

DISPROPORTIONATION OF THE SODIUM SALT OF THE 5-SULFOISOPHTHALIC ACID UNDER CONDITIONS OF GEL CHROMATOGRAPHY

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The behavior of the sodium salt of 5-sulfoisophthalic acid is described under conditions of liquid chromatography with Sephadex LH-20 and water as mobil phase. The original compound undergoes a disproportionation reaction leading to the formation of free acid and trisodium salt. Because of the strong sorption of the free acid the product leaves the column in two separated peaks. Similar behavior was observed in the case of potassium hydrogen phthalate.

In the use of gel chromatography for the separation of low molecular substances in aqueous solution complications may arise due to the influence of processes, which are not encountered of the separation of undissociated molecules in the medium of non-aqueous solvents. For an exact interpretation of chromatograms obtained in the separation of ionogenic compounds in aqueous medium the knowledge of all interactions during the separation process is unavoidable. The sorption effect has to be taken into account with respect to the polarity of the gels, which can be used for separations in aqueous media¹⁻¹⁰. Furthermore, another effect is of importance for the separation in aqueous medium, *i.e.* the specific dependence of the retention of some ionic particles on the character of electrically opposite ions in the mobil phase¹⁰⁻¹². As the electro-neutrality condition in each part of the column must be fulfilled some irregularities of the permeation of individual ions into gel pores and the retention dependence on the pore size may be foreseen, especially if the content of suitable electrolytes in the mobil phase is not sufficient.

The effect of ion exclusion^{3,10,14}, until now not satisfactorily explained¹³, can be one of the factors leading to a change of the permeation coefficient, which cannot be justified by the dimensions of the eluted ions. As a consequence of the complex effect of the sorption, character and concentration of other ions in the mobil phase and the ion exclusion, the permeation alone need not be the decisive factor, influencing the value of the retention volume of the separated ions¹⁵. Investigating the gel-chromatographical behaviour of acidic aqueous molybdate solutions, Streuli and Rogers⁴ observed two peaks, corresponding to different forms of the molybdate anion, but no interpretation has been attempted.

In this work, a similar unusual chromatographic behaviour will be described, observed in the chromatography of aqueous solutions of the esterification products of sodium 5-sulfoisophthalate with ethylene glycol on hydroxypropylated poly-dextrane gel Sephadex LH-20 with water as mobil phase.

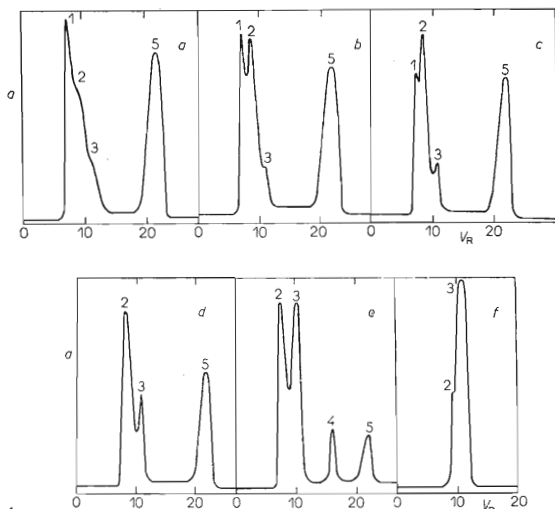


FIG. 1

Chromatograms of Aqueous Solutions of Samples Taken Stepwise from the Reaction Mixture During Esterification of the Sodium Salt of 5-Sulfoisophthalic Acid with Ethylene Glycol

Column 0.8×88 cm, Sephadex LH-20, mobil phase water, flow rate 0.3 ml/min, V_R is expressed as number of siphons, a signal of the detector.

