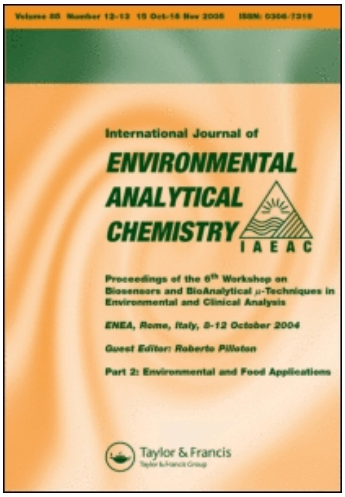

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Ion-Pair Extraction of Aromatic Anionic Surfactants Using the Supported Liquid Membrane Technique

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ION-PAIR EXTRACTION OF AROMATIC ANIONIC SURFACTANTS USING THE SUPPORTED LIQUID MEMBRANE TECHNIQUE

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A supported liquid membrane (SLM) extraction method was developed for anionic surfactants. A porous PTFE membrane was impregnated with a water immiscible organic solvent, forming a selective barrier between the sample and the analytical instrument. With a flowing donor and a stagnant acceptor solution, an enrichment of analytes was obtained. A mixture of linear alkylbenzenesulfonate (LAS) homologues and isomers were used as model system with the components transported across the membrane as ion-pairs formed with a tertiary amine. A slow mass transfer kinetics over the membrane/acceptor interface was noted. By pumping fresh acceptor solution through the acceptor channel for 15 minutes after the enrichment and trapping the analytes subsequently on an anion exchange column, the carry-over effects could be greatly reduced. With 1 hour SLM extraction time, concentrations of LAS down to 2 µg/L could be determined in natural water samples using UV-detection.

KEY WORDS: extraction, supported liquid membrane, anionic surfactant, linear alkylbenzenesulfonate, LAS, ion-pairing

INTRODUCTION

The production of synthetic surfactants has grown world-wide and at the moment the accumulated production in Europe, Japan and US is about 4 million metric tonnes[1]. About 75% of this production refers to anionic surfactants. Of these, the linear alkylbenzenesulfonates (LAS), being more easily biodegradable, have replaced the branched alkylbenzenesulfonates introduced in the 1950s. Most of the surfactants will end up in surface water, ground water and sediment. Normally their concentrations in these matrices are quite low, necessitating an analytical methodology capable of handling concentrations of a few µg/L.

A suitable approach towards low detection limits is to start with a selective enrichment during sample work-up, which substantially decreases the demands on the detection step and separates the analytes from the sample matrix. By introducing such an enrichment step as early as possible, the problem of adsorption of surfactants on various surfaces can be greatly reduced.

Liquid-liquid extraction (LLE) techniques are popular for the routine separation of

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surfactants. Ionic surfactants can be extracted as ion pairs (often with the cationic dye methylene blue as the counter ion) from aqueous media into an organic solvent[2]. Complex matrices imply many sources of error[3]. Problems with emulsion formation and the use of toxic and expensive solvents are strong reasons for replacing LLE by alternative extraction techniques.

The isolation of LAS from complex aqueous matrices using solid-phase extraction (SPE) is a popular approach. High recoveries are often realised and many SPE procedures are given in the literature[4–6]. Both hydrophobic and anion exchanger columns are used. However, problems with overloading, breakthrough, contamination and competitive adsorption are well known.

A new alternative for selective enrichment early in the analysis scheme is the supported liquid membrane (SLM) technique[7,8] developed in our research group. With this approach, humic substances and salts at high concentrations are efficiently removed. The technique can be described as a two-step liquid-liquid extraction. A water immiscible organic solvent is impregnated into a porous PTFE membrane, thus forming a selective barrier between two aqueous phases. The analytes in uncharged form are first extracted from an aqueous donor phase into an organic membrane liquid. Here they diffuse to the other side of the membrane, where they are trapped in a charged form in a second aqueous solution, the acceptor. By pumping the sample through the donor channel and keeping the acceptor stagnant, the analytes are enriched in the acceptor.

