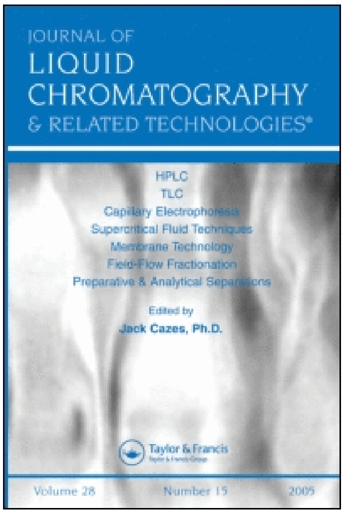

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Simple Method for Separation Monoalkyl and Dialkyl Sodium Phosphates by Liquid Column Chromatography

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Abstract: This paper deals with separation of monoalkyl and dialkyl phosphates by silica gel liquid column chromatography and determination of their structures by various spectrophotometric methods. The pretreatment of the sample and the separation conditions by silica gel column chromatography were studied in detail. In the optimal conditions selected, the monoalkyl sodium phosphate and dialkyl sodium phosphate in industrial products were separated completely. In order to evaluate the separation effect of silica gel column chromatography, the structures of two kinds of alkyl sodium phosphates separated were determined by FTIR, ^{1}H-NMR, ^{31}P-NMR, and atomic emission spectroscopy.

Keywords: Alkyl sodium phosphates, liquid column chromatography, separation, characterization

INTRODUCTION

As anionic surfactants, alkyl sodium phosphates are widely used in the chemical industry.[1,2] In a general way, alkyl sodium phosphates are prepared by fatty alcohol and phosphorus pentoxide, then caustic sodium is added. The products contained mainly monoalkyl sodium phosphate and dialkyl sodium phosphate, and a few inorganic salts, water, and other impurities. So far, only the ^{31}P-NMR spectrum of the products has been determined

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routinely for studying alkyl phosphates[3,4] because the separation was very difficult.

In this work, the industrial products, after thorough pretreatment, were satisfactorily separated by silica gel column chromatography in the selected optimal conditions. The two kinds of alkyl sodium phosphates separated were analyzed by FTIR, ^{1}H-NMR, ^{31}P-NMR, and atomic emission spectroscopy to determine their structures. This separation method is simple, rapid, and efficient.

EXPERIMENTAL

Apparatus

A 210-FTIR spectrophotometer (Nicolet, USA), a AV600 MHz spectrometer (Bruker, Germany), a WSP-1 atomic emission spectrometer (made in Beijing, China), were used for structure analysis of the alkyl sodium phosphates. A AB204-N electron balance (Mettler, Switzerland) was used. The silica gel chromatographic column (800 × 12 mm I.D.) made by the authors[5] was used to separate the samples of alkyl sodium phosphates.

Reagents

The petroleum ether, tetrachloromethane, benzene, methylbenzene, ethyl acetate, chloroform, acetone, absolute ethyl alcohol, methanol, sodium hydroxide (Beijing Chemical Reagent Factory, China) used in this experiment were all of analytical-reagent grade. The silica gel (0.154–0.076 mm grain size) for column chromatography was purchased from China Qingdao Ocean Chemical Plant. The strong acid type styrene cation exchange resin (0.3–1.2 mm grain size, exchange capacity more than 4.2 meq./g Na^+) was purchased from China Shanghai Chemical Reagent Company. The samples (industrial products) were from China Tianjing Petroleum & Chemical Corporation.

Pretreatment, Separation, and Purification

In this work, the strong acid type styrene cation exchange resin was used to separate inorganic salts from the industrial products. The procedure is as follows: about 120 g of the strong acid type styrene cation exchange resin was dipped in hydrochloric acid (5 mol/L) for 2 days, then washed with de-ionized water to $pH = 7$, and water was finally removed. About 5 g of the original industrial product sample was mixed with about 100 mL of de-ionized water in a 500-mL beaker, then the pretreated strong acid type styrene cation exchange resin was added, fully stirred for a moment and rested for 1h, and after they were adequately exchanged, they were filtrated. The filtrate was evaporated to dryness at 100°C. A milky white solid was obtained.

