

✿ Synthesis of EDTA-Monoalkyl Ester Chelates and Evaluation of the Surface Active Properties

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ABSTRACT

Some new chelating agents were synthesized from ethylenediamine-tetraacetic acid dianhydride and long chain alcohols. The equivalent reactions between the chelating agents and several metal ions gave the corresponding chelates in good yields. Surface- and interfacial tensions, dispersing power and emulsifying power of these chelates were determined. These chelates showed excellent surface activities, especially the dispersing and emulsifying powers.

INTRODUCTION

Some metal-containing surfactants are well known, but the studies on synthesis of the chelate surfactants which have hydrophobic alkyl groups with hydrophilic metal ions bonded to them in the chelate configuration have been sparsely reported. It was thought that the chelate surfactants in aqueous or organic solvents might have special adsorption characteristics resulting from the uncoordinated site of the central metal ion, because it is well known that aquo complexes of some transitional metal ions are favorably adsorbed on, e.g., fibers and polyvinyl alcohols.

For the last decade, the authors have synthesized several chelate surfactants and reported that the chelate solutions had good surface activities (1-8). The chelating agents for the surfactants synthesized so far are shown in Figure 1.

Dialkyl- and tetraalkyl esters of ethylenediaminetetraacetic acid (EDTA) have been synthesized (9-16) and reported to be useful for the stabilizer against oxidative degradation of fats and oils (11-14).

The metal complexes of the alkyl esters of EDTA were been reported to be light stabilizers for organic polymers (15,16). However, there is no information on monoalkyl esters of EDTA and their metal chelates.

The metal chelates of the monoalkyl esters of EDTA were expected to have greater stability constants than those of the dialkyl esters and the tetraalkyl esters, and the monoalkyl ester group to have better water-solubility than the dialkyl esters and tetraalkyl esters. The monoalkyl esters would therefore be expected to be useful as surface active agents. The object of this study was to investigate the preparation of the monoalkyl esters of EDTA and the metal chelates, and to clarify the characteristics of the metal chelates with respect to the surface activities.

The general synthetic scheme for the chelating agents and their chelates is shown in Figure 2. In this paper, monoalkyl esters of EDTA from decyl-, dodecyl-, tetradecyl-, hexadecyl-, octadecyl- and oleyl alcohols were expressed by [E-10], [E-12], [E-14], [E-16], [E-18] and [E-Oleyl], respectively.

EXPERIMENTAL PROCEDURES

Materials

EDTA (DOTITE 4H, guaranteed reagent, Dojin Chemicals Co.) was used without further purification. Decyl-, dodecyl-, tetradecyl-, hexadecyl-, octadecyl- and oleyl alcohols were used after vacuum distillation of commer-

cially purified materials. Metal salts used were $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Pb}(\text{NO}_3)_2$. All of these were extra pure grade chemicals and were used after determination of their salt contents.

Synthetic Procedure

EDTA dianhydride. EDTA dianhydride was prepared in 95.3% yield according to the method described by Geigy (17).

EDTA monoalkyl ester. The typical synthetic procedure of monodecyl ester of EDTA is as follows. EDTA dianhydride (15.4 g, 0.06 mol), dissolved in *N,N*-dimethylformamide (DMF) (200 ml), dissolved in *N,N*-dimethylformamide (DMF) (200 ml), was heated with decylalcohol (95.0 g, 0.06 mol) at 95 °C for 8 hr in a 300 ml round-bottomed flask equipped with the reflux condenser protected from atmospheric moisture. The reaction mixture gradually turned orange. Water (20 ml) was added to this solution, and the mixture was heated at 80 °C for an additional 30 min for the unreacted acid anhydride to be hydrolyzed. The reaction mixture was permitted to stand at room temperature for ca. 30 min. The small quantity of the precipitate (EDTA) deposited was removed by filtration. The product precipitated at ice bath temperature was recrystallized from 10 parts of DMF-dioxane (1:2, v/v) to give 3.4 g of pure

