Alkylphosphinic Surfactants With C14-C16 Fatty Chain

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Alkylphosphinates with fatty acid chains are a group of not well known anionic phosphorus-containing surfactants. This group of products has the hydrophobic chain linked directly to the phosphorus atom through a P-C bond.

An alkyl (C14-C16) phosphinate has been prepared by direct reaction between sodium hypophosphite and a commercial α-olefin with detergent range C14-C16, using tert-butyl perbenzoate as reaction initiator. The alkyl phosphinate (25% active matter) obtained has 2.79% of nonphosphinated substance. The surface tension of the sodium salt is 31.9 dynes/cm at 1 g active product/l at pH = 8 and has a moderate foaming power. No significant wetting power has been found.

Alkylphosphinates RP(O)(H)OM are chemical substances with a P-C bond, derivatives of phosphinic or hypophosphorous acid $H_2P(O)OH$. When R is an alkyl chain with eight or more carbon atoms, they show surfactant properties. These products can be obtained in the laboratory by different means (1,2) not useful in general for large production. The most interesting industrial methods would be the direct reaction of the corresponding α-olefin with hypophosphorous acid or its salts (3-6). The reaction product is a mixture of alkylphosphinates. Obtaining sodium octyl, decyl, dodecyl, tetradecyl and hexadecylphosphinates by direct reaction between the pure olefins and sodium hypophosphite monohydrate was studied in previous works (7,8). The reaction conditions to obtain the products with the best surfactant properties were determined using experimental optimization methods.

This method and the conditions found in the former work have been applied to the study of the product obtained using an α-olefin with detergent range C14-C16.

The reaction is carried out in a water/ethanol solution and is initiated by tert-butyl perbenzoate, because the reaction proceeds according to a free radical mechanism.

The reaction is:

$$R{-}CH{=}CH_2 + NaH_2PO_2 \xrightarrow[\text{perbenzoate}]{\text{tert-butyl}} R{-}CH_2CH_2{-}P(O)(H)ONa$$

Tert-butyl perbenzoate $[C_6H_5{-}COOC{-}(CH_3)_3]$ is thermally decomposed into free radicals $C_6H_5{-}COO\cdot$ and $(CH_3)_3CO\cdot$. The mechanism would be similar to that proposed by Stiles, Vaughan and Rust (9), and Griffin (10), for obtaining phosphonic acids from α-olefins:

$$\begin{array}{cccc} C_6H_5COO\cdot & & C_6H_5COOH & \\ \text{or} & +NaH_2PO_2 \rightarrow & \text{or} & +\cdot P(O)(H)ONa \\ (CH_3)_3CO\cdot & & (CH_3)_3COH & \end{array}$$

$$R{-}CH{=}CH_2 + \cdot P(O)(H)ONa \rightarrow R{-}\cdot CH{-}CH_2{-}P(O)(H)ONa$$

$$R{-}\cdot CH{-}CH_2{-}P(O)(H)ONa + NaH_2PO_2 \rightarrow \cdot P(O)(H)ONa + R{-}CH_2CH_2{-}P(O)(H)ONa$$

Reactions like telomerization, double addition and chain termination may be expected. The reaction is quite complex, and the resultant product is a mixture of different substances: mono and di alkylphosphinic sodium salts and telomers that are also alkylphosphinates with branched chains. All of them show surfactant properties, as they have the two hydrophobic and hydrophilic moieties.

EXPERIMENTAL

Materials and apparatus. Sodium hypophosphite monohydrate was reagent grade obtained from Panreac, Montcada, Spain. α-Olefin of detergent range C14-C16 was obtained from Ethyl Corp., Baton Rouge, Louisiana. The mean molecular weight was 206, and the molar percentage of the terminal double bond was approximately 90%. Tert-butyl perbenzoate was technical grade obtained from Perorsa, Barcelona, Spain.