The technique has until now mostly been used for ionizable acidic compounds[9–12] or basic compounds like amines[13] and drugs[14,15]. Recently we demonstrated that also metal ions can be enriched using SLM methodology. Complexing reagents were used to transform the charged metal ion to an uncharged species[16] which then could be extracted as described above.

In this paper we investigate the possibility of using the SLM methodology for extracting anionic surfactants. An ion-pairing reagent (a tertiary amine) was added to the sample solution and the surfactant ions were extracted as uncharged ion-pairs. A commercial LAS product containing a mixture of homologues and isomers was used as a model mixture in the experiments.

MATERIAL AND METHODS

Chemicals

A commercial LAS product, dodecylbenzenesulfonic acid (CAS 27176–87–0), was providing the model compounds. In spite of its marking it consisted of a mixture of homologues, the main part being isomers of dodecylbenzenesulfonic acid (35–40%) and of undecylbenzenesulfonic acid (40–45%). These proportions were obtained from the producer (Acros Chemicals, Beerse, Belgium).

The different membrane liquids used were di-*n*-hexylether (Sigma Chemical Co., St Louis, USA), *n*-undecane (p.a.)(Merck, Darmstadt, Germany), 1-chlorotetradecane (Eastman Kodak Company, Rochester, USA), and 6-undecanone (Acros). Trihexylamine (> 97%), tributylamine (for synthesis), triethylamine (p.a.), and di-*n*-octylamine (> 99%), all from Fluka Chemica AG, Buchs, Switzerland, were used for ion pair formation. Sodium dodecylsulfate, SDS, (99%) (Sigma) was added to the samples in order to prevent adsorption losses. Phosphate buffers were prepared of sodium dihydrogenphosphate (p.a.) and di-sodium hydrogenphosphate (p.a.) from Merck. Sodium hydroxide (p.a.) from Eka Nobel (Bohus, Sweden) was used for pH adjustments.

The mobile phase consisted of acetonitrile, sodium perchlorate and a phosphate buffer, all analytical grade from Merck. All water used was purified with a Milli-Q-RO4 system (Millipore, Bedford, USA). Natural water samples for spiking were collected in the Höje river, located ca 2 km south of Lund.

LC-equipment

The LC-equipment consisted of a high-pressure pump (ConstaMetric III, Laboratory Data control, Rivera Beach, USA), a six-port injector valve (Valco, Houston, TX, USA), an analytical C_8-column (Kromasil 100-5C8, length 150 mm and ID 2.1 mm, Hichrom Ltd., Berkshire, U. K.), and a variable wavelength UV detector (Model 770, Schoeffel Instrument Corp., Westwood, USA). Instead of a sample loop, a precolumn (length 20 mm and ID 2 mm, Upchurch Scientific Inc., Oak Harbor, USA), packed with an anionic exchanger (Dowex 1x8, 100–200 mesh), was connected to the Valco injector. Chromatograms were evaluated using a chromatographic data processor (Perkin Elmer Nelson, model 1020 S/X, Norwalk, CT, USA) equipped with a printer (DeskJet 510, Hewlett Packard, Palo Alto, CA, USA).

Membrane equipment

The membrane holder used was made of two circular PTFE blocks (diameter 120 mm and thickness 8 mm) with machined grooves (depth 0.25 mm, width 1.5 mm, length 250 cm, and a total volume of ca. 1 mL per aqueous phase). One of the blocks had a seal (O-ring). The liquid membrane support was Fluoropore FG (Millipore, Bedford, USA) with an average pore size of 0.2 μm, total thickness of 175 μm of which ca. 115 μm is polyethylene backing, and a porosity of 70%. This was impregnated by soaking for about 15 minutes in an organic liquid. The finished membrane was placed between the two PTFE blocks and clamped tightly and evenly by two aluminium blocks (thickness 6 mm) with eight screws. Hence, two channels (donor and acceptor) separated by the membrane are formed. For a picture of the membrane holder, see ref. 9.

