♨Synthesis of EDTA-Monoalkylamide Chelates and Evaluation of the Surface-Active Properties

TOSHIO TAKESHITA, TAKA-AKI SHIMOHARA and SHIGERU MAEDA, Department of Applied Chemistry, Faculty of Engineering, Kagoshima University, Kagoshima-shi, 890 Japan

ABSTRACT

New chelating agents were synthesized from long-chain amines and ethylenediaminetetraacetic acid (EDTA) monoanhydride which was prepared by partial hydrolysis of EDTA anhydride. The equivalent reactions between the chelating agents and several metal ions gave the corresponding 1:1 metal chelates in good yield. These chelates and the sodium salts of the chelating agents were found to have good surface active properties, especially dispersing power and emulsifying power.

INTRODUCTION

A series of alkyl derivatives of EDTA and their metal chelates have been synthesized; their surface-active properties have been investigated as described in a previous paper (1). The chelates of both bis(N-alkylamide) (2) and bis(N,N-dialkylamide) (3) of EDTA had good surface-active properties, but the application of the divalent metal chelates were limited because of poor water solubility. The main reason for the poor water solubility of those chelates is that they have no charge. The divalent metal chelates of EDTA-monoalkylamides are expected to have a negative charge and, consequently, to have better water solubility than those of the bisalkylamides. The monoalkylamide pentadentate ligand is also expected to have greater chelate stability constant compared to the quadridentate ligands.

The previous paper (1) showed that the equivalent reaction between EDTA-dianhydride and alcohol gave EDTA-monoalkyl ester in poor yield ($\approx$ 13%). Preliminary experiment revealed that the equivalent reaction between EDTA-dianhydride and alkylamine gave predominantly EDTA-dialkylamide, which had been predicted from the above results. The EDTA-monoalkylamide and its chelates, and EDTA-monoanhydride have not been synthesized previously. The object of this study is to investigate the preparation of the monoalkylamides of EDTA in good yield from alkylamines and EDTA by way of EDTA-monoanhydride, and to clarify the characteristics of their metal chelates with respect to their surface-active properties.

The general synthetic scheme for the EDTA-monoalkylamides and their metal chelates is shown in Figure 1. In this paper, EDTA-monoalkylamides prepared from EDTA and decyl-, dodecyl-, tetradecyl-, hexadecyl- and octadecylamine are expressed by C_{10}-amide, C_{12}-amide, C_{14}-amide, C_{16}-amide and C_{18}-amide, respectively.

EXPERIMENTAL PROCEDURES

Materials

EDTA (DOTITE 4H guaranteed reagent, Dojin Chemical Co.) was used without further purification. Decyl-, dodecyl-, tetradecyl-, hexadecyl- and octadecylamine (Tokyokasei's extra pure, Tokyokasei Kogyo Co.) also were used without further purification. Metal salts used for the chelates were $Al(NO_3)_3 9H_2O$, $Fe(NO_3)_3 9H_2O$, $Co(NO_3)_2 6H_2O$, $Ni(NO_3)_2 6H_2O$, $Cu(NO_3)_2 3H_2O$, and $Zn(NO_3)_2 6H_2O$. All of

$R^* = C_{10}H_{21}$ (C_{10}-amide), $C_{12}H_{25}$ (C_{12}-amide), $C_{14}H_{29}$ (C_{14}-amide), $C_{16}H_{33}$ (C_{16}-amide), $C_{18}H_{37}$ (C_{18}-amide)
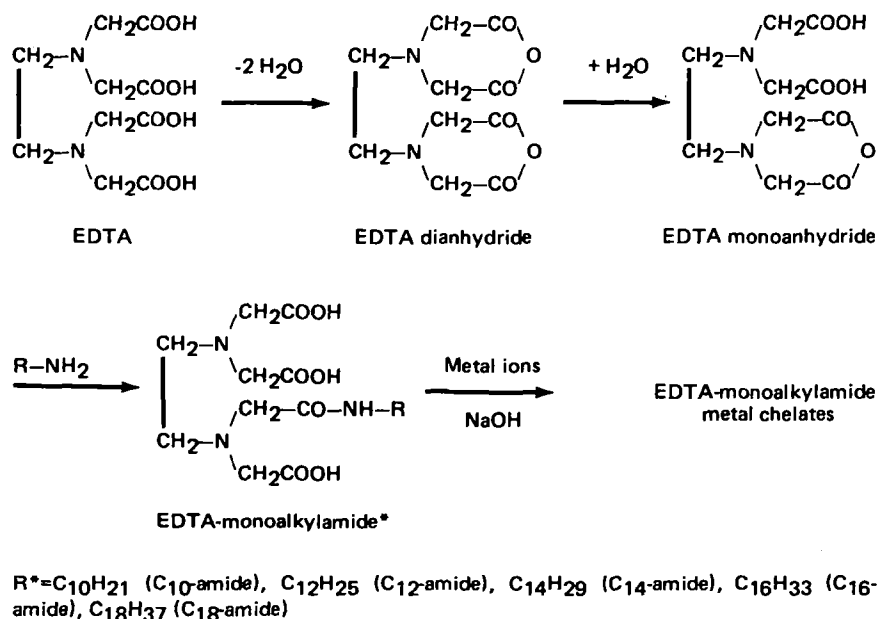
FIG. 1. Synthetic scheme of EDTA-monoalkylamides and the metal chelates.

