Production of Detergent-Grade Trisodium Citrate

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ABSTRACT

An efficient process to produce a technical-grade trisodium citrate suitable for detergent use has been demonstrated. Ammonium citrate is produced as an intermediate by a continuous fermentation approach using *Candida lipolytica* yeast and C_{10}-C_{20} linear paraffin. After removing yeast cells and residual oil by centrifuge, ammonia is distilled off with addition of sodium hydroxide. Trisodium citrate is recovered by methanol precipitation. Impurities, e.g., isocitrate, coloring materials and odorous substances dissolve in methanol and are removed. The methanol is recovered and recycled. A simple approach to convert the trisodium citrate solution directly to a solid for possible use in detergents failed because of the objectionable color, odor and high hygroscopicity.

INTRODUCTION

Although sodium tripolyphosphate, based on its superior over-all cost performance (1), is the work horse of detergent builders, various restrictions on the use of phosphates in detergents necessitate the search for a replacement for the tripolyphosphate (2,3). Trisodium citrate, a naturally occurring derivative, which is nontoxic and readily biodegradable, seems to be a possible choice, but cost-performance, i.e., the high price and the relatively low sequestration value (3), limits its use in detergent formulations to specialty cleaners and liquids. To justify large-scale use of trisodium citrate, the cost-performance of trisodium citrate has to be equal to or better than the present level.

In the United States, citric acid is produced mostly by fungal fermentation of carbohydrates using strains of *Aspergillus niger.* The fermentation cycle is long, 5-14 days for the submerged fermentation process. In addition, the separation and purification of citric acid from the fermentation product is difficult and expensive. The energy involved for submerged fermentation and separation is very high. The quality of citric acid and trisodium citrate, however, is good and meets food and pharmaceutical specifications. So far, all synthetic approaches have been futile because those routes require many steps and give low yields that are not commercially competitive. The purpose of this work is to improve the citric acid fermentation and purification techniques to produce trisodium citrate especially suitable for detergent use.

CONTINUOUS FERMENTATION TECHNIQUE

A recent development using candida yeast and C_{10}-C_{20} normal paraffins to produce citric acid appears to offer many advantages over the prevailing process of fungal fermentation of molasses or corn syrup (4-7). Because the fungal fermentation process to produce citric acid is old, and the process probably has been optimized, I am concentrating on the candida yeast fermentation process. Using a yeast strain given in the literature, e.g., *Candida lipolytica* ATCC 8661 (from the American Type Culture Collection) and *C. lipolytica* IFO-1464 (from the Institute for Fermentation in Osaka, Japan), and a medium containing about 100 g linear paraffin per liter and minor nutrients (7), the rate of citric acid production in a 14-28 L fermentor (New Brunswick Scientific Co., New Brunswick, NJ) at 28 C from the time of innoculation is shown in Figure 1. The pH of the fermentation batch was automatically controlled at 5-6 by the addition of ammonium hydroxide. The citric acid assay is determined by conductivity titration using 0.1 M $FeCl_3$ with a Metroohm conductivity cell (Brinkmann Instruments, Westbury, NY). This procedure does not distinguish between citric and isocitric acid. The amount of isocitric acid and other impurities could be determined by a gas liquid chromatographic (GLC) procedure (8). Depending on the strain of candida yeast, the amount of isocitric acid in the total citric acid varies from ca. 5% (IFO-1464) to ca. 20% (ATCC-8661).

