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Synthesis and Properties of Surface Active Organotitanium Compounds. I

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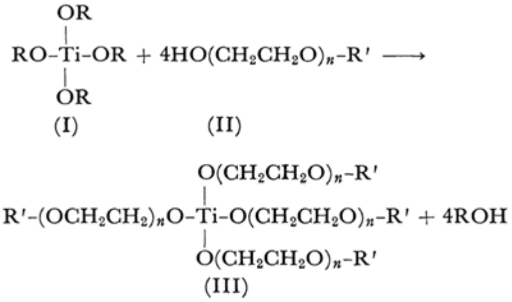
An entirely new series of surface-active polyethenoxy titanium esters which can be prepared by reactions with tetraalkoxy titanium and various polyoxyethylene higher alkyl ethers have been developed. The new series of the titanium compounds are nonionic surface-active agents and have the following general formula: $Ti[O(CH_2CH_2O)_nR']_4$ (the R′ value is higher alkyl radicals). The compounds are viscous liquids or waxy solids; they are soluble in various organic solvents, and some of them are soluble in water. These compounds have dispersing power on titanium oxide in aqueous and non-aqueous media. In this paper, the preparation and properties of these compounds will be described in comparison with the usual nonionic surface-active agents.

Many data have been reported on the synthesis and chemical and physical properties of surfactants, and recently one of the most important problem in research into surfactants is developing of new-type ones. Sowa and Kenny prepared the surface-active complexes of higher alkyl amine by reacting those amines with halogenosilane or titanium tetrahalide.[1] Koehler *et al.* prepared the derivatives of alkanolamine silicate and used them as a dispersant for inorganic pigments in non-aqueous media and some plastics.[2] Sommer investigated organosilanes containing carboxy-substituted alkyl radicals, and used them, as water-repellent agents.[3] Klein obtained water-soluble alkylsilicate esters[4] by reacting silicon esters with polyethylene glycol and found they were useful as water-repellent agents for textile fiber. Organozirconium derivatives[5] were also obtained by Koehler *et al*; they were used as a dispersant in paint, varnish and organic-based ink media.

The present authors intended to synthesize a new type of nonionic surfactant derived from organic titanium esters by an ester exchange reaction with polyoxyethylene higher alkyl ether and tetra *n*-butoxy titanium. This paper will describe the synthesis of a series of polyethenoxy titanium esters and will compare their chemical and physical behavior with that of conventional nonionic surface-active agents of the polyethenoxy type.

Tetraalkoxy titanium (I) was allowed to react with a nonionic surfactant (II) in the presence of an inactive organic solvent such as toluene under unhydrous conditions; a low-molecular-weight alcohol was thus isolated. The reaction was considered to be as follows.



$$\underset{\text{(I)}}{RO-\overset{\displaystyle OR}{\underset{\displaystyle OR}{Ti}}-OR} + \underset{\text{(II)}}{4HO(CH_2CH_2O)_n-R'} \longrightarrow$$

$$\underset{\text{(III)}}{R'-(OCH_2CH_2)_nO-\overset{\displaystyle O(CH_2CH_2O)_n-R'}{\underset{\displaystyle O(CH_2CH_2O)_n-R'}{Ti}}-O(CH_2CH_2O)_n-R'} + 4ROH$$

$R=C_4H_9-$, C_3H_7- , $n=2, 6, 10, 25, 40$
$R'=C_{12}H_{25}-$, $C_{16}H_{33}-$, $C_6H_4C_8H_{17}-$

After the removal of the solvent and alcohol formed through the reaction, the residue was a viscous liquid or a waxy solid, according to the number of "*n*" values in formula (III). Some of the products (III) were found to be soluble in water and showed surface-active characteristics. Table 1 gives the chemical formulas of the products and their appearances.

