

CHROM. 16,108

QUANTITATIVE DETERMINATION OF DODECANOL IN SODIUM DODECYL SULPHATE IN THE NANOGRAM RANGE BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY WITH UV DETECTION

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(Received May 5th, 1983)

SUMMARY

The method described here has been used for the trace analysis of alkanols (carbon number in even-numbered alkyl chain C_8 – C_{16}) in alkyl sulphates, and especially for the determination of residual dodecanol in sodium dodecyl sulphate. The alkanols were determined isocratically with acetonitrile–water (78:22) after derivatization with 1-naphthylurethane at 333°K using a RP-8 10- μ m reversed-phase column. The peaks were monitored at 254 and 290 nm, respectively.

INTRODUCTION

The presence of contaminants with high surface activity is a general problem in the field of investigation of surfactant phenomena. Sodium alkyl sulphates are commonly used surfactants which frequently contain residual alcohol from the synthesis or decomposition (hydrolysis) of the surfactant. Values for the dodecanol content in sodium dodecyl sulphate (SDS) are, however, lacking. Because we wanted to obtain a minimum amount of dodecanol in SDS used as a model surfactant for measurements of surface phenomena, we developed a quantitative method for the determination of trace amounts of dodecanol in SDS.

The low UV absorptivity of long chain alcohols makes the detection of small amounts difficult. To overcome this problem, one must improve the extinction coefficient by derivatization of the alcohol for which we used 3,5-dinitrobenzoyl chloride¹ and phenyl isocyanate². Naphthyl isocyanate was used for the derivatization of alcohols and then following quantitatively by means of high-performance liquid chromatography (HPLC) with fluorescence detection. The derivatization was carried out at 95 and 140°C respectively, in the absence of alkali ions; these would catalyse an ensuing reaction between alkyl urethane and the excess of naphthyl isocyanate to afford biuret as a by-product³.

As the determination of alkanols in alkyl sulphates is in the range of trace analysis (alkanol content 10^{-1} – 10^{-3} %), the aim of this study was to develop a sensitive method by using a reagent which gives a fast quantitative stoichiometric reaction

with the small amount of alcohol, while forming a derivative with high UV absorptivity so as to improve the detection limit.

EXPERIMENTAL

Apparatus

A Hewlett-Packard HP-1084 A liquid chromatograph equipped with a 254-nm fixed wavelength UV detector, a Hewlett-Packard HP-1084 B liquid chromatograph equipped with a variable wavelength UV detector and a data system for processing the chromatograms, a LiChrosorb RP-8 10- μ m reversed-phase column (250 \times 4.6 mm I.D., packing material from E. Merck, F.R.G.) were used for chromatographic separation of the products. Injections of volume 10 μ l were made by an automatic sampler. Solvents were degassed at high temperature under vacuum. A Unicam SP-700 UV-visible spectrophotometer was used for recording the UV spectra.

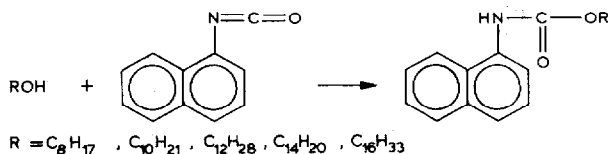
Reagents

The eluent was acetonitrile-water (78:22). The reclaimed acetonitrile-water azeotrope (84% acetonitrile) can be used several times for chromatography without additional purification. *N,N*-Dimethylformamide (DMF) was redistilled twice. For the second redistillation 10 ml of isocyanate C₁₆-C₁₈ per liter of DMF were added to remove isocyanate-consuming compounds. The DMF obtained was UV-pure.

1-Naphthyl isocyanate (α) (purum) (Fluka, Switzerland) was used after two redistillations (b.p. 411–412°K at 12 mmHg). Methanol was redistilled before use. Octanol, decanol, dodecanol, tetradecanol and hexadecanol (puriss.) (Fluka, F.R.G.) were used for preparing the standards for the gas-liquid chromatography tests.

