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ANALYSIS OF NON-IONIC SURFACTANTS OF THE ALKYLPHENOL TYPE IN THE PRESENCE OF MINERAL OIL BY MEANS OF LIQUID CHROMATOGRAPHY

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SUMMARY

A method has been developed for the determination of trace amounts of non-ionic surfactants of the alkylphenol type and mineral oil in waste waters. The separation of different Arkopals, p-$C_9H_{19}\cdot C_6H_4\cdot O\cdot(CH_2\cdot CH_2O)_nH$, according to the number of ethylene oxide units by liquid–liquid chromatography is described. The procedures were elaborated for the discrimination of oil and surfactant components in the sample. Selective detection of both components in the UV region (254 and 285 nm) was used. UV and IR spectra of the surfactants are shown.

An enrichment procedure using a pre-column packed with Porapak Q was tested. Water, in which trace amounts of Arkopal and oil were to be determined, functioned as a very weak mobile phase in the pre-column. After completion of the enrichment procedure, n-hexane was used as a strong mobile phase with simultaneous pre-column heating. Enrichment factors of up to 10^6 were determined, which enabled the components at concentrations down to the parts per million level to be determined. The error of the determinations was calculated.

INTRODUCTION

Non-ionic surfactants are often found in waters together with mineral oils, mostly in the form of oil emulsions. Ethylene oxide adducts of alkylphenols represent a common type of non-ionic surfactants in waters. The most frequent number of ethylene oxide units in a molecule of these surfactants is 6–20.

The concentration of non-ionic surfactants in surface waters is usually about 0.1 mg/l or even less, and up to tens of milligrams per litre in waste waters. In potable waters, non-ionic surfactants mostly occur in trace concentrations. The concentration of mineral oils is usually comparable with or higher than that of non-ionic surfactants.

Both the physico-chemical analysis of non-ionic surfactants of the ethylene oxide adduct type and chromatographic separation methods[1] have received considerable attention[2]. The separation of non-ionic surfactants of the alkylphenol type according to the number of ethylene oxide units added has been carried out, for example by paper and thin-layer chromatography[3–5], but usually with only a semiquantitative evaluation. Analysis by gas chromatography was successful only with ethylene oxide surfactants with a small ethylene oxide content[6–10]. Adsorption column chromatography[11,12] and gel permeation chromatography[6,13,14] have also been used. Liquid chromatography has recently been applied to the separation of non-ionic surfactants[15,16].

The separation of mineral oils and non-ionic surfactants from water is difficult. For example, column adsorption gradient chromatography on silica gel[17] has been used for this purpose. A mixture of non-ionic surfactants containing mineral oil was adsorbed on silica gel and eluted gradually with chloroform and mixtures of chloroform with more polar solvents (diethyl ether, acetone, methanol). The separation of mineral oils and non-ionic surfactants in emulsions was carried out on columns with mixed ion-exchanger in the H^+ and OH^- cycle[18]. In order to separate non-ionic surfactants of the alkylphenol type from fat substances (lanolin), gel permeation chromatography on Sephadex LH-20 has been utilized[19].

EXPERIMENTAL

Materials

Commercial samples of isononylphenols having on average 4–9 molecules of ethylene oxide in one surfactant molecule (Arkopal N-040 to N-090, Hoechst, Frankfort, G.F.R.) were used. These are isononylphenols with *tert.*-butyl and isopropyl[20,21] terminal groups. Samples with up to 13 ethylene oxide units are liquids, while those with higher numbers of ethylene oxide units are pasty, semi-solid or even solids.

Mineral oil B21 is a distillate from a naphthenic aromatic crude oil from the Matzen region of Austria. It is a light mineral oil spin distillate with a viscosity of 4.7–5.5° Engler-degrees at 20 °C. Contents of about 66% of cycloalkanes and 30.2% of aromatics, of which about half comprises mononuclear aromatics, were found by column adsorption chromatography. The average molecular weight is about 280.

