the lime-soap dispersing ability (6).

We have prepared a series of "functional" surfactants by a relatively simple modification of the terminal hydroxyl group of alcohol ethoxylates and have studied their extra functions besides their basic surface active properties (8-11). In this work, we have synthesized three kinds of amide compounds (IIIa-f; Fig. 1) with different terminal structures from the alkyl tetra(oxyethylene) monoethers (Ia,b; alkyl: decyl or dodecyl). There is a patent concerning detergents thickened with terminal dialkanol amide type alcohol ethoxylates which are the familiar types of III, but their properties were not characterized at all (12). Here we report the surface active properties of compounds (III) both in pure water and in hard water, and their lime-soap dispersing ability. We also clarify the effect of the terminal amide structure on these properties and compare these amides with other alcohol ethoxylate derivatives developed by us. The synthetic route for the amides is shown in Figure 1.

EXPERIMENTAL PROCEDURES

Materials. Methyl alkyl[tetra(oxyethylene)]oxyacetates (II) were prepared according to the general method (60-80% yield). Three kinds of alkyl[tetra(oxyethylene)]oxyacetamides (III) with different terminal structures were synthesized by the reac-
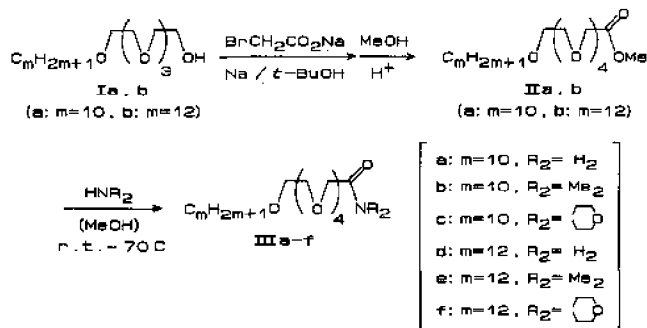
tion of II with ammonia, dimethylamine or morpholine. The reaction was carried out in methanol at room temperature except for IIIc and IIIf, which were prepared at 70°C without any solvent. Pure amides were obtained by the Kugelrohr distillation or recrystallization from hexane.

Alkyl[tetra(oxyethylene)]oxyacetamide (III): Typical procedure. The methyl ester (IIb; 3.0 g, 6.9 mmol) in methanol (5 ml) was dropped into 20 ml of aqueous ammonia (28% solution) at ca. 20°C. After 2 hr of stirring at room temperature and subsequent evaporation of the solvent and excess ammonia, the residue was dissolved in 50 ml of water. After extraction of this solution with ether (100 ml, three times), crude amide (m.p. 37-40° C, 3.0 g) was obtained as a residue after evaporation of the solvent. Recrystallization of the crude product from hexane gave pure 3,6,9,12,15-pentaoxaheptacosanamide (IIIb; m.p. 39.2-39.8°C, 2.0 g, 70% yield).

The structure of III was confirmed by gas liquid chromatography (GLC), spectral (IR, mass and ^{1}H-NMR) and elemental analyses (within ±0.4%). It was also assessed from the observed sharp break in surface tension—concentration curves. Their properties are summarized in Table 1.

Methods. The cloud point (T_{cp}) and other surface active properties of aqueous solutions of these amides were measured by standard methods (9). The stability of these compounds (III) for calcium and magnesium ions was determined in 0.5% solutions by the modified Hart method (13). The solutions contained up to 2000 ppm of total hardness as $CaCO_3$. Surface active properties were also measured in hard water with 1000 ppm of total hardness as $CaCO_3$ which was prepared by the use of $CaCl_2 \cdot 2H_2O$ and $MgCl_2 \cdot 6H_2O$ (a hardness composition of 68% Ca^{2+}, 32% Mg^{2+}). The lime-soap dispersing requirement (LSDR) was determined in 333 ppm of hard water by the Borghetty-Bergmann method (14).