TABLE 1. STATE OF SURFACE-ACTIVE ORGANOTITANIUM COMPOUNDS

Compound	State
$Ti[O(CH_2CH_2O)_2C_{12}H_{25}]_4$	Viscous, slightly yellowish white liquid
$Ti[O(CH_2CH_2O)_6C_{12}H_{25}]_4$	Milky white paste
$Ti[O(CH_2CH_2O)_{10}C_{12}H_{25}]_4$	Waxy white solid
$Ti[O(CH_2CH_2O)_{25}C_{12}H_{25}]_4$	Waxy white solid
$Ti[O(CH_2CH_2O)_{12}C_{16}H_{33}]_4$	Waxy white solid
$Ti[O(CH_2CH_2O)_{25}C_{16}H_{33}]_4$	Waxy white solid
$Ti[O(CH_2CH_2O)_{40}C_{16}H_{33}]_4$	Waxy white solid
$Ti[O(CH_2CH_2O)_{10}C_6H_4C_8H_{17}]_4$	Viscous yellow liquid

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1) F. J. Sowa and E. J. Kenny, U. S. Pat. 2580473.
2) J. O. Koehler and H. Lamprey, *Metal-Organic Compounds*, 217 (1957).
3) L. H. Sommer, U. S. Pat, 2589445.
4) D. X. Klein, U. S. Pat. 2476307.
5) J. O. Koehler *et al.*, U. S. Pat. 2978347.

Experimental

Synthesis of Compounds. The compounds of the III type were prepared by the ester exchange method. The tetra-*n*-butoxy titanium was heated in benzene or toluene together with the calculated amount of polyoxyethylene higher alkyl ether. The butyl alcohol formed through the reaction and the solvent used were distilled *in vacuo*.

On the other hand, whether or not these reactions proceeded was confirmed by another ester exchange reaction in which tetraphenoxy titanium was used instead of tetrabutoxy titanium. Tetraphenoxy titanium has the reddish-orange color[6] which is characteristic of the Ti–O-phenyl bond.[7] During the reaction, the reddish-orange color gradually diminished, until at last the color characteristic of tetraphenoxy titanium vanished. The elimination of this red color was used as an indication of the end of the ester exchange reaction. The properties of this resultant compound coincided with those of that prepared from tetrabutoxy titanium.

Since nonionic surfactants are condensation products of polyoxyethylene with higher alcohol, it is difficult to purify them with such usual organic procedures as distillation and recrystallization.

Our samples were especially supplied by the Laboratory of the Nihon Surfactant Company; the higher alcohol and ethylene oxide were extra pure, and the conditions of the condensation were controlled with care. However, we considered the properties of these compounds to be average.

Polyoxyethylene higher alkylether titanium esters prepared from tetrabutoxy titanium and the polyoxyethylene higher alkyl ethers can not be purified. Therefore, the solvent and the butyl alcohol formed through the reaction were completely removed *in vacuo*.

From the fact that the physical properties of the products are quite different from those of the starting materials, new compounds may be supposed to be obtained from this reaction.

Reagents. *Tetra-n-butoxy Titanium.*[8] The solution of titanium tetrachloride in *n*-butyl alcohol was diluted with benzene and treated with ammonia. After the removal of the ammonium chloride and the solvent, the tetra-*n*-butoxy titanium was distilled under reduced pressure. bp 174°C/6 mmHg. (Found: Ti, 14.06%. Calcd for $C_{16}H_{36}O_4Ti$: Ti, 14.07%)

Nonionic Surface-Active Agents. Employed in this experiment were polyoxyethylene monolauryl ethers ($n=2$, OH value 207.1; $n=6$, OH value 125.0: $n=10$, OH value 89.9; $n=25$, OH value 45.1,) and polyoxyethylene monocetyl ethers ($n=12$, OH value 69.2; $n=25$, OH value 39.8; and $n=40$, OH value 26.9), all supplied by the Laboratory of the Nihon Surfactant Co. Their chemical formulas corresponded to the following: $HO(CH_2CH_2O)_nC_{12}H_{25}$, $HO(CH_2CH_2O)_n \cdot C_{16}H_{33}$. The polyoxyethylene monooctylphenyl ether was a commercial one named Triton-X-100 ($n=10$, OH value 93.6; $HO(CH_2CH_2O)_nC_6H_4C_8H_{17}$.

In each of these polyoxyethylene higher alkyl ethers, it was anticipated that there was some distribution of the chain length of polyethenoxy groups. Therefore, our data on polyethenoxy titanium esters should be considered to be those of the mean properties. As the organic titanates are usually hydrolized with a trace of water, care was taken to remove the water from the starting materials in the synthesis. The water in polyoxyethylene higher alkyl ether was removed by azeotropic distillation with toluene before use.