Procedure

The configuration of the system is shown in Figure 1. The solutions were pumped with a peristaltic pump (A) (Minipuls 3; Gilson Medical Electronics, Villiers-le-Bel, France) using acid resistant pump tubing (Acidflex; Elkay Products, Shrewsbury, MA, USA). The sample and the reagent stream merged together in a PTFE tee connection (B) (60° angle) and were then mixed in a coil (C) (30 cm of 0.5 mm ID coiled PTFE tubing) before entering the donor channel of the membrane device (D). The various parts of the flow system were connected with 0.5 mm ID PTFE tubing and flange-free screw fittings (Alltech Associates Inc., Deerfield, IL, USA). The LAS sample solution and the tertiary amine (concentration ca 100 μg/mL), both in buffer solutions of pH 7, were pumped with a total flow rate of 1.0 mL/min (ratio 1:1) with the peristaltic pump. The acceptor solution, 0.01 M sodium hydroxide containing 200 μg/mL SDS, was kept stagnant during the extraction procedure. After the enrichment, the acceptor was kept stagnant for another 10 minutes, during which time the sample solution was exchanged for 8 mM sulphuric acid for washing of the donor channel. The acceptor channel simultaneousky then rinsed at a flow rate of 0.5 mL/min with new acceptor solution pumped with the

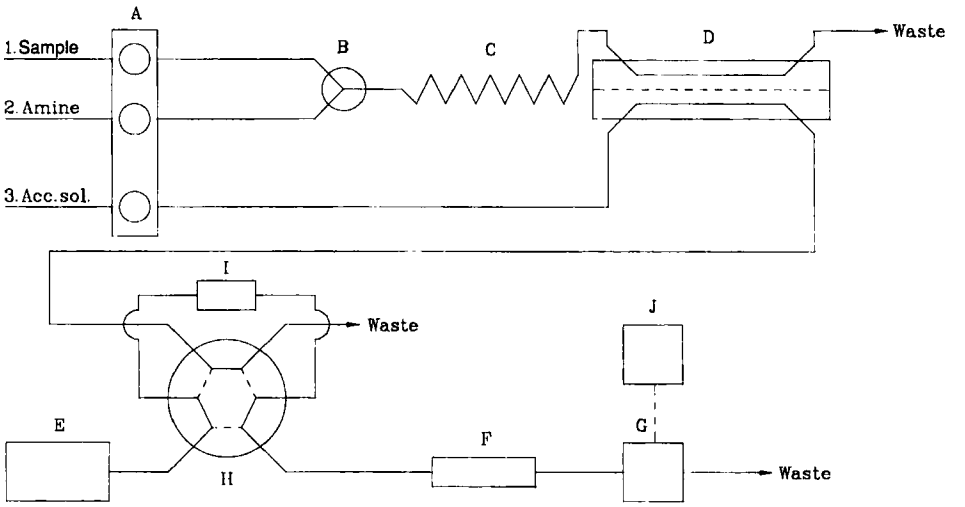

Figure 1 Schematic diagram of the experimental set-up for SLM-extraction of LAS. A- peristaltic pump, B- tee connection, C- mixing coil, D- membrane holder, E- HPLC pump, F- analytical column, G- UV-detector, H- Valco injector, I- precolumn and J- chromatographic data processor.

peristaltic pump while the analytes (LAS homologues and isomers) were trapped on the anion exchanger in the precolumn (I). The analytes were subsequently eluted from the precolumn into the analytical column (F) with the mobile phase pumped with the high-pressure pump (E). The surfactant concentrations were detected at 225 nm in the UV-detector (G) and the results were evaluated with the chromatographic data processor (J)

RESULTS AND DISCUSSION

Chromatography

The LC system used was a modification of the system presented by Nakae *et al.*[17]. The system consisted of a C_8-column and a mobile phase of acetonitrile/phosphate buffer (5 mM, pH 6) at a ratio of 60:40 with 0.10 M sodium perchlorate as modifier. A typical chromatogram is shown in Figure 2 revealing several homologues of the LAS, separated according to chain length[4]. The isomers of each homologue are not separated by this type of LC systems.