Standards

O-Alkyl-N-naphthylurethane standards were prepared by mixing each alcohol with naphthyl isocyanate in the molar ratio 1:1.1. The products were recrystallized three times from light petroleum (b.p. 333–353°K) until the melting points were constant (Table I). The purity of the standards was checked by elemental analysis, mass spectroscopy and liquid chromatography.



Sample derivatization procedure

Samples and standards were dissolved in DMF. A 1-ml volume of sample solution containing 100 mg of SDS (containing *ca.* 1–10⁻³ mg of dodecanol) was pipetted into a glass-stoppered test-tube, 25 μ l of naphthyl isocyanate was added and the tube was shaken vigorously and allowed to stand for 30 min. A 25- μ l volume of methanol was added in order to destroy the excess of naphthyl isocyanate. The reaction mixture should not be heated to exclude ensuing reactions of the urethane with the isocyanate.

TABLE I
MELTING POINTS OF ALKYL NAPHTHYL URETHANES

R	M.p. ($^{\circ}$ K)
C ₈ C ₁₇	339-339.5
C ₁₀ H ₂₁	345.5-346
C ₁₂ H ₂₅	350-350.5
C ₁₄ H ₂₉	355.5-356
C ₁₆ H ₃₃	358.5-359

At an impurity of the SDS sample of 1% dodecanol, the molar ratio of 1-naphthyl isocyanate (mol.wt. 169.2) to dodecanol (mol.wt. 186.3) amounts to 30:1; at an impurity of 0.01% dodecanol in the sample, the ratio amounts to 3000:1. The molar ratio of methanol to naphthyl isocyanate amounts to 3.5:1.

Liquid chromatography

Derivatized samples and standards (10 μ l) were injected into the chromatographic system with an automatic sampler system. The LiChrosorb RP-8 10- μ m reversed-phase column was kept in a thermostated oven at 333 $^{\circ}$ K. O-Dodecyl naphthyl urethane was determined isocratically (acetonitrile-water, 78:22). The column was washed and equilibrated after each separation by means of gradients.

The standard (O-dodecyl naphthyl urethane dissolved in DMF) was injected for each series of measurements for calibration. The peaks were monitored at 254 and 290 nm. Chromatograms were processed quantitatively with the Hewlett-Packard 79850 A LC integrator. The peak-area measurement technique with the tangent skin method gave well reproducible results.

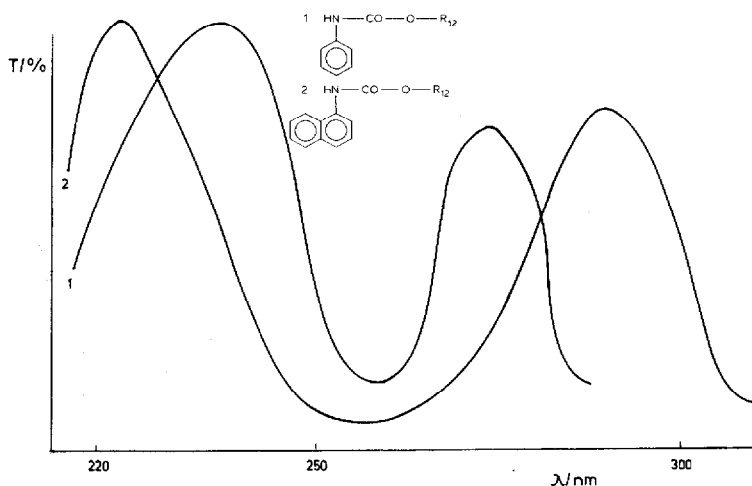
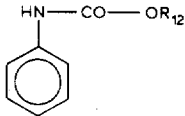
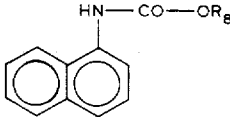
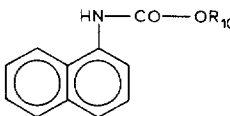
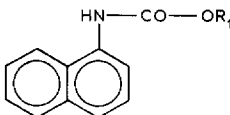
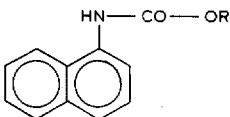
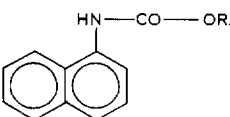


Fig. 1. UV spectra of dodecyl phenyl urethane and dodecyl naphthyl urethane.

