

NMR을 이용한 음이온 및 비이온세제의 혼합물로부터 ABS의 정량

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Quantitative Determination of ABS from Mixture of Anionic and Nonionic Detergents by NMR

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요 약. 음이온세제와 비이온세제의 혼합물에서 alkylbenzene sulfoante 계통의 음이온 세제가 NMR법에 의해서 정량되었다. 음이온세제와 비이온세제의 혼합물에 대한 NMR 스펙트럼에서, 벤젠 그룹은 6.5~8ppm에서 중첩된 피크를 보여주나 sampling 후의 벤젠 그룹은 7~8ppm에서 두개의 doublet을 보여준다. 검량선은 음이온세제의 벤젠그룹과 초산의 메틸그룹의 상대적인 면적비에 의해서 작성되었다(초산은 내부표준물로 사용되었다).

ABSTRACT. Amounts of alkylbenzene sulfonate (ABS) in the mixtures of anionic and nonionic detergents were determined by nuclear magnetic resonance (NMR) method. In the NMR spectrum of anionic and nonionic detergents, benzene group showed peaks overlapping at 6.5~8ppm, but after sampling, benzene group showed two doublet at 7~8ppm. Calibration curve was obtained by relative ratio of area for benzene group in anionic detergent to that for methyl group in acetic acid (acetic acid was used as the internal standard).

INTRODUCTION

Anionic detergents (alkylbenzene sulfonate, ABS; sodium laurylsulfate, SLS; alcohol ether-sulfate, AES) and nonionic detergent (alkyl-phenoxypolyethanol containing 7 to 8 moles of ethylene oxide, APE) are widely used in various industries as well as in household products, and especially ABS is a very valuable synthetic detergent because of its high cleansing powder and low cost.

ABS has two kinds of type; one is linear(1-ABS, soft type), the other is branched (b-ABS, hard type), and hard type is known as a material of water pollution.

The commercial products of 1-ABS are generally a mixture of 10~13 carbon atoms.

Many analytical methods (infrared spectrometry,¹⁻² gas chromatography,³⁻⁷ high performance liquid chromatography,⁸⁻¹² atomic absorption spectrometry,¹³⁻¹⁴ etc.) have been used for the determination, separation, identification of

these detergents.

None of these procedures, however, is effective for the analysis of ABS from mixture of anionic and nonionic detergents.

This paper deals with the separation of anionic detergents from the mixtures of detergents by the difference between solubility in water and that in organic solvent. It also includes the quantitative determination of ABS from the NMR spectrum of anionic detergents, and the purity of 1-ABS is estimated with the method described in the previous paper.^{15,16}

EXPERIMENTAL

Apparatus. NMR spectrometer(60MHz, 360L, Varian) was used.

Reagents. ABS was purchased from Tokyo Kasei Chemical Ind. Co. (Tokyo, Japan), all other reagents were of analytical reagent grade.

Standard solution. 2g ABS, 20ml concentrated hydrochloric acid and 50ml distilled water were placed in 300ml flask equipped with condenser. After heating for an hour, solution was transferred into 250ml separating funnel, 100ml chloroform was added, and was shaken strongly for 5min. After separation, chloroform layer was transferred into 150ml beaker, chloroform was removed by heating in water bath, and the solution was made up to 20ml by adding carbon tetrachloride (containing 2% acetic acid).

Separation of anionic detergent from the mixtures. The mixtures of detergents (containing 0.5g ABS), 50ml distilled water and 50ml chloroform were added in 250ml separating funnel; funnel was shaken vigorously for 5min. If emulsion was formed between water and chloroform, 50ml ethanol was added. After separation, the water layer was transferred into 300ml beaker and 20ml concentrated hydrochloric acid was added. After heating for an hour, 50ml chloroform was added; chloroform

layer was transferred into 150ml beaker, then chloroform was removed by heating in water bath, and carbon tetrachloride (containing 2% acetic acid) was added to make 10ml of solution. NMR spectrum of the solution was obtained using NMR spectrometer.

Calibration. NMR spectrum of each solution containing 3ml, 4ml, 5ml, 6ml of standard solution was obtained by NMR spectrometer. Calibration curve was obtained by plotting relative ratio of area for benzene group in ABS versus that for methyl group in acetic acid; the plot should yield a straight line with an intercept of origin.

