UDC 547.972+541.183+543.544.4

A STUDY OF SORPTION PROCESSES ON A POLYAMIDE SORBENT

I. The Sorption of Quercetin and Dihydroquercetin

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Khimiya Prirodnykh Soedinenii, Vol. 4, No. 6, pp. 349-352, 1968

In spite of the wide use of a polyamide sorbent in the chromatography of flavonoids, the quantitative side of the process has been little studied. There are only isolated papers on the nature of the sorption and desorption of phenols and quinones [1, 2].

In the present communication we give the results of a study of the processes of sorption and desorption of polyamide powder of the flavonoids, quercetin and dihydroquercetin, isolated from the wood of Larix dahurica (Dahurian larch) [3]. We absorbed the flavonoids by the dynamic method [4] from the solvents most frequently used in chromotographic operations (methanol, acetone, and a mixture of methanol and chloroform 15: 85 by volume). The curves obtained (Fig. 1) expressing the equilibrium absorption as a function of the concentration have the form of Langmuir isotherms. Table 1 gives the maximum absorptions of quercetin and dihydroquercetin from various solvents.

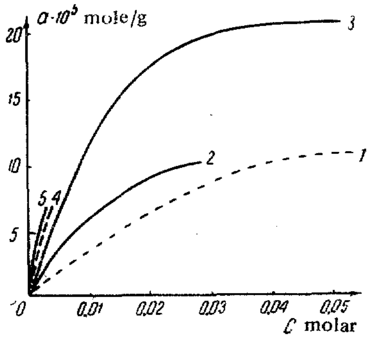

Fig. 1. Isotherms of the sorption of quercetin (2, 3, 5) and dihydroquercetin (1, 4) on polyamides 1, 2) from methanol; 3) from acetone: 4, 5) from a mixture of methanol and chloroform (15 : 85).

The highest figures are obtained for the sorption of a given flavonoid from a mixture of methanol and chloroform (15: 85) and the lowest figures for sorption from methanol. The decrease in polarity in the sequence methanol—acetone—methanol—chloroform (15: 85) leads to a rise in the adsorption of the flavonoid components from these solvents.

By comparing the absorption of quercetin and dihydroquercetin from the same solvents and at the same concentrations of the solutions it can be seen that quercetin possesses a greater affinity for polyamide than dihydroquercetin. Consequently, the presence of a double bond in the C_2-C_3 position in quercetin and its absence in dihydroquercetin increases the activity of quercetin with respect to the polyamide sorbent, all other conditions being the same.

The adsorption of flavonoids on polyamide is completely reversible. Elution takes place most readily with methanol (Fig. 2, A, a, B, a) and least readily with acetone (Fig. 2, A, b and Fig. 2, B, b) and with a mixture of methanol and chloroform (Fig. 2, A, c and Fig. 2, B, c), i.e., the more polar solvent has a greater power of desorption.

When the desorption curves of quercetin and dihydroquercetin prepared under comparable conditions are superposed it can be seen that in all cases dihydroquercetin is desorbed considerably more readily than quercetin.

The sorption of the flavonoids will be affected not only by the nature of the substances themselves and of the solvents but also by the size of the macromolecules of the polyamide sorbent. From a polyamide powder we isolated three fractions with molecular weights of 19 950, 19 050, and 11 220.

Table 1

Limiting Absorption (A_s, mole/g) of Quercetin and Dihydroquercetin on a Polyamide Powder from Various Solvents

Flavonoid	Methanol $\varepsilon = 31.2$		Acetone $\varepsilon = 21.5$		Methanol–chloroform (15 : 85) $\varepsilon = 5.7$	
	$a_s \cdot 10^5$	K	$a_s \cdot 10^5$	K	$a_s \cdot 10^5$	K
Quercetin	18.0	46.0	27.0	88.0	28.5	140.0
Dihydroquercetin	11.0	28.0	—	73.0	19.5	138.0

Note: ε is the dielectric constant of the solvent. For the methanol—chloroform (15: 85) mixture we calculated it as the additive value. K is the adsorption constant from the Langmuir equation.

From the results given in Table 2 it can be seen that the molecular weight also affects the strength of the absorption. Thus, while the absorption of quercetin from methanolic solution (concentration 0.005 M) on polyamide with a molecular weight of 19 959 is $5.3 \cdot 10^{-5}$ mole/g, on polyamide with a molecular weight of 11 220 it falls to $4.2 \cdot 10^{-5}$ mole/g. It is interesting that the number of amide groups in the polyamide rises with an increase in the molecular weight.

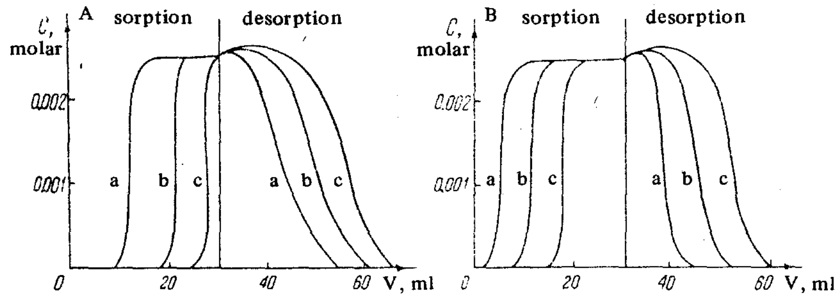

Fig. 2. Desorption of quercetin (A) and dihydroquercetin (B) by methanol (a), acetone (b), and methanol—chloroform (15 : 85) (c).

