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Determination of trace amounts of alcohols in sodium alkyl sulphate mixtures using high-performance liquid chromatography and surface tension measurements

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ABSTRACT

A method was developed for the simultaneous trace analysis of C_8, C_{10} and C_{12} alkanols in sodium alkyl sulphate mixtures. The alkanols determined after derivatization with aromatic isocyanates, RNCO (R = phenyl, 1-naphthyl, 2-anthryl). In the preferred method, microbore high-performance liquid chromatography was applied with acetonitrile–water as eluent after derivatization with 1-naphthyl isocyanate at 333 K using an RP-18 5-μm reversed-phase column. The peaks were monitored at 222 nm.

INTRODUCTION

The contamination of surfactants with highly surface-active impurities is a general problem in the interpretation of measurements in surface and colloid chemistry. Sodium alkyl sulphates (SAS) as commonly used model surfactants frequently contain trace amounts of impurities which change their surface properties fundamentally. In earlier papers we described the kinds of impurities in SAS. It has been demonstrated that long-chain alcohols have the strongest effect on the surface and, therefore, the greatest influence on the adsorption isotherms of SAS because of their high surface activity [1]. The determination of residual alcohols and procedures for their removal are prerequisites for exact surface-chemical investigations.

The conversion of alcohols into urethanes with aromatic isocyanates has been examined for its applicability in high-performance liquid chromatography (HPLC) [2–4]. A method for the determination of trace amounts of dodecanol in sodium dodecyl sulphate has been reported [5].

In this paper, results of the derivatization proce-

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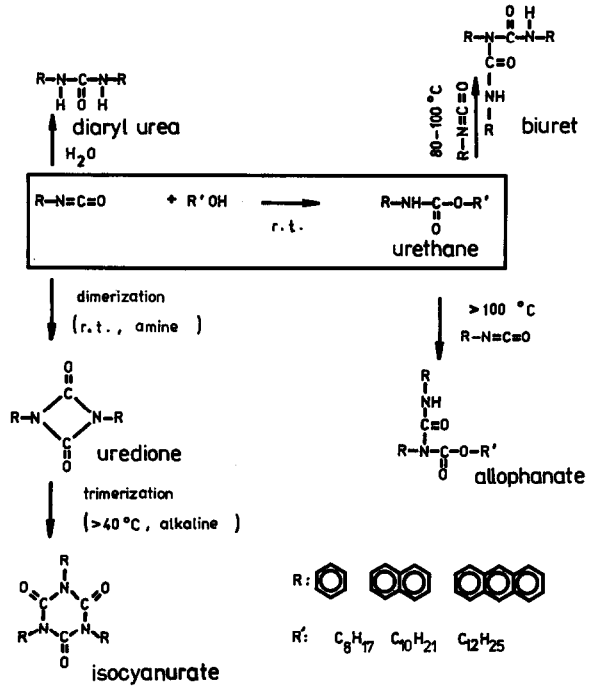

Fig. 1. Derivatization reaction of alcohols with aromatic isocyanates.

dure for phenyl-, 1-naphthyl- and 2-anthrylurethanes are presented. For the simultaneous determination of alcohols in SAS mixtures an improved sensitivity of urethane detection was ascertained by comparing the detection limits of appropriate derivatives using UV detection. In addition, for comparison purposes the influence of alcohols on the surface properties of SAS was studied using surface-tension measurements.

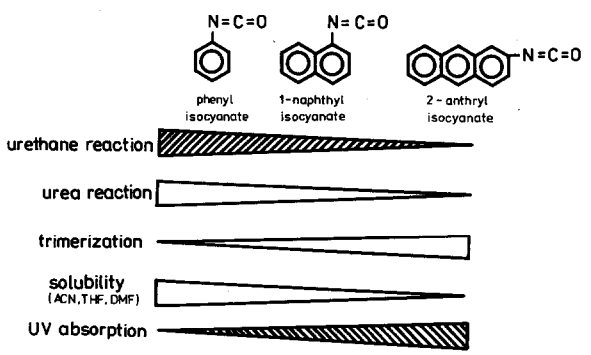

Fig. 2. Effect of coefficients of the derivatization reaction.

