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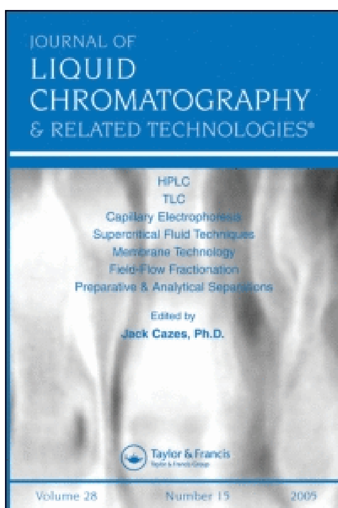

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REVERSED-PHASE HPLC. DETERMINATION OF IONIC SURFACTANTS AS UV-ABSORBING ION PAIRS

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ABSTRACT

Ionic and amphoteric surfactants were separated on reversed-phase columns. Ultraviolet photometry and differential refractometry were employed so that ion pairing and nonpairing compounds could be distinguished. Analysis of ionic surfactants as ultraviolet (UV) absorbing ion pairs improved detection limits 100 fold compared to detection by differential refractometer (RI).

INTRODUCTION

Reversed-phase high-performance liquid chromatography (RPHPLC) has been used for the direct analysis of sulfobetaine amphoteric surfactants (1). These surfactants are (sulfopropyl) dimethyl (alkyl) ammonium inner salts and can be analyzed quantitatively by this method (1). On the other hand, anionic or cationic surfactants or compounds such as long chain acids, amines, and amidoamines, which can be made ionic by the addition or subtraction of a proton, and quaternary ammonium halides are poorly retained. Their chromatographic peaks show considerable tailing in reversed-phase systems and thus make quantitative analysis difficult.

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Analyses of related ionic compounds have been carried out by ion-pair RPHPLC and cited in the literature (2-4). Eksborg and coworkers were able to obtain excellent selectivity and good resolution in the analysis of polar compounds such as aminophenols in aqueous systems by ion-pair RPHPLC with hydrophobic counterions (2). More recently, Knox et al. developed a similar method, which they called soap chromatography, for the separation of catecholamines or sulfonic acids by use of long-chain alkyl sulfates or sulfonates and cetyl trimethylammonium bromide, respectively, as the counterions (3,4).

The present paper describes a method for the quantitative analysis and differentiation of a mixture of ionic and amphoteric surfactants using reversed-phase chromatographic conditions in order to expedite studies of reaction conditions so that optimum yields can be obtained. Ionic surfactants were analyzed as UV-absorbing ion pairs. The compounds chosen for this study were those reactants and products used in the synthesis of sulfopropylated amphoteric surfactants (5) an important class of lime soap dispersants. They were synthesized according to the following scheme:

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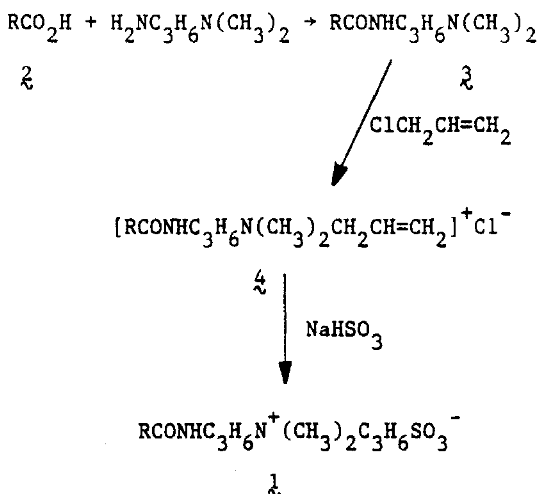

The method of analysis is not limited to ionic surfactants but can be used for any ionic or ionogenic compound which can form an ion pair. Ionic and amphoteric surfactants were separated on commercially available reversed-phase columns with sulfonic acids as counterions in the mobile phase and detected by a UV-photometer and a differential refractometer (RI).

EXPERIMENTAL

Materials

2-Naphthalenesulfonic acid and p-toluene sulfonic acid were obtained from Eastman Kodak Co., Rochester, N.Y. (6). Hyamine 1622 (diisobutylphenoxyethoxyethyldimethylbenzyl ammonium chloride monohydrate) was obtained from Rohm and Haas, Philadelphia, Pa. (6). The above materials were utilized without further purification. 1-Phenylbutane, 1-phenyldecane, and 1-phenyldodecane were purchased from Aldrich Chemical Co., (6) Milwaukee, Wis., and were sulfonated with sulfuric acid (7). The product was recrystallized until the sulfated ash agreed within 0.5% of the theoretical value.