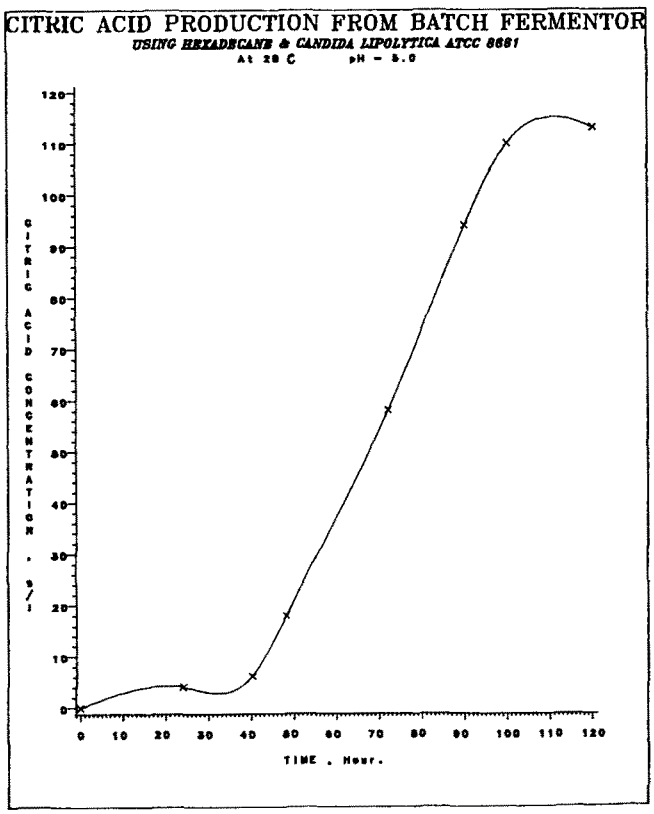

FIG. 1. Citric acid production from batch fermentor using hexadecane and *Candida lipolytica* ATCC 8661 (28 C, pH 5.0).

Figure 1 is a typical S-shaped growth curve. From 0 to 40 hours, the citric acid production rate is controlled by the growth of the yeast cells. During this period, the number of yeast cells are so low that little citric acid is produced. From 40 to 100 hours, the steady citric acid production rate of 1.6 g L^{-1} hr^{-1} apparently is controlled by oxygen transfer rate from aeration. As shown by equation 1, a large amount of oxygen is required to produce citric acid from biological oxidation of hydrocarbons.

$$6H_3C\text{-}CH_2\text{-}(CH_2)_{12}\text{-}CH_2CH_3 + 75O_2 \rightarrow 16HO\text{-}\underset{\displaystyle CH_2COOH}{\overset{\displaystyle CH_2COOH}{\underset{|}{\overset{|}{CH}}}}\text{-}COOH + 38H_2O \quad [1]$$

Theoretically, 226.5 g citric acid should be produced from every 100 g hexadecane. With a yield of 113 g citric acid per 100 g hexadecane, the conversion efficiency is ca. 50%. Besides the CO_2 metabolite, part of the carbon is consumed for yeast cell production (10). In Figure 1, the decrease of citric acid production rate beyond ca. 100 hr could be caused by the low residual hydrocarbon for conversion to

citric acid, but this could be also caused by the citric acid toxic inhibitor effect, as shown by separate experiments. In fermentation batches, when citrates are at concentrations above ca. 100 g/L, the yeast growth and conversion of hydrocarbons to citric acid are inhibited. Using an oxygen enriched air (40% O_2) or high aeration, the initial production rate will increase but the yield will decrease to 75 g citric acid/100 g hydrocarbon in a fermentation cycle, probably because of higher CO_2 metabolite formation. At high oxygen transfer rates at the latter part of the fermentation cycle, near the citric acid toxic level, the hydrocarbon is probably converted primarily to yeast cells, CO_2 and H_2O. In a batch operation, the increased aeration should be confined to the logarithmic growth period.

The concept of continuous fermentation using *C. lipolytica* ATCC-8661 has been reported (7). In the continuous operation, a portion of the fermentation broth is withdrawn and centrifuged. The unconverted hydrocarbon oil layer is skimmed off and returned to the fermentor along with the resuspended yeast cells with fresh medium. The whole recycle operation was accomplished under nonsterile conditions. The continuous operation could run for ca. 10 days before the rate starts to drop. The drop of citric acid productivity after long recycling operations could be caused by the repeated shock experience of recycled cells. No evidence exists that serious contamination of foreign cell growth is the cause of the drop of citric acid production rates. The hypothesis of shock is supported by the fact that the citric acid production rate can be improved by stopping the cell recycle to allow new growth of fresh cells. Although in this work, the continuous fermentation concept is tested only in a pilot plant-sized fermentor, the feasibility of this approach has been demonstrated. The typical composition of the fermentation product is shown in Table I. The composition of yeast cells was determined as 47% C, 6.5 H, 7.5% N, 31% O and 8% ash (10).

