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S. Przeszlakowski[a]
[a] DEPARTMENT OF INORGANIC AND ANALYTICAL CHEMISTRY, MEDICAL SCHOOL, Lublin, POLAND

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Sorption of Salicylic and 5-Sulfosalicylic Acids on Silica Gel Impregnated with Aliquat 336

S. PRZESZLAKOWSKI
DEPARTMENT OF INORGANIC AND ANALYTICAL CHEMISTRY
MEDICAL SCHOOL
20-081 LUBLIN, POLAND

ABSTRACT

Silica gel coated with Aliquat 336 was used as a sorbent for salicylic and sulfosalicylic acid or anions of these acids. It was found that both acids were extracted almost quantitatively if their concentrations in aqueous solutions did not exceed the theoretical capacity of the sorbent. Aliquat 336 extracts a large excess of salicylic acid and only a very small excess of sulfosalicylic acid relative to the amount of quaternary alkylammonium chloride in the sorbent in the form of undissociated molecules of acid. Although the main sorption process of both acids or their anions is an anion-exchange reaction, a physical partition of acids or anions between the two polar phases occurs to a lesser degree.

INTRODUCTION

The immunosuppressing properties of phenolic acids which commonly appear in the plant world (free or connected with sugars as glycosides) have recently been detected and have caused increased interest in these compounds. Small amounts of phenolic acids cannot be analyzed directly from plant material by HPLC (1), and therefore new methods for their isolation and separation are needed. Inczédy and Glósz (2) separated a mixture of benzoic, salicylic, and sulfosalicylic acids by ion-exchange chromatography using a column packed with a strongly basic anion-exchange resin. The anion-exchange properties of solutions of high molecular weight amine salts or quaternary alkylammonium salts in organic solvents are well known (3–5) and many papers have been devoted to the extraction of various (mainly inorganic) acids from aqueous solutions into organic solutions of liquid anion exchangers. Also, chelating reagents for metals (reagents containing strongly acidic sulfonic groups) are strongly extracted with chloroform solutions of liquid anion exchangers (6–10). Salicylic, sulfosalicylic, and γ-resorcylic acids were recently found to be strongly extracted from their aqueous solutions into chloroform solutions of tri-*n*-octylamine or Aliquat 336 (11), and the extraction of an excess of acid relative to the alkylammonium salt concentration occurs for salicylic and γ-resorcylic acids. However, the interpretation of extraction results for salicylic acid has been difficult owing to rather strong extraction of this acid with pure chloroform. The experimental results from the sorption of salicylic and 5-sulfosalicylic acids on silica gel impregnated with Aliquat 336 are used in the present paper to provide an explanation of the extraction mechanism. This sorbent is often used in extraction chromatography of metals (12) as well as for separation of halide ions (13).

EXPERIMENTAL

Materials

Analytical-grade chloroform was additionally purified by distillation. Chloroform solutions of Aliquat 336 (Fluka, Switzerland) were standarized by titration of the residue after evaporation of the diluent with 0.1 $\mathrm{mol \cdot L^{-1}}$ $AgNO_3$ in ethanol–aqueous medium.

Silica gel 100, 0.063–0.2 mm (Merck, Germany), was used as a support for the stationary phase.

Aqueous solutions of salicylic acid (POCh, Poland) and 5-sulfosalicylic acid (Unia, Poland) were standardized by titration with a 0.01 $\mathrm{mol \cdot L^{-1}}$ solution of KOH.

Apparatus

Recording spectrophotometer UV-VIS Specord M40 (Zeiss, Germany) and 1 cm silica cells were used for spectrophotometric measurements. pH measurements were made with a Radelkis OP-208/1 (Hungary) direct reading precision pH meter with a glass-silver chloride electrode assembly. The same apparatus equipped with a chloride ion-selective electrode (Radelkis, Hungary) and a silver chloride reference electrode with a double salt bridge (Metron, Poland) was used for determination of chloride ion concentration as well as for titrimetric determination of chloride ions in Aliquat 336.

A vaccum rotary evaporator (Quickfit, England) was used for impregnation of silica gel with a chloroform solution of Aliquat 336.

Procedure

Two hundred milliliters of 0.02 mol·L^{-1} chloroform solution of Aliquat 336 was mixed with 18.23 g silica gel. The diluent was then evaporated with a vacuum evaporator on a water bath. One gram of the sorbent then contained 0.2 mmol Aliquat 336.