Titanium Oxide. The titanium oxide used was the No. 820 Rutyl type, supplied by the Ishihara Sangyo Co.; it was stored under dried atmosphere.

Solvents. Benzene and toluene were dried over phosphorus pentoxide, distilled, and then stored over metallic sodium.

Analysis of Titanium.[8] Samples were dissolved in dilute nitric acid, and the gravimetric method was used for the determination of the titanium, followed by ignition to TiO_2.

Preparation of the Tetrapolyethenoxy Laurylether Titanium Ester (n=10). A round-bottomed four-necked flask, fitted with a stirrer, a thermometer, and a reflux condenser equipped with a calcium chloride tube, was used. In this flask were placed 50.1 g of polyoxyethylene monolauryl ether ($n=10$), 6.8 g of tetra-*n*-butoxy titanium, and 40 m*l* of benzene. The mixture was then allowed to reflux for half an hour. After the solvent and *n*-butyl alcohol formed through the reaction had been removed out under reduced pressure, there was obtained a waxy white solid which was soluble in benzene and in water. Yield, 94.4%.

(Found: Ti, 1.84%. Calcd for $C_{128}H_{260}O_{44}Ti$: Ti, 1.88%.)

In a similar way the compounds $Ti[OCH_2CH_2O)_n \cdot C_{12}H_{25}]_4$ ($n=2$, 6, 25), $Ti[O(CH_2CH_2O)_nC_{16}H_{33}]_4$ ($n=12$, 25, 40), and $Ti[O(CH_2CH_2O)_{10}C_6H_4C_8H_{17}]_4$ were prepared from tetra-*n*-butoxy titanium with corresponding amounts of polyoxyethylene mono alkyl ethers. The reaction conditions and the results obtained are listed in Table 2.

Determination of Properties. *Stability.* Each sample was weighed (0.5 g) and dissolved in 50 m*l* of distilled water at room temperature. The solution was then allowed to stand in order for its stability to be observed for hydrolysis.

Surface Tension. The surface tension was measured by the drop-weight method, with a tip 0.733 cm in diameter, in a thermo bath at 25°C. There was no appreciable change in surface tension with the time within two minutes after the formation of droplets. The correction of Harkins and Brown[9] was applied.

Cloud Point. Cloud points were determined on solutions containing 0.1 wt% of the compounds. The cloud point was taken as the temperature at which a noticeable turbidity first appeared upon the slow heating of the solution in a water bath.

Dispersion. The apparatus for measuring the settling consisted of a glass tube, 30 cm high and 1 cm in diameter, connected with a stopper. Occasionally, a stopper with two cocks was used. Dried at 110°C overnight, and ground powder of TiO_2 was weighed in a

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[6] T. Yoshino, I. Kijima, M. Ochi, A. Sampei and S. Sai, *Kogyo Kagaku Zassi, (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **60**, 1124 (1957).

[7] J. H. Haslam, *Metal-Organic Compounds,* 274 (1957).

[8] D. C. Bradley, D. C. Hancock and W. Wardlaw, *J. Chem. Soc.,* **1952**, 2773.

[9] W. D. Harkins and F. E. Brown, *J. Am. Chem. Soc.,* **41**, 499 (1919); in International Critical Tables, Vol. IV, 435, McGraw-Hill, New York (1928).

Table 2. Reaction conditions and titanium analysis

Compound	Solvent	Time of reaction min	Yield %	Ti % Found	Ti % Calcd
$Ti[O(CH_2CH_2O)_2C_{12}H_{25}]_4$	Benzene	30	91.0	4.33	4.20
$Ti[O(CH_2CH_2O)_6C_{12}H_{25}]_4$	Benzene	30	94.8	2.61	2.59
$Ti[O(CH_2CH_2O)_{25}C_{12}H_{25}]_4$	Benzene	30	96.1	1.01	0.92
$Ti[O(CH_2CH_2O)_{12}C_{16}H_{33}]_4$	Benzene	30	95.4	1.68	1.53
$Ti[O(CH_2CH_2O)_{25}C_{16}H_{33}]_4$	Benzene	30	95.0	0.99	0.87
$Ti[O(CH_2CH_2O)_{40}C_{16}H_{33}]_4$	Benzene	30	96.6	0.59	0.59
$Ti[O(CH_2CH_2O)_{10}C_6H_4C_8H_{17}]_4$	Benzene	30	96.8	1.81	1.82
$Ti[O(CH_2CH_2O)_{10}C_6H_4C_8H_{17}]_4$	Toluene	30	95.1	1.80	1.82