TABLE II

EXTINCTION COEFFICIENTS, ϵ , AND CALIBRATION COEFFICIENTS, A (AMOUNT/AREA), OF ALKYL PHENYL URETHANES AND ALKYL NAPHTHYL URETHANES AT VARIOUS WAVELENGTHS

Compound	λ (nm)	ϵ ($l \text{ mol}^{-1} \text{ cm}^{-1}$)	A (mg ml^{-3})
	235	16592	—
	254	682	—
	274	829	—
	223	54859	—
	254	1421	$2.8 \cdot 10^{-6}$
	291	6954	—
	223	55359	—
	254	1641	$3.9 \cdot 10^{-6}$
	290	7069	—
	223	49779	—
	254	1633	$4.6 \cdot 10^{-6}$
	291	6703	—
	223	56862	—
	254	1557	$5.3 \cdot 10^{-6}$
	291	7049	—
	223	55771	—
	254	1790	$5.9 \cdot 10^{-6}$
	291	7199	—

RESULTS

Alkyl phenyl and alkyl naphthyl urethanes have three absorption maxima in the UV region, one at 200 nm, another at 220–240 nm and a third at 270–290 nm (in acetonitrile–water azeotrope, Fig. 1, Table II). The first maximum is unsuitable as a detection wavelength because of solvent absorption in this range. At 254 nm the molar extinction coefficients amount to 700 for the phenyl and 1600 $l \text{ mol}^{-1} \text{ cm}^{-1}$ for the naphthyl derivative (ratio *ca.* 1:2.3). This allows detection down to the 10–0.1 μg level. The detection limit can be shifted down to the ng level by use of a variable-wavelength UV detector. The absorption maximum of alkyl naphthyl urethanes at 290 nm will not be shifted by the change of R.

The linearity of the calibration curve over the concentration region employed (Fig. 2) is also shown under various medium influences (amount of naphthyl iso-

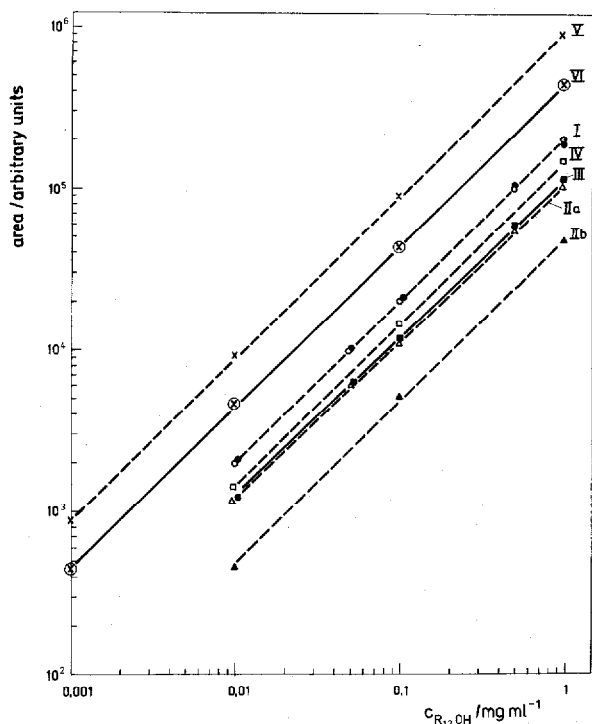


Fig. 2. Investigation of the medium effects. HP-1084 A: I = Calibration with standard and calibration with standard in presence of SDS; IIa = calibration by reaction without SDS (5 μ l of naphthyl isocyanate per 1 ml of sample solution); IIb = calibration by reaction in the presence of SDS (5 μ l of naphthyl isocyanate per 1 ml of sample solution); III = calibration by reaction in the presence of SDS (25 μ l of naphthyl isocyanate per 1 ml of sample solution); IV = calibration by reaction in the presence of SDS (40 μ l of naphthyl isocyanate per 1 ml of sample solution). HP-1084 B: V = Calibration with standard; VI = calibration by reaction in the presence of SDS (25 μ l of naphthyl isocyanate per 1 ml of sample solution).