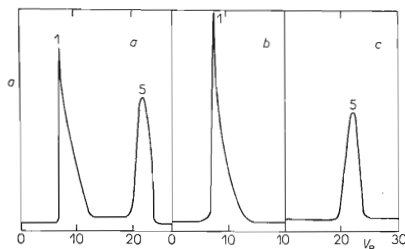


FIG. 2

Chromatogram of Aqueous Solution ($0.04M$) of Sodium Salt of 5-Sulfoisophthalic Acid (a) and Repeated Chromatograms of the First (b) and Second (c) Fractions Obtained in the Separation of Aqueous Solution of Monosodium Salt of 5-Sulfoisophthalic Acid

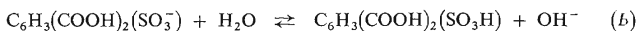
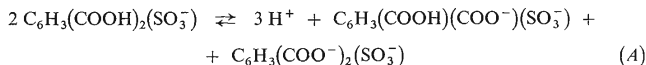
Conditions the same as in Fig. 1.

EXPERIMENTAL

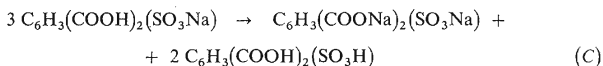
A glass column, i.d. 0.8 cm, contained the gel Sephadex LH-20 (Pharmacia AB, Uppsala), particle size 35–75 μ . Aqueous sample solutions (0.50 \pm 0.05 ml) were introduced with a syringe *via* a stainless steel injection port¹⁶. The flow rate of water as mobil phase varied in the range 0.2–1 ml/min and was measured by the number of overflows of siphon placed at the outlet of the detector. The siphon volume was 2.32 ml. As the detector served the UV₂₅₄-Analyzer (Development Workshop, Czechoslovak Academy of Sciences, Prague) equipped with a low-pressure mercury lamp as optical source, with a quartz capillary cuvette (volume 0.1 ml) and a liquid filter (NiSO₄). Samples of the sodium 5-sulfoisophthalate were obtained from Institute of Organic Syntheses, Pardubice-Rybitví. 5-Sulfoisophthalic acid was prepared from aqueous solution of the corresponding sodium salt by passing it through a column of cation exchanger Dowex 50X8, 50–100 mesh in H⁺-form and evaporation the eluate. The samples from the course of the esterification of sodium 5-sulfoisophthalate with ethylene glycol were provided in our Institute. Potassium hydrogen phthalate as well as other reagents were of the quality P.R. (Lachema, Brno).

RESULTS AND DISCUSSION

In Figs 1a–f the chromatograms are shown, which were obtained with approximately equally concentrated aqueous solution of products, taken at regular time intervals from the reaction mixture of the esterification of the sodium 5-sulfoisophthalate with twenty-fold molar excess of ethylene glycol at 196°C. In place of the assumed three peaks, corresponding to the sodium 5-sulfoisophthalate, its mono- and bis(2-hydroxyethyl) ester five peaks were detected. The chromatography of the aqueous solution of sodium 5-sulfoisophthalate (Fig. 2a) has confirmed that it yields under these conditions two products with largely different elution volumes. The difference of both products was confirmed by repeated injection of the solution of the residues of the corresponding fractions (Figs 2b,c). These components were then isolated in greater amounts from repeated injections of a nearly saturated (3.2M) aqueous sodium 5-sulfoisophthalate under similar conditions and identified with the use of acidity number and sodium content (following ion exchange on an anion-column in carbonate form). It was concluded, that the peak 1 (Fig. 1) corresponds to trisodium 5-sulfoisophthalate and the peak 5 (Fig. 1) with the greatest retention volume from the whole complex of components corresponds to free 5-sulfoisophthalic acid. The rightness of this assumption was proved by a series of chromatograms of 0.4M aqueous solutions of 5-sulfoisophthalic acid stepwise neutralized with sodium hydroxide (Fig. 3). The values of the dissociation constants of 5-sulfoisophthalic acid are not known, however, from the course of the potentiometric titration curve both in aqueous and in nonaqueous solution, it may be concluded, that the differences of the dissociation constant values are small. For this reason, the presence of all ionic forms of the hydrolytic equilibria (A) and (B) can be assumed in solutions of sodium 5-sulfoisophthalate.