(Here the " time of reaction " means the time of reflux; it does not include the time spent for the removal of the solvent.)

glass tube, the air in glass tube was pumped out through the two cock stoppers to examine the effect of the water entered during the operation, and then 30 m*l* of the sample solution was poured on it. The tightly-stoppered cylinder was shaken vigorously and then allowed to stand. The volume of settling was observed at constant time intervals. In this experiment, no remarkable difference could be found between a non-pumped-out system and a pumped-out system. Therefore, most of the experiments were carried out in a non-pumped-out system.

Results and Discussion

Stability. The polyoxyethylene higher alkyl ethers, the original titanium esters, and all the compounds prepared were soluble in benzene, toluene, carbon tetrachloride, and monochloro benzene. There was no difference in solubility in organic solvents among the starting materials and the products. However, some differences in solubility in water were found between tetra-*n*-butoxy titanium and polyethenoxy alkylether titanium esters. Tetra-*n*-butoxy titanium was hydrolyzed rapidly, even with a trace of water, and changed into an insoluble condensed structure. However, the polyethenoxy alkylether titanium esters, consisting of from ten to fifteen polyethenoxy groups, were soluble in water and kept their stability for a few days without decomposition. On the other hand,

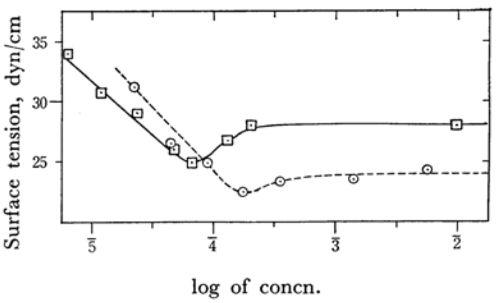

Fig. 1. The surface tension - log concentration curves of tetra polyoxyethylene laurylether titanium ester ($n=10$) and polyoxyethylene monolauryl ether. Temp.: 25°C.

—⊡— Tetra polyoxyethylene laurylether titanium ester

···⊙··· Polyoxyethylene monolauryl ether

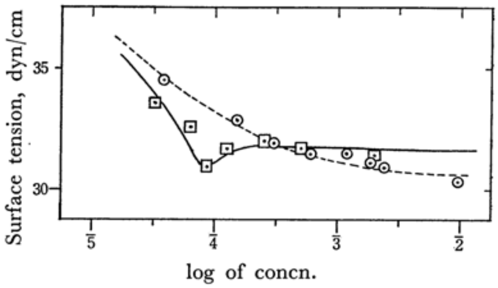

Fig. 2. The surface tension - log concentration curves of tetra polyoxyethylene cetylether titanium ester ($n=12$) and polyoxyethylene monocetyl ether. Temp.: 25°C.

—⊡— Polyoxyethylene cetylether titanium ester

···⊙··· Polyoxyethylene monocetyl ether

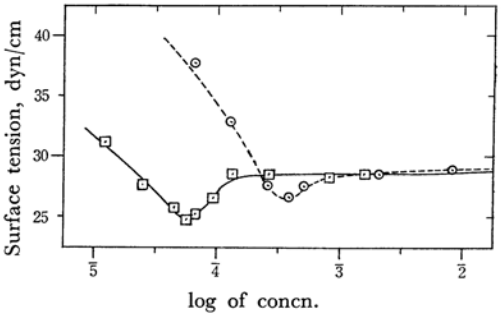

Fig. 3. The surface tension - log concentration curves of tetra polyoxyethylene octylphenylether titanium ester ($n=10$) and polyoxyethylene monooctylphenyl ether. Temp: 25°C

—⊡— Polyoxyethylene octylphenylether titanium ester

···⊙··· Polyoxyethylene mono octylphenyl ether when a mixture of tetra-*n*-butoxy titanium and polyethenoxy lauryl ether ($n=10$) was dissolved in water, the titanium compound hydrolyzed immediately. This fact confirmed that the stability of the compounds in water was caused by the soluble character of the compounds having polyethenoxy groups bonded to the titanium atom. Table 3 lists the behavior of the original nonionic surfactants and the corresponding titanium compounds in water.