Optimisation of the supported liquid membrane enrichment procedure

pH in the donor and acceptor solutions With the ion-pairing extraction mechanism applied here, the guidelines for the acceptor pH which were developed earlier[21] are not valid, but another reasoning must be followed: In the donor phase an ion-pair must be formed between the anionic surfactant and the tertiary amines that were chosen as ion-pair reagents. This is accomplished by choosing the pH in the donor phase below the pK^a of the amine so that the amine is fully protonated and simultaneously above the pK^a of

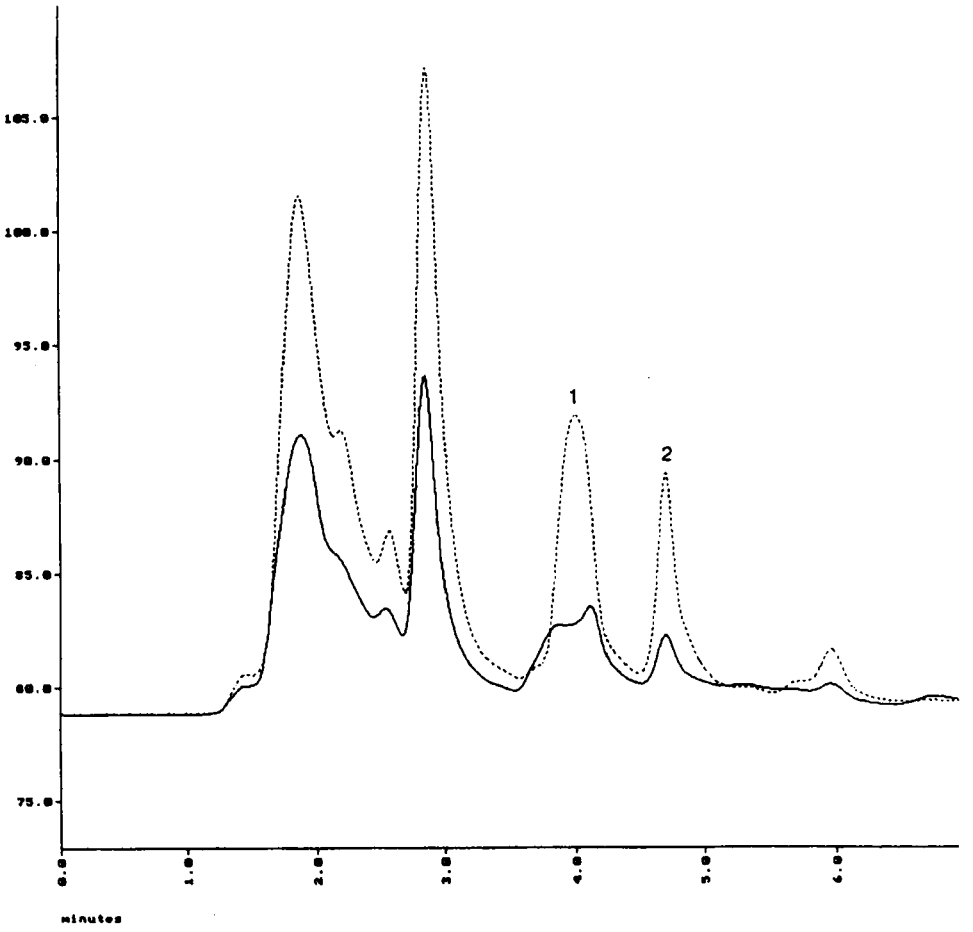

Figure 2 Chromatogram after 60 minutes SLM-extraction of Höje river water (continues line) and after spiking the Höje river water with 7.5 μg/L of LAS-mixture (dotted line). **1**—C_{11} homologue, **2**—C_{12} homologue.

the surfactant so that this compound is negatively charged. The pK^a-values are around 11 for the amines (11. 0 for triethylamine and 10.6 for tridecylamine)[18] and << 0 for the surfactant. It was not possible to find the pK^a for the LAS compounds in the literature, but for similar compounds, e.g. toluene sulfonic acid it is about –6[19]. Also, a value of –1.3 was given elsewhere[20]. Thus any pH < 8 is suitable and a pH of 7 was chosen to avoid as much sample pre-treatment as possible. This pH is expected to give a good selectivity towards potentially interfering low molecular acidic compounds as those can not be extracted as uncharged acids and their ion-pairing constants are expected to be much lower.