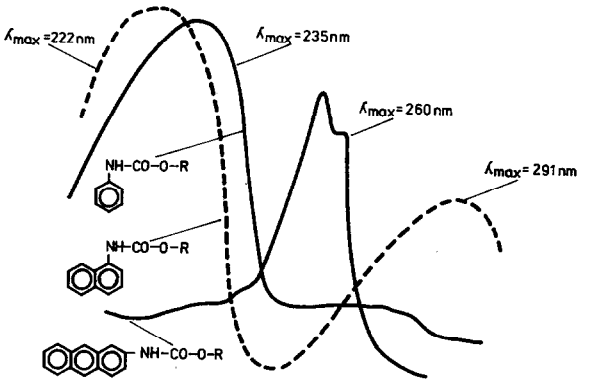

Fig. 3. UV spectra of dodecyl-phenyl-, -naphtyl- and -anthryl-urethane in acetonitrile.

EXPERIMENTAL

HPLC method

The determination of alkanols in SAS was carried out at trace levels (alkanol content 10^{-1}–10^{-3} mol%). For the derivatization of long-chain alcohols with aromatic isocyanates it is important that, on the one hand, the derivatization reaction meets all requirements (fast reaction, complete reaction, relatively few by-products) and, on the other, the detection limit of the derivative is as high as possible. The reaction conditions must be exactly controlled because of various reaction possibilities of isocyanates with alcohols and with themselves (Fig. 1).

The reaction rate of urethane formation decreases from phenyl to anthryl isocyanate and the UV absorption increases in the same direction, which means the sensitivity becomes higher (Fig. 2). From the reaction scheme it also appears that the reaction should be carried out at low temperature and with a short reaction time.

Fig. 3 shows the main maxima for the three urethanes of alkyl chain length C_{12}. The sensitivity limit is shifted depending on the wavelength of UV detection. Considering all these factors (Figs. 1–3), the derivatization reaction for the trace determination of alcohols in SAS was performed with 1-naphthyl isocyanate at room temperature for 30 min and the absorbance was monitored at 222 nm. This method yields excellent results within the derivatizations described. The molar ratio of 1-naphthyl isocyanate to alcohol amounts to 300:1–30 000:1 for 0.1–0.001% alcohol in the SAS, respectively.

Surface tension measurements

Surface tension was measured with an improved ring method as described elsewhere [1]. Special purity of the main component is required in order to characterize trace amounts of highly surface-active alcohols in SAS.

Apparatus

Investigations were carried out on a Hewlett-Packard HP 1090 M liquid chromatograph equipped with a diode-array detector and a ChemStation HP 9000, 300 data system. Microbore columns (100 × 2.1 mm I.D.) packed with 5-μm RP-18 made in the laboratory from silica gel Si 100 and 5-μm Hypersil ODS (Merck, Darmstadt, Germany) were used for chromatographic separations. A 2- or 2.5-μl volume of each sample was injected using an automatic sampler.

Reagents

The eluent was acetonitrile–water. The acetonitrile used was suitable for UV spectrophotometry (Schwedt, Germany).

Liquid chromatography

Derivatized samples (2 or 2.5 μl) were injected into the chromatographic system with an automatic sampler system. Chromatographic separations were carried out at 333 K. The flow-rate was 0.35 or 1 ml min^{-1}, respectively, using gradient elution for optimum separation of urethanes from by-products. The column was washed with acetonitrile and equilibrated after each separation. Standards (O-alkylnaphthylurethanes dissolved in dimethylformamide) were injected for calibration prior to each series of measurements.

TABLE I

MOLAR ABSORPTIVITIES, ε, AND CALIBRATION COEFFICIENTS, *A* (AMOUNT/AREA), OF ALKYLNAPHTHYLURETHANES AT 222 nm

Alkyl chain length	ε (l mol^{-1} cm^{-1})	*A* (mg)
C_8	55 359	$5.3 \cdot 10^{-8}$
C_{10}	54 859	$5.9 \cdot 10^{-8}$
C_{12}	47 779	$6.1 \cdot 10^{-8}$

RESULTS AND DISCUSSION

The absorption maximum of alkylnaphthylurethanes in the UV region at 222 nm was preferred for detection in HPLC (using acetonitrile–water) because of its high molar absorptivity (Table I). The maximum at 200 nm is unsuitable because of solvent absorption in this range and the intensity of the maximum at 290 nm is lower than that at 222 nm.