TABLE I

EDTA-Monoalkylamides

| Monoalkylamide | Elementary analysis | | | | | | Yield (%) | mp (C) |
| | C (%) | | H (%) | | N (%) | | | |
	Found	Calcd	Found	Calcd	Found	Calcd		
C_{10}-amide	55.53	55.67	8.64	8.64	9.56	9.74	53	98.5 ~ 99.0
C_{12}-amide	57.80	57.49	9.21	8.99	9.02	9.14	56	91.0 ~ 92.0
C_{14}-amide	59.30	59.11	9.40	9.30	8.55	8.62	73	98.0 ~ 100.0
C_{16}-amide	60.57	60.56	9.59	9.58	8.05	8.15	74	104.0 ~ 105.0
C_{18}-amide	61.56	61.85	10.01	9.82	7.47	7.73	84	108.0 ~ 109.5

these were extra pure grade chemicals and were used after determination of their salt contents.

Synthetic Procedure

EDTA dianhydride. EDTA dianhydride was prepared in 95% yield according to the method described by Geigy (4).

EDTA monoanhydride. EDTA dianhydride (64.1 g, 0.25 mol) was dissolved in N,N-dimethylformamide (DMF) (guaranteed grade, 400 mL) at 76 C in a 1,000-mL round-bottomed flask equipped with stirrer, micro-syringe and reflux condenser in a system protected from atmospheric moisture. Water (4.5 g, 0.25 mol) was injected by drops in the course of 50 min from the micro-syringe. When the reaction mixture became turbid after being stirred for another 2 hr at 76 C, the mixture was allowed to stand at room temperature for 2 hr. The mixture was filtered, and the residue was washed with DMF and dried for 5 hr at 70 C under vacuum.

EDTA-monoalkylamides. The typical synthetic procedure for EDTA-monohexadecylamide (C_{16}-amide) is as follows. EDTA-monoanhydride (13.7 g, 0.05 mol) and hexadecyl-amine (0.05 mol) were dissolved in dry DMF (600 mL) in a 1,000-mL round-bottomed flask. The mixture was stirred for 10 hr at 98-100 C in a system protected from atmospheric moisture and oxygen. After being cooled, the mixture was poured into a large excess of water and filtered, and the residue was washed with water to give the crude product. A portion of the crude product (3-5 g) was dissolved in aqueous sodium hydroxide (120 mL) at pH 10. The solution was shaken with ether (100 mL). The etherial and emulsified phases containing unreacted amine were discarded. The water phase was neutralized with 10% HCl, heated at 70-80 C to remove the dissolved ether, and acidified to pH 4 to give precipitate. The precipitate was separated, washed with distilled water, and dried for 5 hr at 80 C under vacuum giving purified C_{16}-amide. Other portions were similarly treated, and the purified products were combined.

Metal chelates of EDTA-monoalkylamides. The metal chelates were synthesized by the same method as mentioned in the previous paper (1). The crude products of the copper and nickel chelates from C_{18}-amide and of the copper chelate from C_{16}-amide were purified as follows. The crude chelate was dissolved in hot ethanol containing the minimal quantity of water necessary to dissolve it, and cooled gradually in ice-water. The crystals formed were then separated. The other crude chelates were purified by extraction with toluene/butanol (5:3). Thirty metal chelates (5 chelating agents × 6 metals) were thus obtained in 42-100% yield (Table II, vide infra). The metal chelates obtained were analyzed for the central metal ions by the same method as described in the previous paper (1).

Surface Activities

The measurements of surface tension, interfacial tension, dispersing power, and emulsifying power were made by the same methods as described in the previous paper (1).