cyanate, presence of SDS, method of preparation). Derivatization was carried out separately for each concentration. The family of straight lines has similar gradients, which means the extinction coefficient will hardly be influenced. The accompanying compounds in the sample cause variations in the absorption behaviour of the sample solution.

Curve I shows that the calibration leads to the same values both in the presence and absence of the surfactant. The medium influence on the reaction between dodecanol and naphthyl isocyanate in the presence and absence of SDS is shown in curves IIa and IIb. By increasing the amount of isocyanate from 5 μ l (curve IIb) to 25 μ l for each sample (molar ratio of dodecanol to naphthyl isocyanate *ca.* 1:30 up to 1:3000), one obtains curve III. The influence of the surfactant in this measurement range can be regressed by increasing the amount of isocyanate. If the amount of isocyanate is increased any further, the samples become inhomogeneous by precipitation (curve IV). Therefore, optimum conditions were selected and used for calibration and determination; these were ascertained as calibration curve III (HP-1084 A

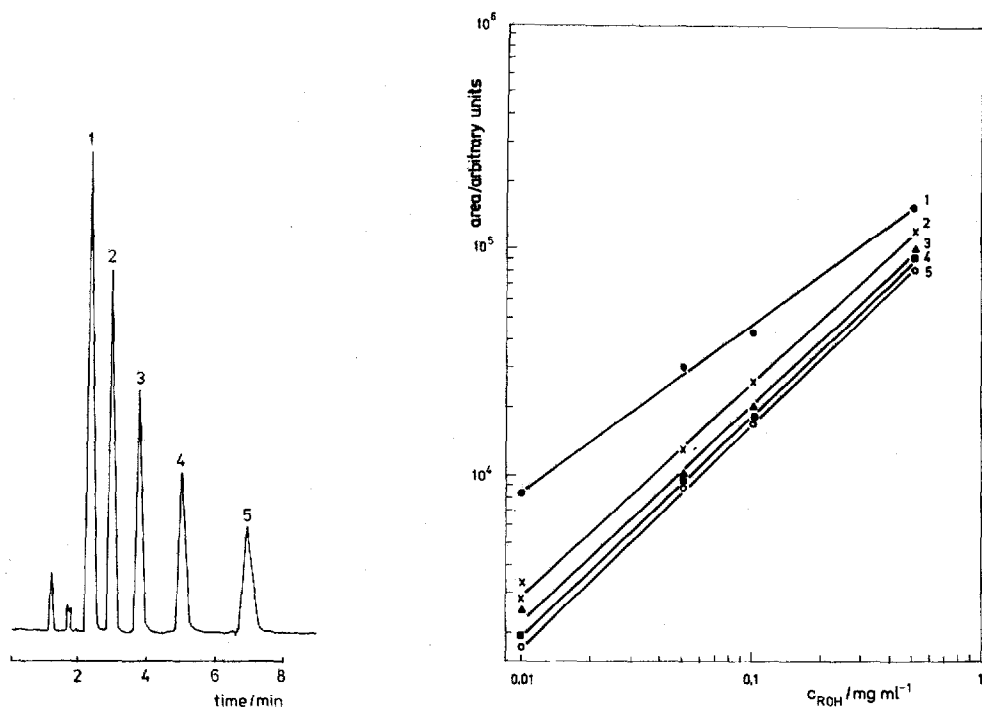


Fig. 3. Separation of alkyl naphthyl urethanes. Column LiChrosorb RP-8 ($10\ \mu\text{m}$), $250 \times 4.6\ \text{mm}$ I.D.; eluent, acetonitrile-water (78:22); UV detection at 254 nm. Peaks: 1 = octanol; 2 = decanol; 3 = dodecanol; 4 = tetradecanol; 5 = hexadecanol.