As the value of the retention volume of free acid (peak 5) is much larger than the total column volume, the sorption mechanism of the separation of this component is thus proved. With respect to the high concentration of the introduced sample solutions the ion exchange properties of the gel used cannot participate in the separation process, if there are any. The most probable mechanism of the process, seems to be such, that both equilibria (A) and (B) are shifted as a result of the sorption of the free acid on the gel. The resulting not sorbed trisodium salt is eluted in a separated peak before the peak of the free acid. The overall balance is expressed by Eq. (C):



It may be seen from Fig. 3 that the dismutation according to Eq. (C) does not proceed quantitatively, because the peak 5 of the free acid (H_3SiF) disappears before the equivalence $3 \text{Na}^+/\text{H}_3\text{SiF}$ has been reached. This may be also the reason for the tailing of the peak 1, attributed to the trisodium salt Na_3SiF . The disagreement of this fact (Fig. 3) with the results of the analysis of the fractions in the preparation experiments, when the total concentration of all H_3SiF forms was approximately $3 \cdot 2\text{M}$, can be caused by the influence of the concentration of the injected samples

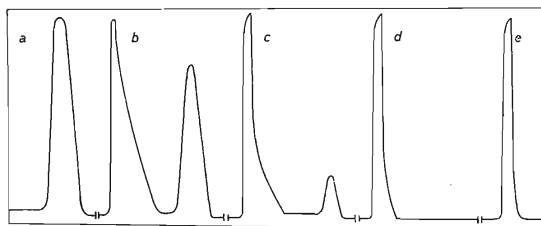


FIG. 3

Chromatograms of Aqueous Solutions (0.4M) of 5-Sulfoisophthalic Acid, Stepwise Neutralized by Sodium Hydroxide

Flow rate 1 ml/min, other conditions the same as in Fig. 1. Equivalence acid: NaOH ratio; a 10:0, b 10:4, c 10:8.9, d 10:9.7, e 10:11.0.

on the course of the dismutation reaction (C). The disagreement of the surface areas of the peaks 1 and 5 (Fig. 3) with the corresponding content of both components is caused, beside the non-linear function of the employed detector also by the great variability of the molar absorbances of pH-dependent dissociation forms of 5-sulfoisophthalic acid at the wavelength of the used optical source (254 nm). Sorption of the free acid is probably due to the interaction of undissociated carboxyl groups with the gel material, which is also confirmed by the finding that the retention volume of bis(2-hydroxyethyl) ester does not depend on whether its sulfo group is in acid or neutralized form (Fig. 4*a,b*). Under these circumstances peak 4 in Fig. 1*e* belongs probably to the sorption wave of the acid form of monoester, whose neutralized form is represented by peak 2. Fig. 4*c* is in accordance with this inter-

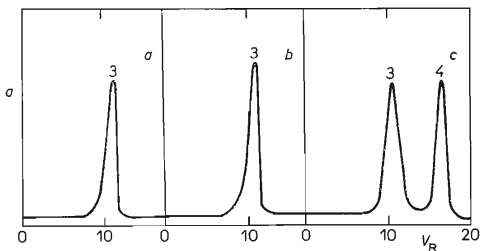


FIG. 4

Chromatograms of Aqueous Solution of Bis-(2-hydroxyethyl) Ester of Monosodium Salt of 5-Sulfoisophthalic Acid after Passing through the Column of Cation Exchanger in H^+ -Form (*a*) and in Na^+ -Form (*b*) and of the Solution of Compounds Obtained from Fractions 2 and 3 (Fig. 1*e*) after Conversion into Acid Form by Passing through the Column of Cation Exchanger in H^+ -Form (*c*)

The same conditions as in Fig. 1.

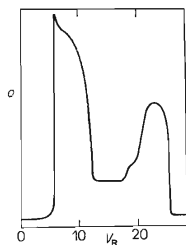


FIG. 5

Chromatogram of Aqueous Solution (0.5M) of Potassium Hydrogen Phthalate

The same conditions as in Fig. 1.

pretation. In order to verify a more general validity of the described phenomenon we had carried out chromatographic analysis of potassium hydrogen phthalate under the same conditions. As can be seen in Fig. 5, even in this case two peaks are formed.

The found behaviour can be applied in practice to a very effective separation of mixtures of 5-sulfoisophthalic acid, its hydroxyethyl ester and bis(2-hydroxyethyl) ester which can be obtained from the esterification mixtures of the sodium salt of 5-sulfoisophthalic acid and ethylene glycol after their conversion to acid form by means of a cation exchanger.

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