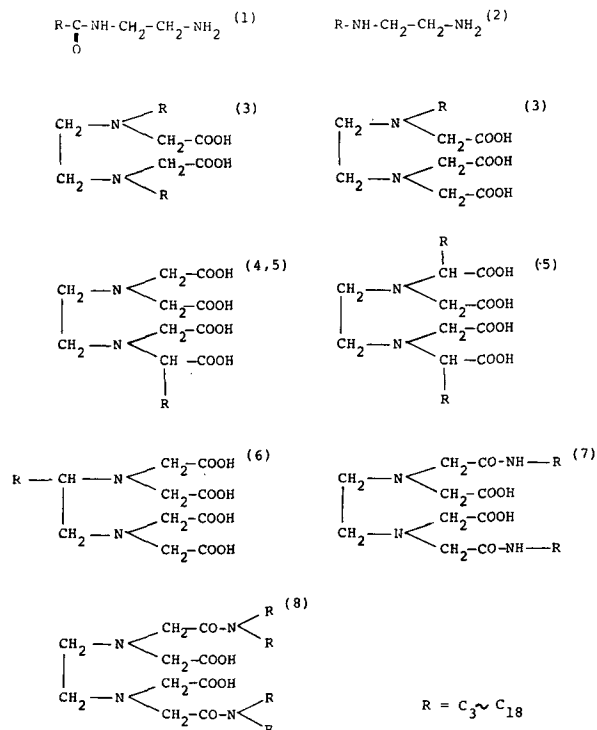


FIG. 1. Chelating agents for the chelate surfactants synthesized by authors.

product (0.0079 mol, 13% theoretical). Analysis calculated for $C_{20}H_{36}N_2$: C, 55.54; H, 8.39; N, 6.48, neutralization value (NV), 389. Found: C, 55.49; H, 8.35; N, 6.45; NV, 389. The dodecyl-, tetradecyl-, hexadecyl-, octadecyl- and oleyl homologs were synthesized in an analogous manner and were obtained in about the same yield, i.e., 13-23%. In the analytical results for carbon, hydrogen and nitrogen of the homologs, the observed values differed from the calculated values by not more than $\pm 0.4\%$.

Metal chelate of EDTA-monoalkyl esters. The general procedure is given as follows. EDTA-monoalkyl ester (1 mmol) was dissolved in the mixture of ethanol (20 ml) and N/10 sodium hydroxide (20 ml). A 0.05 g-ion/1 solution of metal nitrate (20 ml) and N/10 sodium hydroxide were alternately added by drops to the solution. The pH of the reaction mixture was maintained at the neutral point in the course of the reaction. The total volume of N/10 sodium hydroxide added was recorded. The solution was heated to dryness under reduced pressure. The crude product was purified by removal of coexisting inorganic salts using extraction with a toluene-butanol mixed solvent (40 ml). The mixing ratios of toluene to butanol for the individual metal chelates were: 1:3 for the aluminum chelate; 1:8 for the iron chelate; 1:1 for the other chelates. The solvent of the extract was evaporated. The residual solid was dried in vacuo at 60 C for 5 hr to give pure product. The 54 metal chelates were thus obtained in 60-99% yield.

The metal chelate obtained was analyzed for the sodium and the central metal by the atomic absorbance method or the EDTA titration method, after wet-decomposition (18) of the chelate. The analytical results thus obtained were in fair agreement with the calculated values for the 1:1 chelates.

Surface Activities

The measurements of surface tension and interfacial tension were made by the vertical plate method (19).

Dispersing power. The test of the dispersing power was made according to the industrial standards of Kao-Atlas Co., Ltd. (20) as follows. Titanium oxide (0.3 g; TITONE R-310; Sp.Gr. 4.2; without surface treatment; Sakai Chemical Industry Co.), the metal chelate (0.006 g; 2.0 wt% to the titanium oxide), and organic solvent (ca. 30 ml; toluene-butanol (2:1v/v), were mixed in a sedimentation glass tube (diam., 1.13 cm; height, 30 cm). After 50 vigorous shakes, the glass tube was allowed to stand undisturbed at room temperature. The height (cm) of the dispersed layer of the titanium oxide was plotted against standing time (hr) (see Fig. 5).