Fig. 4. Linearity plots for alkyl naphthyl urethanes. Alkyl groups as in Fig. 3.

equipped with a fixed-wavelength detector at 254 nm) and VI (HP-1084 B equipped with a variable-wavelength detector at 290 nm), respectively.

Fig. 3 shows that alkyl naphthyl urethanes of various carbon numbers in the alkyl chain are well detectable and appear adjacent to one another (even-numbered $\text{C}_8\text{--C}_{16}$). The change in the retention time of the alkyl naphthyl urethanes by varying the water content in the eluent is described in Table III. The molar extinction coefficients at 254 and 290 nm are almost constant (Fig. 4).

TABLE III

DEPENDENCE OF ALKYL NAPHTHYL URETHANE RETENTION ON THE COMPOSITION OF THE ELUENT

Column and detection as in Fig. 3.

Volume of water in the eluent (%)	k' Values				
	C_8	C_{10}	C_{12}	C_{14}	C_{16}
32	1.58	2.63	4.35	7.15	11.75
27	1.08	1.75	2.78	4.41	6.96
22	0.72	1.14	1.75	2.67	4.04
17	0.51	0.78	1.15	1.68	2.45

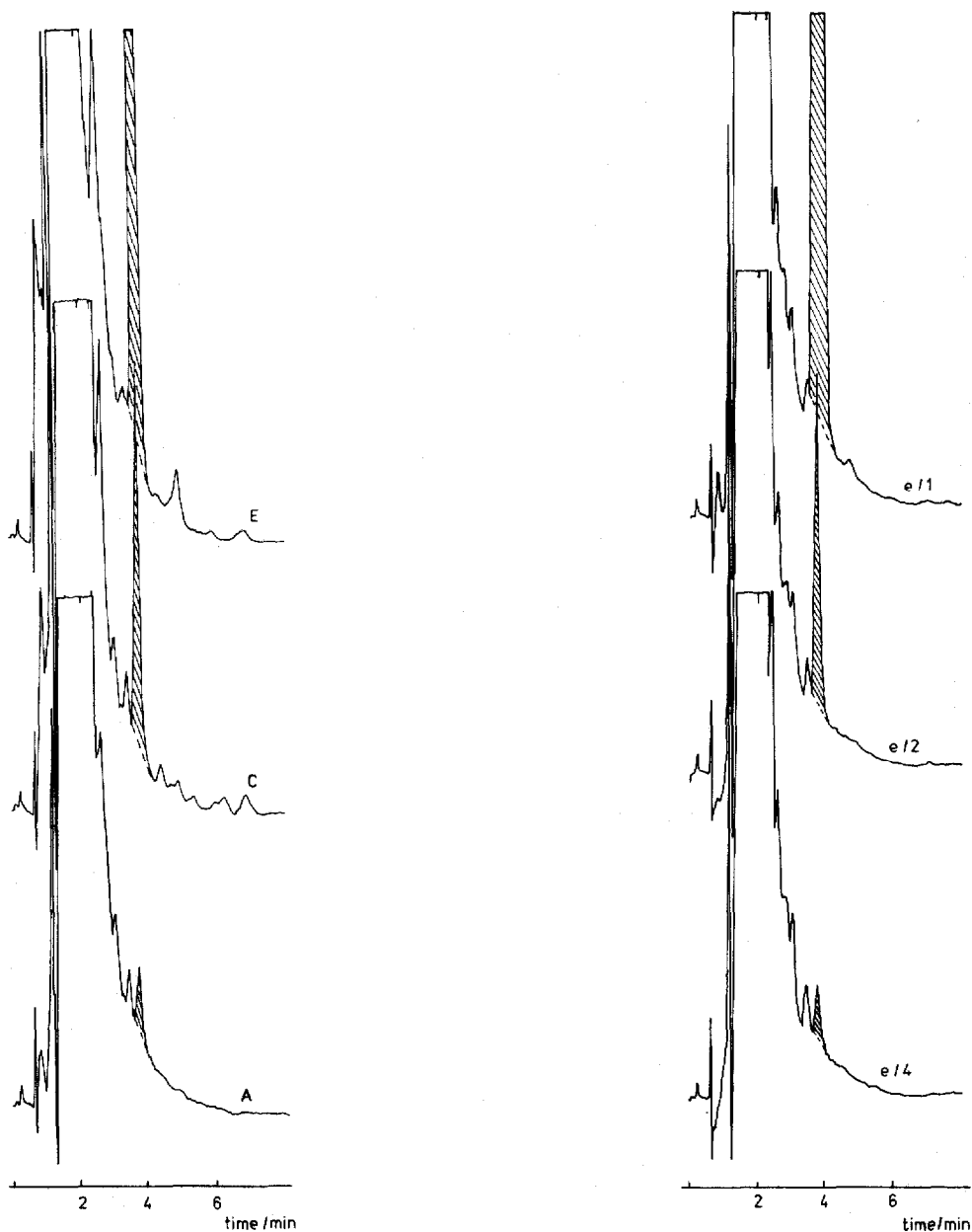


Fig. 5. Chromatograms of dodecyl naphthyl urethanes from the residual dodecanol in commercial sodium dodecyl sulphates. Column and eluent as in Fig. 3. UV detection at 290 nm.

Fig. 6. Chromatograms of dodecyl naphthyl urethanes from the residual dodecanol in home-synthesized sodium dodecyl sulphates prepared using different crystallization steps. Column and detection as in Fig. 5. Symbols for the dodecyl sulphates as in Table IV.

