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1957

SovietRxiv

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Abstract

Full Text

PHYSICAL CHEMISTRY

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THE MECHANISM OF SORPTION OF DIPOLAR IONS BY ION EXCHANGERS

(Presented by Academician P. A. Rebinder on February 6, 1957)

Dipolar ions (amino acids, polypeptides, proteins in solutions of a definite acidity) simultaneously carry positive and negative charges. This property cannot but affect the process of their sorption by ion exchangers, which is based on the electrostatic interaction of ions with the ion exchanger.

In the case of sorption of dipolar ions, in contrast to the sorption of ions with charges of the same sign, along with electrostatic attraction electrostatic repulsion should also be observed. This circumstance has not been taken into account until now. In the most significant works carried out in this field ([1],[2]), in which the dynamics of the sorption of amino acids by ion-exchange resins was studied and the task was set of establishing the laws governing the sequence of displacement of amino-acid ions from ion exchangers, the usual concepts of the mechanism of ion sorption were used and the distinctive character of dipolar ions was not taken into account.

As a result of the investigations we have carried out, it was possible to show that the sorption of dipolar ions proceeds according to laws substantially different from the laws of sorption of ions carrying charges of one sign. The experiments were carried out with amino acids. The concentration of amino acids was determined by the ninhydrin method. The concentration of sodium ions was determined by the uranyl acetate method, and that of hydrogen ions with the aid of a glass electrode.

Fig. 1. Equivalence of exchange of alanine cations with hydrogen ions on SDV-3 resin during displacement of alanine by a 0.01 *N* HCl solution.

1—concentration of alanine cations; **2**—concentration of hydrogen ions; **3**—total concentration of alanine cations and hydrogen ions.

First of all, experiments were set up to study the equivalence of exchange. The amino acids glycine, alanine, and leucine were sorbed under dynamic conditions on the sulfonic resin SDV-3 (in the H-form). In each experiment 1 g of resin was taken; the concentration of the initial amino-acid solutions was 0.01 *N*. In all experiments it was established that, in the process of sorption of amino acids by the hydrogen form of the sulfonic resin, no release of hydrogen ions into the solution occurs; the acidity of the solutions does not change.

The equivalence of exchange was also studied in the reverse process—during displacement of amino acids by a 0.01 *N* HCl solution. As is seen from Fig. 1, in this case complete equivalence is observed between the amount of absorbed hydrogen ions and the amount of displaced alanine ions (in this case it is necessary to take into account only that part of the alanine which is present in the solution in the form of cations).

The results obtained make it possible to suggest a mechanism for the sorption of dipolar ions on H-exchangers. Sorption proceeds according to the scheme

$$\mathrm{RSO_3^-H^+ + NH_3^+R_1COO^- \rightleftarrows RSO_3^-NH_3^+ + R_1COOH;}$$

R is the radical of the polymeric cation exchanger; R_1 is the radical of the dipolar ion.

In accordance with this scheme, it should be assumed that the hydrogen ion does not enter the solution, but jumps over to the negatively charged end of the dipolar ion, as a result of which the dipolar ion is converted into a cation and is sorbed without electrostatic hindrance.

The reverse process—the displacement of the amino acid—proceeds as follows:

$$\mathrm{RSO_3^-NH_3^+R_1COOH + H^+ \rightleftarrows RSO_3^-H^+ + NH_3^+R_1COOH.}$$

The amino acid in solution here is present in the form of a cation, since the solution has considerable acidity; moreover, it is essential that the equivalence applies only to the process indicated here. The portion of alanine that is converted into a dipolar ion (the proximity of pH and pK) should not be taken into account.

Neutralization of the carboxyl group in a dipolar ion bound to an ion exchanger can quite well be admitted, despite the high pH value (7), since interaction with the ion exchanger sharply changes the properties of the ion. However, neutralization of the charge of the carboxyl group is, naturally, impossible when using the sodium or, in general, the salt form of the resin, since the salt of carbonic acid is always dissociated. In view of this, dipolar ions must be sorbed with great difficulty on the sodium form of resins because of the competition

between electrostatic attraction and repulsion. The results presented in Table 1 fully confirm this. The sodium form of the sulfonic resins SDV-3 and SBS-2 sorbs many times smaller amounts of amino acids than the hydrogen form of the same resins. The sorption capacities here and below were determined by the dynamic method.