Instrumentation

Chromatographic measurements were carried out in the apparatus shown in Fig. 1. The mobile phase, analytical grade *n*-hexane (Lachema, Brno, Czechoslovakia), was aspirated from a glass reservoir (1) by an MC 300 pump (4) (Mikrotechna, Prague, Czechoslovakia) through a degasifier (2), whose bath was heated at 54°, and a three-way stopcock (3). The mobile phase was delivered from the pump (4) through a device for damping pressure pulses (5) according to Locke[22] and manometer (6) to a brass saturation column (7) of length 50 cm and I.D. 0.4 cm. Then it was delivered into a sampler (8) and analytical column (9), 250 cm long and I.D. 0.2 cm, which was assembled from five 50 cm long stainless-steel pieces. The saturation column (7) was packed with Chezasorb (Lachema), grain size 0.1–0.25 mm, coated with 30% polyethylene glycol 400 (Carlo Erba, Milan, Italy); the separation column (9) was packed with Chezasorb, grain size 60–80 μm (graded[23] in this Institute), coated with 15%

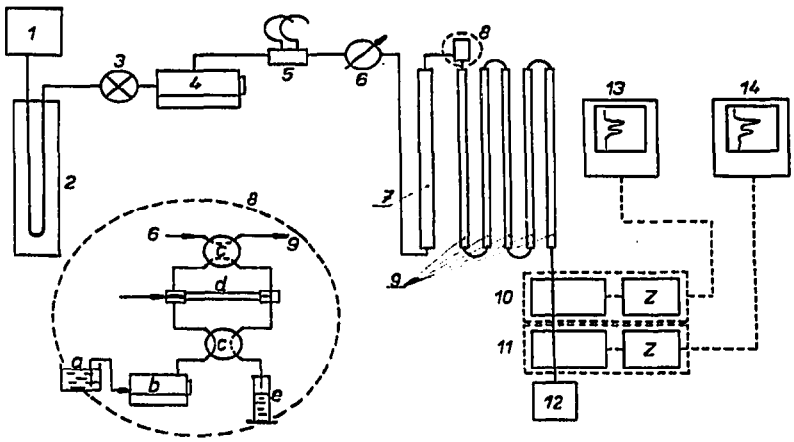

Fig. 1. Diagram of the chromatograph. For description, see text.

polyethylene glycol 400. The eluate from the analytical column was transferred into a flow-through cell of a UV analyzer (wavelength 285 nm) (10), then through a PTFE capillary, about 15 cm long and I.D. 1 mm, into a flow-through cell of another UV analyzer (wavelength 254 nm) (11) (both of the UV analyzers were manufactured in the Development Workshop of the Czechoslovak Academy of Sciences, Prague, Czechoslovakia) and then into a waste collector (12). The responses of both detectors were led to two EZ 11 recording millivoltmeters (13, 14) (Laboratory Instruments, Prague, Czechoslovakia). The operating pressure in the overpressure part of the arrangement was 9 atm and the mobile phase flow-rate was 0.45 ml/min. Both flow-through cells were manufactured in this Institute, and their volume was *ca.* 45 μl and optical path 1 mm.

An LC M2 wire detector (Pye Unicam, Cambridge, Great Britain) was used for some of the measurements.

The sampling equipment (8) was replaced for the enrichment procedure (see Fig. 1) with a device consisting of two four-way stopcocks (c) (Development Workshop, Czechoslovak Academy of Sciences), between which a brass enrichment pre-column (d) (8 cm long, I.D. 0.8 cm) packed with Porapak Q, grain size 80–100 mesh, was inserted. Another MC 300 pump (b) was connected additionally to the system, which permitted the delivery of water under analysis (a) through the enrichment column (see Fig. 1).

Procedure for measurements

Standard mixtures of Arkopal N-040, N-060 and N-090 with mineral oil B21, prepared by weighing, and pure compounds were sampled by Hamilton injection syringes into a flow of the mobile phase and the detector responses were followed on both recorders. The calibration and quantitative determination of Arkopals and mineral oil were also carried out in this way. The capacity of the pre-column was tested for the enrichment procedure by injecting the mixture prepared on the pre-column and washing with a known volume of distilled water.