PRODUCTION OF TRISODIUM CITRATE FROM FERMENTATION PRODUCT

Three different approaches to produce trisodium citrate from fermentation product have been investigated. These approaches vary from the existing purification process for producing high purity trisodium citrate to new, lower-cost, potentially acceptable detergent-grade sodium citrate as shown by Figures 2-4.

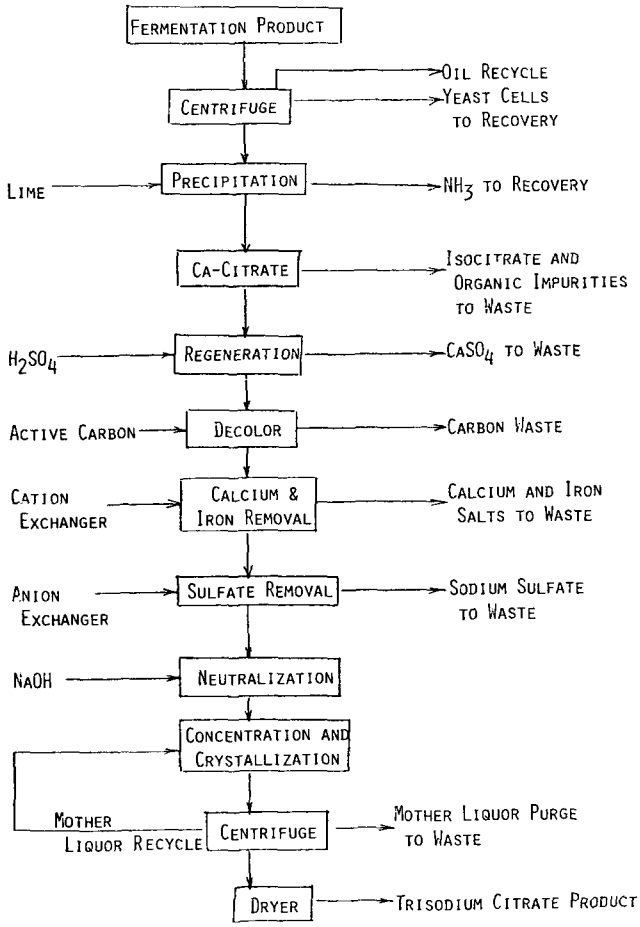

FIG. 2. Process 1—production of high-purity trisodium citrate.

Process 1—High Purity

The citrate-laden fermentation product is first centrifuged and washed to remove yeast cells and a small amount of oil. If the yeast cells are not recycled to the fermentor, cells could be dried and used as feed supplement (10). A considerable amount of work to satisfy potential safety concerns for using the cells as a feed supplement will be required. Surplus cells could be burned as fuel. The small

TABLE I

Typical Composition and Appearance of Citric acid Fermentation Liquid Using Hexadecane and *Candida lipolytica* (ATCC-8661) Yeast

Characteristics	Analyses
Color	Yellowish
Odor	Noticeable barn-type odor
pH	5-6
Density, g/mL at 25 C	1.04-1.05
Composition, g/1000 g of decelled liquor	
Total citric acid	90-96
$(NH_4)_2SO_4$	3-4
KH_2PO_4	0.02-0.2
$MgSO_4$	0.2-0.5
$CaCO_3$	0.4-0.7
NaCl	0.2-0.5
Others	0.1-1.0
Water	Balance
Yeast cell, wt. % of fermentation product	10-11

