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Abstract

Full Text

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ON THE EQUILIBRIUM DISTRIBUTION OF AN AMINO ACID

IN THE WATER–ION EXCHANGER SYSTEM

(Presented by Academician V. A. Kargin on 9 II 1965)

The basic proposition advanced by us for describing equilibrium in the system aqueous amino-acid solution–ion exchanger is that, in such cases, it is necessary to take into account both the ionization of the amino acid in both phases and the existence of interphase equilibrium for each of the forms of the amino acid, i.e., to proceed from the usual principles of thermodynamic equilibrium of the system. Thus, we have a heterogeneous system (swollen ion exchanger–solution) in which the amino acid dissociates in both phases, while in the ion-exchanger phase the total concentration of all counterions is a constant quantity. Investigators who have dealt with this problem up to the present have not taken into account the ability of the amino acid to ionize in the ion-exchanger phase (1-4).

Fig. 1. Scheme of the equilibrium distribution of an amino acid between an aqueous solution and a cation exchanger. AH^+—amino-acid cation, $A^\pm$—amino-acid zwitterion, A^-—amino-acid anion, $\bar{K}_1$ and K_1—first dissociation constants of the amino acid in the ion exchanger and in solution. $\bar{K}_2$ and K_2—second dissociation constants in the ion exchanger and in solution; K_H^{am}—ion-exchange constant; K_p—distribution coefficient of the zwitterion; K_D—distribution coefficient of the amino acid as a nonexchange electrolyte

The case analyzed by us of the equilibrium distribution of a substance between an aqueous solution and the ion-exchanger phase is schematically represented in Fig. 1.

In the present work we give the results of a study of equilibrium in the pH region of solutions in which it is possible to neglect the Donnan distribution of the nonexchange electrolyte, i.e., when two processes occur in the system: ion exchange of the amino-acid cation for hydrogen between the solution and the cation exchanger, and distribution of the zwitterion between the two phases. We measured the equilibrium constant of the ion exchange of the amino-acid cation for hydrogen. This made it possible to calculate the first dissociation constant (of the COOH group) of the amino acid in the ion-exchanger phase. From the known concentrations of the amino acid and other ions in the system and the first dissociation constants of the amino acid in both phases, the distribution of the zwitterion was calculated. Thus, knowing the first dissociation constants of the amino acid in the ion exchanger and in solution and the ion-exchange constant or distribution coefficient, one can obtain a complete picture of the equilibrium in the ion exchanger—amino-acid solution system at different values of pH, of the analytical concentration of the amino acid, and of the concentration of the sodium ion in solution.

First, the sorption of amino acids in ternary systems was determined over a wide range of equilibrium concentrations of hydrogen ions, sodium ions, and amino acid. The results obtained are presented in Table 1.

Table 1

Sorption of glycine by a sulfonic acid cation exchanger in a ternary system

g_{am}, mg-eq per 1 g H-form	C_{Na^+}, mg-eq/ml	C_{H^+}, mg-eq/ml	C_{am}, mg-eq/ml	g_{Na^+}, mg-eq per 1 g H-form	g_{H^+}, mg-eq per 1 g H-form	g_{AH^+}, mg-eq per 1 g H-form	K_{H}^{am}
1.79	$4.3 \cdot 10^{-2}$	$4.79 \cdot 10^{-2}$	$3.16 \cdot 10^{-2}$	1.54	1.73	1.82	1.71
2.50	$1.6 \cdot 10^{-2}$	$1.88 \cdot 10^{-2}$	$2.65 \cdot 10^{-2}$	1.22	1.42	2.46	1.55
1.96	$4.1 \cdot 10^{-2}$	$1.20 \cdot 10^{-2}$	$3.06 \cdot 10^{-2}$	2.40	0.705	1.98	1.52
2.95	$9.7 \cdot 10^{-4}$	$2.30 \cdot 10^{-4}$	$2.16 \cdot 10^{-2}$	1.70	0.40	2.96	1.64
							$K_{\text{H,avg}}^{\text{am}} = 1.6$

