N-Lauroyl-Ethylenediamine Chelates: Preparation and Evaluation of Surface Tension and Dispersant Properties

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Abstract

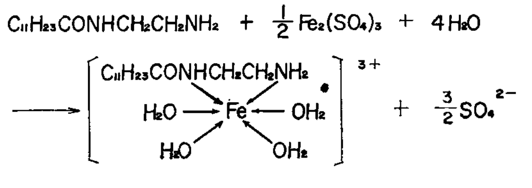
A chelate surfactant was synthesized having a hydrophobic alkyl group and hydrophilic metal ion bonded to the former in the chelate configuration, and its properties were investigated. N-lauroyl-ethylenediamine (LEDA) was used as the hydrophobic chelating agent and salts of some transitional metals (e.g. iron, cobalt, nickel, copper and chromium) were reacted therewith. The reaction of LEDA with ferric sulfate on 1:1 equivalent reaction ratio afforded $[Fe(LEDA)(H_2O)_4]\,{}^3\!/_2SO_4$. In other reactions pure chelates were not obtained, but the products showed good surface activity.

Introduction

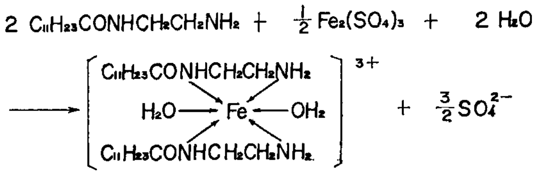
Some metal-containing surfactants are known. These are compounds of silicon or titanium, and have some interesting properties, but have not been studied extensively.

A chelate surfactant which contains a metal element in the chelate configuration as a hydrophilic component has not yet been synthesized. So we prepared some chelate surfactants by the reaction of N-lauroyl-ethylenediamine (LEDA) with metal salts.

The reaction of LEDA with ferric sulfate is shown in equations 1 to 3.



[1]



[2]

$$3\ C_{11}H_{23}CONHCH_2CH_2NH_2 + \frac{1}{2}Fe_2(SO_4)_3 \longrightarrow [Fe(C_{11}H_{23}CONHCH_2CH_2NH_2)_3]^{3+} + \frac{3}{2}SO_4^{2-} \qquad [3]$$

Experimental Procedures

Materials

Lauric acid was of certified reagent grade mp. 43.5 C, acid value 284.9 (calculated, 280.1). Ethylenediamine was used after vacuum distillation of commercially purified material. Metal salts used were:

$Al_2(SO_4)_3$, $Cr_2(SO_4)_3nH_2O$, $MnSO_4nH_2O$, $Fe_2(SO_4)_3nH_2O$,
$CoSO_47H_2O$, $NiSO_47H_2O$, $CuSO_45H_2O$:
$CrCl_36H_2O$, $FeCl_3$, $CoCl_26H_2O$, $CuCl_22H_2O$, $ZnCl_2$,
$AgNO_3$, $CdCl_22\frac{1}{2}H_2O$, $SnCl_22H_2O$:

All of these were extra pure grade chemicals. The reagents for which the water of crystallization were unknown were used in aqueous solution after determining their salt contents.

LEDA

LEDA was prepared according to the method of Takase (1) and Agre et al. (2) as follows: 240 g (4 mole) of ethylenediamine were put in a 1000 ml four-necked flask attached to a condenser, a thermometer, a nitrogen tube and a sealed stirrer; then 200 g (1 mole) of lauric acid dissolved in 100 ml of ethanol was added. The flask was dipped in an oil bath, and heated slowly under flowing nitrogen gas. The reaction reached 145 C after distilling off the ethanol, then a reflux condenser replaced the distillation condenser, and the reaction was continued at this temperature for 3 hr under reflux. Then the distillation condenser was re-attached to the flask in place of the reflux condenser, the reaction mixture was heated to 200 C, and the reaction was stopped. After cooling, a waxy solid substance was removed, milled and dissolved in 300 ml of ethanol. The mixture was permitted to stand overnight in a refrigerator after warming the solution once. Insoluble material (N,N′-dilauroyl-ethylenediamine) was filtered out, ethanol was recovered from the filtrate by distillation, and the crude product was obtained as residue (yield 21%). A flaky crystal of the product was gained from the crude after recrystallization from ligroin. Analysis: Calculated for LEDA ($C_{14}H_{30}N_2O$); MW, 242.4; N, 11.6%; mp, 80–82 C. Found: MW, 246; N, 11.6%; mp, 80–81 C.