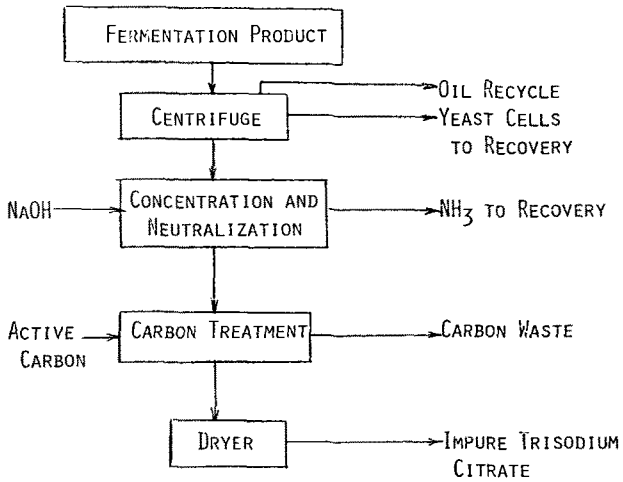

FIG. 3. Process 2—impure trisodium citrate.

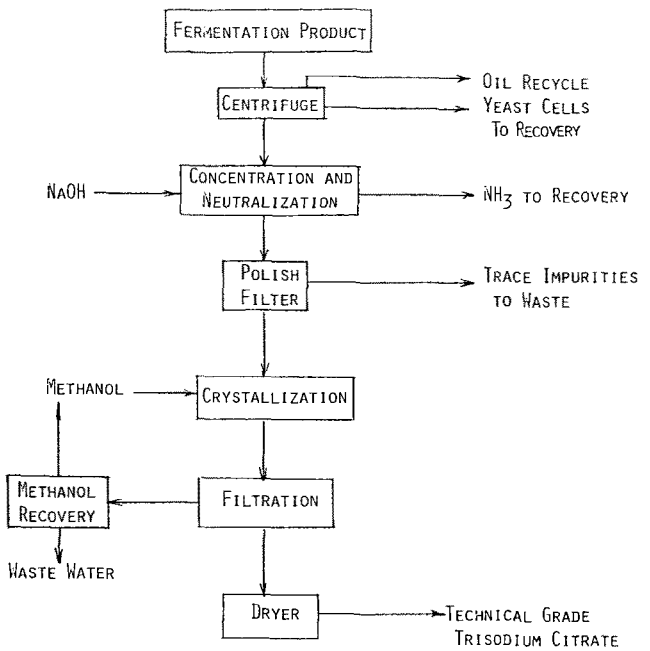

FIG. 4. Process 3—production of technical grade trisodium citrate suitable for detergent use.

TABLE II

Quality of Trisodium Citrate from Various Recovery Schemes

Composition (wt. %)	Process 1 high purity	Process 2 inpure grade	Process 3 technical grade
$Na_3C_6H_6O_7 \cdot 2H_2O$	99.5+	96.6	99.0
Na_2SO_4	nil	1.6	0.2
Ca(II)	nil	0.4	0.4
Other inorganic impurities	<0.1	0.6	0.1
Minor organic impurities	<0.1	0.6	0.3

amount of oil is removed by a decanter and is recycled to the fermentor.

The citrate in the filtered liquor actually is in the form of ammonium citrate. The filtered liquor is treated with calcium hydroxide to ca. pH 9-11 so that ammonia can be boiled off, recovered and recycled to the fermentation operation. Calcium citrate, probably in the form of tricalcium dicitrate hydrate salt, together with minor inorganic salts, e.g., calcium sulfate, aluminum, magnesium and iron phosphate or hydroxides will be recovered by filtration. Calcium isocitrate is quite soluble and is removed by washing the filter cake with hot water. The calcium citrate is resuspended in an equal weight of water and decomposed with 93-96% sulfuric acid. The temperature is kept below ca. 60 C to form easily filterable $CaSO_4 \cdot 2H_2O$ crystals. The filtration rates of calcium citrate and calcium sulfate are about 2 mL min^{-1} $(cm^2)^{-1}$. The filtrate has a yellow color. Together with the wash, the crude acid passed through a cation exchanger such as Amberlite IR-120 to remove dissolved calcium and iron and, if needed, an anion exchanger could be used to remove the residual amounts of sulfate.

The dilute citric acid is concentrated by evaporation to contain ca. 35-40% anhydrous citric acid. Although multiple-effect vacuum evaporation is preferred, atmospheric evaporation is acceptable. A small amount of turbidity develops and the color intensifies.

