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SEPARATION OF ALCOHOL ETHOXYLATES BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

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SUMMARY

A high-performance liquid chromatographic method has been developed for the separation of alcohol ethoxylates according to their alkyl chain lengths, C₁₂, C₁₆ and C₁₈ alcohol ethoxylates were separated according to their alkyl groups using a chemically bonded stationary phase (C₁₈) and acetone-water as mobile phase. Elution of the alcohol ethoxylates is not influenced by the ethylene oxide group.

INTRODUCTION

Alcohol ethoxylates are widely used as emulsifiers, wetting agents and detergents. Many chromatographic analyses of these non-ionic surfactants have been reported. For example, the molecular weight distribution of ethylene oxide adducts has been determined¹⁻⁸. However, there have been only a few reports on the separation according to their alkyl groups which is of interest in industrial analysis. Thomas and Rocca⁹ reported the high-performance liquid chromatographic (HPLC) separation according to the alkyl group of alcohol ethoxylates using methanol-water as mobile phase, pH 9.5. Ohtsuki and Shiraishi¹⁰ reported the separation between octylphenol ethoxylate and nonylphenol ethoxylate by reversed-phase chromatography using gradient elution. Although the method of Thomas and Rocca is the only one for separating alcohol ethoxylates in accordance with their alkyl groups, their method has a lack of reproducibility because of the lack of information on experimental conditions such as the buffer and its concentration.

In this paper, I describe a systematic investigation of the reversed-phase HPLC separation of alcohol ethoxylates according to their alkyl groups. The logarithm of the capacity factor, $\log k'$, is used as an index of separation of alcohol ethoxylates.

EXPERIMENTAL

Chemicals

Alcohol ethoxylates, C₁₂, C₁₆ and C₁₈, were purchased from Kao-Atlas (Tokyo, Japan). These non-ionic surfactants have degrees of ethoxylation varying between 3 and 20. All reagents used for chromatographic analysis were analytical-reagent grade.

HPLC apparatus and procedure

Chromatographic analyses were performed with a liquid chromatograph (Model 638-50; Hitachi Scientific Instruments, Tokyo, Japan) equipped with a variable loop injector, a differential refractometer (SE-31; Showa Denko K.K., Tokyo, Japan) and a data processor (Chromatopac C-R1A; Shimadzu Corporation, Kyoto, Japan). The separation columns (150×4 mm I.D. and 150×8 mm I.D.) were packed with LiChrosorb RP-18, RP-8 and RP-2 (Merck, Darmstadt, F.R.G.), and Hitachi gel No. 3053 (C_{18} type), all of particle size $5 \mu\text{m}$. Packing of these stationary phases was carried out by the balanced density method. Acetone-water mixtures were used as mobile phase. Flow-rates were 1.0 ml/min for the 4 mm I.D. column and 2 ml/min for the 8 mm I.D. column. Sample solutions of *ca.* 10% were prepared using the mobile phase and $10 \mu\text{l}$ of each solution were injected into the chromatographic system. The logarithm of the capacity factor, $\log k'$, of each alcohol ethoxylate was calculated from the chromatograms. k' was calculated according to the equation $k' = V_n/V_m$, where V_m is the mobile phase interstitial volume and V_n is the net retention volume. V_m was determined by measuring the retention volume of non-retained water.

RESULTS AND DISCUSSION

As the separation of alcohol ethoxylates in accordance with their alkyl groups is required without influence of the ethylene oxide (EO) group on the elution, various kinds of hydro-organic mobile phase were tested. The results of mobile phase selection showed that acetone-water was suitable for the separation of alcohol ethoxylates according to their alkyl groups, but that other solvents such as methanol, acetonitrile and tetrahydrofuran were not suitable because the elution was strongly affected by the EO group.

The retention behaviour of lauryl alcohol ethoxylates using acetone-water as mobile phase is shown in Fig. 1. The mobile phase composition was varied from 65:35 to 90:10, and the stationary phase was Hitachi gel No. 3053 (150×4 mm I.D.). As shown, the retention time of the alcohol ethoxylate decreased with increasing acetone content in the mobile phase, and moreover, the slope of the linear

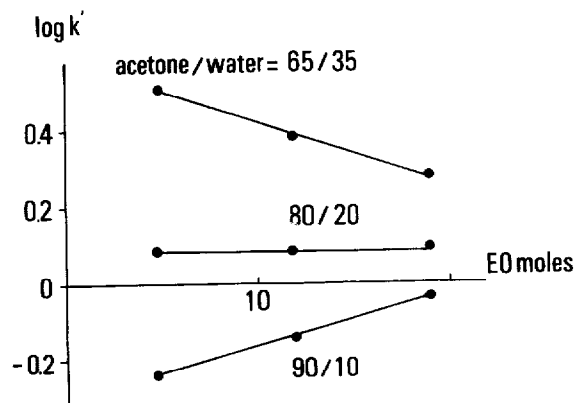


Fig. 1. Relationship between $\log k'$ and the degree of ethoxylation for lauryl alcohol ethoxylate.