Emulsifying power. The emulsifying power essentially was estimated according to the manner described by Schulman and Cockbain (21) and Yoshizaki and Terashima (22). The aqueous solution of the metal chelate (3 ml; 3×10^{-3} mol/l) and kerosene (2 ml) were mixed in a test tube (25 ml). After 20 vigorous shakes, the test tube was allowed to stand undisturbed until any separation of the oil phase appeared at room temperature. The time until the appearance of the oil phase was recorded.

RESULTS AND DISCUSSION

Synthesis of EDTA-Monoalkyl Esters and Metal Chelates

The overall yields of the desired EDTA-monoalkyl esters were generally poor because the occurrence of the side reaction, dialkyl-esterification, required repeated recrystallization from DMF-dioxane to obtain the pure compounds.

In the reactions of the colored metal ions (iron, cobalt, nickel and copper) with EDTA-monoalkyl esters, the color

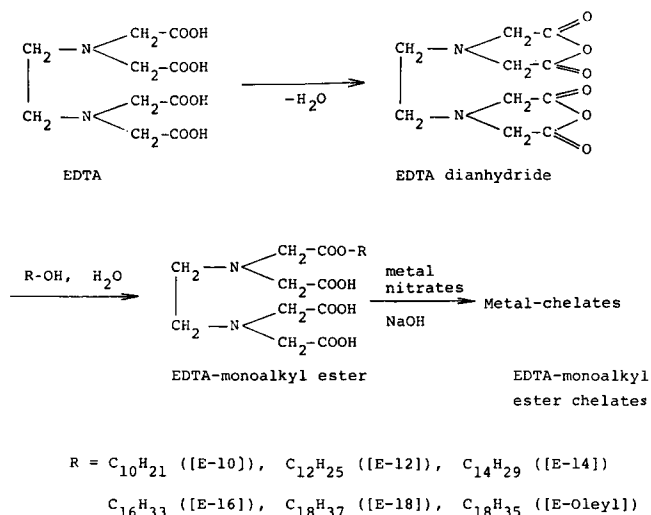


FIG. 2. Synthetic scheme of EDTA-monoalkyl ester chelates.

change of the solutions occurred similar to that of the reaction of these metal ions with EDTA. No precipitate was formed in the course of the reaction in any metal ion. This finding suggested that the metal ion which was not coordinated by the chelating agent was absent in this neutral aqueous solution, because if the metal ion being uncoordinated was present in the solution, it should precipitate as hydroxide.

Figure 3 shows typical infrared (IR) spectra of the iron chelate and the trisodium salt of EDTA-mono-hexadecyl ester in region $1700-1300 \text{ cm}^{-1}$. It was seen, by comparing the chelate with the sodium salt of IR spectra in Figure 3, that antisymmetric stretching vibration band ($\gamma_{as}C=O$) of the chelate shifted from 1595 cm^{-1} to 1632 cm^{-1} and the symmetric stretching vibration band ($\gamma_{s}C=O$) of that shifted from 1410 cm^{-1} to 1385 cm^{-1} . Busch and Bailar

