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Note

Analysis of the sulphonation products of 2-amino-1-naphthalenesulphonic acid by high-performance liquid chromatography

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A knowledge of chemical kinetics is very important when designing chemical reactors and optimization of their operation. In order to establish the kinetics of chemical reactions, it is necessary to analyse a series of reaction mixtures and to determine their contents both qualitatively and quantitatively. The lack of simple, precise and rapid analytical methods has been the main obstacle in investigating many complex chemical reactions.

An example is the sulphonation of 2-amino-1-naphthalenesulphonic acid, a process that yields many isomers with different numbers of sulphonic groups. The analytical methods applied so far to these compounds have been based on paper chromatography¹, conversion into volatile derivatives, *e.g.*, sulphochlorides, and their separation², separation of salts of these acids and microscopic investigation of crystals^{3,4}.

These methods are inadequate in terms of sensitivity, accuracy and the time required for analysis. High-performance liquid chromatography (HPLC) techniques have used recently for the investigation of aminonaphthalenesulphonic acids. In "soap chromatography", a quaternary ammonium detergent was added to the water-propanol mobile phase for the separation of aminonaphthalenesulphonic acids⁵. Reversed-phase chromatography of aminonaphthalenesulphonic acids may be also performed using a mobile phase containing a strong electrolyte⁶⁻¹⁰, but the retention of acids is lower than in ion-pair reversed-phase chromatography¹¹. This may be a disadvantage for the separation of aminonaphthalenesulphonic acids with two or three sulphonic groups. Ion-pair reversed-phase chromatography seems to be the most advantageous method for the separation of aminonaphthalenesulphonic acids^{12,13}. The separation can be optimized by adjusting the proportions of methanol and water in the eluent and its flow-rate through the column and by changing the type and concentration of the counter ion in the mobile phase^{13,14}.

In the papers cited above the separation of isomeric aminonaphthalenesulphonic acids was mainly described. There were no attempts to separate aminonaphthalenesulphonic acids with one, two or three sulphonic groups simultaneously. In this work, the separation of nine 2-aminonaphthalene sulphonic acids

with different numbers of sulphonic groups is demonstrated. In addition, the separation of 2-aminonaphthalenesulphonic acids present in the sulphonation mixture during the process for the production of 2-amino-1,5-naphthalenedisulphonic acid and 2-amino-1,5,7-naphthalenetrisulphonic acid was performed.

EXPERIMENTAL

Reagents

A 0.5 M solution of tetra-*n*-butylammonium phosphate was obtained by mixing 52 ml of 1.11 M potassium dihydrogen phosphate in water with 25 ml of 1.54 M tetra-*n*-butylammonium hydroxide in water at pH 7.2. The solution was mixed thoroughly and kept in the dark. It was used to prepare the eluent that served as the mobile phase and as the solvent for the sulphonation mixture and standard samples.

Standard samples of 2-aminonaphthalenesulphonic acids were obtained as sodium and potassium salts by repeated crystallization of the technical products from water and ethanol.

Apparatus

A Waters Model 440 liquid chromatograph equipped with a UV detector (254 nm), a 6000 A pump, a U6K injector and a 300 × 4 mm I.D. μ Bondapak C₁₈ column (Waters Assoc., Milford, MA, U.S.A.) was used.

Procedure

The eluent was a 0.005 M solution of tetra-*n*-butylammonium phosphate in 50, 30 and 20% methanol (10 μ l of 0.5 M tetra-*n*-butylammonium phosphate in water

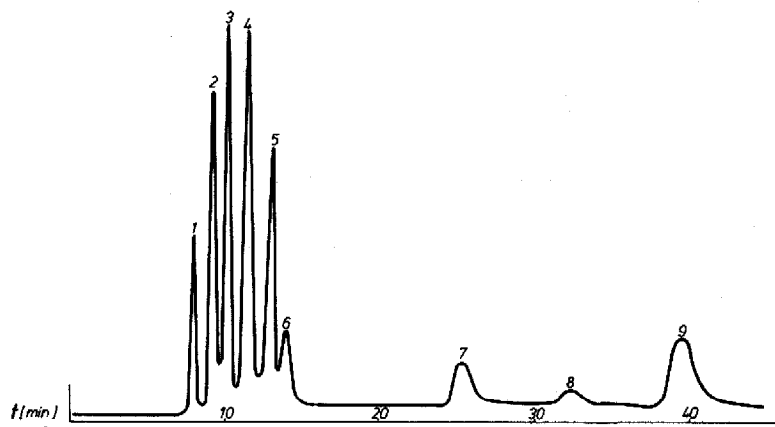


Fig. 1. Reversed-phase HPLC separation of aminonaphthalenesulphonic acids. Isocratic elution with 0.005 M tetra-*n*-butylammonium phosphate in methanol-water (1:4). Column: μ Bondapak C₁₈, 300 × 4 mm I.D. Flow-rate: 1.5 ml/min. Detection: UV, 254 nm, 1.0 a.u.f.s. Compounds: 1 = 2-aminonaphthalene-5-sulphonic acid; 2 = 2-aminonaphthalene-5,7-disulphonic acid; 3 = 2-aminonaphthalene-1,5-disulphonic acid; 4 = 2-aminonaphthalene-1,6-disulphonic acid; 5 = 2-aminonaphthalene-6,8-disulphonic acid; 6 = 2-aminonaphthalene-7-sulphonic acid; 7 = 2-aminonaphthalene-8-sulphonic acid; 8 = 2-aminonaphthalene-1,5,7-trisulphonic acid; 9 = 2-aminonaphthalene-1-sulphonic acid.