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TABLE 1

Properties of Amides (IIIa-f)[a]

Compound (m,R₂)	Yield[b] (%)	Mp (°C) or Bp (°C/Torr)[c]	¹H-NMR[d] (CDCl₃) (d)	MS (70 eV) m/z (rel. intens.)	Anal. found (calcd)
IIIa (10, H₂)	66	waxy product	0.83(t,3H), 1.2–1.8(m,16H), 3.42(t,2H), 3.6–3.8(m,16H), 3.97(s,2H), 5.6–6.2(br, 2H)	391(M⁺,Amp[e]), 102(100), 89(25), 45(50)	C, 61.33(61.35) H, 10.32(10.55) N, 3.45(3.58)
IIIb (10,Me₂)	78	140/0.02	0.85(t,3H), 1.2–1.8(m,16H), 2.90(s,3H), 2.97(s,3H), 3.42(t,3H), 3.6–3.8(m,16H), 4.20(s,2H)	419(M⁺,Amp), 130(100), 87(34), 45(41)	C, 62.98(62.97) H, 10.81(10.81) N, 3.09(3.39)
IIIc (10,O)	71	180/0.06	0.88(t,3H), 1.2–1.7(m,16H), 3.44(t,2H), 3.5–3.8(m,24H), 4.21(s,2H)	461(M⁺, 18), 172(100), 128(30), 57(28)	C, 62.23(62.44) H, 10.38(10.26) N, 2.98(3.03)
IIId (12, H₂)	70	39.2–39.8	0.83(t,3H), 1.2–1.8(m,20H), 3.42(t,2H), 3.6–3.8(m,16H), 3.97(s,2H), 5.6–6.2(br,2H)	419(M⁺,Amp), 102(65), 89(71), 45(100)	C, 62.78(62.97) H, 10.83(10.81) N, 3.22(3.39)
IIIe (12,Me₂)	72	150/0.02	0.85(t,3H), 1.2–1.8(m,20H), 2.90(s,3H), 2.98(s,3H), 3.42(t,2H), 3.6–3.8(m,24H), 4.20(s,2H)	447(M⁺,Amp), 130(100), 87(40), 45(40)	C, 64.58(64.39) H, 11.08(11.03) N, 2.89(3.13)
IIIf (12,O)	70	160/0.06	0.85(t,3H), 1.2–1.7(m,20H), 3.42(t,2H), 3.6–3.8(m,24H), 4.20(s,2H)	489(M⁺, 2), 172(100), 128(40), 57(55)	C, 63.82(63.77) H, 10.52(10.50) N, 2.97(2.86)

[a]IR spectra: IIIa,d: 3400, 2940, 2850, 1650, 1460, 1350, 1290, 1250, 1110 and 960 cm⁻¹ (neat); IIIb,c,e,f: 2920, 2850, 1650, 1450, 1350, 1280, 1110 and 950 cm⁻¹ (neat).
[b]Based on methyl ester (II).
[c]Kugelrohr distillation.
[d]100 MHz; s: singlet, br: broad, t: triplet and m: multiplet.
[e]Amp: amplified.

RESULTS AND DISCUSSION

The preparation of the amides was very easy, and they were isolated in good yield. All these amides (III) were readily soluble in water. It was shown by the measurement using the modified Hart method that compounds (III) were stable in hard water above 2000 ppm of total hardness as CaCO₃.

The surface tension-concentration plots of III, both in pure water and in hard water measured by the Wilhelmy method, 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 III both in pure water and in hard water are summarized in Table 2.

In the case of amides with the same alkyl group, the T_{cp} values of the dimethylamides (IIIb,e) or acyl-morpholines (IIIc,f) were higher than those of the corresponding N-unsubstituted amides (IIIa,d) by about 15–25 °C. This means that these N,N-disubstituted amides are more hydrophilic than the N-unsubstituted amides. It may be considered that the intramolecular hydrogen bond of a terminal amide group with carbonyl or ether oxygens contributes to the hydrophobic character of the N-unsubstituted amides. The T_{cp} values of all compounds in hard water are about from 1–9 °C lower than those in pure water, probably because of the salting-out effect (15). Because the T_{cp} of the most hydrophobic, IIId with a dodecyl group, is higher than room temperature, all these compounds seem to

possess sufficient hydrophilicity even in hard water.