The silica gel was washed by petroleum ether, acetone, methanol, de-ionized water in turn, then activated at 110°C for 2.0 h; the silica gel chromatographic column was prepared by a natural settling method,[5] and the silica gel in the chromatographic column was about 40 cm high. The sample (500 mg) after pretreatment (the milky white solid) was dissolved with a little hot chloroform, and added to the silica gel column while still hot; then the mixtures of chloroform and methanol with different proportions (9 : 1, 8 : 1, 7 : 1, 6 : 1, 5 : 1, 3 : 1) were used to elute the silica gel column in turn. Two kinds of components were collected and purified once again by silica gel column chromatography.

Determination of Structures

The original industrial product sample, after thorough pretreatment and separation and purification yielding two kinds of components, were investigated by atomic emission spectroscopy, FTIR, ^{1}H-NMR, and ^{31}P-NMR. These spectra were analyzed to determine their structures.

RESULTS AND DISCUSSION

Pretreatment of the Sample

The sample containing mainly monoalkyl and dialkyl sodium phosphates and a few inorganic salts was a milky white liquid. It could not be directly separated by a silica gel column because there were no appropriate solvents to dissolve it. In this work, a cation exchange resin was used to separate inorganic salts from the sample. The sample after pretreatment was a milky white solid. The pretreated sample (500 mg) was dissolved with a little hot chloroform, added to the silica gel column while hot, and the complete separation could be obtained.

Temperature and Time of Silica Gel Activation

In the experiments of the activation temperature (80, 90, 100, 110, 120°C) and time (0.5, 1.0, 1.5, 2.0, 2.5 h) of silica gel, the best separation result was obtained at 110°C for 2.0 h.

Eluents of Silica Gel Column

Petroleum ether, tetrachloromethane, benzene, methylbenzene, chloroform, ethyl acetate, acetone, absolute ethyl alcohol, methanol, and de-ionized water were used to elute the silica gel column in turn. Components were eluted between chloroform and methanol, so the mixtures of chloroform and methanol with different proportions (9 : 1, 8 : 1, 7 : 1, 6 : 1, 5 : 1, 3 : 1) were used as eluents, resulting in a good separation.

Evaluation of Separation Effect

The ^{31}P-NMR spectra were taken on the samples, after their separation and purification. They are shown in Fig. 1, Fig. 2, and Fig. 3, respectively. Because it is difficult to find a solvent to dissolve them, the mixture of chloroform -methanol (5 : 1) was used as solvent in which the temperature was 30°C, and the apparent pH of the solution was adjusted to 9–10 with the proper amount of sodium hydroxide, and determined with a precise pH-test paper. It can be seen in Fig. 1 that there are two kinds of phosphorus in the sample after pretreatment, the peak at $\delta = 1.72$ corresponds to dialkyl sodium phosphate, and the peak at $\delta = 6.45$ corresponds to monoalkyl sodium phosphate. So, it is clear that the component in Fig. 2 is dialkyl sodium phosphate and the component in Fig. 3 is monoalkyl sodium phosphate; showing that the separation of the industrial sample was excellent.

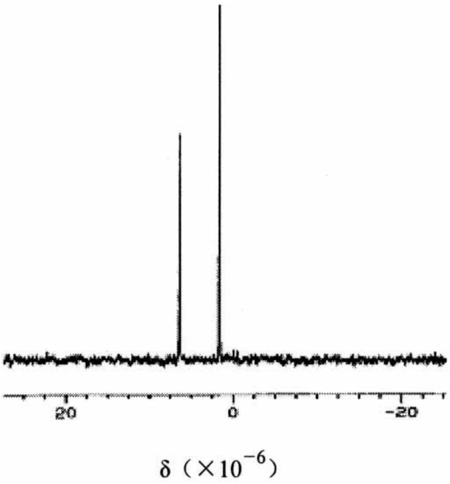


Figure 1. The ^{31}P-NMR spectrum of the sample unseparated by column chromatography.

