

SEPARATION OF THE HOMOLOGOUS SERIES OF ALKYL BENZYL DIMETHYLAMMONIUM HALIDES
AND ALKYL PYRIDINIUM HALIDES BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

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Separations of the homologous series of alkylbenzyl dimethylammonium chlorides and alkylpyridinium halides having the alkyl groups of C-10, C-12, C-14, C-16 and C-18 were carried out by high performance liquid chromatography. All components were well resolved and the logarithm of the capacity factor was directly proportional to the alkyl chain length.

Alkylbenzyl dimethylammonium chlorides (BzAC) and alkylpyridinium halides (APH), typical cationic surfactants, have been widely used as germicides, textile softeners and in many other industrial applications. These commercial products are usually mixtures of alkyl homologue of C-10 to C-18. The composition of them are usually determined by gas chromatography. This method, however, requires some prior derivations of them into volatile species.

Liquid chromatography has been made a great progress in recent years due to the developments of detector and column packings, and has become comparable to gas chromatography in convenience, speed and efficiency. The present paper is concerned with an application of high performance liquid chromatography to direct analysis of the homologous series of BzAC and APH without pretreatment of the samples.

The liquid chromatograph used was constructed from the separate components; the pump was a Kyowaseimitsu reciprocating pump and the detector was a Hitachi-Perkin Elmer 139 spectrophotometer with 20mm × 2mm I.D. Teflon flow cell. BzAC was detected at 263.5nm and APH at 260nm. All flow paths were of Teflon. The column packing material was Hitachi gel 3010, porous spherical particles of copolymer of styrene and divinylbenzene and of 25μm average diameters, which was packed in a 500mm × 4mm I.D. glass column by slurry method. BzAC and APH having the alkyl groups of C-10, C-12, C-14, C-16 and C-18 were prepared and purified by recrystallizations from acetone. A mixture of each homologue was dissolved in methanol and injected in the column with a microsyringe through the septum injector.

Methanol eluted all components of BzAC and APH at the solvent front. With a 0.5M hydrochloric acid-methanol solution as an eluent, each member of the homologous series of BzAC and APH was eluted in the order of the alkyl chain

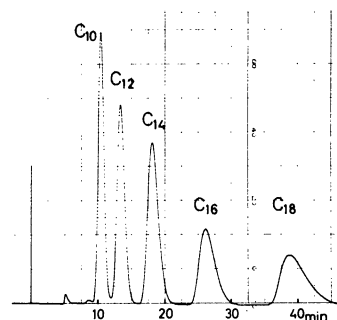


Fig.1. Chromatogram of BzAC.
column Hitachi gel 3010
500mm × 4mm I.D.
eluent 0.5M HCl-CH₃OH
flow rate 1.18 ml/min.
pressure 41 kg/cm²
column temp. 30°C.

length and separations were good as shown in Fig.1 and 2. As an increase of the concentration of hydrochloric acid, the retention volume and the resolution value increased in both cases of BzAC and APH. Alkylpyridinium bromides were eluted at the same retention volume as that of alkylpyridinium chlorides of the same alkyl chain length. This might suggest that the counter ion of the surfactants is exchangeable to the ions in the eluents.

Perchloric or sulfuric acid instead of hydrochloric acid also gave satisfactory separations. The use of lithium chloride or ammonium chloride in place of an acid gave the same results that obtained using hydrochloric acid of the same chlorine contents. When using perchlorate, the situation was the same. These results indicate that the cations in the eluents have no influence on the capacity factor and that the only anions have influence on the separation aspects. In other words, capacity factors are affected by the species of anions and also by the concentration of them.

The linear relationships between the logarithm of the capacity factor and the carbon number of the alkyl groups are shown in Figs.3 and 4. Both the capacity factor and the specific retention volume are proportional to the net retention volume^{2,3)} and therefore, the capacity factor is linear to the specific retention volume. In liquid-liquid partition chromatography, Locke and Martire³⁾ reported the logarithm of the specific retention volume of each member of the homologue was directly proportional to the carbon number. This results, therefore, might be explained in terms of the theory of partition chromatography.

The present results may suggest that this method may be applicable to the determination of the homologue of other surfactants such as alkylsulfates, alkylbenzenesulfonates and so on. The detailed studies of these series are now in progress.

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References and Footnotes

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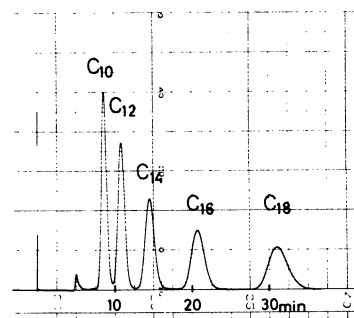


Fig.2. Chromatogram of APH. conditions same as Fig.1.

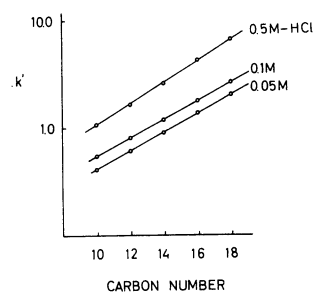


Fig.3. Relationship between k' and alkyl chain length of BzAC.

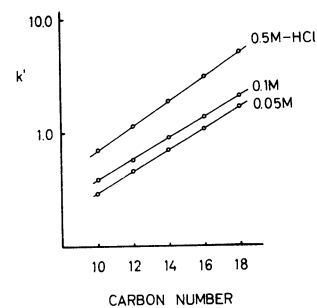


Fig.4. Relationship between k' and alkyl chain length of APH.

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