RESULTS AND DISCUSSION

Preparation of EDTA-Monoanhydride

The attempt to prepare EDTA-monoanhydride from EDTA gave poor results, whereas the preparation from EDTA dianhydride gave good yield (75%) of the EDTA-monoanhydride: mp 200.5-202.0; IR(KBr) 1820 and 1775 (anhydrous ring νC=O), and 1690 (carboxy νC=O) cm^{-1}. Analysis calcd for $C_{10}H_{14}N_2O_7$: C, 43.80; H, 5.15; N, 10.21. Found: C, 43.59; H, 5.23; N, 10.26. The purity of the EDTA monoanhydride was proven from the experimental data already mentioned and from the solubility behavior in DMF compared to that of EDTA (almost insoluble) and EDTA-dianhydride (fully soluble).

Synthesis of EDTA-Monoalkylamides

The EDTA-monoalkylamides were obtained in good yield, 53-84% (Table I). Such a high yield could not be expected if the monoalkylamides were synthesized by the reaction of EDTA-dianhydride with the amines. Table I shows the results of elementary analysis, yield and mp measurement of the monoalkylamides obtained. The typical characteristics of C_{16}-amide are: IR(KBr) 3400 (amide νNH), 1715 and 1675 (carboxy νC=O), 1650 (amide I), 1540 (amide II) cm^{-1}; NMR of the trisodium salt (D$_2$O), δ 3.07-3.18 (br, 9.5, N-CH$_2$-CO + CO-ND-CH$_2$-R), δ 2.54 (t, 4.0, N-CH$_2$-CH$_2$-N), δ 1.25 (br, 28.0, CO-ND-CH$_2$-(CH$_2$)$_{14}$-CH$_3$), and δ 0.83 (t, 3.0, -CH$_3$). Similar data corresponding to the other EDTA-monoalkylamides were also obtained. These IR and NMR data and the elementary analysis and mp data in Table I show that EDTA-monoalkylamides obtained are all satisfactorily pure.

TABLE II

Yield of EDTA-Monoalkylamide Metal Chelates[a]

| Chelating agent | Central metal ion of chelate | | | | | |
	Al	Fe	Co	Ni	Cu	Zn
C_{10}-amide	42	100	70	60	65	97
C_{12}-amide	74	87	53	93	91	63
C_{14}-amide	88	95	84	80	95	75
C_{16}-amide	100	65	72	92	88	94
C_{18}-amide	85	69	60	85	89	92

[a]Data are calcd on the basis of the presumed formula shown in Table III.

TABLE III

EDTA-Monohexadecylamide Metal Chelates and Sodium Salt

Central ion of chelate	Consumption of alkali[a] (mol)	Content of central metal (%)		Presumed formula[b]	IR, $\nu COO^-(cm^{-1})$			
		Found	Calcd[c]		ν_{as}^1	ν_{as}^2	ν_s	$\Delta[(\nu_{as}^1-\nu_s)]$
Al^{3+}	4	4.72	4.65	Na[M(OH)A] (octahedral)	1660	–	1382	278
Fe^{3+}	4	9.50	9.18	Na[M(OH)A] (octahedral)	1632	–	1380	252
Co^{2+}	3	9.57	9.62	Na[M(OH$_2$)A] (octahedral)	1638	–	1381	257
Ni^{2+}	3	9.54	9.59	Na[M(OH$_2$)A] (octahedral)	1620	1600	1398	222
Cu^{2+}	3	10.75	10.60	Na[MA] (square planar)	1630	1610	1390	240
Zn^{2+}	3	10.44	10.88	Na[MA] (tetrahedral)	1610	1595	1393	217
Na salt	–	–	–	Na$_3$ A	–	1597	1410	187

[a]The consumption of NaOH (mol) when 1 mol of chelate was being prepared.

[b]AH$_3$: chelating agent; A: trivalent anion of chelating agent; M: central metal ion.

[c]Calcd value for the presumed formula.

Preparation of the Metal Chelates of EDTA-Monoalkylamides

Table II shows the yield of the EDTA-monoalkylamide metal chelates obtained. Table III shows typical results of the preparation of C$_{16}$-amide metal chelates. Similar results corresponding to the other EDTA-monoalkylamide chelates were also obtained.

In the reaction of the colored metal ions (iron, cobalt, nickel and copper) with the monoalkylamides, the color changes of the solution occurred similarly to those of the reactions of these ions with EDTA. This finding implies that the mechanism of the reactions must be same as that of chelate formation with EDTA.