The acceptor pH should be chosen so high that the amine becomes uncharged which breaks the ammonium—LAS ion pair. The surfactant will still be charged and thus trapped in the acceptor. It was found that an acceptor pH of 12 gave good extraction efficiencies. Minor changes around the selected pH-values did not significantly affect the extraction.

Carry-over effects Ideally, neglecting the small effect of diffusive dispersion, all of the extracted analyte should be quantitatively transferred from the acceptor channel to the analytical column by one channel volume of acceptor buffer. In practice, a considerably larger volume is needed to obtain a complete transfer. This can be due to two different reasons. Firstly, some analyte might be adsorbed (in the channel, on the membrane surface or in the connecting tubing) and secondly, slow mass transfer kinetics could delay the transport through the membrane/acceptor interface. In either case, incomplete transfer will lead to carry-over to the next analysis. These two types of carry-over effects must he handled in different ways.

To decrease adsorption, SDS has been added to surfactant samples in other investigations[3]. The benefits of this displacer in the SLM extraction were tested by addition of SDS to the acceptor solution. It can be seen (Table 1) that the observed extraction efficiency increased when SDS was added to the acceptor. SDS was also added to all sample solutions in order to avoid adsorption in the donor channel and connecting tubing.

The relation between the pumping time of the acceptor (after enrichment and washing) and the observed extraction efficiency reflects the kinetics in the system. Figure 3 shows this relation for the C_{11} fraction with three different membrane liquids. The other homologue fractions behaved almost identically. It is seen that a plateau is reached after about 15 minutes. This experiment was performed with a constant flow rate of 0.5 mL/min, and an alternative interpretation of the results may thus be that 7.5 mL of liquid is needed to reach the plateau. To settle this question an investigation was designed with two series of experiments, the first one involving pumping a constant volume of liquid (8 mL) with different flow rates, and the second one with pumping different volumes with the same flow rate (0.5 mL/min). Figure 4 shows the observed extraction efficiency versus total pumping time for both these series, and it is apparent that the onset of the plateau depends on the rinsing time (15 min), irrespectively of the volume pumped. This means that the losses mainly depend on slow mass transfer kinetics rather than adsorption effects and incomplete rinsing of the acceptor channel. Thus, a pumping time of 15 minutes was selected which leads to negligible carry-over effects. When extracting natural water at unknown and varying analyte concentrations, a somewhat longer rinsing time may be needed for safety.

Such carry-over effects are found to vary considerably between different extraction systems, and they are often negligible. For example, in enrichment of Cu^{2+} by complexing with 8-hydroxyquinoline and di-*n*-hexylether as membrane liquid in the same type of membrane unit as above, it has previously been shown[16] that with an acceptor pumping time of 5 min after enrichment, the carry-over was less than 1%, i.e. the mass transfer was much faster than in the present investigation. On the other hand we

Table 1 Extraction efficiency for the two main homologue fractions of LAS with and without addition of an adsorption suppressing agent sodiumdodecylsulphate (SDS) (200 µg/mL) to the acceptor solution. Di-*n*-hexylether was used as membrane liquid and trihexylamine as the ion-pairing reagent (n = 6).

	Extraction efficiency (RSD)	
Analyte	*without SDS*	*with SDS*
C_{11} homologue fraction	0.58 (4.9%)	0.71 (4.2%)
C_{12} homologue fraction	0.50 (4.1%)	0.62 (3.9%)