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HPLC apparatus and operating conditions

The apparatus consisted of a minipump (Milton Roy, Riviera Beach, Fla.) with an injection valve (Rheodyne, Berkeley, Calif.), fitted with a 20-μl loop. The analytical columns were μ-Bondapak C_{18} stationary phase (Waters Assoc., Milford, Mass.), and LiChrosorb RP-8, stationary phase (E. M. Labs., Elmsford, N.Y.). The detectors used were a differential refractometer, Model R-401, and a UV-photometer (254 nm) Model 440 (Waters Assoc., Milford, Mass.). The mobile phase was aqueous methanol, and the flow rate was maintained at 1 ml/min. All solvents were filtered through a 0.45-μm Millipore filter (Millipore, Bedford, Mass.) before use. The counterion was added directly to the mobile phase, and the system was allowed to equilibrate for 1 hr before determinations were made. The concentration of counterions was varied between 0.3 and 4.2 m*M* depending on their molar absorptivity.

Test samples were dissolved in the mobile phase, and 20-μl samples were injected onto the column. When concentrations or types of counterion were changed, the column was washed with several column volumes of aqueous methanol. When the column was not in use, the counterion was washed from the column with several volumes of aqueous alcohol.

RESULTS AND DISCUSSION

Simultaneous use of the UV and RI detectors in ion pair chromatography was found to be useful in these studies to distinquish between ion pairing and nonpairing components in a mixture. The concentration range of counterion in the mobile phase, varied between 0.3 and 4.2 m*M*, was in agreement with that recommended by Gloor and Johnson (8). The application of both detectors for the detection of the separated reactants and products required for the synthesis of surfactant **1** is shown in Fig. 1. Peak 1 is due to the amphoteric product (**1**), which is internally neutral and did not form an ion pair under the chromatographi conditions described. The second peak represents the long-chain acid (**2**), which cannot form an ion pair with the counterion in the mobile phase; it was detected quantitatively by ionic suppression. Since compounds **1** and **2** did not form ion pairs, they were detected by RI only. The amidoamine (**3**) and the long-chain ally quaternary ammonium chloride (**4**) were detected as ion pairs by both UV photometer and RI. Detection of ionizable surfactants as UV-absorbing ion pairs can improve detection limits 100-fold over those obtained with RI. Ten mg of surfactant **4** was detected by RI and 0.1 μg by UV using p-toluene sulfonic acid as the counterion (Table 1). Improved detection limits was due to increased response and greater stability of the UV detector.

Quantitation was limited because of variation in $\underline{k}^1$ with sample size. For example, the capacity factor of surfactant **4** increased with decreasing sample size (Fig. 2). Variation in $\underline{k}^1$ with sample size was most dramatic when 2-napthalene sulfonic acid was the counterion. This may be due to its low concentration

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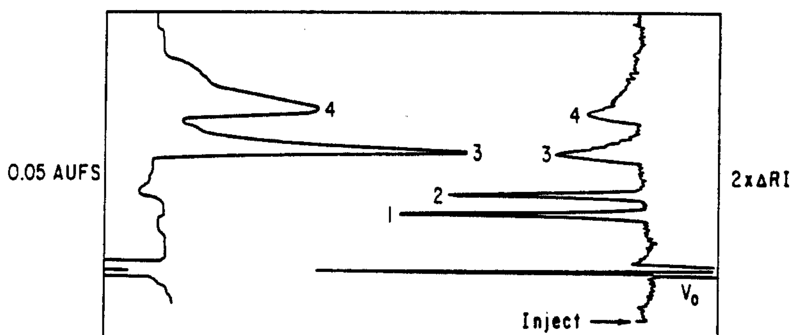

Fig. 1. HPLC separation of a mixture of Compounds 1, 2, 3, and 4 (see scheme). Column, μ-Bondapak C_{18}; mobile phase, methanol-water (9:1) containing 0.2% (v/v) acetic acid and 4.2 mM sodium decylbenzenesulfonate (pH = 4). Sensitivity was 0.05 AUFS and 2X for the UV and RI detector, respectively.

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TABLE 1 Detection Limits

$RN^+(CH_3)_2CH_2CH = CH_2$* 4 (μg)	RI** Peak height (mm)	UV*** Peak height (mm)
20	28	424
10	13	220
1	ND	23
0.6	ND	14
0.1	ND	3

*Counterion was p-toluene sulfonic acid.