We have found that the T_{cp} of a series of alcohol ethoxylate derivatives changes considerably with the structure of the terminal group (9,11). The T_{cp} values of dodecyl tetra(oxyethylene)oxy derivatives with various terminal groups (Z) previously developed by us are illustrated in Figure 3.
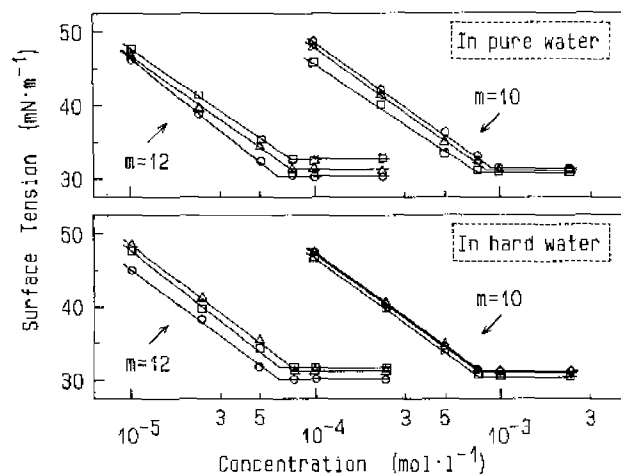

FIG. 2. Surface tension-concentration plots of amides (III) in pure water and in hard water with 1000 ppm of total hardness (as CaCO₃) at 20°C. O, IIIa,d (R₂ = H₂); △, IIIb,e (R₂ = Me₂); □, IIIc,f [R₂ = –(C₂H₄OC₂H₄)–].

TABLE 2

Surface Active Properties of Amides (IIIa-f)[a]

Compound (m,R$_2$)	Condition[b]	T$_{cp}$[c] (°C)	10^{4}CMC (mol•1^{-1})	γ_{CMC} (mN•m^{-1})	10^{2}A (nm^2)
IIIa	P	45.9	9.1	31.2	54
(10, H$_2$)	H	45.7	8.0	31.2	50
IIIb	P	66.8	8.5	31.1	54
(10,Me$_2$)	H	57.0	8.3	31.4	54
IIIc	P	59.5	7.6	30.9	57
(10,O)	H	57.0	8.0	30.7	56
IIId	P	26.0	0.60	30.3	47
(12, H$_2$)	H	25.8	0.60	30.1	47
IIIe	P	50.5	0.75	31.2	52
(12,Me$_2$)	H	45.0	0.75	31.8	52
IIIf	P	50.8	0.75	32.7	55
(12,O)	H	49.8	0.60	32.0	52

[a]CMC, γ_{CMC} and A: at 20°C.
[b]P, in pure water; H, in hard water (total hardness, 1000 ppm as CaCO$_3$).
[c]At 1 wt%.

Acylmorpholine and dimethylamide showed the highest T$_{cp}$ values among these alcohol ethoxylate derivatives. The N-unsubstituted amide showed a nearly similar T$_{cp}$ value to that of the alcohol ethoxylate with one more oxyethylene unit (C$_{12}$E5). Therefore, it can be considered that the hydrophilicity of these amides (III) is very good for this series of alcohol ethoxylate derivatives.
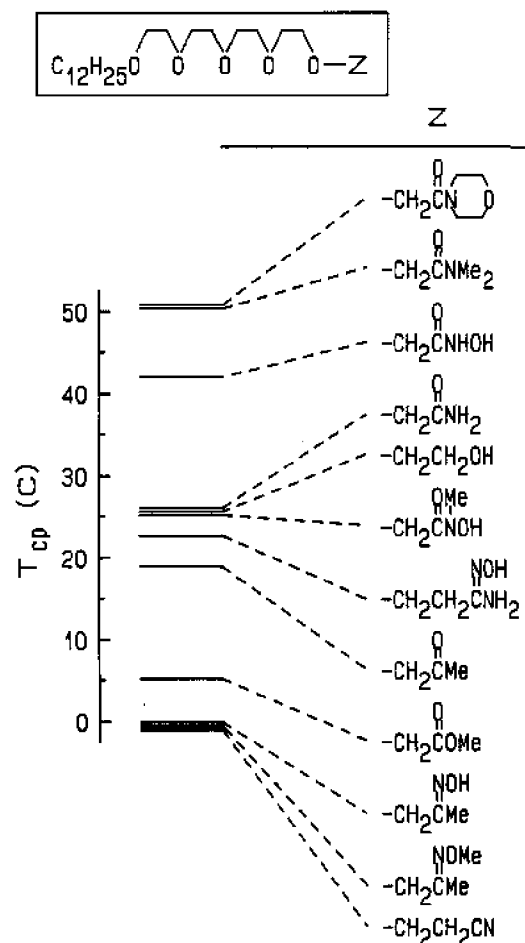
The CMC values of each compound in pure water and in hard water almost the same. In addition, amides with the same alkyl group showed similar CMC values regardless of the structure of the terminal group. The CMC values of amides with a dodecyl group were about one-tenth smaller than those of amides with a decyl group. As a result, it is clear that the CMC of III also depends on the type of hydrophobic groups rather than the structure of the hydrophilic group like other "functional" alcohol ethoxylates (9,11). The γ_{CMC} values of each compound in both solution systems were almost the same and were good for a series of nonionic surfactants.