RESULTS AND DISCUSSION

Solubilities of Detergents. Detergents form emulsion with water and organic solvent since they have both hydrophilic group and lipophilic group.

In *Fig. 1*, we can see nonionic detergent was transferred to organic solvent in the mixture of water and organic solvent when alcohol is added; that is, chloroform layer has λ max at 242, 278nm, but water layer does not.

ABS acid was obtained by the hydrolysis of ABS and was extracted with chloroform. As shown in *Fig. 2*, chloroform layer has λ max at 242, 258, 263 and 268nm, while water layer does not. This means nonionic detergent and ABS acid are more soluble in organic solvent than in water.

Analysis of NMR Spectrum and of Sample. The NMR spectrum of ABS acid in carbon tetrachloride containing 2% acetic acid is displayed in *Fig. 3*. In NMR spectrum, benzene group shows peak at 7~8ppm in ABS; methyl group at 2ppm in acetic acid.

The NMR spectrum of the mixture of anionic and nonionic detergents is shown in *Fig. 4*.

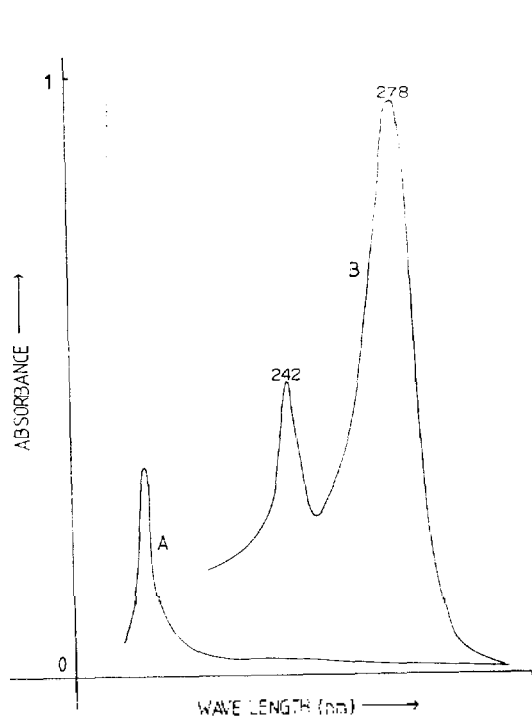


Fig. 1. Absorption spectra of (APE) (A, in H₂O; B, in CHCl₃).

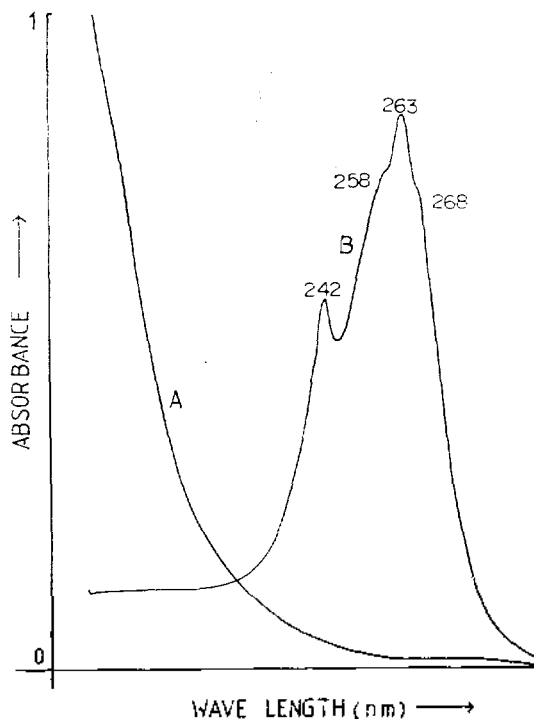


Fig. 2. Absorption spectra of ABS acid (A, in H₂O; B, in CHCl₃).