Table 1

Sorption capacity for amino acids by sulfonic resins in the hydrogen and sodium forms

Resins	Amino acids	Sorption capacity, mg-eq/g: H-form of resin	Sorption capacity, mg-eq/g: Na-form of resin
SDV-3	Glycine	2.2	0.02
SDV-3	Alanine	1.75	0.011
SDV-3	Leucine	1.92	0.08
SBS-2	Glycine	1.2	0.044

Table 2

Sorption capacity for amino acids by sulfonic resin SNF(Na) and carboxylic resin KFU(Na) from aqueous and aqueous-acetone solution

Resins	Amino acids	Sorption capacity, mg-eq/g: from aqueous solution	Sorption capacity, mg-eq/g: from 75% acetone solution
KFU	Glycine	0.14	0.82
KFU	Alanine	0.086	0.67
SNF	Glycine	0.098	0.62
SNF	Alanine	0.054	0.286

The influence of the negative charge of the carboxyl group in the process of sorption of dipolar ions can be reduced to a certain extent by using solutions of increased ionic strength, as a result of screening of the charge of the carboxyl group. Experiments carried out to study the sorption of alanine by the sodium form of the SDV-3 resin from a solution containing alanine at a concentration of 0.01 N and sodium chloride of various concentrations confirmed this consideration. As can be seen from Fig. 2, with an increase in the concentration of sodium chloride, the sorption capacity for alanine first increases and then decreases. The increase in capacity is associated with screening of the charge of the carboxyl group, and the decrease in capacity—with the competing action

sodium ions. It is necessary to emphasize that, in the sorption of ions with charges of the same sign, an increase in the concentration of the competing ion can lead only to a decrease in the sorption capacity.

Fig. 2. Dependence of the total dynamic sorption capacity for alanine by SDV-3 resin on the concentration of NaCl. Initial alanine concentration 0.01 N. C is the concentration of NaCl (in normalities)

Figure 2: Fig. 2. Dependence of the total dynamic sorption capacity for alanine by SDV-3 resin on the concentration of NaCl. Initial alanine concentration 0.01 N. C is the concentration of NaCl (in normalities)

The second way of weakening the action of the carboxyl group in the process of sorption of amino acids consists in using acetone as the solvent, since in an acetone solution the carboxyl group of amino acids is not dissociated (ˆ3). Table 2 gives the results of determining the sorption capacity for glycine and alanine by the carboxyl resin KFU and the sulfocation-exchange resin SNF (both resins in the Na form) from a 0.01 N solution of amino acids in 75% acetone and in water. From an aqueous solution the amino acid is sorbed only very slightly. On going to the water–acetone solution, the sorption capacity increases considerably.

Fig. 2. Dependence of the total dynamic sorption capacity for alanine by SDV-3 resin on the concentration of NaCl. Initial alanine concentration 0.01 N. C is the concentration of NaCl (in normalities).

The influence of the carboxyl group on the sorption of amino acids by cation exchangers should evidently also be weaker when the distance between the amino and carboxyl groups is increased. To study this regularity, the sorption capacities were determined for the amino acid (glycine), a dipeptide (diglycine), and a tripeptide (leucyl-leucylglycine) by SBS-2 resin in the Na form. The sorption capacity for glycine is 0.044 mg-eq/g, for the dipeptide 0.208 mg-eq/g, and for the tripeptide 0.214 mg-eq/g, which confirms the importance of the distance between the positive and negative charge in the process of sorption of dipolar ions on the salt form of resins.

The results obtained raise the question of revising the entire system of interpretation of the processes of sorption of amino acids, peptides, and proteins and open up new possibilities for the selective separation of dipolar ions from all other ions, for example, by using two filters with resins in the salt and hydrogen forms. In this purification system, cations are sorbed on the first filter, and on the second only dipolar ions. This indicates one of the practical applications of the mechanism of sorption of dipolar ions established by us. On the basis of the concepts developed, it is possible to propose a large number of variants of the method of selective sorption of dipolar ions.

We express our gratitude to R. B. Ponomareva, who took part in setting up some of the experiments.

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Received

7 VII 1956

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Note: Figure translations are in progress. See original paper for figures.