Table 2

Adsorption of Quercetin as a function of the Molecular Weight of the Polyamide Sorbent (from Methanolic Solution, Concentration 0.005 M)

Fraction no.	Mol. wt. of the polyamide fraction	Content of the fraction in the initial polyamide, %	Absorption of quercetin, moles/g	Number of amide groups per g of polyamide
1	19 950	66.0	$5.3 \cdot 10^{-5}$	$5.25 \cdot 10^{21}$
2	19 050	3.3	$4.9 \cdot 10^{-5}$	$5.20 \cdot 10^{21}$
3	11 220	15.0	$4.2 \cdot 10^{-5}$	$5.09 \cdot 10^{21}$

The adsorption of quercetin under the same conditions on ordinary unfractionated Kapron was $4.4 \cdot 10^{-5}$ mole/g, i.e., it approximated to the adsorption on the polyamide with the lowest molecular weight. This shows the necessity for standardizing the powder used with respect to its molecular weight.

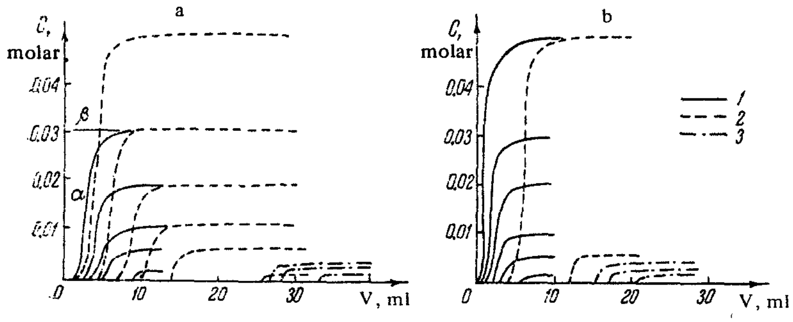

Fig. 3. Elution curves at various concentrations of quercetin (a) and dihydroquercetin (b) from methanol (1), acetone (2), and methanol—chloroform (3).

Experimental

Polyamide (Kapron) powder. The polyamide sorbent was prepared by the acetic acid method [5] from polycaprolactam fiber wastes. From 0.4 kg of the fiber 0.38 kg (95%) of powder was obtained. The slightly moist powder was passed through a sieve (0.25 mm) and dried in vacuum at 50° C. The specific surface of the powder was 90 m^2, determined by the adsorption of benzene and hexane vapors by the BET method [6].

Sorption isotherms. A column 0.8 cm in diameter was charged with 1.0 g of polyamide powder (the height of the column of sorbent was 9.0 cm), and the flavonoid solution was passed through. The rate of passage was kept constant at 3 ml/min. The solution issuing from the column was collected in the form of 1.0-ml fractions, and the concentrations of flavonoid in each of them was determined from the difference in the refractive indices of the solvent and the solution (measured by means of an ITR-2 interferometer). Figure 3 gives the elution curves for concentrations 0.001–0.05 M. The amount of substance adsorbed at each concentration was calculated from the formula [4].

$$a = \frac{S \cdot K}{m},$$

where a is the adsorption at the given concentration of flavonoid, mole/g;

S is the area delimited by the elution curve α, the axis of ordinates, and the line β parallel to the axis of abscissas at the equilibrium concentration, cm^2 (Fig. 3, a);

K is the number of moles of flavonoid per cm^2 of surface S; and m is the weight of polyamide sorbent, g.
To exclude the possible dissolution of the polyamide in the solvents that we had selected, the solvent was previously treated with them.

Isolation of the polyamide fractions [7]. One hundred and twenty grams of the polyamide powder was dissolved in 3360 ml of m-cresol (concentration 3.6%). With constant stirring, 3000 ml of methanol was added to the solution thermostated at 20° C. After 24 hr, the precipitate that had deposited was filtered off, washed with methanol, and dried. This gave 80 g of powder of the first fraction (66.0% of the initial weight). Another 800 ml of methanol was added to the filtrate and the precipitate that deposited after a day was filtered off. This gave 3.9 g of the second fraction (3.3% of the initial weight.) Another 400 ml of methanol was added to the filtrate after the second precipitation and after 48 hr the third fraction was obtained—18 g, or 15% of the initial weight. The polyamide remaining in the solution was not precipitated by methanol in the form of a powder.

Molecular weight determination. The molecular weights were determined viscosimetrically in m-cresol solution, the calculation being carried out by means of the formula $\eta_{sp} = 0.522 \cdot 10^{-6} \cdot C \cdot M^{1.26}$ [8], where C is the concentration of the polyamide solution. In our experiments, it was 5 g/l.

Conclusions

Using quercetin and dihydroquercetin as examples, it has been shown that the adsorption of flavonoids increases with a decrease in the polarity of the solvent and depends on the molecular weight of the polyamide sorbent. The presence of a double bond in quercetin leads to a higher sorption activity than the dihydroquercetin.

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27 June 1967

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