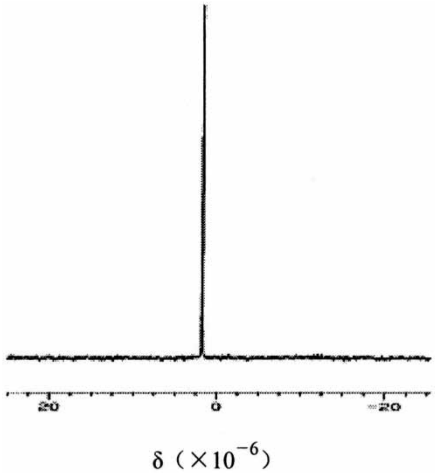


Figure 2. The ^{31}P-NMR spectrum of the component separated (dialkyl sodium phosphate).

Structure Analysis of the Components

As mentioned, it could be proven, preliminarily, that two kinds of components separated were dialkyl sodium phosphate and monoalkyl sodium phosphate. In this work, FTIR and ^{1}H-NMR also were used to determine their structures, because the IR and ^{1}H-NMR spectra of the two kinds of components separated

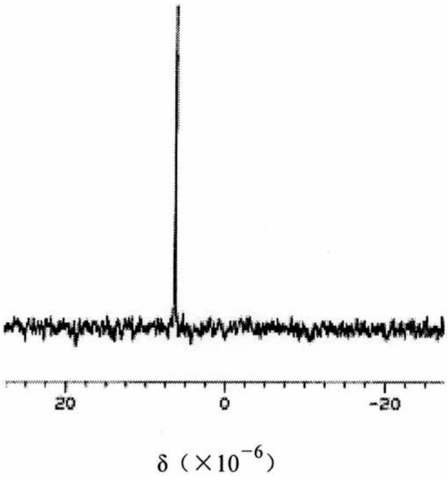


Figure 3. The ^{31}P-NMR spectrum of the component separated (monoalkyl sodium phosphate).

are very similar; the IR and ^{1}H-NMR spectra of dialkyl sodium phosphate are shown in Fig. 4 and Fig. 5 only.

As shown in Fig. 4, the peaks at 2956, 2919, 2849, 1378, and 721 cm^{-1} belong to long chain alkyl; the middle strong peak at 1213 cm^{-1} is the result of an P=O stretching vibration, the strong peak at 1051 cm^{-1} is the result of an P–O stretching vibration. In the IR spectrum of monoalkyl sodium phosphate, there was the same peak of the long chain alkyl as dialkyl sodium phosphate, but the peak at 1213 cm^{-1} shifts to 1230 cm^{-1} and the peak at 1051 cm^{-1} shifts to 1090 cm^{-1}.

Because of the special properties of the component, $CDCl_3$-CD_3OD (5 : 1) was used as solvent. The explanation of the peaks in Fig. 5 is shown in Table 1.

As is obvious from Table 1, after thorough calculation, each long chain alkyl in dialkyl sodium phosphate has sixteen carbons. Using the same method, it can be proven that the long chain alkyl in monoalkyl sodium phosphate also has sixteen carbons.

According to the analysis above, the two kinds of components separated by silica gel column chromatography are dihexadecyl sodium phosphate and monohexadecyl sodium phosphate.

Preliminary Discussion of Separation Process

The original industrial product sample, after thorough pretreatment and yielding two kinds of components by silica gel column chromatography, were determined by atomic emission spectroscopy. The results showed that

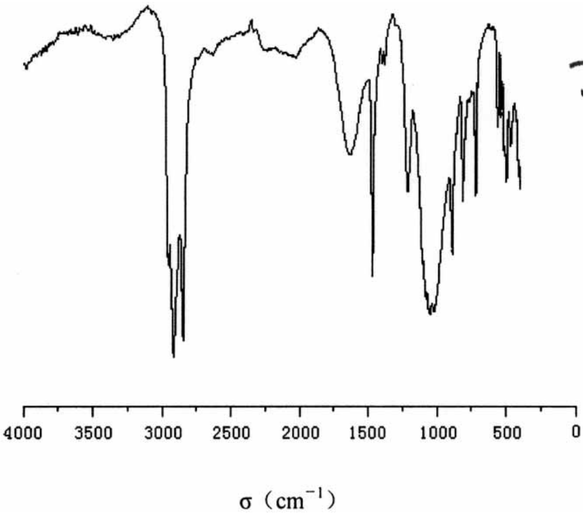


Figure 4. The IR spectrum of dialkyl sodium phosphate.

