RELATIONSHIPS BETWEEN THE STRUCTURE OF ALKYLPHENOL-POLYETHYLENEGLYCOL ETHER TENSIDES AND THEIR ULTRAVIOLET SPECTROSCOPICAL PROPERTIES

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Summary

UV spectroscopy was used for the determination of the ethoxylation degree of alkylphenol polyethylenglycol ether (alkylphenol-ethylene oxide) condensates. The method is based on a transformed Lambert–Beer law, i.e. the specific absorbance is a linear function of the reciprocal molecular mass. Two types of tensides were examined. It was found that the three *para*-alkyl derivatives (octyl, nonyl, dodecyl) have similar molecular absorption coefficients, but 2,4,6-tributyl-substitution decreased this value. The fact is in accordance with the characteristic bandshapes. The practical significance of the work in the analysis of tensides is also presented.

Researchers have dealt for long with the determination of the average condensation degree of alkylphenol-ethylene oxide condensates and several "classical" methods [1] have been developed. Izawa described an UV spectroscopic method [2] for the quantitative determination of tensides of this type, but his method did not provide information about the composition of the measured surfactant. Drugarin et al. worked out a modern and quick instrumental analytical method for determining the degree of ethoxylation (hereinafter marked EO) by measuring the refractive index of tensides [3]. Recently UV and IR spectroscopic methods were reported by De la Guardia et al. [4, 5]; they determined the degree of condensation and the molecular mass of nonylphenol-ethylene oxide condensates.

The purpose of our work was to apply UV spectroscopy to the determination of the EO, the molecular mass and the HLB (hydrophobic-lipophilic balance). Besides, the influence of the structure of the substituted phenol polyethyleneglycol ether and the length of the alkyl chain upon the wavelength of the UV absorption maximum, the molecular absorption coefficient ($\varepsilon(\lambda)$) and the shape of the absorption band has been studied.

A transformed form of the Lambert–Beer law of absorption spectroscopy has been used as the basis of our work

$$A^{1\%}_{1\,\mathrm{cm}}(\lambda) = 10 \cdot \varepsilon(\lambda)\ M^{-1} \qquad (1)$$

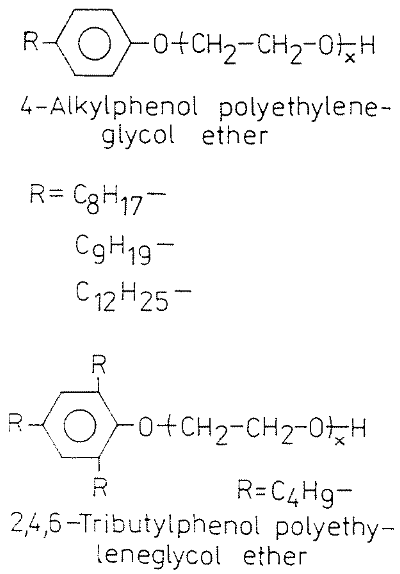

Fig. 1

where $A^{1\%}_{1\,\mathrm{cm}}(\lambda)$ = specific absorbance
$\varepsilon(\lambda)$ = molecular absorption coefficient
M^{-1} = reciprocal molecular mass

According to Eq. (1) the specific absorbance is a linear function of the reciprocal molecular mass, the slope of the function being $\varepsilon(\lambda)$, which is a specific feature of "UV-active" substances. Eq. (1) is suitable for determining the molecular mass in all cases where the UV-chromophores are the same and the molecule is increased by a "UV-inactive" part. An important group of surfactants of this kind are the alkylphenol-ethylene oxide condensates (alkylphenol polyethyleneglycol ethers). The UV-chromophore part is the substituted benzene ring, the "UV-inactive" part being the repeated ethylene oxide units.

Figure 1 shows the formulas of the two types of compounds examined.

Experimental

The UV data were obtained using a Pye Unicam Model SP-1800 UV spectrophotometer with 1 cm quartz cell. The tensides were dissolved in spectroscopic grade methanol. The accuracy of the weighing of the tensides was 0.1 mg.

Results and discussion

Examination of the UV spectra of the two types of tensides shown in Fig. 2 reveals the interesting feature that their absorption maxima are at the same wavelength (278 nm), but the average ε (278) values and the shapes of the bands are different.

