

CHROMSYMP. 754

## RETENTION OF ALIPHATIC ANIONIC SURFACTANTS IN ION CHROMATOGRAPHY

JOACHIM WEISS

*Dionex GmbH, Einsteinstrasse 1, D-6108 Weiterstadt (F.R.G.)*

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### SUMMARY

Mobile-phase ion chromatography with suppressed conductivity detection provides an efficient technique for the analysis of aliphatic and olefinic anionic surfactants. A porous resin, derived from divinylbenzene, was used as the stationary phase. Ammonium and tetra-alkylammonium salts were used as the ion-pair reagents.

Retention parameters, such as hydrophobicity, solvophobic surface area and the effect of polar substituents, are discussed to explain the different retention behaviours of the compounds investigated, which are consistent with the theory of ion-pair formation in the mobile phase.

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### INTRODUCTION

#### *General remarks*

Ion chromatography (IC) was introduced as a new analytical technique in 1975 by Small *et al.*<sup>1</sup>. It involves ion-exchange, ion-exclusion and ion-pair mechanisms, which in almost every case is accompanied by non-specific interactions, such as adsorption and solvophobic effects. Mobile-phase ion chromatography (MPIC) is a patented technique, combining the classical elements of reversed-phase ion-pair chromatography (RPIPC)<sup>2-4</sup> and suppressed-conductivity detection. MPIC serves as an alternative to ion-exchange chromatography, because both anions and cations can be analysed with the same stationary phase.

#### *Stationary phase*

The stationary phase is a non-derivatized porous resin, derived from divinylbenzene (DVB), having a high specific surface area of *ca.* 350 m<sup>2</sup>/g. Due to its structural elements (alkyl residues and benzene rings), it is only slightly polar and essentially hydrophobic.

#### *Mobile phase*

The mobile phase is an aqueous solution of an ion-pair reagent. An organic modifier, usually acetonitrile or methanol, is added in varying amounts to support ion-pair formation and to adjust the eluent polarity.

### Analysed compounds

While the separation of aromatic anionic surfactants is almost trivial, the analysis of aliphatic and olefinic sulphonates and sulphates demands carefully optimized MPIC conditions. The compounds investigated include:

alkyl sulphonates	$\text{R-CH}_2\text{-SO}_3^- \text{Na}^+$
alkyl sulphates	$\text{R-CH}_2\text{-O-SO}_3^- \text{Na}^+$
hydroxyalkyl sulphonates	$\text{R-CH-CH}_2\text{-SO}_3^- \text{Na}^+$
	OH
olefine sulphonates	$\text{R-CH}_2\text{-CH=CH-CH}_2\text{-SO}_3^- \text{Na}^+$

### EXPERIMENTAL

#### Equipment and chemicals

All experiments were performed on a Dionex 2010i ion chromatograph. The column was a 250 × 4.6 mm I.D. MPIC-NS1 (neutral DVB resin from Dionex, Sunnyvale, CA, U.S.A.). Water for the eluent was purified in a Barnstead PCS still. The ion-pair reagent, ammonium hydroxide, was purchased from Merck (Darmstadt, F.R.G.) as an aqueous solution of 25% ammonia. Tetramethylammonium hydroxide was purchased from Fluka (Buchs, Switzerland), tetrapropylammonium hydroxide from Dionex, and the modifier acetonitrile from Promochem (Wesel, F.R.G.).

The sample components were a donation from Akzo Chemie (Düren, F.R.G.).

#### Chromatographic conditions

Column, MPIC-NS1; eluent, 0.01 *M* ammonium hydroxide [or 0.002 *M* tetramethylammonium hydroxide (TMAOH) or tetrapropylammonium hydroxide (TPAOH)] + 28–40% (v/v) acetonitrile; flow-rate, 1 ml/min; conductivity detection; fibre suppressor, type AFS-2; regenerant, 0.0125 *M* sulphuric acid; injection volume, 50  $\mu\text{l}$ ; solute concentration, 100 ppm.