APPLICATIONS

Fig. 5 shows chromatograms of dodecyl naphthyl urethanes from residual dodecanol in the commercial sodium dodecyl sulphates of various producers. The products differ in content of dodecanol (Table IV). Fig. 6 shows chromatograms of dodecyl naphthyl urethanes in home-made sodium dodecyl sulphates. The content of dodecanol decreases with the number of crystallization steps (Table V).

A surface method for the determination of dodecanol in SDS of various qualities is the quantitative processing of the minimum in the region of critical micelle concentration (c.m.c.) by surface tension measurements of aqueous surfactant solutions⁴. Fig. 7 shows the standard plot for this determination method.

TABLE IV

DODECANOL CONTENT IN COMMERCIAL SODIUM DODECYL SULPHATES

Sodium dodecyl sulphate	Dodecanol (%)		
	HPLC method		C.m.c. method
	$\lambda = 254 \text{ nm}$	$\lambda = 290 \text{ nm}$	
A	—	$1.8 \cdot 10^{-3}$	—
B	$9.4 \cdot 10^{-3}$	$1.6 \cdot 10^{-2}$	$1.2 \cdot 10^{-2}$
C	$2.9 \cdot 10^{-2}$	$2.9 \cdot 10^{-2}$	$3.0 \cdot 10^{-2}$
D	$9.3 \cdot 10^{-2}$	$9.0 \cdot 10^{-2}$	$1.0 \cdot 10^{-1}$
E	$1.0 \cdot 10^{-1}$	—	$0.7 \cdot 10^{-1}$
F	$2.7 \cdot 10^{-1}$	—	$3.2 \cdot 10^{-1}$