The absorption maximum of alkylnapthylurethanes at 222 nm is slightly shifted by a change in R. Fig. 4 shows the linearity of the calibration graphs over the concentration range employed. The most suitable concentration range of the alcohols for the determination was 0.001–0.1 mg/ml. Optimum conditions for the determination procedure (amount of naphthyl isocyanate, presence of sodium dodecyl sulphate, method of preparation) selected in a pre-

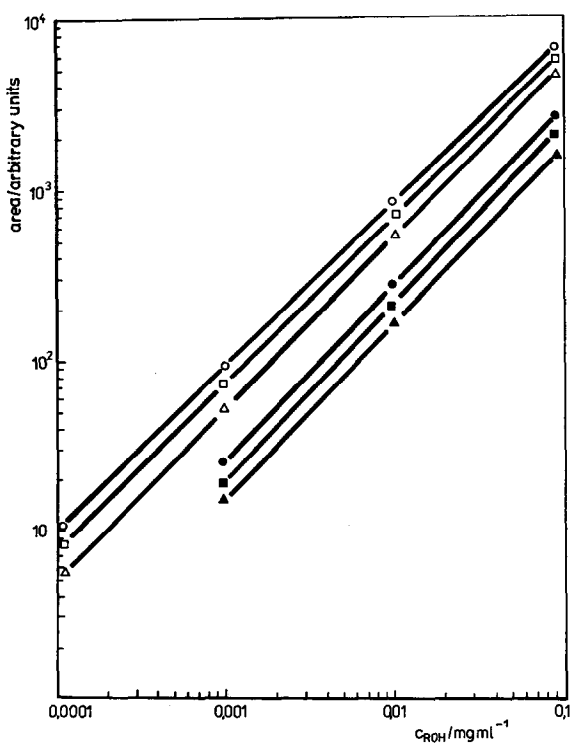

Fig. 4. Calibration with standard urethanes with alkyl chain lengths of (○) C_8, (□) C_{10} and (△) C_{12} and calibration after derivatization in the presence of SAS with alkyl chain lengths of (●) C_8, (■) C_{10} and (▲) C_{12}.

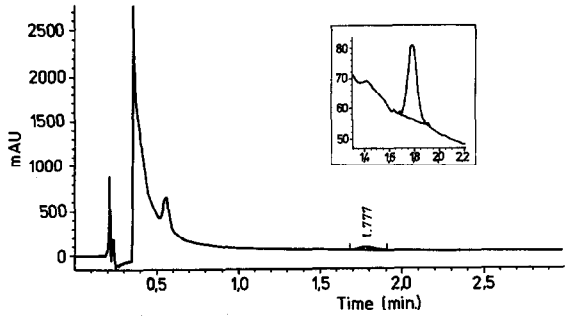

Fig. 5. Chromatogram of dodecylnaphthylurethane from the residual dodecanol (0.01%) in sodium dodecyl sulphate, Column, 5-μm RP-18 (100 × 2.1 mm I.D.). Eluent, A = water, B = acetonitrile; gradient, 0–2.5 min from 78% to 80% B, 2.5–3.75 min from 80% to 100% B, 3.75–6.25 min 100% B, 6.25–6.50 min from 100% to 78% B. Post time, 4.00 min; flow-rate, 1.0 ml min^{-1}; injection volume, 2.5 μl.

vious study [5] were used for calibration and determination. The efficiency of the derivatization process without medium effects was found to be >95% quantitative. The accompanying compounds in the sample caused variations in the adsorption behaviour of the sample solution. Alkylnaphthylurethanes with various carbon numbers in the alkyl chain appear to be adjacent to one another. Good reliability and reproducibility were achieved by using microbore columns and a computer for processing chromatograms. The retention volumes were found to be reproducible.