**Baseline noise was 5 mm at 2X.

***Baseline noise was 0.5 mm at 0.005 AUFS.

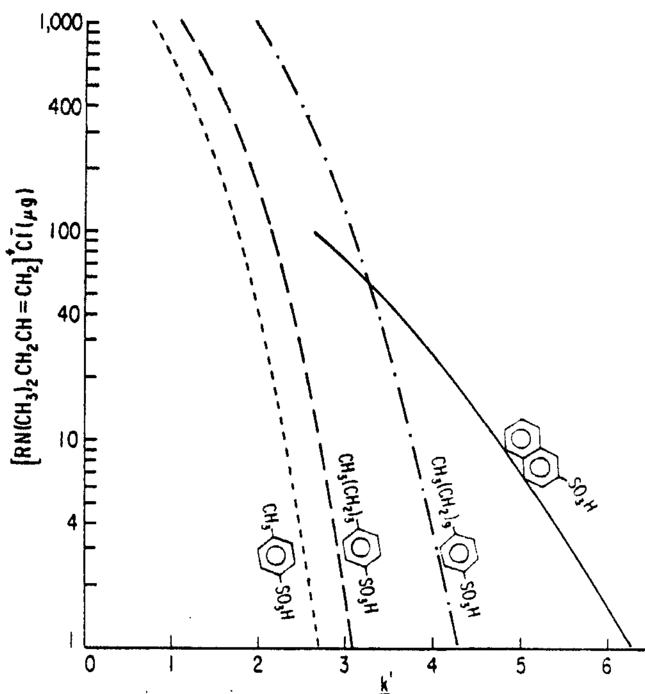

Fig. 2. Effect of solute sample size on $\underline{k}^1$ for different counter-ions. Column, μ-Bondapak C_{18}; mobile phase, methanol-water (9:1) containing 0.2% (v/v) acetic acid and either 0.3 m$\underline{M}$ 2-naphthalenesulfonic acid, 2.9 m$\underline{M}$ p-toluenesulfonic acid, 4.2 m$\underline{M}$ sodium butylbenzenesulfonate, or 4.2 m$\underline{M}$ sodium decylbenzene sulfonate.

(0.3 m$\underline{M}$) in the mobile phase because of its large extinction coefficient.

In spite of this limitation, relatively constant $\underline{k}^1$ values and good quantitation were obtained for sample sizes less than

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TABLE 2 Determination of Known Mixtures*

	$RN^{+}(CH_3)_2CH_2CH=CH_2$** 4			$RN^{+}H(CH_3)_2$** 3			RCO_2H*** 2		
Sample	Actual (μg)	Found (μg)	Relative error (%)	Actual (μg)	Found (μg)	Relative error (%)	Actual (μg)	Found (μg)	Relative error (%)
1	14.4	14.4	0	10.8	10.6	1.9	20.0	20.5	2.5
2	9.2	9.5	3.2	10.2	10.2	0	10.0	10.3	3.0
3	13.4	13.7	2.2	8.6	8.8	2.3	15.8	15.5	1.3
4	12.0	11.8	1.7	16.5	17.0	3.0	7.9	7.9	0

*Chromatographic conditions same as Fig. 1.

**Analysis based on peak height of UV-absorbing ion pair.

***Analysis based on peak height of nonpairing long-chain acid.

****% Relative error = $\frac{\text{error}}{\text{actual}}$ x 100 for three consecutive analyses.

100 μg when chromatographic conditions described in Fig. 1 were used. Recoveries of known surfactant mixtures were determined as UV-absorbing ion pairs and nonpairing components, and accuracy was expressed as percent relative error in Table 2. Cationic compounds 3 and 4 were detected as UV-absorbing ion pairs and the long-chain acid 2 was detected unpaired. The relative error for ion paired components is of the same order of magnitude as nonpairing components. Alternatively, long-chain acids can also be detected as UV-absorbing ion pairs at a neutral pH with Hyamine 1622, used as the counterion.

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REFERENCES AND NOTES

1 N. Parris, W. M. Linfield and R. A. Barford, Anal. Chem., 49, 2228. 1977 .

2 S. Eksborg, P. Lagerström, R. Modin and G. Schill, J. Chromatogr., 83, 99. 1973.

3 J. H. Knox and G. R. Laird, Ibid., 122, 17. 1976.

4 J. H. Knox and J. Jurand, Ibid., 125, 89. 1976

5 N. Parris, C. Pierce and W. M. Linfield, JAOCS, 54 294. 1977.

6 Reference to brand or firm name does not constitute endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.

7 L. F. Fieser, Organic Experiments, D .C. Heath and Co., Boston, Mass., Ch. 32, p.168. 1964.

8 R. Gloor and E. L. Johnson, J. Chromatog. Sci., 15, 413. 1977.

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