TABLE V

DODECANOL CONTENT IN HOME-MADE SODIUM DODECYL SULPHATES PREPARED USING VARIOUS CRYSTALLIZATION STEPS

Sodium dodecyl sulphate	Dodecanol (%)		
	HPLC method		C.m.c. method
	$\lambda = 254 \text{ nm}$	$\lambda = 290 \text{ nm}$	
a	—	$1.7 \cdot 10^{-3}$	—
b/1	$2.3 \cdot 10^{-1}$	—	$2.8 \cdot 10^{-1}$
c/2	$5.8 \cdot 10^{-2}$	—	$7.3 \cdot 10^{-2}$
d/2	$5.4 \cdot 10^{-2}$	—	$7.3 \cdot 10^{-2}$
e/1	$8.2 \cdot 10^{-1}$	$7.8 \cdot 10^{-1}$	$7.9 \cdot 10^{-1}$
e/2	$1.3 \cdot 10^{-2}$	$1.5 \cdot 10^{-2}$	$1.3 \cdot 10^{-2}$
e/3	—	$1.6 \cdot 10^{-3}$	—
e/4	—	$1.5 \cdot 10^{-3}$	—
f/2	$3.8 \cdot 10^{-2}$	$4.0 \cdot 10^{-3}$	$3.9 \cdot 10^{-2}$
f/3	—	$1.3 \cdot 10^{-3}$	—
f/4	—	$< 10^{-3}$	—

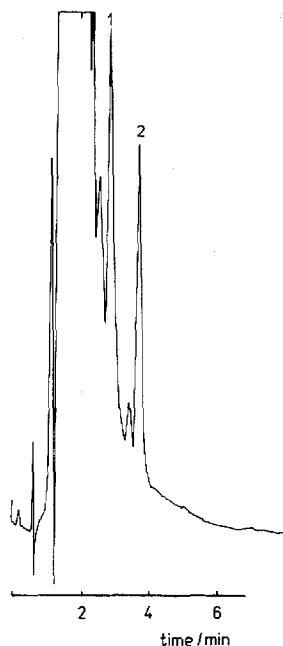
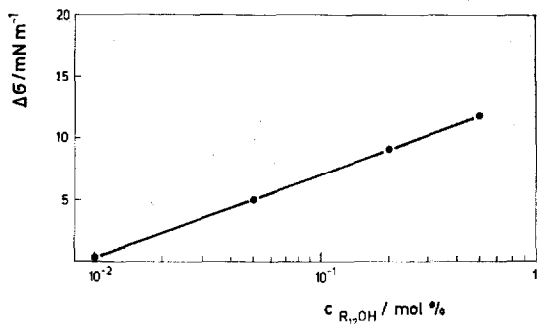


Fig. 7. Detection of dodecanol in sodium dodecyl sulphate by quantitative evaluation of the c.m.c. minimum in the surface tension-concentration curve.

Fig. 8. Separation of alkyl naphthyl urethanes. Column and detection as in Fig. 5. Peaks: 1 = decyl naphthyl urethane from decanol in sodium decyl sulphate; 2 = dodecyl naphthyl urethane from dodecanol in sodium dodecyl sulphate.

At 254 nm the same detection limit was found for the c.m.c. method and the HPLC method while at 290 nm the HPLC method is more sensitive. The results of the two methods are compared in Tables IV and V for commercial and home-made sodium dodecyl sulphates.

Fig. 8 shows a chromatogram for the separation of dodecanol and decanol in a mixture of sodium dodecyl sulphate with sodium decyl sulphate.

CONCLUSIONS

The method described here has been used for the determination of alkanol traces (carbon number in even-numbered alkyl chain: C_8 - C_{16}) in alkyl sulphates, and especially for the determination of residual alcohol (dodecanol) in sodium dodecyl sulphate. The method works well and can be used for any alcohol provided that the corresponding urethane can be eluted. It is shown that the HPLC method is more sensitive than the surface-tension method (determination of the amount of dodecanol by measurement of the minimum in the region of critical micelle concentration of the surface tension-concentration curve).

ACKNOWLEDGEMENTS

We thank Mrs. B. Drescher and Mrs. U. Modrow for expert technical assistance and good nerves during the development of the method. We are grateful to Dr. K. Schwarz and Mrs. K. Kleiner for registering the UV spectra and for determining the extinction coefficients.

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