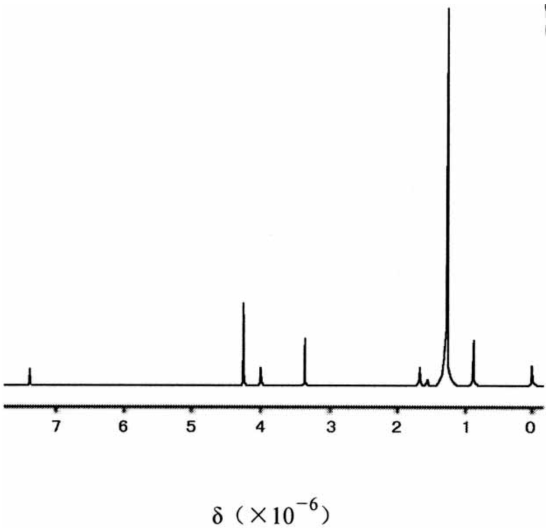


Figure 5. The ^{1}H-NMR spectrum of dialkyl sodium phosphate.

in the original sample, the sodium was much higher in concentration than the phosphorus. After thorough pretreatment of the sample the sodium and phosphorus were almost equal. There was no sodium in the two kinds of the components separated by silica gel column chromatography. It was shown that the sample after pretreatment was the salt form of alkyl sodium phosphates, and the components separated by silica gel column chromatography existed as the anion form of alkyl phosphates. On the other hand, there was no peak of P–OH stretching vibration in the IR spectrum (Fig. 4), and also there was no peak of OH in the ^{1}H-NMR spectrum (Fig. 5). All of this showed that the two kinds of components separated by a silica gel column existed as the anion form of alkyl phosphates.

Based on the difference of their adsorption, these components can be separated by silica gel column chromatography. The Si–O–H on the surface of silica gel is a weak acidic and can form a hydrogen bond from –OH on the silica gel and these polar compounds. Separation occurs because the

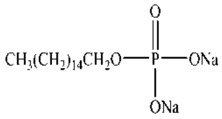
Table 1. The explanation of the peaks in ^{1}H-NMR spectrum

δ (×10^{-6})	Character group	Integral value	Character group number
0.87–0.89	$-CH_3$	1.359	2
1.27–1.67	$-(CH_2)_n-$	14.024	28
3.47, 4.25, 7.42	Solvent		
3.97–3.98	$\underline{-CH_2}$OP-(Standard)	1.000	2

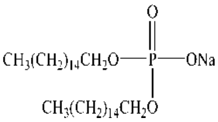
polarity of different compounds is dissimilar, and their ability of forming hydrogen bonds is also dissimilar. According to the above, it could be proven that the sample was a mixture of two kinds of alkyl sodium phosphates, and the two kinds of components separated by silica gel column chromatography were alkyl phosphate anions. The sodium ion of these components can pass through the silica gel column first, and not adsorb on the silica gel surface; but the alkyl phosphate anions can be adsorbed on the silica gel surface by forming hydrogen bond with Si–O–H. The polarities of dialkyl phosphate anion and monoalkyl phosphate anion are different, caused by the different length of alkyl chain, allowing them to be separated by silica gel column chromatography.

CONCLUSIONS

Silica gel column chromatography was used to separate dialkyl sodium phosphate and monoalkyl sodium phosphate effectively; ^{31}P-NMR method was used to evaluate the effect of separation; the components separated by silica gel column chromatography were determined by ^{31}P-NMR, ^{1}H-NMR, FTIR, and atomic emission spectroscopy, and the structures are as follows:



$$CH_3(CH_2)_{14}CH_2O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle ONa}{|}}{P}}{-}ONa$$



$$CH_3(CH_2)_{14}CH_2O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle CH_3(CH_2)_{14}CH_2O}{|}}{P}}{-}ONa$$

The results of the experiment showed that the proposed method for separating dialkyl sodium phosphate and monoalkyl sodium phosphate was efficient, simple, and of low cost.

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