The stopcocks on the modified apparatus were first correctly adjusted and pump b was switched on. After washing all tubing with water, the sample (Arkopal,

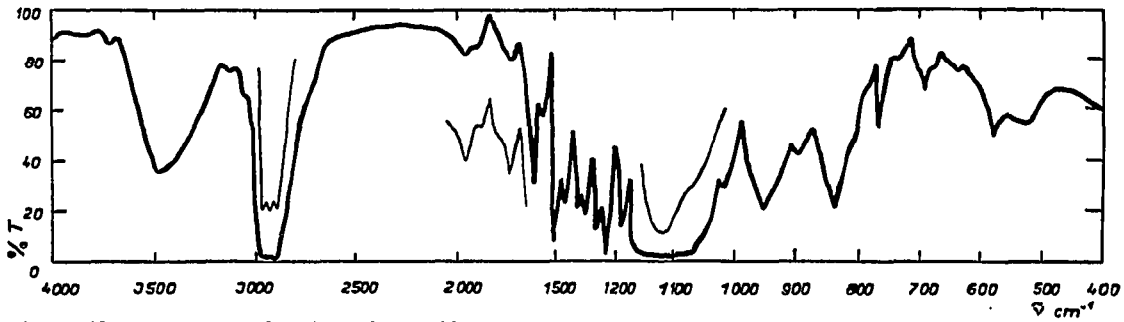

Fig. 2. IR spectrum of Arkopal N-060.

mineral oil and mixture) on the enrichment column. After a known volume of water had been passed, the stopcocks were adjusted in such a way that the mobile phase (*n*-hexane) would also pass through the enrichment column. At the same time, the heating of the enrichment column was switched on at *ca.* 50°. The sample was thus washed out from the column. The further procedure of the analysis was identical with the procedure described above.

RESULTS AND DISCUSSION

The production of surfactants of the type under study provides preparations with a relatively wide range of molecular weights, *i.e.*, with varying numbers of ethylene oxide units in the molecule of the surfactant. Even in commercial preparations, with stated average numbers of ethylene oxide units in the molecules, a distribution of molecular weights can always be found, which has recently been studied by Huber *et al.*[16]. Fig. 2 shows the IR spectrum of Arkopal N-060. The distribution of individual components in Arkopal N-040, N-060 and N-090 preparations is shown in Fig. 3. The content was evaluated from the heights of the peaks obtained by the separation in the system *n*-hexane (mobile phase)–polyethylene glycol 400 on

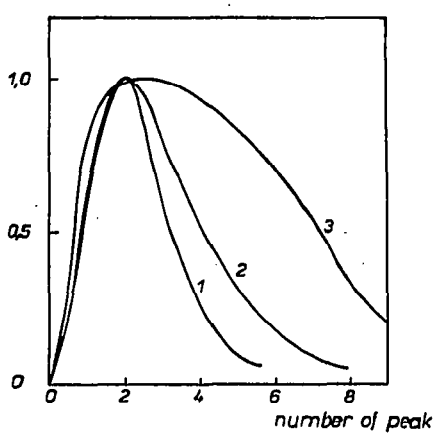

Fig. 3. Distribution of the peak heights for Arkopals: 1, N-040; 2, N-060; 3, N-090.

Chezasorb (stationary phase). The peak heights were normalized to the peak corresponding to the largest content of the component.

In order to verify that the purity of the fractions separated was satisfactory, the spectra from the first fraction collected were measured in the UV and IR regions. The UV and IR spectra corresponded to the spectra of Arkopal. In Fig. 4, the UV

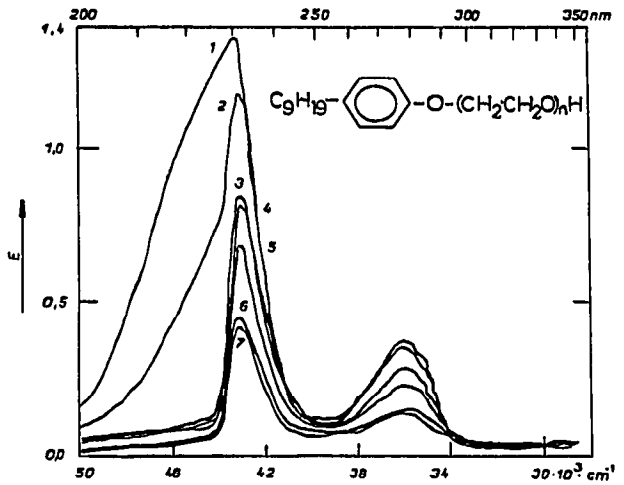

Fig. 4. UV spectra of Arkopals: 1, N-040; 2, N-060; 3, N-090; 4, N-100; 5, N-150; 6, N-230; 7, N-300.

spectrum is shown for various molecular weights of Arkopal. Despite the fact that the separation of the non-ionogenic surfactants according to molecular weight is possible, the first fraction could not be separated successfully from the fraction of mineral oil without using a gradient.