The sorption of salicylic acid and sulfosalicylic acid (or their potassium salts, obtained by potentiometric titration of acids with 0.1 mol·L^{-1} KOH) from aqueous solutions was investigated by the static method. The sorbent (0.025 g) was then usually shaken with 10 mL acid or salt solution. The mixture was subsequently centrifuged, and the remaining acid or anion in the solution was determined spectrophotometrically on the basis of appropriate calibration graphs obtained for standard solutions of both acids or their potassium salts.

The concentration of chloride ions in the aqueous solution displaced from Aliquat 336 by salicylate or sulfosalicylate anions after sorption was determined potentiometrically with the use of a chloride ion-selective electrode calibrated with standard sodium chloride solutions (correcting for the concentration of chloride ions washed from the sorbent with distilled water). In these experiments, 20 mL volumes of the aqueous solutions of the acid or salt being investigated were shaken for 5 minutes with 50 mg of the sorbent (salicylic acid or its salt) or with 100 mg of the sorbent (sulfosalicylic acid or its salt).

RESULTS AND DISCUSSION

Neither salicylic acid nor 5-sulfosalicylic acid were adsorbed from their aqueous solutions on activated silica gel in control experiments. The sorption process of these acids takes place between the aqueous phase and the liquid anion exchanger phase. Aqueous solutions of both acids contain undissociated molecules of salicylic acid (H_2A) and mononegative anions (H_2A^-) from sulfosalicylic acid. It is assumed that the strongly acidic sulfonic group is completely dissociated, and that the HA^- and HA^{2-} anions are produced from dissociation of the carboxylic groups; the presence of anions A^{2-} and A^{3-} from dissociation of the phenolic group is practically excluded in acidic or neutral aqueous solutions because of the very low dissociation constants (K_2) of both acids (14). If extraction of these acids follows only from an anion-exchange reaction, their sorption on silica gel coated with Aliquat 336 should decrease with the concentration of acid in the aqueous solution and increase with the pH of the solution and the dissociation constant K_1 of the acid.

Figure 1 shows the dependence of sorption efficiency of salicylic and 5-sulfosalicylic acids and their anions, HA^- and HA^{2-}, on their concentration in aqueous solutions. Both acids are very strongly sorbed from very dilute aqueous solutions. (The stronger sulfosalicylic acid was somewhat more strongly sorbed than salicylic acid.) However, the distinctly lower sorption of salicylate and sulfosalicylate anions in comparison with the sorption of both acids investigated suggests the following anion-exchange reactions:

$$\overline{R_4N^+, Cl^-} + HA^- \Leftrightarrow \overline{R_4N^+, HA^-} + Cl^-$$

$$\overline{2R_4N^+, Cl^-} + HA^{2-} \Leftrightarrow \overline{(R_4N^+)_2, HA^{2-}} + 2Cl^-$$

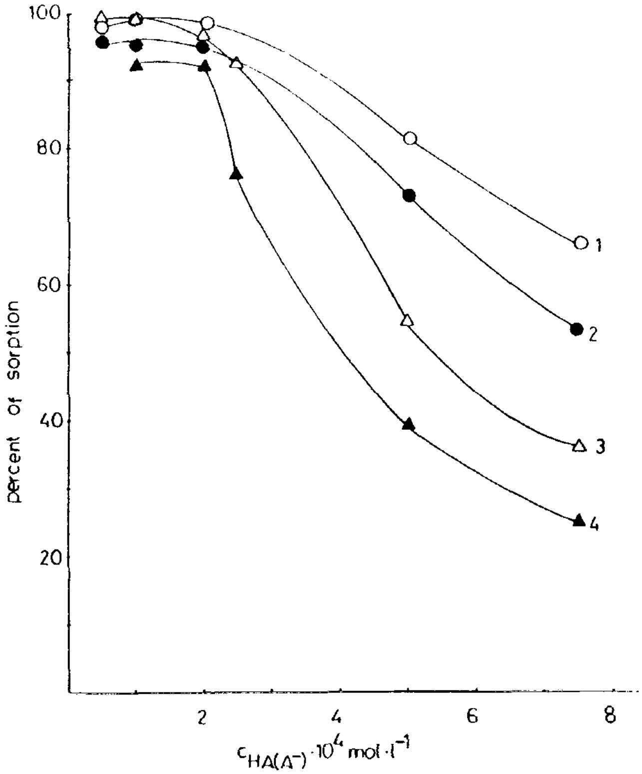

FIG. 1 Percent of salicylic (1) and 5-sulfosalicylic (3) acids or salicylate (2) and 5-sulfosalicylate (4) anions sorbed vs initial concentration of acid or anion in the aqueous solution relationships. The aqueous solution (10 mL) was shaken with 25 mg sorbent containing 5 μmol Aliquat 336.