TABLE I
Reaction of LEDA With Ferric Sulfate

LEDA: Fe^{3+} equivalent ratio	LEDA		Fe^{3+} gram ion	Reacting solution		Products		Precipitates		Products yield[a] (%)
	mol	(g)		pH	Color	Yield (g)	Color & appearance	Yield (g)	Color	
1:1	$\frac{10}{1000}$	2.424	$\frac{10}{1000}$	2.55	Red: Clear	5.243	Yellowish red: Rosinous	0	....	102
2:1	$\frac{1}{1000}$	0.242	$\frac{0.5}{1000}$	4.10	Yellowish red Cloudy	0.334	Yellowish red Waxy	0.045	Light brown	92.6
3:1	$\frac{1.2}{1000}$	0.290	$\frac{0.4}{1000}$	5.80	Orange Cloudy	0.351	Yellowish red	0.044	Brown	94.6

[a] Calculated values respectively from formulas [1], [2], [3].

TABLE II

Synthesis of LEDA-Metal (1:1) Sulfate Chelates

Metal ion	Solution of metal salts		pH of reacting solution	Products			Yield[a] (%)	Precipitates	
	Color	pH		Yield (g)	Color	Appearance		Color	Yield (g)
Al^{3+}	Colorless	2.5	3.2	0.379	Ivory	Waxy	78	White	0.031
Cr^{3+}	Deep greenish blue	1.6	4.0	0.379	Deep green	Waxy	74	Grayish blue	0.091
Mn^{2+}	Pink	3.9	8.2	0.378	Yellowish gray	Paraffin like	81	Brown	0.050
Co^{2+}	Red	4.2	7.0	0.313	Red purple	Paraffin like	67	Grayish blue	0.082
Ni^{2+}	Green	5.3	7.7	0.318	Yellowish green	Waxy	68	Yellowish green	0.088
Cu^{2+}	Blue	3.1	4.6	0.317	Light green	Waxy	72	Light blue	0.122

[a] Yield (%) = Yield (g) of product/theoretical yield (g) × 100. Theoretical yield (g): Calculated values as LEDA-metal monochelate, coordinated with 4 water molecules (but only 2 water molecules in the case of Cu^{2+}).

Synthesis and Analysis of LEDA Chelate Sulfates

LEDA-Fe Sulfate Chelates. LEDA ethanol solution (12%) was added to a ferric sulfate aqueous solution (0.518×10^{-3} g ion/g) as shown in Table I. Then water was added to the mixture to a volume equal to that of ethanol. When any precipitate was formed, it was filtered out, and the filtrate was heated to dryness on a water bath and then was completely dried at 60 C in vacuum for 2 hr.

Other LEDA-Metal Sulfate Chelates. LEDA (0.001 mole) and various metal sulfates (0.001 g ion) were reacted by the same method as above, and the chelates of Table II were synthesized. The precipitates in the cases of aluminium, cobalt and nickel chelates were incompletely recovered.

Analyses. Nitrogen by Kjeldahl Method: After adding a small amount of conc. nitric acid and heating, the sample was decomposed, and the metal was determined by the following methods:

Iron, aluminium, chromium and cobalt: Ignited, metallic oxides weighed.

Manganese: Sodium bismuthate method.

Nickel: Dimethylglyoxime-acetate method.

SO_4^{2-}: Weighed as $BaSO_4$ (instantly isolated after addition of $BaCl_2$).