The spectra in the UV region provide the basis for a relatively simple solution of the quantitative determination of surfactants in the presence of mineral oil. Non-ionic surfactants of the alkylphenol type with an ethylene oxide chain have second maxima in *n*-heptane in the region of 276–284 nm (ref. 20), while the spectrum of oil decreases monotonously from the maximum at *ca.* 230 nm. As the spectrum of Arkopals has a minimum in the region of 250 nm, two UV spectrophotometers, connected either in series or in parallel, can be used for the determination of oil (254 nm) and Arkopals (285 nm). Also, it is evident that in both instances, absorption caused by the other component occurs. Chromatograms 1 and 2 in Fig. 5 are shown as examples.

In order to evaluate quantitatively the concentration of Arkopal in waters in the presence of mineral oil, the regular distribution of molecular weights in the preparations under study was used. After analyzing the pure preparation, the content of the first component that overlaps the oil fraction can be determined. The contents of both mineral oil and Arkopal can be determined in the first fraction by means of calibration curves. The precisions of both procedures were compared. When two detectors were used, the standard deviations of the determination of Arkopal N-040

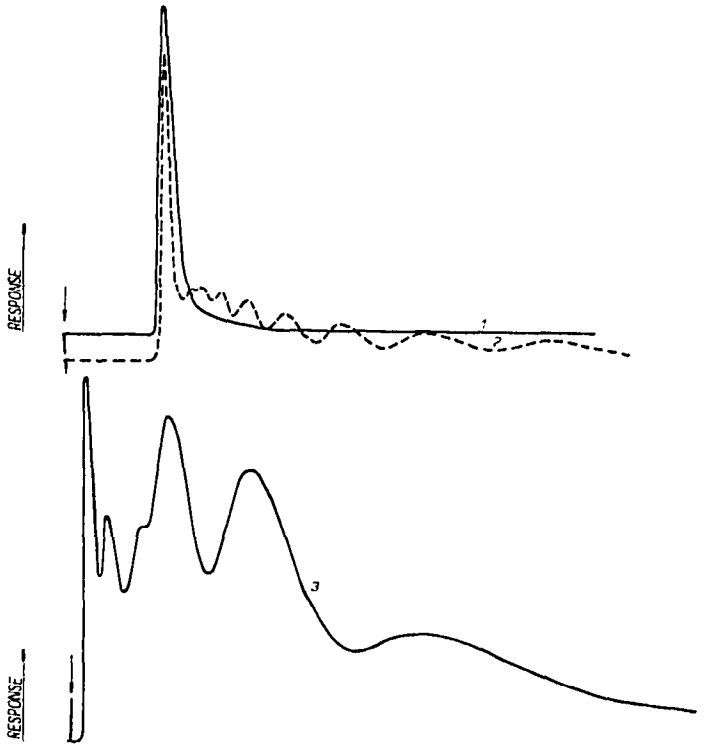

Fig. 5. Chromatograms of (1) a mixture of Arkopal N-060 and mineral oil, UV detector, 254 nm; (2) a mixture of Arkopal N-060 and mineral oil, UV detector, 285 nm; (3) a mixture of Arkopal N-040 and mineral oil, wire detector (Pye Unicam LC M2).

and N-060 were ± 21.2 and 5.2% (relative), respectively, while when one UV detector (285 nm) was used for the determination of the content, the standard deviations were 11.2 and 2.6% (relative), respectively.

The oil fraction could partially be separated from the surfactant by using a separation column 25 cm long and I.D. 2 mm, packed with Porapak T, grain size 200–325 mesh, with the LC M2 wire detector, as shown in chromatogram 3 in Fig. 5.