Both the color and the turbidity are removed by treating the solution with 0.1-0.2% carbon and by filtration, respectively. The carbon-treated solution is neutralized with 50% NaOH to pH 8.9. Trisodium citrate crystals, $Na_3C_6H_6O_7 \cdot 2H_2O$ are recovered after concentration. With recycling the mother liquor, the recovery of trisodium citrate from the starting fermentation product is ca. 85%. The crystal product is clear, white and free-flowing. The typical analyses are shown in Table II. The high purity trisodium citrate seems to be comparable in quality to so-called USP/FCC grade available commercially, although the purification process is somewhat simpler than that described in the literature (11).

Process 2—Impure Trisodium Citrate

Because purity is not essential for use in detergents, an attempt has been made to produce a low-cost, impure trisodium citrate for possible use in detergents. After removing yeast cells and residual oil from the fermentation product, 50% NaOH was added to increase the pH to ca. 11. The neutralized liquor was concentrated to strip off ammonia, which is recovered and recycled as an ammonia solution. After about half of the water is vaporized, the concentrated liquor is free of ammonia odor. While the ammonia is boiled off, a brown precipitate is formed, consisting of ferric oxide and coagulated organic material. This precipitate is difficult to filter without a filter aid. Active carbon is a convenient filter aid. It also serves as a decoloration and deodorization agent. As high as 10 g carbon per 1000 g concentrated liquor is necessary. Even at this high level of carbon, the filtered liquor and the product recovered later has a slightly yellowish tint and an objectional odor. The odor is difficult to mask with perfume in a detergent.

The carbon-decolorized sodium citrate solution is concentrated to a slurry containing ca. 40-50% by weight of crystalline $Na_3C_6H_6O_7 \cdot 2H_2O$. The slurry is mixed with 5-10 times recycled, dried solid in a pug-mill similar to that used in producing granular fertilizer, before drying in convenient drying equipment.

Because, in this process, most soluble impurities are included in the product, the citrate assay is the lowest of the 3 processes. Depending on the starting fermentation product, trisodium citrate produced from this approach contains an appreciable level of trisodium isocitrate, which is hygroscopic. The hygroscopicity of trisodium citrate from various processes, compared with sodium tripolyphosphate, is shown in Table III. Trisodium citrate produced by this approach contains ca. 0.2-0.5% NaOH, which also contributes to the hygroscopicity. Although the amount of weight gain after 43.5 hr at 25 C and 88% RH

TABLE III

Hygroscopicity of Trisodium Citrate Containing Varying Amounts of Impurities at 25 C (Weight Gain Percentage)

Sample description	Relative humidity (71.2%) Exposure time, hr 4.5	20.0	27.8	44.3	Relative humidity (88.0%) Exposure time, hr 3.5	20.2	26.8	43.5
Sodium tripolyphosphate (form II, powder)	0.09	0.57	0.76	1.56	0.21	6.02	7.64	10.95
Food grade trisodium citrate	0.03	0.03	0.03	0.08	0.04	0.06	0.06	0.14
Process 1 trisodium citrate	0.03	0.03	0.05	0.07	0.06	0.08	0.10	0.25
Process 2 trisodium citrate	1.97	3.47	4.67	5.28	2.83	9.19	9.32	10.21
Process 3 trisodium citrate	0.06	0.07	0.10	0.25	0.05	0.10	0.25	0.45
Food grade trisodium citrate + 4.7% Na_3 isocitrate	0.71	1.22	2.09	2.17	1.48	3.57	4.05	4.18
Food grade trisodium citrate + 1.0% NaOH	0.73	0.73	0.73	0.73	1.49	3.22	3.34	3.69
+ 4.8% NaOH	4.52	10.18	10.39	10.76	6.40	18.52	18.73	19.30
+ 9.0% NaOH	13.74	35.70	41.85	59.96	12.47	54.17	69.38	–

from the impure trisodium citrate is similar to the weight gain of Form II sodium tripolyphosphate, the impure trisodium citrate is badly caked. The Form II sodium tripolyphosphate apparently converted to fluffy crystalline sodium tripolyphosphate hexahydrate. Handling the impure sodium citrate under hot, humid weather could require special attention, e.g., using a moisture-barrier material for packing. In the author's opinion, the impure trisodium citrate probably has too many problems to be accepted for use in detergents. The yields of detergent grade trisodium citrate dihydrate are shown in Table IV.