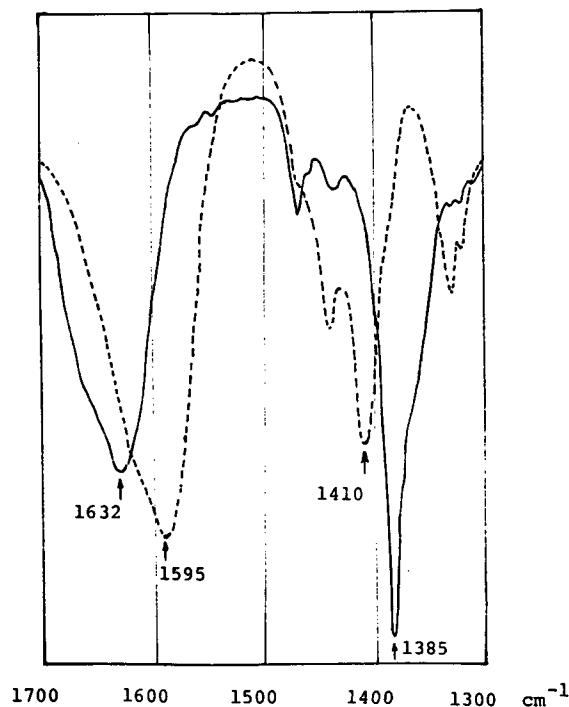


FIG. 3. Infrared spectra of the iron chelate (solid line) and the trisodium salt (dotted line) of EDTA-mono-hexadecyl ester.

TABLE I

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

Chelating agent	Central ion of chelate									
	Al	Ca	Fe	Co	Ni	Cu	Zn	Cd	Pb	Na ^a
Surface tension										
[E-10] ^b	38.4	48.8	37.8	55.9	53.4	49.3	48.0	31.4	41.1	36.6
[E-12]	27.7	35.7	34.1	42.9	36.5	39.4	42.0	31.5	36.0	25.1
[E-Oleyl]	30.2	29.2	29.2	39.1	34.0	38.4	38.4	32.3	36.8	30.8
Interfacial tension										
[E-10]	11.3	21.0	10.2	19.6	13.3	21.9	13.6	8.8	23.9	23.6
[E-12]	5.1	13.3	5.3	7.4	11.0	9.3	6.8	8.3	11.4	13.2
[E-Oleyl]	2.7	4.8	3.7	4.8	7.3	4.8	4.2	5.0	6.9	7.9

Chelate concentration: 1×10^{-3} mol/l.^aNa means trisodium salt of EDTA-monoalkyl ester.^bAbbreviations used in the table: [E-10], [E-12] and [E-Oleyl], see Fig. 2.

(23) distinguished clearly between the 3 types of carboxyl groups of EDTA and IR spectra: (a) free carboxyl group ($1750-1690\text{ cm}^{-1}$); (b) free carboxylate ion ($1610-1580\text{ cm}^{-1}$); (c) coordinated carboxylate ion ($1650-1640\text{ cm}^{-1}$). Sawyer and his co-workers (24-26) described (a) the difference in frequency between the major peak for the symmetric stretching vibration ($1450-1350\text{ cm}^{-1}$) and the peak for the antisymmetric stretching vibration ($1660-1570\text{ cm}^{-1}$) of the COO^- group indicates the degree of covalent metal-oxygen bonding for the EDTA chelates; (b) the frequency difference increases as the bonding becomes more covalent; (c) in chelates for which the difference is 225 cm^{-1} or greater the bonding is primarily covalent; (d) if the difference is less than 225 cm^{-1} the bonding is primarily ionic. Figure 3 shows that the difference in the frequency of these 2 C=O stretching bands was 247 cm^{-1} . The result led to the conclusion that the bonding of the iron ion and carboxylate is primarily covalent (24-26). In Figure 3, the absence of the shoulders at 1595 cm^{-1} and 1410 cm^{-1} indicates that all 3 COO^- groups of the chelating agent are bonded to the iron ion. In the preparation of the iron chelate, 4 mol of sodium hydroxide for 1 g-ion of iron were needed to keep the mixture neutral. It was speculated from that finding that 3 hydroxy ions were used for neutralization of the 3 carboxyl groups of the chelating agent and that 1 hydroxy ion was bonded to the iron ion. The elementary analysis of the chelate suggested that 1 molecule of water also was bonded to the iron ion.

It has been shown by Hoard et al. (27-29) that the iron chelate with EDTA is able to form a pentagonal bipyramid type of the structure in which iron is coordinated by the hexadentate EDTA and a water. They reported that the heptacoordinated structure of the iron chelate was not so unusual. This discussion and our experimental results support (but do not prove) that the structure of the iron chelate of EDTA-monoalkyl ester is $\text{Na}[\text{Fe}(\text{OH})\text{A}(\text{H}_2\text{O})]$, where A means the triacetate-form of EDTA monoalkyl ester.