H_2O: Karl Fischer Method (methanol solvent).

LEDA-Metal Chloride or Nitrate Chelates. Silver nitrate and some other metal chlorides were reacted with LEDA in 1:2 equivalent ratio by the same method as in the case of sulfate chelates. LEDA was dissolved in ethanol (containing water–4:1), then used as a 9% solution. Nitrate was used only in the case of silver. Chromium, iron and silver chelates were prepared by adding 0.185×10^{-3} g ion of chromium, iron and silver to 0.370×10^{-3} mole of LEDA. Other metal chelates were prepared by adding the metal ion (1×10^{-3} g ion) to 2×10^{-3} mole of LEDA. Results are listed in Table III. Color changes were observed, and precipitates occurred in all cases.

Analyses. Silver: by adding a small amount of conc. nitric acid and heating, the mixture was dissolved in dilute nitric acid, dilute hydrochloric acid was added, and precipitated silver chloride was filtered and weighed. Other metals: determined as metallic oxides by the method similar to the case of sulfate chelates.

Specific Surface Tension. A stalagmometer method was adopted (Japanese Industrial Standard K 3362). Measurement was done within 1 hr after dissolving the chelate surfactants.

Dispersing Power. Dispersing power for inorganic pigment (Titanium oxide—rutile type) was measured by using sedimentation tubes. Organic solvent: For sulfate chelates, toluene-butanol (20:1) mixture. For other chelates, toluene. Sedimentation tube: Dia., 1 cm; height, 30 cm. Titanium oxide (0.3 g), chelate surfactants (0.006 g, 2.0% to the pigment) and organic solvent (30 cm height) were mixed in the tube, and the mixture was allowed to stand overnight,

TABLE III

Synthesis of LEDA-Metal (2:1) Chloride or Nitrate Chelates[a]

Metal ion	CN[b]	Color of metal salt solution	pH of reacting solution	Products			Theoretical yield (g)[c]	Yield (%)[d]	Precipitates	
				Yield (g)	Color	Appearance			Color	Yield (g)
Cr^{3+}	6	Deep green	4.3	0.128	Grayish green	Paraffin like	0.126	102	....	0.001
Fe^{3+}	6	Yellowish brown	2.2	0.121	Yellowish red	Waxy	0.126	96	....	0
Co^{2+}	6	Pink	8.3	0.457	Blue	Waxy	0.651	70	Light blue	0.153
Cu^{2+}	4	Blue	7.8	0.463	Dark green	Waxy	0.619	75	Blue	0.148
Zn^{2+}	4	Colorless	8.2	0.398	Yellowish orange	Paraffin like	0.621	64	White	0.193
Ag^{+}	4	Colorless	9.9	0.122	Yellowish gray	Waxy	0.121	100	....	Trace
Cd^{2+}	4	Colorless	10.5	0.588	Yellowish white	Waxy	0.668	86	White	0.139
Sn^{2+}	6	Milky white	10.3	0.577	Yellow	Waxy	0.710	81	White yellow	0.131

[a] Nitrate was used only in the case of Ag^{+}.

[b] Coordination number.

[c] Calculated values as LEDA-metal bis-chelates coordinated with 2 water molecules in cases of Cr^{3+}, Fe^{3+}, Co^{2+} and Sn^{2+}, and 0 water molecule in cases of Cu^{2+}, Zn^{2+}, Ag^{+} and Cd^{2+}.

[d] Yield of product (g)/Theoretical yield (g) × 100.