TABLE 1

Distribution Coefficients (D_m) for Salicylic and 5-Sulfosalicylic acids or Their Anions between Silica gel Impregnated with Aliquat 336 and an Aqueous Solution of Acid or Salt, Calculated from Experimental Data (molar amount of acid or anion in the aqueous solution was equivalent to the molar amount of alkylammonium chloride in the sorbent)

	Dissociation constant, K_1	pH of 5×10^{-4} mol·L^{-1} (initial) aqueous solution	D_m
Salicylic acid	10^{-3}	3.43	4.2
5-Sulfosalicylic acid	4×10^{-3}	3.09	11.2
Salicylate	—	5.22	2.6
5-Sulfosalicylate	—	5.45	3.5

This is based on the distribution of salicylate and sulfosalicylate anions between the aqueous and organic phases.

At equivalent amounts of both acids in aqueous solutions and quaternary alkylammonium chloride in the sorbent, the distribution coefficient for 5-sulfosalicylic acid is almost three times as high as for salicylic acid (see Table 1). Distribution coefficients for both acids are higher than those for their anions.

Salicylic acid is extracted into the liquid anion exchanger phase to an extent that exceeds the theoretical capacity of the sorbent. Only a small excess of 5-sulfosalicylic acid can be extracted with Aliquat 336 (see Fig. 2). On the other hand, the mole ratio of anions of these acids to Aliquat 336 never approached the theoretical values (1.0 for salicylate and 0.5 for sulfosalicylate). Our results indicate that in addition to the extracted anions, the undissociated salicylic acid and to lesser extent sulfosalicylic acid are also extracted.

$$\overline{R_4N^+, Cl^-} + HA^- + nH_2A \Leftrightarrow \overline{R_4N^+, HA^-(H_2A)_n} + Cl^-$$

Extraction of excess acid, relative to the stoichiometric amount of amine, is well known from liquid–liquid extraction data and occurs normally at high concentrations of acids in aqueous solutions (additional extraction increases with decreasing acid strength). However, extraction of an excess of weak acetic acid takes place even when its concentration is as low as 0.2 mol·L^{-1} (15). The additional extraction of undissociated molecules of salicylic acid takes place at very low concentrations in aqueous solutions, (as low as 10^{-3} mol·L^{-1}), and therefore the tendency to extract undissociated molecules of aromatic acids depends not only on the acid strength but also on the hydrophobicity of the acid molecule.

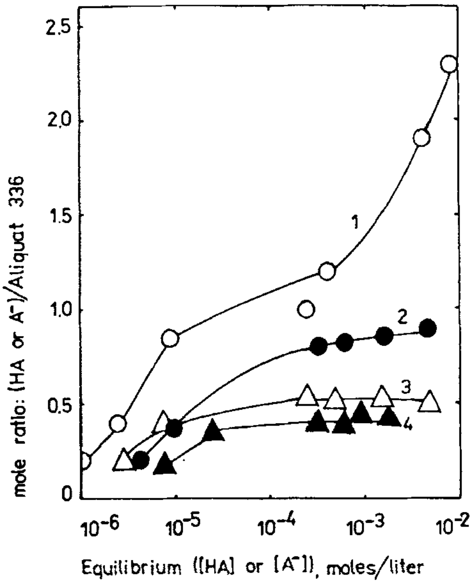

FIG. 2 Mole ratio of salicylic (1) and 5-sulfosalicylic (3) acids or salicylate (2) and 5-sulfosalicylate (4) anions to Aliquat 336 in the sorbent vs equilibrium concentration of both acids or anions in the aqueous solution relationships. Experimental conditions are the same as in Fig. 1.