### RESULTS

As shown in Fig. 1, retention times of alkyl sulphonates increase exponentially with increasing alkyl chain length. For a given chain length,  $\text{R-CH}_2\text{-SO}_3^- \text{NR}_4^+$  is more weakly retained than  $\text{R-CH}_2\text{-O-SO}_3^- \text{NR}_4^+$  (Fig. 2). Hydroxyalkyl sulphates are less strongly retained than alkyl sulphonates, both having the same chain length. A hydroxyl group in the 3-position lowers retention more strongly than one in the 2-position. The hydroxyl group in the 3-position on a  $\text{C}_{16}$  chain is more effective in lowering retention than the loss of one methylene group in a 2-substituted  $\text{C}_{16}$  chain (Fig. 3). Olefine sulphonates are less strongly retained than alkyl sulphates, both having the same chain length (Fig. 4). Technical olefine sulphonates are highly complex mixtures. Resolution can be improved by pairing with a more strongly solvophobic counter-ion (Fig. 5). In general, the retention of all the compounds investigated decreases with increasing acetonitrile content of the eluent.

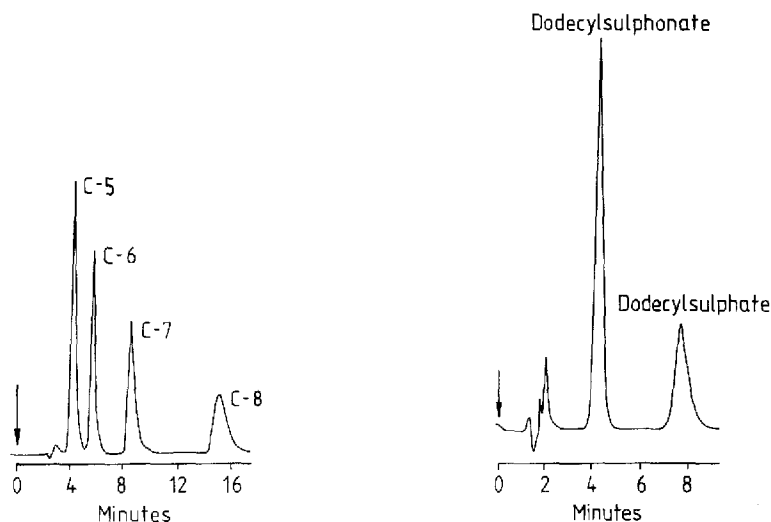


Fig. 1. Separation of long-chain (C<sub>5</sub>–C<sub>8</sub>) alkyl sulphonates. Eluent, 0.002 M TBAOH–acetonitrile (72:28, v/v); suppressed-conductivity detection; flow-rate, 1 ml/min.

Fig. 2. Separation of dodecylsulphonate and dodecylsulphate. Eluent, 0.01 M ammonium hydroxide–acetonitrile (65:35, v/v); suppressed-conductivity detection; flow-rate, 1 ml/min.

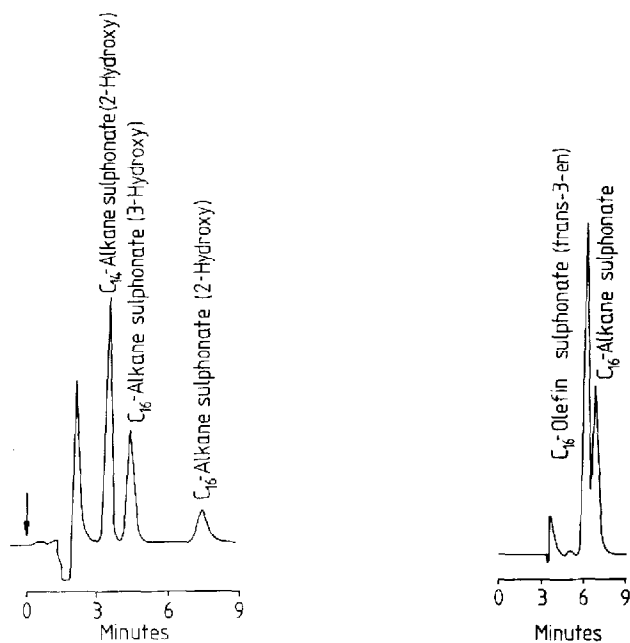


Fig. 3. Separation of different hydroxyalkyl sulphonates. Eluent, 0.01 M ammonium hydroxide–acetonitrile (62.5:37.5, v/v); suppressed-conductivity detection; flow-rate, 1 ml/min.

Fig. 4. Separation of alkyl and olefin sulphonates with equal carbon chain length. Eluent, 0.01 M ammonium hydroxide–acetonitrile (65:35, v/v); suppressed-conductivity detection; flow-rate, 1 ml/min.