The equilibrium analytical concentration of the amino acid C_{am} in solution was determined by the ninhydrin method (^{5}); the concentration of Na^+ in solution (C_{Na^+}) was determined with a flame photometer; the concentration of hydrogen ions in solution (C_{H^+}) was determined potentiometrically and by titration with alkali (5). The sorbed amount of sodium ions (g_{Na^+}) was determined by combusting a weighed portion of the ion exchanger (sulfate ash), or with the aid of a flame photometer, and the sorbed amount of amino acid (g_{am}) after elution of the amino acid from the cation exchanger with alkali at pH 12 (5). The sorbed amount of hydrogen ions (g_{H^+}) was calculated from the known ion-exchange constant $K_{\mathrm{H}}^{\mathrm{Na}}$, determined in the binary system H—Na-sulfonic acid cation exchanger. The amount of amino acid cation sorbed by the cation exchanger (g_{AH^+}) was calculated from the difference $g_0 - (g_{\mathrm{Na}^+} + g_{\mathrm{H}^+})$, where g_0 is the static exchange capacity of the cation exchanger ($g_0 = 5.08$ mg-eq per 1 g H-form, KU-2 sulfonic acid cation exchanger containing 4% divinylbenzene, fraction 0.25—0.5 mm). From the experimental data presented in Table 1 it is seen that, under these conditions, the quantities g_{AH^+} and g_{am} are practically equal. This indicates that the concentration of H-ions in the ion-exchanger phase is such that the equilibrium between the amino acid cation and the zwitterion within the resin is shifted toward the cation. Therefore, for calculating the concentration constant $K_{\mathrm{H}}^{\mathrm{am}}$, equal to

$$g_{\mathrm{AH}^+} \cdot f(x) / g_{\mathrm{H}^+} \cdot C_{\mathrm{am}}, \tag{1}$$

where

$$f(x) = \frac{C_{\mathrm{H}^+}^2 + K_1 \cdot C_{\mathrm{H}^+} + K_1 \cdot K_2}{C_{\mathrm{H}^+}},$$

Fig. 2. Sorption isotherm of glycine in a ternary system. Left—at pH = 1.3—3.6; $C_{\mathrm{Na}^+} = 9 \cdot 10^{-4}$—$4.5 \cdot 10^{-2}$ n; $\operatorname{tg}\alpha = 1.2 \cdot 10^{-1}$; $K_{\mathrm{H}}^{\mathrm{am}} = 1.6$; point* $= 1/g_0$; $B = \dfrac{f(x)\,[C_{\mathrm{Na}^+} K_{\mathrm{H}}^{\mathrm{Na}} + C_{\mathrm{H}^+}]}{C_{\mathrm{H}^+} \cdot C_{\mathrm{am}}}$; right—at pH = 6.12; $C_{\mathrm{Na}^+} = 2 \cdot 10^{-2}$ n; $\operatorname{tg}\alpha = 0.356$; $\bar{K} = 3.26 \cdot 10^{-3}$.

and K_1 and K_2 are the first and second dissociation constants of the amino acid in solution, it is convenient to use a linear equation analogous to the Langmuir isotherm. It has the following form:

$$\frac{1}{g_{\mathrm{AH}^+}} = \frac{1}{g_0} + \frac{1}{g_0 K_{\mathrm{H}}^{\mathrm{am}}} \left\{ \frac{f(x)\,[C_{\mathrm{Na}} K_{\mathrm{H}}^{\mathrm{Na}} + C_{\mathrm{H}^+}]}{C_{\mathrm{H}^+} C_{\mathrm{am}}} \right\}. \tag{2}$$

Then the ion-exchange constant $K_{\mathrm{H}}^{\mathrm{am}}$ is equal to $1/\operatorname{tg}\alpha \cdot g_0$. The value $\operatorname{tg}\alpha$ was obtained from the equation of a straight line calculated by the method of least squares (see Fig. 2a). In parallel, the sorption of the amino acid was measured in binary systems amino acid—hydrogen—sulfonate in the region where g_{am} varied from 0.28 to 4.58 mg-eq/g of the H-form, while the value g_{H^+} was in every case not less than 0.5 mg-eq/g. Under these conditions the value g_{am} is equal to g_{AH^+}. The ion-exchange constant $K_{\mathrm{H}}^{\mathrm{am}}$, calculated in binary systems, is a constant quantity equal, like $K_{\mathrm{H}}^{\mathrm{am}}$ measured in ternary systems, to 1.6. These data show that $K_{\mathrm{H}}^{\mathrm{am}}$ is practically independent of the degree of loading of the ion exchanger with amino acid and of the form in which the ion exchanger is present.

The equilibrium in ion-exchanger—amino-acid solution systems was then studied under conditions in which g_{H^+} becomes a small quantity. In these cases it is necessary to take into account the equilibrium between the cation and the zwitterion in the ion exchanger. The first dissociation constant in the ion-exchanger phase $\overline{K}_1$ is equal to

$$\frac{g_{\mathrm{A}^\pm} \cdot g_{\mathrm{H}^+}}{g_{\mathrm{AH}^+} v}, \tag{3}$$

where $g_{\mathrm{A}^\pm}$ is the amount of zwitterion in the ion-exchanger phase in mg-eq/g, and v is the volume of the ion exchanger in the equilibrium system, measured pycnometrically. The experiments were carried out over a wide interval of amino-acid concentrations, and the equilibrium values of C_{H^+}, C_{Na^+}, g_{Na^+}, and g_{am} were determined by the methods indicated above. The results obtained were treated with the aid of an equation expressing the relation between the analytically determined sorbed amount of amino acid ($1/g_{\mathrm{am}}$) and the analytical concentration of amino acid in solution ($1/C_{\mathrm{am}}$) (see equation (4) and Fig. 2b).