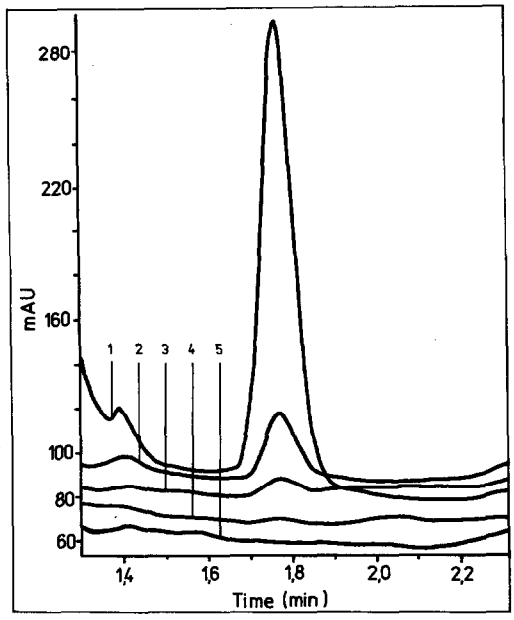

Fig. 6. Integrated peaks of dodecylnaphthylurethanes from dodecanol in sodium dodecyl sulphates of different quality from various producers (1–4) and laboratory-made (5). Column and detection as in Fig. 5. Dodecanol content: 1 = $6.5 \cdot 10^{-2}$; 2 = $1.1 \cdot 10^{-2}$; 3 = $2 \cdot 10^{-3}$; 4 = $1 \cdot 10^{-3}$; 5 = $< 10^{-3}$%.

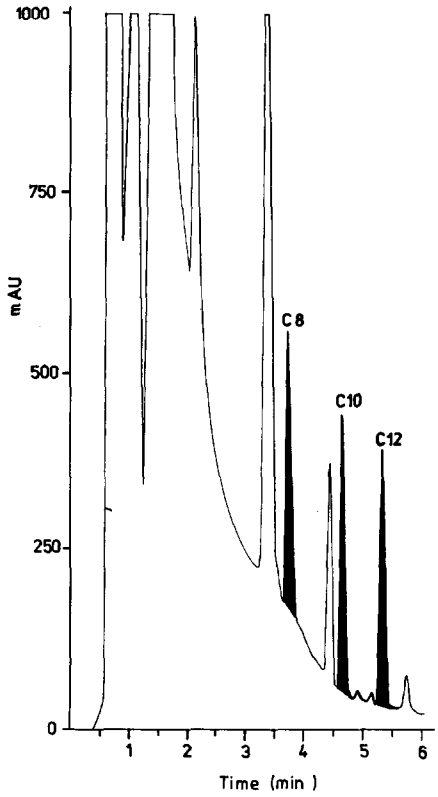

Fig. 7. Separation of alkylnaphthylurethanes of the chain lengths C_8, C_{10} and C_{12} from the mixture of SAS after alcohol derivatization. Column, 5-μm RP-18 (100 × 2.1 mm I.D.). Eluent, A = water, B = acetonitrile; gradient, 0–1 min 55% B, 1–4.5 min from 66% to 100% B, 4.5–5 min, 100% B, 5–6 min, from 100% to 66%. Post time, 2.75 min; flow-rate, 0.35 ml min^{-1}; injection volume, 2.0 μl.

Figs. 5 and 6 show chromatograms and integrated peaks of dodecylnaphthylurethane from residual alcohol in sodium dodecyl sulphates from various commercial producers as well as a laboratory-made product with different dodecanol contents. The lowest impurity content (dodecanol) was found in the laboratory-made product (Fig. 6, curve 5). Fig. 7 shows a chromatogram for the separation of C_8,