In Table III, the trisodium salt of C$_{16}$-amide (Na$_3$ A) has strong COO⁻ stretching vibration bands at 1597 (ν_{as}^2) and 1410 (ν_s) cm^{-1}. The chelates of nickel, copper and zinc have 2 asymmetric stretching bands, ν_{as}^1 and ν_{as}^2, respectively: the ν_{as}^1 is assigned to the carbonyl of which bonding with metal is covalent, and the ν_{as}^2 is assigned to that of which bonding with metal is ionic. There is only one of the stretching bands, ν_{as}^1, in IR spectra of aluminum, iron and cobalt chelates. Table III also shows that the frequency differences, $\Delta(\nu_{as}^1 - \nu_s)$, increased when the C$_{16}$-amide formed metal chelates. These findings led to the conclusion from the same discussion as mentioned in the previous paper (1) that the bondings of the aluminum, iron and cobalt ions with the carboxylate groups of the chelating agents are primarily covalent, respectively, and that the chelates of nickel, copper and zinc contain the 2 types of bonding with respect to the carboxylate groups: one is covalent and the other is ionic.

The consumption of sodium hydroxide for the preparation of the C$_{16}$-amide chelates is shown in the second column of Table III. Three mol of sodium hydroxide were consumed to neutralize the 3 carboxyl groups of C$_{16}$-amide in the case of cobalt, nickel, copper and zinc chelates; consequently, the 3 carboxyl groups had to be changed to carboxylate groups. In the aluminum and iron chelates, 4 mol of the alkali were consumed, in spite of which the C$_{16}$-amide had 3 carboxyl groups to be neutralized. This fact can be interpreted as follows: 3 mol of the sodium hydroxide neutralized 3 carboxyl groups to give 3 carboxylate groups and the residual hydroxide ion was coordinated by the central metal ion. These C$_{16}$-amide chelates were thus presumed to have the formula shown in Table III on the basis of our discussion on IR spectra and the alkali consumption, and the usual coordination number of the respective metal ions. The analytical results for the central metal of the chelates agreed with the calcd values

for the presumed formula (Table III). The chelates of C$_{10}$-amide, C$_{12}$-amide, C$_{14}$-amide and C$_{18}$-amide with the 6 metals must have the same structure as the C$_{16}$-amide chelates.

Surface and Interfacial Tensions

Table IV shows the experimental results for surface and interfacial activities on water-soluble chelates. The water-solubility of the chelates of EDTA-monoalkylamide was better than those of EDTA-monoalkyl esters: C$_{14}$-amide chelates were soluble in water, whereas chelates of tetradecyl derivative of the latter were insoluble. As shown in Table IV, the chelates of C$_{12}$-amide were generally superior to the chelates of C$_{10}$-amide and C$_{14}$-amide in both surface and interfacial activities, with few exceptions.

The critical micelle concentrations (cmc) of C$_{12}$-amide chelates were observed from the surface tension-concentration curves at 5×10^{-5}, 1.3×10^{-4}, 6×10^{-5}, 8×10^{-5}, 1.5×10^{-4} and 1.5×10^{-4} mol/L for aluminum, iron, cobalt, nickel, copper and zinc chelates, respectively. These cmc values are fairly lower than those of EDTA-monoalkyl ester iron chelates (C$_{10}$-ester: 13×10^{-4}; C$_{12}$-ester: 9.2×10^{-4}; oleyl-ester: 6.7×10^{-4} mol/L) (1).

Dispersing Power

The chelates having shorter alkyl length than C$_{16}$-amide did not dissolved in toluene/butanol (20:1) at concentration of 6 mg/30 mL. Figure 2 shows the sedimentary pattern of pigment (TiO$_2$) in the toluene/butanol. The pigment completely settled within few minutes in the solvent without

TABLE IV

Surface Tension and Interfacial Tension (against kerosene) of Aqueous Chelate Solution (dyne/cm)

Chelating agent	Central ion of chelate						
	Al	Fe	Co	Ni	Cu	Zn	Na[a]
Surface tension							
C$_{10}$-amide	35.2	43.5	28.9	40.2	30.2	41.9	58.9
C$_{12}$-amide	30.9	30.1	31.0	31.4	31.4	31.1	31.4
C$_{14}$-amide	36.5	40.4	34.6	44.1	43.9	38.4	62.6
Interfacial tension							
C$_{10}$-amide	10.3	6.6	0.0	3.4	5.0	6.5	4.7
C$_{12}$-amide	0.9	3.3	0.0	1.7	0.0	1.2	5.3
C$_{14}$-amide	2.3	10.6	5.3	5.7	2.1	4.1	4.6

Chelate concentration: 1×10^{-3} mol/L.