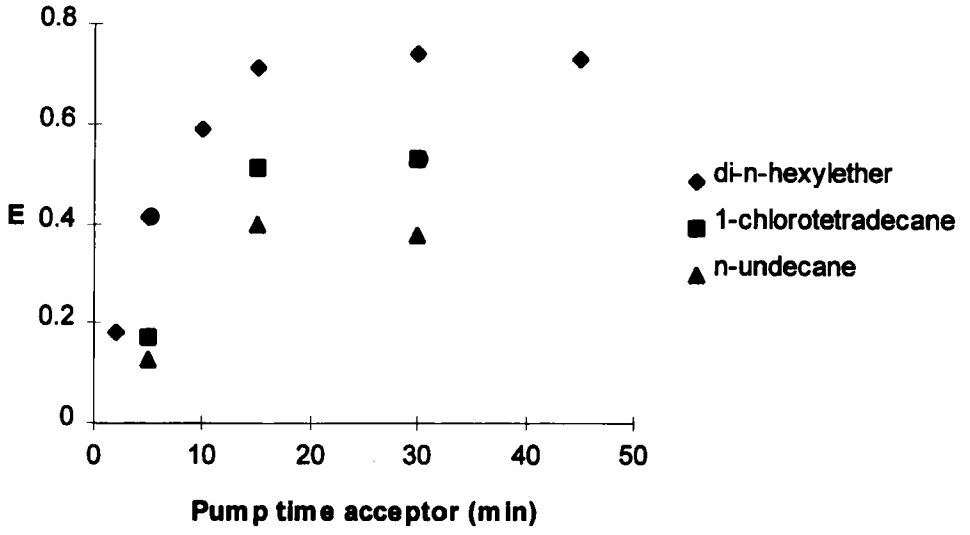

Figure 3 Extraction efficiencies for LAS (C_{11} homologue fraction) with three different membrane liquids (di-*n*-hexylether, *n*-undecane and l-chlorotetradecane) as function of washing time (min) of the acceptor.

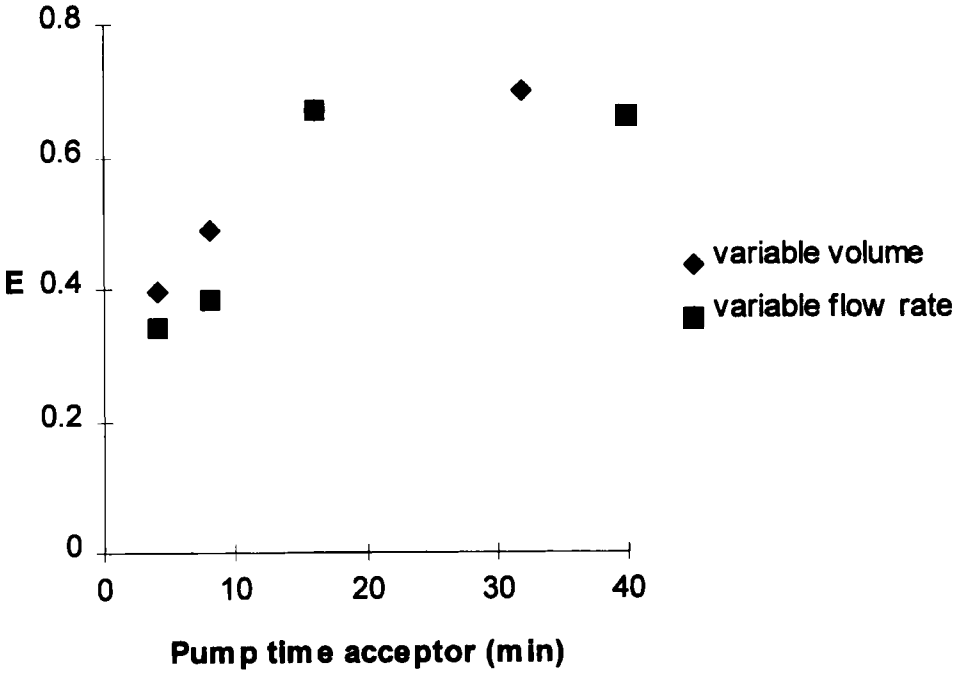

Figure 4 Extraction efficiency for LAS (C_{11} homologue fraction) as function of washing time (min) of the acceptor, with variable acceptor volume (mL) (constant flow rate 0.5 mL/min) respectively variable acceptor flow rate (mL/min) (constant volume 8 ml.). Di-*n*-hexylether membrane.

have found a slower mass transfer in other systems for metal enrichment, e.g. with alkyl phosphoric acid as carrier.

Precolumn The anionic precolumn used to focus the analytes transferred from the acceptor was able to trap 50 mL of a 1 mg/L surfactant solution. Thus, the required transfer volume of ca 8 mL, as discussed above, will not cause breakthrough problems. The capacity of the precolumn was evaluated by injecting different volumes of the LAS mixture dissolved in acceptor solution.