Process 3—Technical Grade Trisodium Citrate

Because the impure trisodium citrate from Process 2 shows undesirable color, odor and hygroscopicity properties, a somewhat higher quality trisodium citrate than the product from Process 2 is needed. After various investigations, coloring matters, odorous substances and hygroscopic sodium isocitrate and sodium hydroxide were found to be removable by methanol extraction. Process 3 is based on an optimized methanol precipitation and separation scheme. The initial steps of removing the yearst cells, oil and ammonia for Process 3 are the same as for Processes 1 and 2. The hot sodium citrate solution is first flash-cooled to ca. 60 C and filtered to remove the small amount of coagulated material. A filter aid is required to give a fast filtration rate. The filtered citrate solution is then mixed with recycled and extra methanol to give the desired level of methanol. Temperature is important to give the desired crystalline phase. At 25 C, the citrate is crystallized as the 5.5 hydrate. Using the lower temperature has the advantage of using a lower amount of methanol because of the lower solubility of trisodium citrate and the water removed by the formation of a higher hydrate. At temperatures above the phase transition temperature, 47.5 C, the dihydrate is recovered. The dihydrate crystals are blocky and larger than the so-called pentahydrate. The solubilities of trisodium citrate in methanol solution and the equilibrium phase are shown in Figure 5.

The recovery efficiency and purity of trisodium citrate depend on the final concentration of methanol in the aqueous phase. The optimum concentration appears to be within a methanol-to-water-weight ratio of 1.5-1.6. At a higher ratio than the optimum, too much trisodium isocitrate will be precipitated with trisodium citrate. At a lower ratio than the optimum, the amount of trisodium citrate loss in the methanol phase is too high.

The filter cake is washed with methanol before it is dried in a dryer with indirect heat. The vapor from the dryer

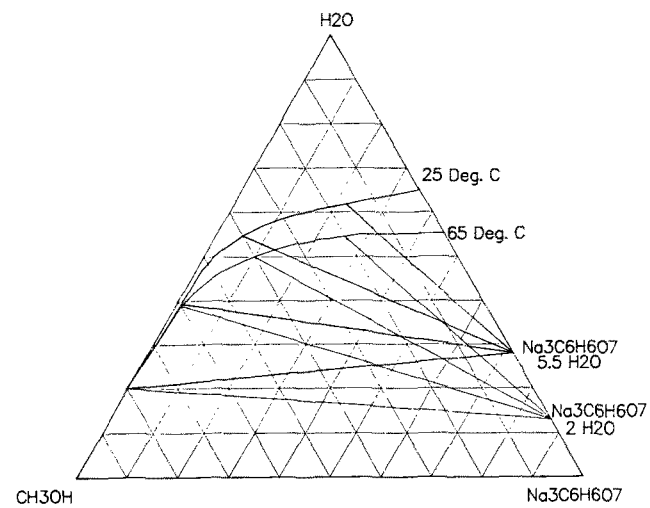

FIG. 5. System H_2O–CH_3OH–$Na_3C_6H_6O_7$.

TABLE IV

Raw materail Requirement to Produce a Hundredweight of Trisodium Citrate

Raw material	Weight required per hundredweight product Process 1	Process 2	Process 3
n-Paraffin	55.78	43.37	46.69
NH_3	6.54	5.09	5.47
Inorganics (nutrients)	3.77	2.93	3.15
H_2SO_4	68.42	0	0
$Ca(OH)_2$	50.57	0	0
Active carbon	2.35	1.82	0
Ion exchangers	0.1	0	0
Filter aid	4.7	0	1.5
50% NaOH	85.03	85.8	91.97
Yield based on n-paraffin (%)	51.5	66.2	61.5

feeds into a distillation column where the methanol in the filtrate is recovered. The bottom portion of the distillation column contains free sodium hydroxide and organic impurities that can be oxidized by air under pressure (12) before being discharged into a biological treatment unit. The amount of aqueous waste from Process 3 is ca. 1/2-1/3 the amount from Process 1.