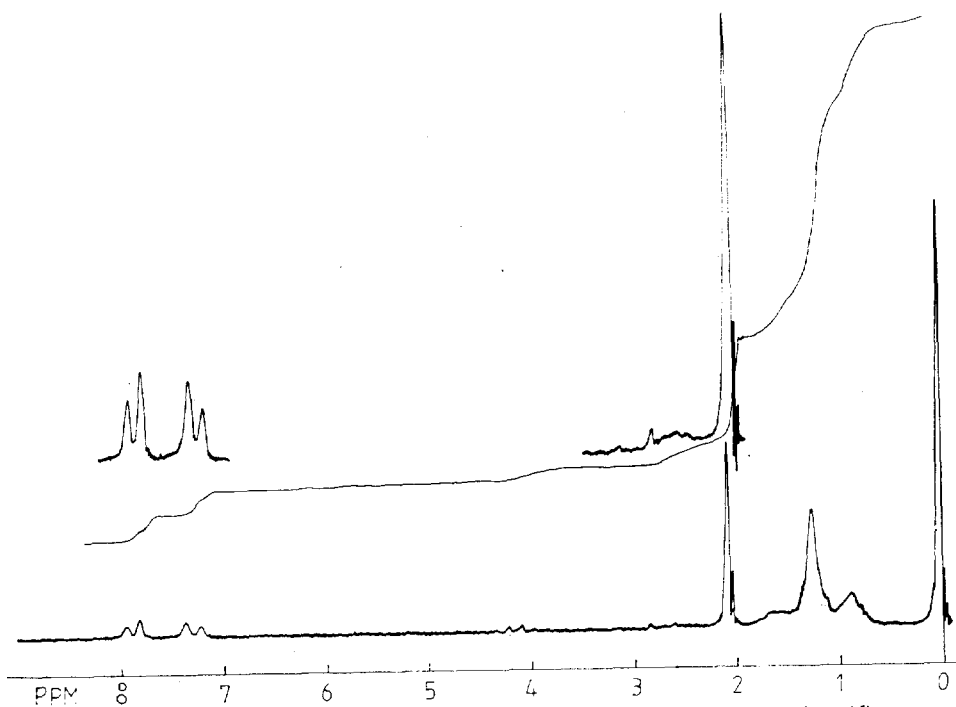


Fig. 3. NMR Spectrum of ABS acid in CCl₄ (Containing 2% acetic acid)

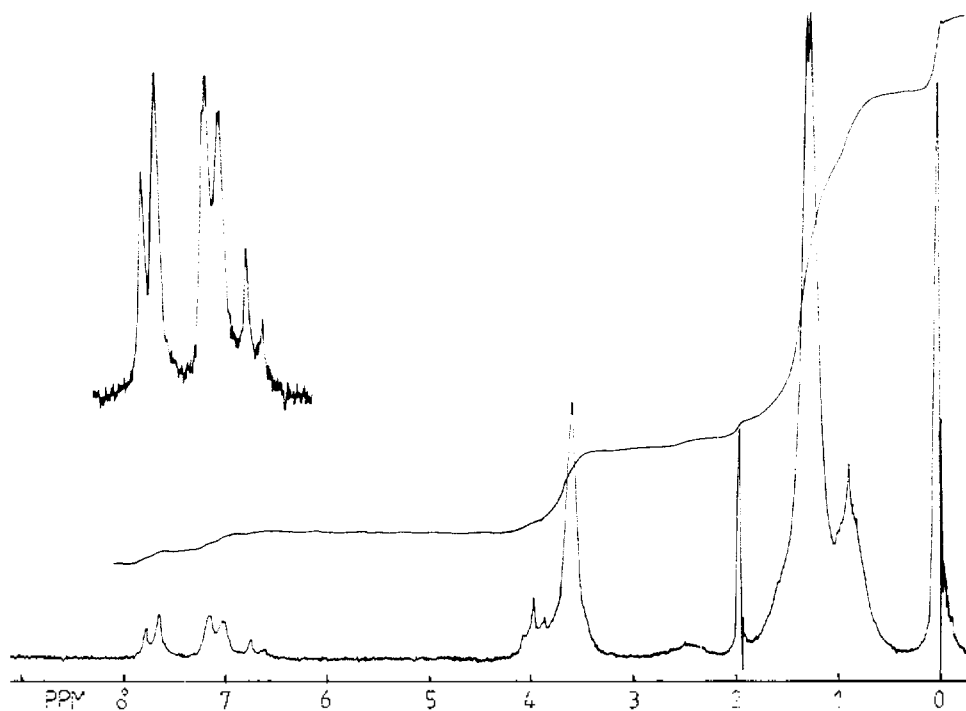


Fig. 4. NMR Spectrum of the mixture of anionic and nonionic detergents in CCl_4 (Containing 2% acetic acid)