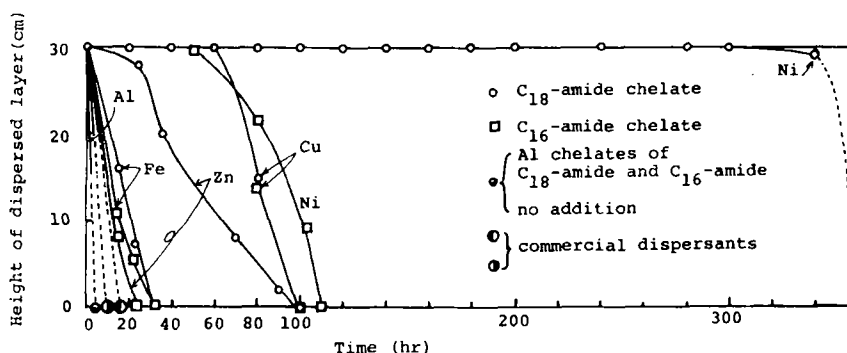[a]Na means trisodium salt of EDTA-monoalkylamide.

FIG. 2. Dispersing power of the chelates of EDTA-monooctadecylamide (C_{18}-amide) and EDTA-monohexadecylamide (C_{16}-amide). Pigment: TiO_2 (without surface treatment, rutile type), 0.3 g; surfactants: 0.0006 g; solvent: toluene/butanol (20:1), 30 mL.

TABLE V

Emulsifying Power (Time [hr] Needed for Appearance of the Oil Phase) in the System of Oil (kerosene, 2 mL) and Aqueous Chelate Solution (3×10^{-3} mol/L, 3 mL)

Chelating agent	Central ion of chelate						
	Al	Fe	Co	Ni	Cu	Zn	Na[a]
C_{10}-amide	0(21)	>100 (54)	0 (41)	>100(44)	0(0)	100(44)	>100(51)
C_{12}-amide	>100(49)	>100 (57)	0.1(9)	>100(55)	>100(50)	>100(54)	13(37)
C_{14}-amide	>100(65)	>100 (53)	0.1(35)	>100(69)	>100(63)	>100(68)	>100(55)
C_{16}-amide	>100(52)	>100 (52)	0 (19)	>100(64)	—	>100(60)	>100(51)
C_{18}-amide	>100(50)	0.4(18)	0 (0)	>100(53)	—	>100(50)	>100(54)

Figures in parentheses mean the volume ratio (%) of the emulsified phase to the total volume of emulsified, oil and water phases after 100 hr of standing.

[a]Na means trisodium salt of EDTA-monoalkylamide.

any surfactant. The addition of commercial dispersants, Homogenol L-12 (Kao-Atlas Co.) and Duomeen TDO (Lion-Armour Co.), delayed the sedimentation for 10 and 15 hr, respectively. The aluminum and iron chelates showed poor dispersing power in contrast with these metal chelates of EDTA-monoalkyl esters and of the other EDTA-derivatives (1). No clear interpretation was obtained for why these metal chelates of only this series had poor dispersing power. Figure 2 also shows that the chelates of C_{18}-amide were superior to those of C_{16}-amide and the nickel chelate of C_{18}-amide was particularly good.

Emulsifying Power

Results of emulsifying test are shown in Table V. The kerosene could not be emulsified in the control solution containing 3×10^{-3} mol/L sodium palmitate. The kerosene phase appeared 0.1 hr after shaking in the control solution of sodium dodecylbenzenesulfonate. Table V shows that the chelates had excellent emulsifying power compared to the sodium dodecylbenzenesulfonate. Many chelate solutions emulsified the kerosene for 100 hr or longer while the water phase was separated.

These results on the properties of chelate solution confirm that the central metal ion of the chelate has a specific affinity for anionic surface and water; accordingly, the chelate has excellent dispersing power for the solid such as TiO_2 in organic solvent, and strong emulsifying power for kerosene in water. Koide et al. (5) successfully applied these complexane-type surfactants to the ion flotation collector. In preliminary experiments, the authors found that some EDTA-derivatives and the chelates had very high efficiency for dispersing coal in heavy oil (coal-oil mixture) (6). The chelating agents and the chelates in this paper can be expected to be used for various applications.

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