TABLE IV
Analysis of LEDA-Fe Sulfate Chelates

LEDA:Fe^{3+} equivalent ratio	Products								Precipitates	
	N (%)		Fe (%)		SO_4 (%)		H_2O (%)		Found Fe (%)	Calc. as $Fe(OH)_3$ Fe(%)
	Found	Calc.[a]	Found	Calc.[a]	Found	Calc.[a]	Found	Calc.[a]		
1:1	5.41	5.44	10.22	10.86	27.6	28.1	14.7	14.0	......	......
2:1	8.42	7.77	3.73	7.75	......	......	5.1	5.0	43.1	52.3
3:1	9.02	9.06	0.36	6.02	......	......	5.3	0	47.5	52.3

[a] Calculated from formulas [1], [2], [3].

then shaken severely 50 times. Any change of sedimentation above the top of pigment layer was measured at 20 C.

Results and Discussion

LEDA-Fe Sulfate Chelates

The aqueous solution of ferric sulfate had a yellowish brown color. However when adding the colorless LEDA ethanol solution to the aqueous solution (1:1 equivalent ratio), the color of the solution changed from yellowish brown to red. This color change was similar to that in the case of adding ethylenediamine to ferric sulfate solution.

In the cases of the reactions of LEDA:$Fe^{3+} = 2:1$ and of LEDA:$Fe^{3+} = 3:1$, the color changes of the reacting solution were less than the former case. The 1:1 reactant did not give any precipitate and the product was soluble in butanol, so that it became clear that the product did not contain unreacted ferric sulfate and also did not include the 2:1 chelate [2] and the 3:1 chelate [3].

Table IV lists the analytical data for LEDA-Fe sulfate chelates. In Table IV, since the sulfate part of the 1:1 reactant was instantly precipitated as barium sulfate by adding barium chloride aq. solution, it seems that the sulfate part was not directly combined to iron by coordination. Then we can conclude from Table IV that the product (1:1) is a chelate molecule which is constructed from a center iron atom, one LEDA molecule which is bonded to iron atom by chelate bond and 4 coordinated water. However, the product (1:1) showed low pH in aq. solution (Table VIII) and indicates that the water molecules coordinated to iron are substituted partly with hydroxo ion in aq. solution.

Reactants (2:1) and (3:1) gave precipitates respectively, and each precipitate contained much iron, hence it seemed that the chelate component contents were small in these products. Solubility of LEDA-Fe (1:1) chelate is: soluble solvents: water, methanol, ethanol, butanol, ethanol-ligroin (3:100), ethanol-benzene (5:100), butanol-toluene (1:10); insoluble or partially soluble solvents: acetone, ligroin, benzene, toluene. The test was made by dissolving about 30 mg of the sample in about 1.5 ml of the solvent at 27 C.

TABLE V
Analysis of LEDA-Metal (1:1) Sulfate Chelates

Metal ion	**Products**						Precipitates	
	N (%)		Metal (%)		H_2O (%)		Found metal (%)	Calc. as hydroxide metal (%)
	Found	Calc.[a]	Found	Calc.[a]	Found	Calc.[a]		
Al^{3+}	6.8	5.8	3.6	5.6	14.8	14.9	20.7	34.6
Cr^{3+}	6.1	5.5	6.2	10.2	8.9	14.1	29.0	50.5
Mn^{2+}	6.6	6.0	8.6	11.8	8.6	15.5	47.4	63.4
Co^{2+}	8.0	6.0	2.4	12.6	6.1	15.4	47.4	63.4
Ni^{2+}	8.6	6.0	3.5	12.5	12.2	15.4	15.5	63.3
Cu^{2+}	8.9	6.4	2.4	14.5	9.0	8.2	46.7	65.1

[a] Calculated values as LEDA-metal mono-chelates, coordinated with 4 water molecules, but 2 water molecules in the case of Cu^{2+}.

TABLE VI
Analysis of LEDA-Metal (2:1) Chloride or Nitrate Chelates

Metal ion	Products metal (%)		Precipitates	
	Found	Calc.[a]	Found metal (%)	Calc. as hydroxide metal (%)
Cr^{3+}	7.6	7.6	......	......
Fe^{3+}	8.3	8.2	......	......
Co^{2+}	0.8	9.0	49.1	53.6
Cu^{2+}	5.3	10.3	24.3	65.1
Zn^{2+}	5.5	10.5	20.2	65.8
Ag^{+}	15.9	16.5	......	......
Cd^{2+}	5.0	16.8	46.6	76.8
Sn^{2+}	3.3	16.7	79.0	77.7

[a] Based on the theoretical yield (Table III, c).