Membrane liquid Four different membrane liquids (di-*n*-hexylether, 6-undecanone, undecane and 1-chlorotetradecane) were investigated using the same experimental conditions. From other studies[15] the 6-undecanone membrane was supposed to give the highest extraction efficiency, but the extraction efficiencies obtained in this study were irreproducible and difficult to evaluate. The reason for these problems is probably the larger solubility of this liquid in water, which results in considerably lower long term stability than for the other membrane liquids. The 6-undecanone membrane liquid had to be replaced after less than one working day and was omitted from further investigations. The other membrane liquids could be used for a period of at least a week.

The extraction efficiencies for those membrane liquids obtained after 15 min acceptor pumping time are shown in Table 2. It can be observed that with the most hydrophobic membrane, *n*-undecane, the extraction efficiency for the C_{12} homologue fraction is larger than for the C_{11} fraction, while the contrary is true for the more polar membranes. From the chromatographic retention order, the organic/water partition coefficient must be larger for C_{12} than for C_{11}. In an earlier work[21], the detailed theory for SLM extraction was worked out. In short, the extraction is either *membrane-controlled*, (characterised by relatively low partition coefficients and that the efficiency is controlled by the partition coefficient and the diffusion coefficient in the membrane) or *donor-controlled* (with larger partition coefficients and controlled by the diffusion coefficient in the donor phase, i.e. the aqueous sample). Calculations with the actual membrane dimensions and flow rates and assuming realistic values for diffusion coefficients reveal that the extraction process with the *n*-undecane membrane is membrane-controlled, leading to the observed extraction efficiencies. With the other membranes, the partition coefficients are much higher, making them insignificant to the mass transfer as the process goes donor-controlled. The differences in extraction efficiency (which are hardly statistical significant) can then be explained as differences in diffusion coefficients between the LAS homologues.

For the further work, di-*n*-hexylether was selected as membrane liquid, as the extraction efficiency is considerably higher than with the two more unpolar liquids

Table 2 Extraction efficiencies after 20 minutes extraction of a 1.0 µg/mL LAS solution for different membrane liquids, 15 minutes pumping of the acceptor. Ion-pairing reagent: trihexylamine.

Membrane liquid	*Extraction efficiency (RSD, n)*	
	C_{11} *fraction*	C_{12} *fraction*
di-*n*-hyxylether	0.71 (4.2%, 4)	0.62 (7.6%, 4)
1-chlorotetradecane	0.51 (1.2%, 3)	0.43 (4.1%, 3)
n-undecane	0.40 (7.1%, 3)	0.55 (5.8%, 3)

Ion-pairing reagent Three different tertiary amines, trihexylamine, tributylamine and triethylamine were used as ion-pairing reagents. As can be seen in Table 3, trihexylamine gave the highest extraction efficiency. This is probably due to its longer carbon chain giving a more hydrophobic ion-pair with a higher partition coefficient for the extraction of analyte from aqueous donor solution into the organic membrane liquid.

A secondary amine, di-*n*-octylamine, was used to compare tertiary and secondary amines. Although di-*n*-octylamine has more carbon atoms than tributylamine, the extraction efficiency using di-*n*-octylamine was much lower. The reason is probably that the hydrogen-bonding ability of the secondary amine leads to larger water solubility and thus to a lower partition coefficient.

Concerning the concentration of the ion-pairing reagent it was found that an excess by a factor of 6–7 was sufficient to get acceptable and reproducible extraction efficiencies. An amine concentration around 100 mg/L will be more than sufficient for extraction of LAS at a low μg/L level.

Quantification

Quantification of individual LAS components in natural waters is very complicated. This needs a highly efficient separation system, a selective clean up from the large number of other components which may be present, and access to reference substances of different isomers within each LAS homologue. In this paper the efforts have been directed towards the possibility of using SLM technique to simplify the sample work-up procedure and at the same time achieving a low detection limit.

One of the dominating LAS homologues (C_{11}) was used for investigating the possibility for quantification by spiking surface water samples from Höje river with the LAS mixture. As seen in Figure 2, this river water contains different LAS compounds, why the standard addition method was needed to establish the calibration graph.