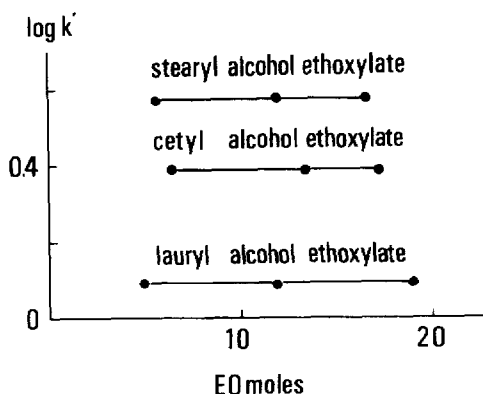


Fig. 2. Retention behaviour of stearyl, cetyl and lauryl alcohol ethoxylates.

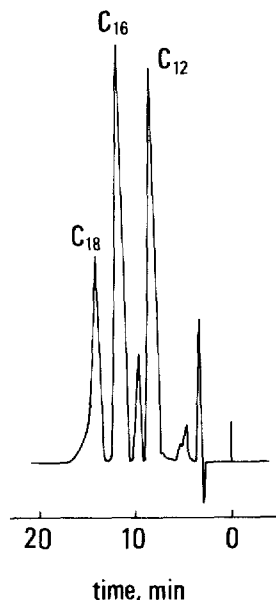


Fig. 3. Typical separation of stearyl, cetyl and lauryl alcohol ethoxylates.

relationship between $\log k'$ and the degree of ethoxylation was reversed in direction between acetone-water compositions of 65:35 and 90:10. The mobile phase acetone-water (80:20) gives a zero slope in the relationship between $\log k'$ and the degree of ethoxylation, which means that lauryl alcohol ethoxylates are eluted without influence from the degree of ethoxylation.

Fig. 2 shows the retention behaviour of lauryl, cetyl and stearyl alcohol ethoxylates using the mobile phase acetone-water (80:20). The alcohol ethoxylates having different alkyl groups are eluted only according to these groups and not according to the degree of ethoxylation.

Fig. 3 shows a typical separation of stearyl, cetyl and lauryl alcohol ethoxylates. The degrees of ethoxylation are 4.3 for lauryl alcohol ethoxylate, 6.0 for cetyl alcohol ethoxylate and 5.2 for stearyl alcohol ethoxylate. The identification of the eluted peaks was carried out by field-desorption mass spectrometry (FD-MS). Peaks which appeared during chromatography were fractionated and then their FD-MS spectra were measured. From the FD-MS measurements, the elution order of these non-ionic surfactants was found to be lauryl, cetyl and stearyl alcohol ethoxylate. The peak eluted between lauryl and cetyl alcohol ethoxylates was identified by FD-MS as C_{14} alcohol ethoxylate. As shown in Fig. 3, these alcohol ethoxylates were separated only according to the difference in their alkyl groups.

Analytical columns packed with various kinds of stationary phase and of various dimensions were used to confirm whether the change of slope in the relationship between $\log k'$ and the degree of ethoxylation was due to the stationary phase or not. The stationary phases were LiChrosorb RP-18, RP-8 and RP-2. The last two were not suitable for the separation of homologous alcohol ethoxylates because of the

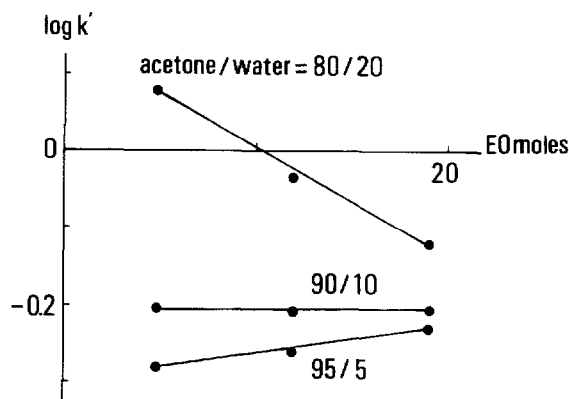


Fig. 4. Retention behaviour of lauryl alcohol ethoxylates using LiChrosorb RP-18 as stationary phase.

lower interaction between these stationary phases and the alkyl groups of the alcohol ethoxylates.

Fig. 4 shows the retention behaviour of lauryl alcohol ethoxylates using column (150 × 8 mm I.D.) packed with LiChrosorb RP-18. The results obtained were similar to those obtained on the column packed with Hitachi gel No. 3053. From these results, the retention behaviours of alcohol ethoxylates illustrated in Figs. 1 and 4 are functions of the hydration and solvent effects of the mobile phase, not of the stationary phase.

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