TABLE 3. STABILITY OF AQUEOUS SOLUTIONS OF COMPARABLE NONIONIC SURFACTANTS AND CORRESPONDING POLYETHENOXY TITANIUM ESTERS

Surfactants used as starting materials	Stability
$HO(CH_2CH_2O)_2C_{12}H_{25}$	Insoluble in water
$HO(CH_2CH_2O)_nC_{12}H_{25}$ $n=6,\ 10,\ 25$	Soluble in water
$HO(CH_2CH_2O)_nC_{16}H_{33}$ $n=12,\ 25,\ 40$	Soluble in water
$HO(CH_2CH_2O)_{10}C_6H_4C_8H_{17}$	Soluble in water
$Ti(OC_4H_9)_4$	Insoluble, decomposed rapidly
Titanium compounds	
$Ti[O(CH_2CH_2O)_2C_{12}H_{25}]_4$	Insoluble
$Ti[O(CH_2CH_2O)_6C_{12}H_{25}]_4$	Cloudy or dispersed
$Ti[O(CH_2CH_2O)_{10}C_{12}H_{25}]_4$	Soluble
$Ti[O(CH_2CH_2O)_{25}C_{12}H_{25}]_4$	Soluble, but slightly cloudy
$Ti[O(CH_2CH_2O)_{12}C_{16}H_{33}]_4$	Soluble
$Ti[O(CH_2CH_2O)_{25}C_{16}H_{33}]_4$	Soluble, but slightly cloudy
$Ti[O(CH_2CH_2O)_{40}C_{16}H_{33}]_4$	Soluble, but slightly cloudy
$Ti[O(CH_2CH_2O)_{10}C_6H_4C_8H_{17}]_4$	Soluble

Surface Tension. The water-soluble polyethenoxy titanium esters exhibit surface activity in the aqueous phase. The relation between the surface tension of an aqueous solution of these compounds and the concentration showed a trend similar to that obtained in a conventional surfactant solution. This trend is characterized by a sharp initial decrease of surface tension to a minimum, followed by a short rise and a further, gradual flattening.

The surface tension - log concentration curves of some typical water-soluble titanates are shown in Figs. 1, 2, and 3. For the sake of comparison, the data for polyoxyethylene higher alkyl ethers are also included. It was considered that the inflections in the curves correspond to the CMC values of nonionic surfactants. From Figs. 1, 2, and 3 it may be observed that the CMC values of the new surfactants shift towards a lower concentration region than do the corresponding nonionic surface-active agents in each case.

Cloud Point. When the temperature of 0.1% solutions of the polyethenoxy titanium esters were raised by slow heating, some of the solution became cloudy. These cloud points appeared when the "*n*" values of the polyethenoxy chain $(CH_2CH_2O)_n$ were between 6 and 12. The cloud points of the new surfactants were very similar to those of the nonionic surfactants used as starting materials. The cloud points determined are summarized in Table 4.

TABLE 4. CLOUD POINT OF COMPARABLE NONIONIC SURFACTANTS AND THE CORRESPONDING POLYETHENOXY TITANIUM ESTERS

Surfactant used as starting material	Cloud point °C
$HO(CH_2CH_2O)_6C_{12}H_{25}$	48.0
$HO(CH_2CH_2O)_{10}C_{12}H_{25}$	83.5
$HO(CH_2CH_2O)_{12}C_{16}H_{33}$	97.0
$HO(CH_2CH_2O)_{10}C_6H_4C_8H_{17}$	64.0
Polyethenoxy titanium ester	
$Ti[O(CH_2CH_2O)_6C_{12}H_{25}]_4$	48.0
$Ti[O(CH_2CH_2O)_{10}C_{12}H_{25}]_4$	84.0
$Ti[O(CH_2CH_2O)_{12}C_{16}H_{33}]_4$	98.0
$Ti[O(CH_2CH_2O)_{10}C_6H_4C_8H_{17}]_4$	64.0

Dispersion. In non-aqueous systems, the polyethenoxy titanium esters exhibited a dispersing power on inorganic pigments. Even in aqueous systems, the water-soluble titanium esters containing a chain of at least ten ethenoxy groups exhibited a good dispersing power on inorganic pigments. On the other hand, the dispersing power of such starting materials as the polyoxyethylene higher alkyl ethers were very weak in both aqueous and non-aqueous media.