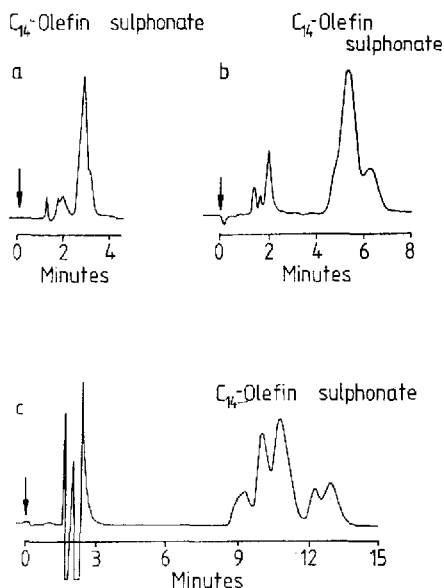


Fig. 5. Separation of a technical olefin sulphonate with different ion-pair reagents in the mobile phase. Eluent, (a) 0.01 *M* ammonium hydroxide-acetonitrile (60:40, v/v); (b) 0.002 *M* TMAOH-acetonitrile (60:40, v/v); (c) 0.002 *M* TPAOH-acetonitrile (60:40, v/v); suppressed-conductivity detection; flow-rate, 1 ml/min.

## DISCUSSION

The retention of alkyl chains is determined by their respective surface area (*SA*), which, in turn, depends linearly on chain length:

$$\ln k' \propto SA \propto n_{\text{CH}_2}$$

The low retention of alkyl sulphonates as compared to that of alkyl sulphates with equal carbon chain length appears to be related to an effect observed with thia-alkanes in reversed-phase liquid chromatography (RPLC). As shown in Fig. 6, a CH<sub>2</sub>-S or CH-S arrangement in both dialkyl sulphides and alkyl sulphonates represents a local polar centre which permits an increased interaction with the polar eluent via solvation. For each such group, a retention decrease equivalent to the loss

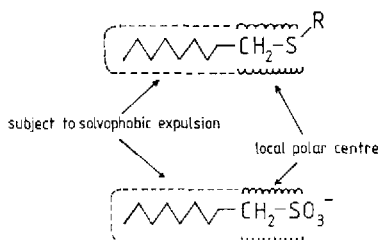
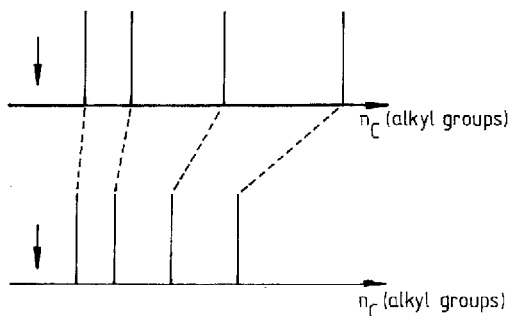


Fig. 6. Schematic representation of the cavity surface area decrease via solvation of local polar centres comprising an S-atom and adjacent aliphatic CH-fragments.

of *ca.* 1–3 methylene groups is observed, depending on the eluent water content. Furthermore, the retention contribution of methylene groups is appreciably lowered in the presence of sulphur atoms.

In the case of alkyl sulphates, lowering of methylene retention is not observed (Fig. 7). Retention-lowering, compared to the parent alkane, is only due to the sulphate eluent interaction. Introducing a hydroxyl group in the 2- or 3-position decrease retention equivalent to the loss of two or three methylene groups, respectively, in the solvophobically active alkyl group. The retention-lowering effect of a hydroxyl group is caused by direct hydrogen bond formation to the eluent constituents, while the influence on methylene groups within the chain is negligible.

Alkyl sulphates



Alkyl sulphonates

Fig. 7. The separation of alkyl sulphonates and alkyl sulphates, having almost equal total molecular surface areas, due to the increased solute–eluent interaction of alkyl sulphonates, as indicated in Fig. 6.

The lower retention of olefine sulphonates as compared to that of alkyl sulphonates with equal carbon chain length is caused by induced dipole moments at the double bond, which, in turn, result in an increased interaction with the eluent constituents via solvation. The retention behaviour of olefine sulphonates in MPIC is very similar to that observed in RPLC.

With a given acetonitrile content of the eluent, retention increases with increasing solvophobic character of the counter-ion, *i.e.* with increasing chain length of the alkyl substituents of the quaternary ammonium group. The least solvophobic is the ammonium ion itself. The  $\ln k'$  of olefine sulphonates increases almost linearly with the alkyl chain length. This observation can be attributed to two effects; (i) an increase in the solvophobic surface area of the solute ion-pair, and (ii) a decrease in the sulphonate ammonium bond polarity which, in turn, leads to a diminished solute–eluent interaction.

## REFERENCES

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