The reaction was conducted at atmospheric pressure in batch conditions and at constant temperature. The sodium hypophosphite, dissolved in ethanol/water (3:1) was placed in the reaction vessel and the temperature raised until reflux. Forty-five g of α-olefin were slowly and continuously fed into the reactor through a Harvard type 2205 syringe metering pump with electronically variable DC motor (Harvard Apparatus Co. Inc., Millis, Massachusetts) using a 100-ml Hamilton 699 CH syringe. The molar ratio of sodium hypophosphite/α-olefin was 0.95. The α-olefin was added in 45 min. The total amount of the initiator, t-butyl perbenzoate, 2.7% in weight respect to the charge weight, was divided into two equal parts. One part was introduced into the reaction system dissolved with the hypophosphite, while the second was dissolved in the α-olefin, thus being added during the reaction. The reflux time was 45 hr.

The amount of water/ethanol mixture was that necessary to keep the final solid content, excluding the organic peroxide, equal to 25%.

The reaction conditions were those which were found to be the best during the synthesis of sodium octylphosphinate (7), and also used in obtaining the C10 to C16 alkylphosphinates (8).

The product obtained was a one-phase liquid when hot, separating a white solid when cooled.

RESULTS AND DISCUSSION

Analysis of the sodium salt. The nonphosphinated product has been determined by ion exchange, according to the standard method of the C.I.D. (11). The result found has been 2.79%. This result agrees with the previous values determined in the synthesis of the C10 to C16 alkylphosphinates.

Infrared spectroscopy. (i) On the reaction product the following absorption bands have been found: P-H absorption, 2300 cm^{-1}; O=P-O absorption, 1670 cm^{-1}; P=O absorption, 1100-1250 cm^{-1} and 1000-1100 cm^{-1}, and C-CH absorption, 2800-2950 cm^{-1} and 1450 cm^{-1}.

The double bond band at 1620 cm^{-1} is absent, confirming the very low residual α-olefin content.

(ii) On the anionic fraction after purification by ion exchange, the spectrum of the anionic fraction is identical to the corresponding spectrum of the reaction product. The double bond band at 1620 cm^{-1} is absent.

(iii) The spectrum of the nonphosphinated product obtained by ion exchange shows only the characteristics of saturated hydrocarbons. Probably, the nonphosphinated product is composed of polymeric substances obtained from the α-olefin.

SURFACTANT PROPERTIES

Surface tension. The surface tension of solutions of 1 g active product/l water at pH 8 and 20 C has been measured in a Lauda automatic tensiometer. The value obtained has been 31.9 dynes/cm.

At the same time, the surface tensions of solutions of the sodium and the ammonium alkylphosphinate were determined under the same conditions, once they had been purified by ion exchange. The values obtained were: Sodium alkyl (C14-C16) phosphinate 29.95 dynes/cm, and ammonium alkyl (C14-C16) phosphinate 29.0 dynes/cm.

These results show that the alkyl (C14-C16) phosphinate is a good surfactant. Surface tension of the purified product is similar to that obtained for the reaction product.

The results are of the same order as those previously reported (7,8) for pure products.

Foaming power. The foaming power of a solution of 2.5 g active reaction product/l water, at pH 8 and 25 C has been measured according to the method UNE 55.502. The results obtained were 350 ± 15 cm^3 at 30 seconds, 326 ± 14 cm^3 at 3 min and 312 ± 16 cm^3 at 5 min.

The limits shown have been calculated at the 0.05 probability level.

These results agree with those obtained for pure C14 and C16 products. Since the C14 fraction is predominant, the values obtained are closer to the pure C14 than to pure C16 product (388 cm^3 and 158 cm^3 respectively).

Wetting power. The product has no significant wetting power on disks of cotton at the concentration of 10 g reaction product/l in aqueous solution at pH 8 and 20 C.

ACKNOWLEDGMENTS

F. Comelles of the AID measured surface tensions, and F.J. Domingo of Marchon Surfac S.A. provided technical assistance.

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[Received April 22, 1986]