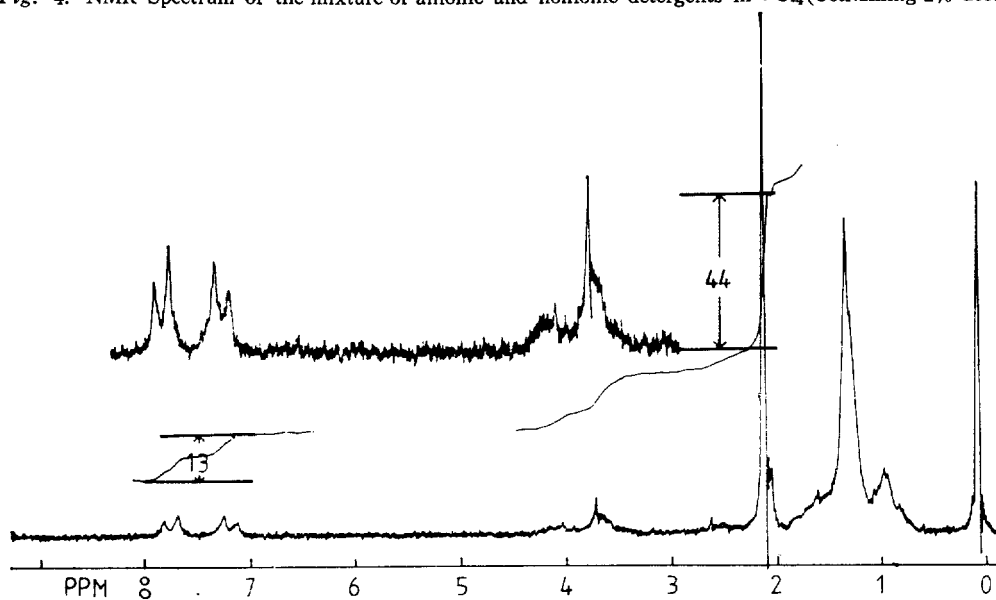


Fig. 5. NMR Spectrum of the mixture after sampling.

Here benzene groups are overlapped at 6.5~8 ppm; methyl groups at 0.7~0.9ppm; methylene groups at 1~1.5ppm; ethylene oxide groups and methoxy group at 3.5~4ppm; but methyl

group of acetic acid shows singlet at 1.9ppm.

Fig. 5 is the NMR spectrum of the mixture of detergents after sampling and it does not have peaks near 6.5~7ppm; that is, nonionic

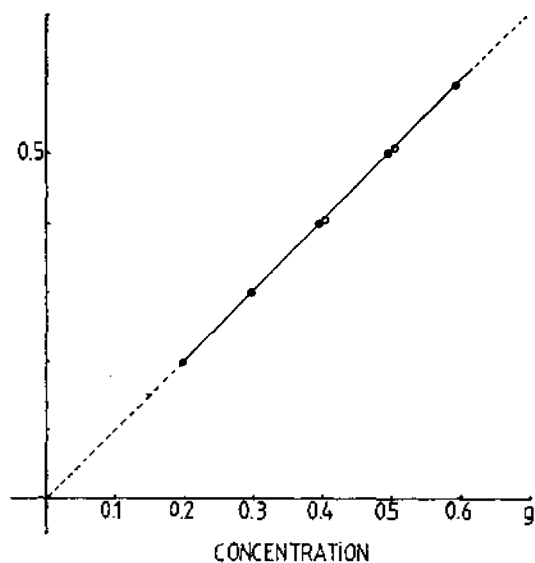


Fig. 6. Calibration curve of standard solution.

Table 1. The relative ratio of area for benzene group (in ABS, acid) to that for methyl group (in acetic acid)

ABS(g)	Relative ratio of area benzene group/methyl group		Effect
	Standard	Sample	
0.2	0.198		
0.3	0.300	0.295	98.3%
0.4	0.391	0.402	102.8%
0.5	0.501	0.504	100.6%
0.6	0.599		

detergent does not exist in mixture of detergents after sampling.

The relative ratio of area for benzene group in anionic detergents to that for methyl group in acetic acid are summarized in Table 1.

Fig. 6 is the calibration curve of standard solution; the experimental values are in very good agreement with the theoretical ones. This suggests that this method is effective for the quantitative analysis of ABS in the mixture of

detergents.

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