Similarly, the following formulas were given on the basis of the experimental results (the consumption of sodium hydroxide, IR spectra and elementary analysis) and the usual coordination numbers of metals when AH_3 designates the chelating agent and M metal ion: $\text{Na}[\text{Al}(\text{OH})\text{A}]$ for aluminum chelate (octahedral); $\text{Na}[\text{M}(\text{A})(\text{H}_2\text{O})]$ for calcium-, cobalt-, nickel-, cadmium-, and lead chelates (octahedral); $\text{Na}[\text{M}(\text{A})]$ for copper (square planar)- and zinc (tetrahedral) chelates, respectively.

Surface and Interfacial Tensions

The water-solubility at room temperature of the chelates of [E-10], [E-12], and [E-Oleyl] were fairly good compared to those of dialkyl esters of EDTA, bis (N-alkylamide) of EDTA ([7] in Fig. 1), and bis (N,N-dialkylamide) of EDTA ([8] in Fig. 1) which had the comparable total alkyl chain length. The better water-solubility of the monoalkyl ester chelates is considered to be a result of anionic charge in the aqueous solution; almost all chelates of the dialkyl esters or the dialkyl amides of EDTA had neutral charge. It was found that the water-solubility of the chelates decreased with an increase in the alkyl chain length of the esters, but the chelate of [E-Oleyl] had similar solubility to that of the chelates of [E-10].

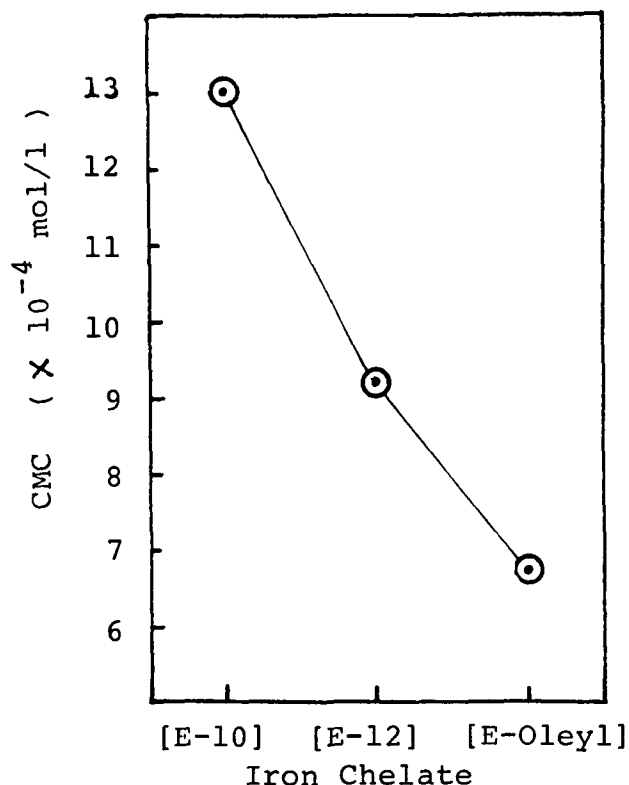


FIG. 4. Relationship between CMC and alkyl chain length of EDTA-monoalkyl ester iron chelates.

TABLE II

Dispersing Power (Time [hr] for the Complete Sedimentation of TiO_2 Pigment in the Chelate Solution of Toluene-Butanol)

Chelating agent	Central ion of chelate								
	Al	Ca	Fe	Co	Ni	Cu	Zn	Cd	Pb
[E-10]	—	—	90	20	58	63	—	—	—
[E-12]	50	—	103	42	64	85	47	—	—
[E-14]	60	—	113	45	65	63	45	—	—
[E-16]	70	60	109	53	64	85	62	—	67
[E-18]	260	100	105	52	65	103	63	70	69
[E-Oleyl]	70	88	108	55	63	110	63	98	38

Symbol (—) means the chelate is insoluble in the toluene-butanol (20:1).