The sedimentation of titanium oxide (Rutyl) in aqueous media containing polyethenoxy titanium esters is shown in Figs. 4, 5, and 6. The dispersed systems were relatively stable for several

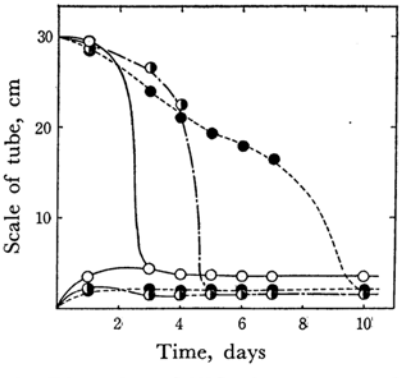

Fig. 4. Dispersion of TiO_2 in aqueous solutions of tetra polyoxyethylene laurylether titanium ester ($n=10$).

—○— 0.707 (% by wt.)
···●··· 0.089
---◑--- 0.044

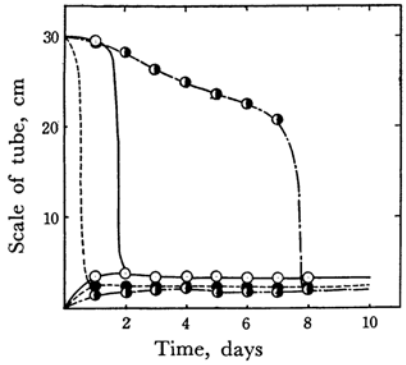

Fig. 5. Dispersion of TiO_2 in aqueous solutions of tetra polyoxyethylene cetylether titanium ester ($n=12$).

—○— 0.667 (% by wt.)
---◑--- 0.167
···●··· 0.084

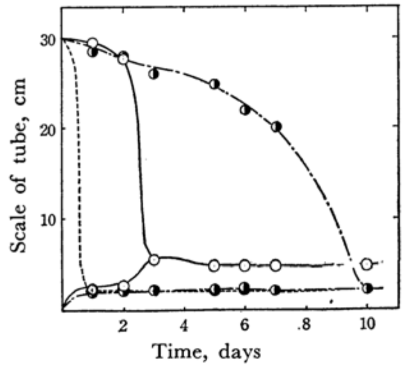

Fig. 6. Dispersion of TiO_2 in aqueous solutions of tetra polyoxyethylene octylphenylether titanium ester ($n=10$).

—○— 0.705 (% by wt.)
---◑--- 0.074
--●-- 0.038

days; the most stable systems were obtained at concentrations of about 0.1 wt%.

In non-aqueous systems, a relatively stable dispersion was obtained for a polar medium such as monochloro benzene; this tendency was observed in each compound. Typical data for the (tetra polyethenoxy octylphenylether titanium ester solutions) are shown in Fig. 7.

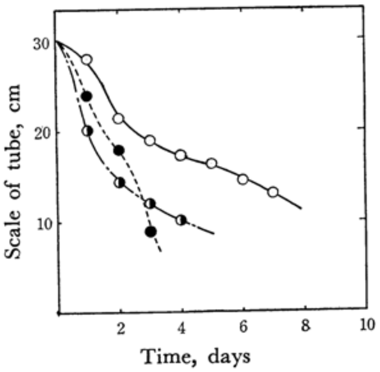

Fig. 7. Dispersion of TiO_2 in benzene, carbon tetrachloride and monochloro benzene solutions of tetra polyoxyethylene octylphenyl ether titanium ester. (2.0 wt.%)

···●··· benzene
-·◑-· carbon tetrachloride
—○— monochloro benzene

By the reaction of tetrabutoxy titanium with a nonionic surfactant of the $HO(CH_2CH_2O)_n$-R′ type, surface-active agents containing titanium were obtained.

All the compounds were soluble in the usual organic solvents; moreover, some of these compounds were found to be soluble in water.

These compounds were submitted to surface-tension measurements; it was thus observed that the CMC of the surface-active agents containing titanium shifted towards a lower concentration region than that of the related nonionic surface-active agents.

From the determination of the sedimentation volume, it was found that these compounds had good properties for the dispersion of TiO_2 in both aqueous and non-aqueous media.