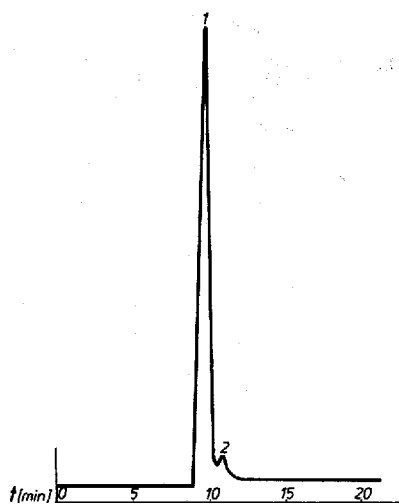


Fig. 2. Reversed-phase HPLC separation of sulphonation mixture. First stage of sulphonation of 2-aminonaphthalene-1-sulphonic acid; temperature, 30°C; oleum concentration, 7.5% SO₃. Conditions as in Fig. 1. 1 = 2-aminonaphthalene-1,5-disulphonic acid; 2 = 2-aminonaphthalene-1,6-disulphonic acid.

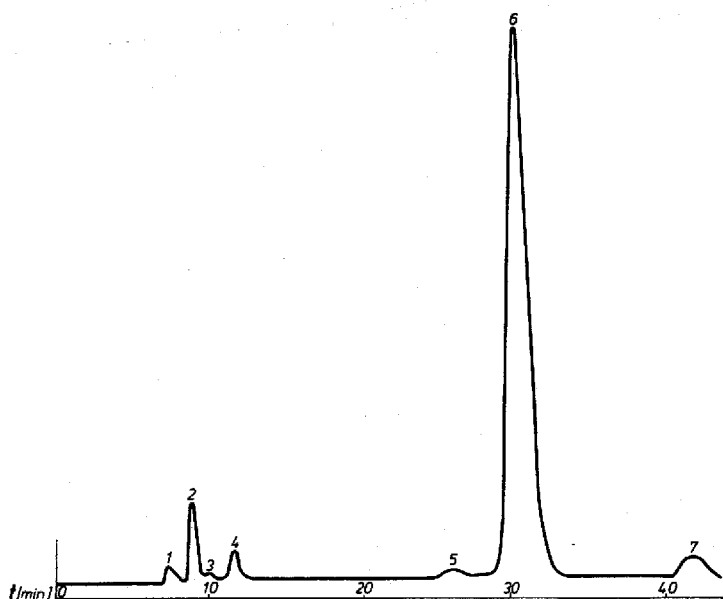


Fig. 3. Reversed-phase HPLC separation of sulphonation mixture. Second stage of sulphonation of 2-aminonaphthalene-1-sulphonic acid; temperature, 114°C; oleum concentration, 7.5% SO₃. Conditions as in Fig. 1. Compounds: 1 = 2-aminonaphthalene-5,7-disulphonic acid; 2 = 2-aminonaphthalene-1,5-disulphonic acid; 3 = 2-aminonaphthalene-1,6-disulphonic acid; 4 = 2-aminonaphthalene-6,8-disulphonic acid; 5 = unidentified; 6 = 2-aminonaphthalene-1,5,7-trisulphonic acid; 7 = unidentified.

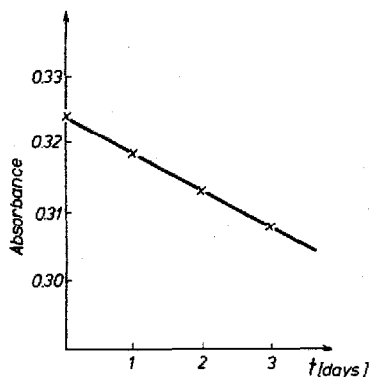


Fig. 4. Change of absorbance of 2-aminonaphthalene-1,5-disulphonic acid in aqueous solution. Concentration = $1.3 \cdot 10^{-3}$ M.

were added per 1 l of solvent). All standard sample solutions and the eluent were filtered through $0.45 \mu\text{m}$ organic filters.

For identification and quantitative analysis, standard solutions of 2-aminonaphthalenesulphonic acids of concentration 0.4 mg/ml of the eluent were used. The concentrations of the reaction mixtures were 1–2 mg/ml of the eluent. The amounts of solution chromatographed ranged from 2 to $10 \mu\text{l}$.

RESULTS AND DISCUSSION

The separation of standard mixtures of 2-aminonaphthalene sulphonic acids was achieved successfully (Fig. 1).

The chromatograms of sulphonation mixtures in the process for the production of the 2-amino-1,5-naphthalenedisulphonic acid and 2-amino-1,5,7-naphthalenetrisulphonic acid are shown in Figs. 2 and 3, respectively.

In the first stage of sulphonation, leading to 2-amino-1,5-naphthalenedisulphonic acid, only isomeric aminonaphthalenedisulphonic acids were observed. In the process for the production of 2-amino-1,5,7-naphthalenetrisulphonic acid, aminonaphthalenedisulphonic and aminonaphthalenetrisulphonic acids are present in the sulphonation mixture.

Solutions of sulphonation mixtures and standard acids samples are unstable and change their molar absorptivities with time. For example, 2-amino-1,5-naphthalenedisulphonic acid changes its absorbance with time, as shown in Fig. 4. Reversed-phase ion-pair chromatography ensures a good separation of aminonaphthalenesulphonic acids present in the reaction mixture. With aminonaphthalenesulphonic acids there is no direct dependence between retention time and the number of sulphonic groups in the molecule.

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