When the solution of LEDA-Fe (1:1) chelate was heated or permitted to stand for several hours, some precipitates were formed. Recrystallization of this chelate by using the above solvents was not successful.

Other LEDA-Metal (1:1) Sulfate Chelates. With regard to the products of which reactants gave both a small quantity of precipitate and plenty of the products (Table II), the determined values agreed relatively well with those calculated for N% in Table V. The precipitates showed relatively higher contents of metal; consequently the products had higher contents of nitrogen and lower contents of metal than the calculated values. The chromium chelate in Table V was insoluble in water.

LEDA-Metal (2:1) Chloride or Nitrate Chelates. The changes of color of the reactant solutions were also observed in these cases (Table III). In the case of iron no precipitate was formed, of silver and chromium very little formed, and of other metals much precipitate formed.

Table VI shows the analytical data for these chelates. The observed metal contents of the products were appreciably less than the calculation except for the cases of iron, silver and chromium. This must be attributed to the fact that much metal ion was precipitated in that reaction, and it is presumed that these products contain the tris-chelates or the LEDA-

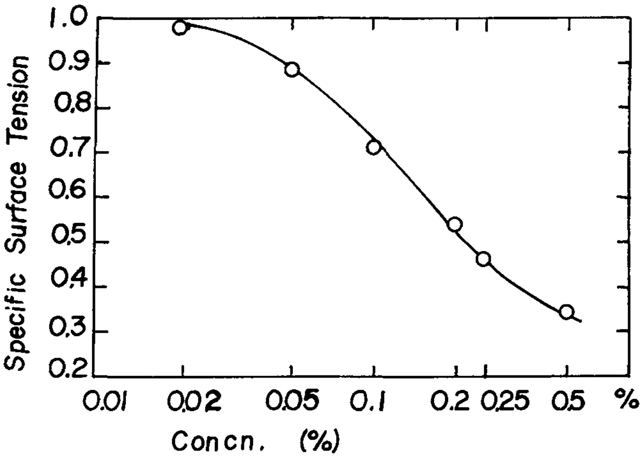


FIG. 1. Specific surface tension of LEDA-Cu (2:1) chloride chelate in aq. solution.

TABLE VII

Specific Surface Tension and pH of LEDA-Fe(1:1) Sulfate Chelates in Aq. Solution

	0.02%	0.05%	0.1%	0.2%	0.25%	0.5%
Specific surface tension	0.98	0.86	0.77	0.64	0.64	0.48
pH	3.9	3.3	3.1	3.1	3.0	2.9

TABLE VIII

Specific Surface Tension and pH of LEDA-Metal (1:1) Sulfate Chelates in 0.25% Aq. Solution

Metal ion	Specific surface tension	pH
Al^{3+}	0.51	4.4
Cr^{3+}	insoluble	....
Mn^{2+}	0.47	5.7
Co^{2+}	0.44	5.7
Ni^{2+}	0.45	5.9
Cu^{2+}	0.49	4.5

TABLE IX

Specific Surface Tension and pH of LEDA-Metal (2:1) Chloride or Nitrate Chelates in 0.25% Aq. Solution

Metal ion	Specific surface tension	pH
Cr^{3+}	0.63	4.9
Fe^{3+}	0.65	3.2
Co^{2+}	0.59	7.2
Cu^{2+}	0.47	6.6
Zn^{2+}	0.64	6.9
Ag^{+}	0.86	....
Cd^{2+}	0.68	6.9
Sn^{2+}	0.69	6.5
(LEDA · HCl)[a]	0.68	....