TABLE 2

Results of the Determination of Salicylic Acid (H_2A) or Salicylate Anions (HA^-) and Chloride Ions in the Aqueous Solution, Obtained after Shaking 20 mL of the Aqueous Solution of Acid or Its Potassium Salt with 50 mg of the Sorbent Containing 10 μmol Aliquat 336

Initial aqueous solution $C_{H_2A\,(HA^-)}$ (mol·L^{-1})	H_2A (HA^-) in 20 mL initial aqueous solution (μmol)	H_2A (HA^-) sorbed (μmol)	Cl^- eluted (μmol)	μmol Cl^- / μmol H_2A (HA^-) sorbed
H_2A, 2×10^{-4}	4	3.78	2.10	0.56
H_2A, 5×10^{-4}	10	8.06	3.42	0.42
H_2A, 5×10^{-3}	100	17.40	5.72	0.33
HA^-, 2×10^{-4}	4	3.68	3.18	0.86
HA^-, 5×10^{-3}	100	7.50	6.72	0.90

TABLE 3
Results of the Determination of 5-Sulfosalicylic acid (H_3A) or Sulfosalicylate Anion (HA^{2-}) and Chloride Ions in the Aqueous Solution after Shaking 20 mL 5×10^{-4} mol·L^{-1} Aqueous Solution of Acid or its Salt with 100 mg Sorbent Containing 20 μmol Aliquat 336

H_3A (HA^{2-}) in 20 mL of initial solution (μmol)	H_3A (HA^{2-}) sorbed (μmol)	Cl^- eluted (μmol)	μmol Cl^- eluted / μmol H_3A (HA^{2-}) sorbed
H_3A, 10	9.18	7	0.76
HA^{2-}, 10	7.4	7	0.95

The results of chloride ion determinations in aqueous solution (displaced from Aliquat 336) after sorption of salicylic acid (Table 2) and 5-sulfosalicylic acid (Table 3) confirms the importance of the anion-exchange reaction in the sorption process of these acids, and especially of salicylate and sulfosalicylate anions.

Although the amount of chloride ions displaced from Aliquat 336 by salicylic acid increased with acid concentration in the initial aqueous solution, the mole ratio of chloride ions eluted to acid sorbed decreased with acid concentration (in the same direction as the dissociation of this acid decreases). Thus, if the concentration of salicylic acid in the aqueous solution exceeds the capacity of the sorbent, the relative significance of the anion-exchange reaction decreases and the extraction of undissociated molecules of acid increases. On the contrary, in aqueous solutions with only salicylate or sulfo-salicylate anions present, the main sorption mechanism is anion exchange. However, even in this case the mole ratio of chloride ions eluted to anions sorbed does not approach the theoretical value of 1. Thus sorption of both acids or their anions probably occurs, but to a low degree, and affects the physical distribution of acids or anions between the aqueous phase and the liquid anion-exchanger phase.

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REFERENCES

1. E. Heftman (Ed.), *Chromatography. Part B—Applications*, Elsevier, Amsterdam, 1985.
2. J. Inczédy and L. Glósz, *Acta Chim. Acad. Sci. Hung.*, *62*, 241 (1969).
3. A. S. Kertes, Y. Marcus, and E. Yanir, *Equilibrium Constants of Liquid–Liquid Distribution Reactions. Part 2. Alkylammonium Salt Extractants*, Butterworths, London, 1974.
4. V. S. Shmidt, *Extraction with Amines*, Atomizdat, Moscow, 1970 (in Russian).
5. E. A. Mezhov, *Extraction with Amines, Amine Salts and Quaternary Alkylammonium Salts*, Atomizdat, Moscow, 1977 (in Russian).
6. S. Przeszlakowski and E. Habrat, *Analyst*, *107*, 1320 (1982).
7. S. Przeszlakowski and H. Wydra, *Talanta*, *31*, 401 (1984).
8. S. Przeszlakowski and H. Wnuk, *Chem. Anal.* (*Warsaw*), *30*, 535 (1985).
9. R. Kocjan and S. Przeszlakowski, *Ibid.*, *33*, 753 (1988).
10. S. Przeszlakowski, *Ibid.*, *37*, 285 (1992).
11. S. Przeszlakowski and E. Karczmarczyk, *Acta Pol. Pharm.-Drug Res.*, *51*, 301 (1994).
12. T. Braun and G. Ghersini (Eds.), *Extraction Chromatography*, Elsevier, Amsterdam, 1975.
13. S. Przeszlakowski and R. Kocjan, *Chromatographia*, *13*, 175 (1980).
14. S. Kortüm, W. Vogel, and K. Andrussov, *Dissoziationskonstanten organischer Säuren in wässeriger Lösung*, Butterworths, London, 1961.
15. A. S. Vieux, *Bull. Soc. Chim. Fr.*, p. 3364 (1969).

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