The adsorption area/molecule (A) of amides with a dodecyl group (IIId-f) was smaller than A of IIIa-c

FIG. 3. The effect of terminal structures of alcohol ethoxylate derivatives on the T$_{cp}$.

TABLE 3

Foaming Properties of Amides (IIIa-f)[a]

Compound (m,R$_2$)	Condition[b]	Foam Volume (ml)					
		0′	0.5′	1′	1.5′	2′	5′ (min)
IIIa	P	90	20	0			
(10, H$_2$)	H	110	20	0			
IIIb	P	210	140	90	50	20	0
(10,Me$_2$)	H	160	70	30	20	0	
IIIc	P	180	110	30	20	0	
(10,O)	H	175	110	30	20	0	
IIId	P	240	220	200	170	130	0
(12, H$_2$)	H	240	200	140	120	90	0
IIIe	P	240	160	90	50	20	0
(12,Me$_2$)	H	260	200	100	50	20	0
IIIf	P	130	30	0			
(12,O)	H	140	40	10	0		

[a]At 20°C, 1 wt% solution.
[b]P, in pure water; H, in hard water (total hardness, 1000 ppm as CaCO$_3$).

TABLE 4

Lime-Soap Dispersing Requirement (LSDR) of Amides (IIIa-f) and Reference Compounds at 20°C

Amide	(m,R_2)	LSDR	Reference compound	LSDR
IIIa	$(10, H_2)$	14.0	Linear alkylbenzene sulfonate[a]	40
IIIb	$(10,Me_2)$	15.2	Sodium dodecyl sulfate	30.0
IIIc	$(10,O)$	13.4	$C_{10}H_{21}O(CH_2CH_2O)_6H$	26.5
IIId	$(12, H_2)$	6.5	$RC(=O)N[(CH_2CH_2O)_7H]_2$[b]	2
IIIe	$(12,Me_2)$	6.0		
IIIf	$(12,O)$	6.0		

[a]See (17).

[b]See (2); R refers to a tallow-derived alkyl group.

with a decyl group. In each compound, the A value in hard water was almost the same or a little smaller than that in pure water. The A values of the acylmorpholines (IIIc,f) were larger than other amides, probably because of the bulkiness of the hydrophilic terminal group.

The foaming properties determined by the semi-micro TK method (16) both in pure water and in hard water are given in Table 3. The foaming ability and foam stability of III in both solution systems were almost the same. Unexpectedly, the foaming properties of acylmorpholine with a dodecyl group (IIIf) were inferior to those of IIIc with a decyl group. But, overall, the foaming properties of these amides are judged as medium for a series of our prepared alcohol ethoxylate derivatives (9,11).

Finally, results of the LSDR of III and some reference compounds are listed in Table 4. Because the LSDR of amides with a decyl group was about 14 and that of amides with a dodecyl group was about 6, it was found that III had better lime-soap dispersing ability than LAS, SDS and a normal alcohol ethoxylate. But our results were not beyond the LSDR of an oxyethylated fatty amide with a tallow-derived alkyl group. Linfield et al. have reported that the LSDR of oxyethylated fatty amides decreased with an increase in the number of oxyethylene units (6). Therefore, there is a possibility that our type of compounds with longer alkyl and oxyethylene groups may show smaller LSDR values.

Amide compounds (III) in this work showed excellent surface active properties, not only in pure water but also in hard water, and had good lime-soap dispersing ability. Though many other factors, such as detergency, dispersing ability and so on, must be considered

for practical use, these amides may be applied to an active ingredient in phosphate-free detergents.

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ERRATA

In the article "Evaluation of Turkish Sulphur Olive Oil as an Alternative Diesel Fuel" by Aksoy et al., which appeared in the June 1988 issue of JAOCS (65:936-938), the term "Fusel oil" incorrectly appeared nine times as "fuel oil." "Fusel oil" should have appeared in the seventh and ninth lines of the abstract, the 13th line of the second paragraph and the 12th line of the fourth paragraph in the "Materials and Methods" section; in the headings for Tables 4 and 5, and the sixth line of the sixth paragraph, the third line of the seventh paragraph, and the fourth line of the final paragraph of the "Results and Discussions" section.