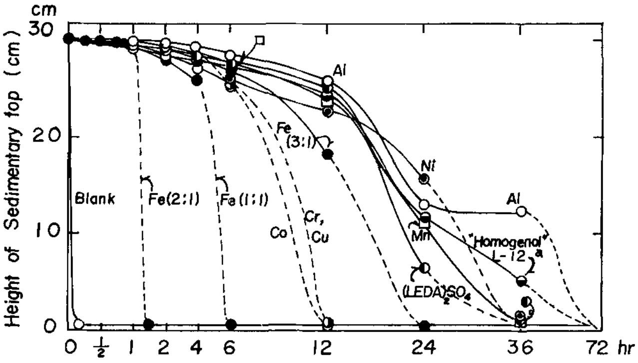
[a] LEDA chloride.

chloride. In the cases of iron, chromium and silver chelates, their metal contents agreed with the calculated values as bis-chelates, but their molecular structures were not apparent because of coordination of chlorine in the cases of the chelates formed from chloride.

Specific Surface Tension. Table VII shows specific surface tension and pH of LEDA-Fe (1:1) sulfate chelate aq. solutions in various concentrations. As to other sulfate chelates, the same properties are tabulated in Table VIII in 0.25% aq. solution.

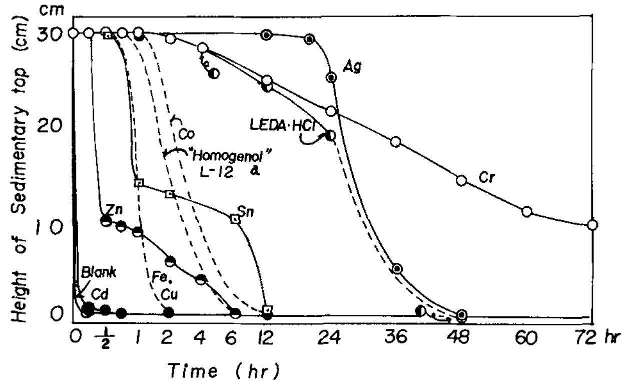
The specific surface tension-concentration curve of LEDA-Cu (2:1) chloride chelate is drawn in Figure 1. Table IX shows specific surface tension and pH values of other metal chloride or nitrate chelates in 0.25% aq. solution.

LEDA-Fe (1:1) sulfate chelates have little appreciable surface activity as shown in Table VII, however LEDA-Cu (2:1) chloride chelate is somewhat superior (Fig. 1). LEDA-Co (2:1) chloride chelate has also considerable surface activity (Table IX).



a Dispersing agent (KAO products)

FIG. 2. Dispersing power of LEDA-metal (1:1) sulfate chelates (TiO_2/toluene-butanol).



a Dispersing agent (KAO products)

FIG. 3. Dispersing power of LEDA-metal (2:1) chloride or nitrate chelates (TiO_2/toluene).

Dispersing Power. Figures 2 and 3 show respectively the dispersing power of LEDA-Metal (1:1) sulfate chelates and LEDA-Metal (2:1) chloride or nitrate chelates for titanium oxide.

In Figure 2, the aluminium chelate has excellent dispersing power, such that the sedimentation was not completed after 36 hr and is superior to LEDA-sulfate. In Figure 3, it is shown that chromium and silver chelates have superior dispersing power (especially chromium chelate). And the dispersing power of these chelates (Fig. 2–3) was compared with that of other commercial dispersant "Duomeen TDO" (Lion Armour Co., Ltd.). According to these results in both cases of toluene-butanol and toluene solvents, more effective chelates in their dispersing powers (Fig. 2–3) were as effective as "Duomeen TDO." These chelates must be mixtures with LEDA sulfate or chloride. The fact that these chelates are better dispersants than the LEDA salts means that the pure chelates are superior. The excellent dispersing power of these chelate compounds shows that there is an attractive force between the chelate parts of the compounds and the surface of the titanium oxide. These chelates did not affect the color of the white titanium oxide pigment except the dark color chelates (iron and chromium) at their use concentration.

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