Aluminum and iron chelates had better solubility compared to the other metal chelates of the same chelating agent, which presumably was caused by these chelates being coordinated by hydrophilic hydroxo ions. The sodium salts of the chelating agents were, of course, the most soluble in water because of the tribasic ion.

Table I shows the experimental results of surface and interfacial tensions of the water-soluble chelates. As shown in Table I, the chelates having longer alkyl chain length ([E-12]) were superior to that having shorter alkyl chain ([E-10]) in both surface and interfacial activities. It also was found that the chelates of trivalent metals such as aluminum and iron generally had good surface and interfacial activities. The strong hydrophilic characteristic of the aluminum and iron chelates resulting from the hydroxo ions apparently was the reason for the superiority of these chelates in surface and interfacial activities.

The relationship between the alkyl length and the CMC of the iron chelates which was obtained from the surface tension-concentration curve is shown in Figure 4. The CMC of the [E-12] chelate was less than that of the [E-10] chelate. This phenomenon agreed with the general trends expected (30,31). The CMC of [E-Oleyl] chelate was slightly lower than that of the [E-12] chelate. No clear interpretation was obtained of why some chelates had minimal activity in the relationship between the surface

activities and the alkyl chain length, and why the other chelates didn't. Further experiments are in progress.

Dispersing Power

The data plotting the time until the complete sedimentation of TiO_2 in the chelate solution of toluene-butanol are summarized in Table II. All chelates in Table II had better dispersing power than the commercial dispersants (Fig. 5). The dispersing power of many chelates increased with an increase in the saturated alkyl chain length of the chelates. Figure 5 shows the sedimentary patterns of pigment (TiO_2) in the system of the aluminum chelates and the organic solvent. As shown in Figure 5, the pigment powder settled within a few minutes in the solvent with no surfactants. The addition of commercial dispersants, "Homogenol L-12" (Kao-Atlas Co.) and "Duomeen TDO" (Lion-Armour Co.), delayed complete sedimentation for 10 and 15 hr, respectively. The aluminum chelate of [E-18] delayed the sedimentation most effectively as a dispersant in all chelates tested.

It has been shown in earlier papers (3, 5 and 6) that the aluminum or iron chelates of the same series of EDTA-derivatives ([3], [5] and [6] in Fig. 1) which are also monoanionic surfactants have the best dispersing power in the individual series. It is unclear why the aluminum and iron chelates have such superior dispersing powers. It can be