The water from the river was spiked with three different concentrations of LAS; 7.5 μg/L, 30 μg/L and 75 μg/L (n = 3 for each addition). A linear standard addition calibration curve was obtained for the C_{11} homologue (correlation coefficient = 0.999). Assuming that 45% of the LAS mixture is the C_{11} homologue, this leads to a C_{11} concentration in the river of 1.8 ± 1.1 μg/L. From the slope of the curve an extraction efficiency of 0.75 for the C_{11} fraction was obtained in approximate agreement with the value (0.71) observed in standard solutions. Further assuming that the relation between the LAS homologues in the river water is the same as in the commercial LAS mixture, the total LAS concentration is ca 4 μg/L.

Table 3 Extraction efficiencies (C_{11} fraction) after 20 minutes extraction of a 1.0 μg/mL LAS solution with different ion-pairing reagents, 15 min pumping of the acceptor. Membrane liquid: di-*n*-hexylether.

Ion-pairing reagent	*Extraction efficiency (RSD, n)*
Triethylamine	0.16 (6.2%, 4)
Tributylamine	0.59 (4.7%, 3)
Trihexylamine	0.71 (4.2%, 4)
Di-*n*-octylamine	0.26 (4.9%, 3)

One contribution to the uncertainty of this determination may be differences in extraction efficiencies between different isomers in the C_{11} mixture. Such differences are expected to be small, since the isomers elute simultaneously with approximately the same partition coefficients in the LC column. Thus it can be assumed that the partition coefficients between the organic membrane liquid and the aqueous phase are very close for the different isomers. According to theory developed by us previously[21] this will give the same extraction efficiencies, especially since the size of the isomers and their ion-pairs are very similar leading to similar diffusion constants. On the other hand, there are differences both in the sizes and in chromatographic retention between homologue fractions, which will manifest as differences in extraction efficiency (c.f. Table 2).

It can be estimated that a detection limit of ca 2 μg/L of LAS can be achieved after extraction of 30 mL sample during 60 minutes with the carry-over effects under control, i.e. after careful cleaning of the membrane system, provided that the relative extraction efficiencies of the various LAS homologues (and isomers) are known.

Comparison with SPE

Although this work is in its preliminary stage, some comparisons can be made with the SPE approach. The detection limit found here with UV-detection (2 μg/L in a 30 mL sample) compares favourably to those found in the literature e.g. 2 μg/L (ref 4), 0.8 μg/L (ref 6) and a quantitation limit of 20 μg/L (ref 5). All these values are based on the extraction of about 200 mL of sample and the more sensitive fluorescence detection. This difference is partly due to the fact that with the SLM technique all of the extracted analytes is injected and partly to higher selectivity giving cleaner extracts.

As the problems with breakthrough volumes and overloading with the SLM technique typically are much smaller than with SPE[8], it should be possible to extract larger volumes of sample (on the expense of time) hence decreasing the detection limits further. This also gives the possibility of time integrating field sampling[22].

Another aspect is that with SPE usually disposable cartridges are used leading to considerable expenses and labour costs. The SLM units can be used for many samples (the di-*n*-hexylether membranes used in this investigation lasted at least 80 hours of operation), are easily cleaned between samples and are therefore potentially more economical. Furthermore, the potential for automation of the SLM technique is large which has been realised in several other applications[8,11,14].

The extraction efficiency in SLM is often considerably less than 100%. This is sometimes interpreted as a low recovery. However, the unextracted fraction of the analyte can then be found in the outlet from the donor channel. In SLM, the recovery can be defined as the sum of analyte amount found in the acceptor phase and in the donor outlet divided by the analyte amount input to the system. It is always possible to increase the extraction efficiency towards 100% by decreasing the donor flow rate. This leads to very slow extraction and it is usually more efficient in terms of detection limit to work with higher flow rates giving lower extraction efficiencies[8,21].

CONCLUSION

We have shown that aromatic anionic surfactants can be selectively enriched using SLM methodology permitting determination at low μg/L concentrations. In order to improve the quantitative certainty, separate standards for the various isomers and homologues of LAS are needed. With similar SLM-systems, the extension to aliphatic anionic surfactants as well as to cationic surfactants should be possible.

Acknowledgments

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