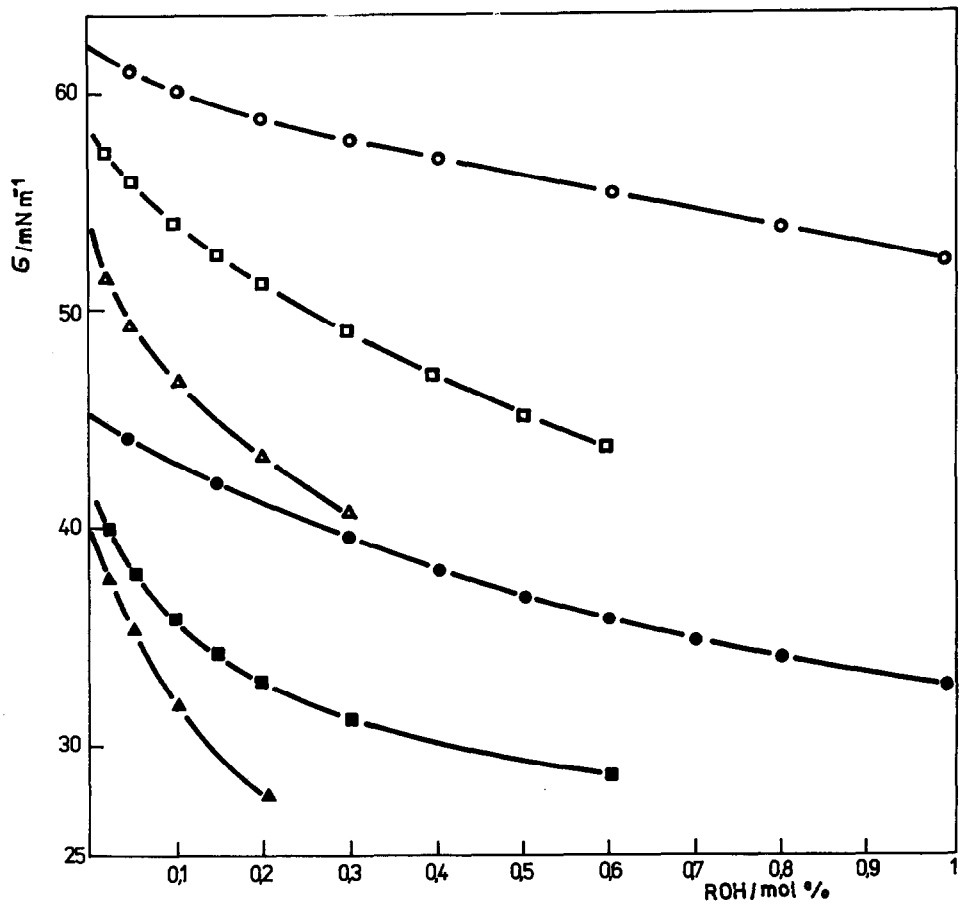

Fig. 8. Depression of the surface tension decreased by alcohols in aqueous solutions of SAS with alkyl chain lengths of C_8, C_{10} and C_{12}. ○ = 0.03, ● = 0.1 *M* sodium octyl sulphate; □ = 0.01, ■ = 0.03 *M* sodium decyl sulphate, △ = 0.003, ▲ = 0.007 *M* sodium dodecyl sulphate.

C_{10} and C_{12} urethanes in a mixture of corresponding SAS.

For comparison, the effect of defined amounts of alcohols on SAS of the same chain length was systematically investigated using surface tension (σ) measurements. The calibration graphs for the alcohol content of sodium octyl, decyl and dodecyl sulphate were measured for selected SAS concentrations near or below the critical micelle concentration. The surface tension changes of an optimally purified SAS solution due to increasing amounts of alcohol of the same alkyl chain length are shown in Fig. 8. In the region between 0.01 and 1 mol% of alcohol the surface tension changes continuously with increasing alcohol ratio, but there is no straight line for σ *vs.* log $c_{alcohol}$ ($\sigma = \sigma_{SAS+alcohol}$) or for σ *vs.* $c_{alcohol}$. Corresponding to the dependence of the surface activity on the alkyl chain length, the sensitivity increases with increasing chain length of the alcohol. Note the concentration differences of sodium octyl, decyl and dodecyl sulphate in Fig. 8.

In conclusion an HPLC method has been introduced for the determination of trace amounts of alcohols into surface-active sodium alkyl sulphates. The procedure is based on the conversion of alcohols into urethanes. The sensitivity of the HPLC method is high, the detection limit being about 10^{-3}%. Compared with surface-tension measurements, the main advantage of the HPLC method is its selectivity to alcohols of different chain lengths. Other trace surface-active compounds do not interfere in the determination of alcohols by HPLC. The

sensitivity of the HPLC method increases slightly with decreasing alkyl chain length of the alcohols, whereas that of the surface-tension measurement increases strongly with increasing alkyl chain length. In this connection the two methods are complementary.

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