The raw material requirements for producing various grades of trisodium citrate have been estimated and sum-

marized in Table IV. The technical-grade trisodium citrate is comparable in appearance and other physical properties to the high-purity material. The slight amounts of impurities in technical-grade trisodium citrate appear to be unobjectionable for detergent use, and its cost-performance is significantly better than the currently available high-purity trisodium citrate. In summary, an efficient process to produce technical-grade trisodium citrate suitable for detergent use has been demonstrated.

ACKNOWLEDGMENT

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Determination of Surfactant Mixtures in Shampoos and Detergents by HPLC

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ABSTRACT

A technique for separating 4 nonionic, 7 anionic and 4 amphoteric surfactants with n-dodecyl groups was studied by high performance liquid chromatography (HPLC) and applied to the determination of these surfactants in commercial shampoos and household detergents. Conditions used for the separation were: column packing and size, TSK-LS 410 (5μ) and 6 mm i.d. × 500 mm (2 connected, 250 mm columns); mobile phase, water/methanol (25/75, v/v) containing 0.25 M sodium perchlorate adjusted to pH 2.5 with phosphoric acid; column temp., 50 C; detector, RI. Surfactants in shampoos and detergents were clearly distinguished from each other and determined without column chromatographic pretreatment, e.g., ion-exchange chromatography.

INTRODUCTION

Commercial shampoos and household detergents usually consist of different ionic surfactants, and general properties of these commercial products depend on the combination of surfactants. A combination of fatty acid diethanolamides and sodium alkylsulfates or polyoxyethylene (POE) sodium alkylsulfates has been most widely used. Recently, other surfactants, e.g., alkyldimethylamino acetic acid betaine, sodium N-acyl-N-glutamates, alkyldimethylamine oxide and so forth, have often been used in these products. These surfactants are formulated in the products in small amounts, but strongly affect the properties.

Thin layer chromatography (TLC) (1,2), ion-exchange chromatography (3,4), salting-out chromatography (5) and other column chromatographies (6,7) have been used to separate and determine surfactants in commercial shampoos and household detergents. However, TLC is not suitable for quantitative analysis and column chromatographic techniques often take a long time to analyze.

In recent years, several papers (8-10) have been published on the separation of surfactants by means of high performance liquid chromatography (HPLC). In these papers, however, the emphasis is on the separation of individual surfactant homologs. Parris (11) successfully separated a combination of long-chain fatty acids; weakly anionic surfactant, sulfopropylated-type amphoteric surfactant and long-chain quaternary ammonium chloride; cationic surfactant with a combination of ion-suppression and ion-pair technique by using acetic acid and sodium dodecylbenzenesulfonate. However, strongly anionic surfactants, e.g., sodium alkylsulfate, are not applicable to the technique developed by Parris because they are not suppressed in an acid medium, as described in our previous papers (12,13), and are not ion-paired with an anionic counterion, e.g., sodium dodecylbenzenesulfonate. As sodium alkyl sulfate is the surfactant most widely used in commercial shampoos and household detergents, Parris's technique is not suitable for separating surfactant mixtures in these commercial products.

We have been studying the separation of surfactant homologs by HPLC using reversed-phase packing containing an octadecyl silane group chemically bonded to silica gel (ODS/Silica) (12-14). In our previous paper (14), nonionic, anionic, cationic and amphoteric surfactants were separated into their individual homologs and simultaneously distinguished from each other with a mixture of methanol, water, sodium perchlorate ($NaClO_4$) and phosphoric acid as the mobile phase.

In order to develop a rapid analytical method, the technique described in the previous paper (14) was applied to the determination of individual surfactant in commercial shampoos and household detergents that usually contain nonionic, anionic and amphoteric surfactants. Although the