The two latter observations indicate that the substitutions of the benzene ring and, consequently, the UV-chromophore parts are different. We suppose that the 2,4,6-substitution gives rise to a vibrational transition, which is different from that caused by parasubstitution, and the former is superimposed onto the absorption band. This characteristic shape of the band can be found in all the five members of 2,4,6-substituted compounds. In the spectra of the *para*-alkyl-substituted derivatives only a small shoulder can be seen on the absorption peak.

Table 1 presents the determined specific absorbance values. Table 1 shows well the linear relationship between the reciprocal molecular mass and the specific absorbance. In the case of the three *para*-alkyl-substituted compounds the average *ε(278) = 1400;* for the 2,4,6-trialkyl-substituted derivatives this value is lower, *ε(278) = 850.* The deviation of the two molecular absorption coefficients may be explained by the difference between the delocalization energies or by the disparate symmetry conditions. The established connections have great practical importance.

Examining a group of tensides having the same UV-chromophore part, it is sufficient to measure the specific absorbances of only two or three known members of the series (which differ in EO) and the unknown molecular masses and EO values of the other members can be readily calculated by Eqs (2) and (3).

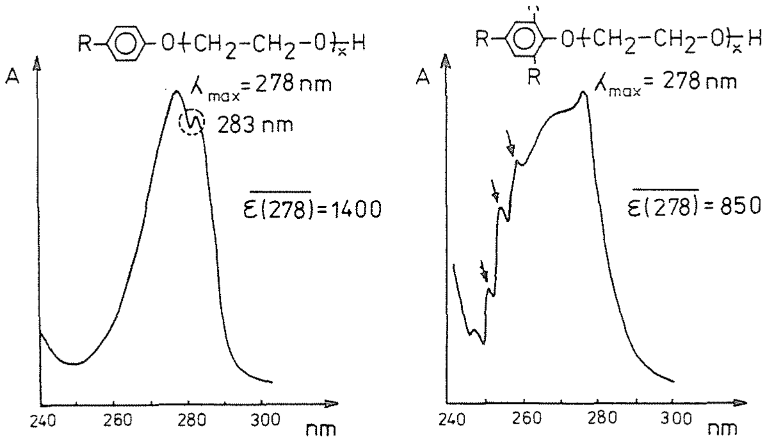

Fig. 2. UV spectra of the two types of compounds examined

Table 1

Summary of the measured results

4-Octylphenol polyethyleneglycol ether

Molecular mass	Ethylene oxide number	10^{-4} M^{-1}	$A_{1\,cm}^{1\%}(278)$	$\varepsilon(278)$
2406	50	4.2	5.8	1400
1086	20	9.2	13.4	1455
426	5	23.5	34.4	1465
338	3	29.6	43.5	1470
250	1	40.0	57.0	1425

2, 4, 6-Tributylphenol polyethyleneglycol ether

Molecular mass	Ethylene oxide number	10^{-4} M^{-1}	$A_{1\,cm}^{1\%}(278)$	$\varepsilon(278)$
2462	50	4.1	3.5	858
1054	18	9.5	8.1	853
834	13	12.0	10.2	851
614	8	16.3	13.9	853
438	4	22.8	19.4	849

$$M_{\text{tenside}}\,(\text{unknown}) = \frac{10 \cdot \varepsilon(\lambda)\,(\text{average})}{A_{1\,\text{cm}}^{1\%}(\lambda)\,(\text{unknown})} \tag{2}$$

$$EO = \frac{M_{\text{tenside}} - M_{\text{phenol}}}{44} \tag{3}$$

The EO is a very important number in the application of tensides. Increasing the number of the ethylene oxide units, the hydrophilic character of the tensides of this kind becomes stronger.

By the use of this simple method the splitting of the ether bonds with hydrogen iodide, which is the usual procedure is tenside analysis, is unnecessary. The HLB (hydrophobic-lipophilic balance) values of the surfactants, being characteristic of polarity, can be simply calculated by Eq. (4) from the determined molecular mass.

$$HLB = 20\left(1 - \frac{M_{\text{phenol}}}{M_{\text{tenside}}}\right) \tag{4}$$

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