$$\frac{1}{g_{\mathrm{am}}} = \frac{g_{\mathrm{H}^+}}{g_0(\overline{K}_1 \cdot v + g_{\mathrm{H}^+})} + \left\{ \frac{g_{\mathrm{H}^+} \cdot f(x)\,[C_{\mathrm{Na}} K_{\mathrm{H}}^{\mathrm{Na}} + C_{\mathrm{H}^+}]}{(\overline{K}_1 \cdot v + g_{\mathrm{H}^+}) K_{\mathrm{H}}^{\mathrm{am}} \cdot g_0 \cdot C_{\mathrm{H}^+}} \right\} \cdot \frac{1}{C_{\mathrm{am}}}. \tag{4}$$

The dissociation constant $\overline{K}_1$ is equal to

$$\frac{g_{\mathrm{H}^+} \cdot A - \operatorname{tg}\alpha \cdot g_{\mathrm{H}^+}}{\operatorname{tg}\alpha \cdot v},$$

where

$$A = \frac{f(x)\,[C_{\mathrm{Na}} K_{\mathrm{H}}^{\mathrm{Na}} + C_{\mathrm{H}^+}]}{K_{\mathrm{H}}^{\mathrm{am}} \cdot g_0 \cdot C_{\mathrm{H}^+}}.$$

The value $\operatorname{tg}\alpha$ was obtained from the equation of a straight line calculated from the experimental data by the method of least squares. The $\overline{K}_1$ calculated from the experimental data for glycine is equal to $3.26 \cdot 10^{-3}$ ($p\overline{K}_1 = 2.49$), i.e., it is close in magnitude to the first dissociation constant of glycine in aqueous solution ($pK_1 = 2.34$). In analogous fashion, the first dissociation constants in the ion-exchanger phase were calculated for α-alanine and asparagine ($p\overline{K}_1 =$ 2.46 and 2.22).

For the isoelectric region of the amino acid, a curve of the dependence of g_{am} on the concentration of sodium ions in the equilibrium solution was obtained experimentally (at $C_{\mathrm{am}} = 0.01$ n). At the same time, for these same conditions,

Fig. 3 and Fig. 4

Figure 2: Fig. 3 and Fig. 4

the quantities g_{AH^+}, $g_{\mathrm{A}^\pm}$, g_{am}, and also the concentration of H-ions in the ion-exchanger phase were calculated from the known ion-exchange constant ($K_{\mathrm{H}}^{\mathrm{am}}$) and the first dissociation constants of the amino acid ($\overline{K}_1$ and K_1). Figure 3 shows how the experimental points fit the calculated curve of the dependence of ($g_{\mathrm{AH}^+} + g_{\mathrm{A}^\pm}$) on C_{Na^+}.

In Fig. 4 a complete picture is presented of equilibrium in the ion exchanger—amino-acid (glycine) solution system at different values of pH, analytical concentration of the amino acid, and a specified concentration of the Na^+ ion in solution ($C_{\mathrm{Na}^+} = 0.01$ N), calculated by us from the known dissociation constants of the amino acid $\overline{K}_1$, K_1, K_2 and the ion-exchange constant $K_{\mathrm{H}}^{\mathrm{am}}$. In the calculations it was assumed that $\overline{K}_2 = K_2$.

Fig. 3. Dependence of g_{am}, g_{AH^+}, $g_{\mathrm{A}^\pm}$, and $\lg \overline{C}_{\mathrm{H}^+}$ inside the resin on the concentration of Na^+ in solution.
1—g_{am}; 2—g_{AH^+}; 3—$g_{\mathrm{A}^\pm}$; 4—$\lg \overline{C}_{\mathrm{H}^+}$. *I*—experimental points.

Fig. 4. Equilibrium in the ion exchanger—amino-acid solution system, $C_{\mathrm{am}} = 0.2$ N: 1—g_{am}, 2—g_{AH^+}, 3—$g_{\mathrm{A}^\pm}$, 4—g_{A^-}, as a function of the pH of the solution.

The data obtained show in what region and under what conditions the processes of ion exchange, distribution of the zwitterion, and Donnan distribution of the amino acid predominate. The regularities established are fully applicable to the equilibrium distribution of an amino acid between water and an anion exchanger, and also to the distribution of weak acids and bases between the ion-exchanger phase and solution.

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