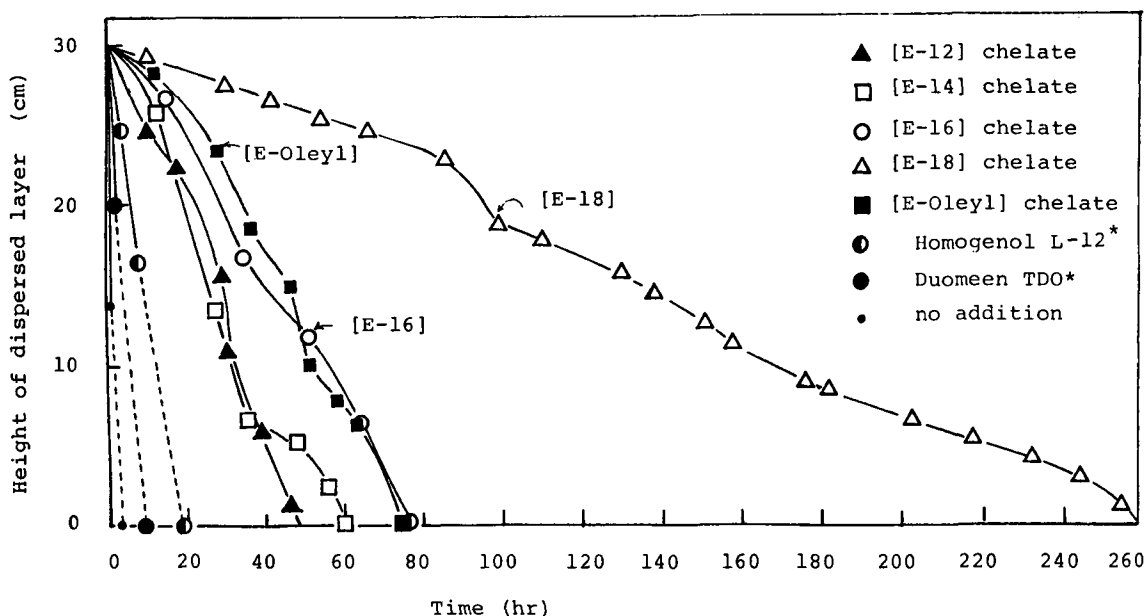


FIG. 5. Dispersing power of aluminum chelates of EDTA-monoalkyl esters and commercial dispersants. Pigment: TiO_2 (without surface treatment, rutile-type), 0.3 g; surfactants: 0.006 g; solvent: toluene-butanol (20:1), 30 ml.

TABLE III

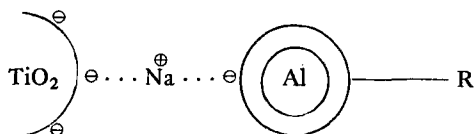
Emulsifying Power: Time Needed for Appearance of the Oil Phase in the System of Oil (Kerosene, 2 ml) and Chelate Aqueous Solution (3×10^{-3} mol/l, 3 ml)

Chelating agent	Central ion of chelate									
	Al	Ca	Fe	Co	Ni	Cu	Zn	Cd	Pb	Na ^a
[E-10]	40	4	>100	>100	21	1.0	20	0.1	21	0
[E-12]	70	20	>100	>100	>100	>100	>100	70	>100	15
[E-14]	>100	—	>100	—	—	—	>100	—	>100	14
[E-16]	>100	—	>100	—	—	—	—	—	>100	>100
[E-18]	>100	—	22	—	—	—	—	—	56	>100
[E-Oleyl]	43	55	—	>100	>100	0	>100	>100	>100	>100

Symbol (—) designates no determination.

^aNa means trisodium salt of EDTA-monoalkyl ester.

speculated that these hard acids (32), Al³⁺ and Fe³⁺, which have small ionic radii (0.50 and 0.64 Å, respectively), make hard monoanionic spheres of the chelate ring; consequently, these hard anionic spheres tightly bind to the anionic surface of TiO₂ through hard sodium ions as illustrated in Scheme I. It is implied that, the more tightly the chelate binds to the surface of the TiO₂, the more effectively the TiO₂ is protected with the alkyl group of the chelate. And,



SCHEME I.

the longer alkyl chain of the chelate gives the better affinity for the organic solvent (toluene-butanol).

Emulsifying Power

Results of the emulsifying test are shown in Table III. The tests were made for the chelates which were fully soluble in water (all chelates of [E-10], [E-12] and [E-Oleyl] and for some chelates of [E-14], [E-16] and [E-18] which were appreciably soluble in water. The kerosene could not be emulsified in the control solution containing 3×10^{-3} mol/l sodium palmitate. Kerosene was completely emulsified in the aqueous chelate solution, and no kerosene phase appeared for several hours in many cases. Table III shows that many chelates had very good emulsifying power.

These results on the properties of the chelate solution suggest that the central metal ion of the chelate has specific affinity for anionic solid surfaces or water, and consequently has excellent dispersing power for the solid such as TiO₂ in organic solvent or strong emulsifying power for the kerosene in water. The monoalkyl esters of EDTA have such exceptional chelating power that they also are expected to have specific metal-deactivating activity in organic solution. These chelate surfactants in this series are expected to have various uses because some of them are soluble in water and the others are soluble in organic solvents.

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[Received December 26, 1979]