The sensitivities that can be obtained by using UV detectors in a direct analysis are not sufficient for the determination of the contents of the substances under investigation in waters. The actual concentrations vary in the concentration range from parts per million downwards. We therefore decided to apply to liquid chromatography the technique of enrichment[24]. In contrast to gas–solid systems, in liquid–solid systems, the solute is adsorbed only up to the capacity of the monolayer of the adsorbent. An adsorbent with a sufficiently large specific surface area is therefore advantageous. It is known from the character of adsorption isotherms[25] that it is advantageous if the activity of the sorbent towards the solute is high and as different as possible from its activity towards the basic component. Polymer sorbents[26], particularly Porapak Q, meet these demands if water is used as the basic component. Water is a very weak mobile phase for this sorbent and, as a consequence, the conditions for obtaining a sufficiently high enrichment factor are fulfilled.

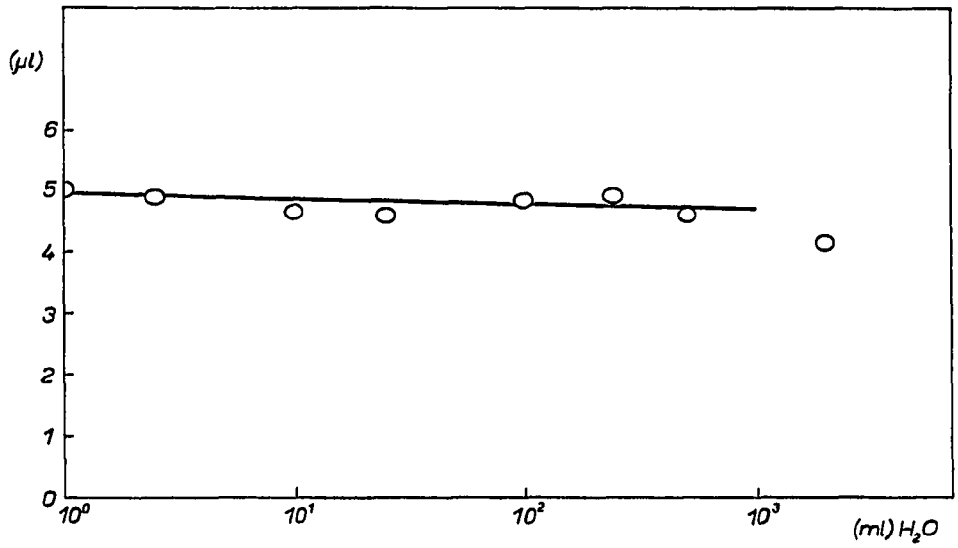

Fig. 6. Dependence of the volume of Arkopal N-040 collected (μl) on the volume of water passed through the enrichment column.

The results obtained by the enrichment technique are shown in Fig. 6. It is evident that even with the passage of 1500 ml of water through the pre-column, no sample losses occur. An enrichment factor greater than 10^6 is obtained, *i.e.*, the components under investigation can be determined in water at concentrations less than 1 ppm. In our experiments, the standard deviation of the determination of the samples injected without being enriched was $\pm$ 0.267 μl, *i.e.*, $\pm$ 5.3% (relative). A standard deviation of $\pm$ 0.273 μl, *i.e.*, $\pm$ 5.9% (relative), was found for the procedure using the enrichment.

Desorption from the enrichment column was carried out by introducing *n*-hexane as a very strong mobile phase. The desorption process was speeded up by heating the enrichment pre-column during the desorption. Even under these conditions, a loss in efficiency of the separation system occurred, which was caused by an incorrect concentration profile of the sample introduced into the column. The application of a dynamic temperature gradient[27] could improve this situation substantially.

When using the enrichment technique, a certain amount of water, corresponding to the dead volume of the enrichment pre-column, is introduced into the separation column in every experiment. As a result, liquid–liquid systems cannot be used (polyethylene glycol 400 in the present work) as extensive washing of the stationary phase from the column occurs. Therefore, systems must be used in the separation column that are inert towards water, and adsorption systems are the most satisfactory. Porapak Q and T were therefore used in the separation column. The separation on this material was not as good as that on the column that was used originally, but it is sufficient for the quantitative determination of the contents of the individual components under investigation in waters. By using the procedures described above, mineral oil and surfactants can be separated and quantitatively determined simultaneously. Water, being eluted from the pre-column, increases its short-time noise

on passing through the UV detector, but the quantitative interpretation of the chromatogram is still possible. On using the wire detector, the content of water in the effluent increased the detector noise to such a level that the quantitative interpretation of the chromatogram was impossible. The wire detector was therefore not used for the experiments using the enrichment column.

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