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Abstract

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ON THE CATALYTIC ACTIVITY OF H-IONS IN SULFOPOLYSTYRENE CATION EXCHANGERS AND IN SULFURIC ACID SOLUTIONS

(Presented by Academician V. A. Kargin, 7 VII 1964)

The aim of this work was to measure the acidity function (1) in cation-exchange synthetic resins and to compare the catalytic activity of the H-counterions of the ion exchanger and the H-ions of an aqueous acid solution. To determine the acidity function in cation exchangers, a method was developed that made it possible to apply the Hammett indicator method to such objects. The kinetics of the process occurring under the action of H-ions of the acid solution and H-counterions located in the insoluble macromolecule of the ion-exchanger bead were studied by examining the rate of dehydration of tetracycline (2).

Method for determining the acidity function in acid solutions (H_0) **and in ion exchangers** ($\overline{H}_0$)**.** As the indicator, n-nitroaniline was used (m.p. 148°, $\varepsilon_{\lambda=382} = 12\,900$).

The ratio $C_{\mathrm{BH^+}}/C_{\mathrm{B}}$, where $C_{\mathrm{BH^+}}$ is the concentration of the protonated form and C_{B} is the concentration of the molecular form of the indicator, was determined from the molar extinctions of the indicator solutions in acids (at λ382 mμ).

$$\frac{C_{\mathrm{BH^+}}}{C_{\mathrm{B}}} = \frac{\varepsilon_{\mathrm{B}} - \varepsilon}{\varepsilon - \varepsilon_{\mathrm{BH^+}}}, \tag{1}$$

where ε_{B} is the molar extinction of the indicator in the molecular form, $\varepsilon_{\mathrm{BH^+}}$ is the molar extinction of the protonated form of the indicator, and ε is the molar extinction of the indicator in acid of a given concentration. The concentration of the acid solution was determined by titrating weighed portions of the acid. H_0 was calculated in the usual way:

$$H_0 = \mathrm{p}K - \lg \frac{C_{\mathrm{BH}^+}}{C_{\mathrm{B}}}, \qquad (2)$$

where p$K = 1.1$, and

$$K = \frac{a_{\mathrm{H}^+} C_{\mathrm{BH}^+} f_{\mathrm{BH}^+}}{C_{\mathrm{B}} f_{\mathrm{B}}}.$$

As ion exchangers we used strongly acidic sulfopolystyrene cation exchangers containing 5.06 g (ion exchanger I) and 0.76 g (ion exchanger II) of H_2O per 1 g of dry H-form. The ion-exchanger particles were spherical, $d = 0.5$–1 mm in the swollen state. The main difficulty lay in developing a method for measuring the molar extinctions of the indicator in the ion-exchanger phase. First, sorption of the indicator by the ion exchanger from an aqueous indicator solution was carried out. Then the ion exchanger with the sorbed indicator was separated from the solution by filtration on a Büchner funnel, the resin was transferred to a cuvette of an SF-4 spectrophotometer ($l = 1$ mm or 3 mm), and the resin beads were covered with *n*-octane. In another cuvette the original ion exchanger in the swollen state was placed and likewise covered with *n*-octane. The extinctions were measured at $\lambda = 390$ mμ.

Figure 1 shows the absorption spectra of *n*-nitroaniline in water and in the Na- and H-forms of the ion exchanger. As is seen from Fig. 1, on passing from water to the ion exchanger there is [[unclear: inverted/overprinted text in the source]] of the molar extinction, which is apparently caused by a change in the medium.

Despite the heterogeneity of the resin—*n*-octane system, the reproducibility of the results in measuring optical density was quite satisfactory (mean error $±$10%).

In the salt (Na-form) of the ion exchanger, the sorbed indicator is in the molecular form. Then the ratio of the concentrations of the indicator in the ionic and molecular forms,

$$\frac{\overline{C}_{\mathrm{BH}^+}}{\overline{C}_{\mathrm{B}}},$$

is equal to

$$\frac{\overline{C}_{\mathrm{BH}^+}}{\overline{C}_{\mathrm{B}}} = \frac{\varepsilon_{\mathrm{B}} - \overline{\varepsilon}}{\overline{\varepsilon}}, \qquad (3)$$

where ε_{B} is the molar extinction of the indicator in the Na-form of the ion exchanger, and $\overline{\varepsilon}$ is the molar extinction of the indicator in the ion exchanger under study (in the Na—H- or H-form). Equation (3) does not include the

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

extinction of the protonated form of the indicator in the ion exchanger, $\varepsilon_{\mathrm{BH}^+}$, which may be neglected ($\varepsilon_{\mathrm{BH}^+} \ll \varepsilon_{\mathrm{B}}$).

Fig. 1. Absorption spectra of *p*-nitroaniline in water and in the ion exchanger. 1 –water; 2 –Na-form of the ion exchanger; 3 –H-form of the ion exchanger

In Fig. 2 are presented the results of measurements of the optical density of ion exchangers containing the indicator, as a function of the indicator concentration. As can be seen from the figure, Beer' s law is obeyed sufficiently well. This provides a basis for calculating the molar extinctions of the indicator in ion exchangers. The acidity function of the ion exchanger ($\overline{H}_0$) was calculated in the same way as for solutions, assuming that the pK of the indicator is unchanged.

Fig. 2. Dependence of the optical density of *p*-nitroaniline D in ion exchangers on the concentration of *p*-nitroaniline C: *a* –ion exchanger I in different forms: 1 –Na; 2 –Na–H ($C_{\mathrm{H}^+} = 0.26$ N); 3 –Na–H ($C_{\mathrm{H}^+} = 0.50$ N); 4 –H ($C_{\mathrm{H}^+} = 0.87$ N). *b* –ion exchanger II: 1 –Na; 2 –H ($C_{\mathrm{H}^+} = 2.9$ N)

The concentration of H-ions in the ion exchanger was calculated from the quasi-homogeneous state of the ion exchanger and expressed in normalities. The content of H-ions per unit weight of ion exchanger was determined by potentiometric titration, and the volume of the ion exchanger in the swollen state was measured by the pycnometric method.

Figure 3 presents the relationship between the acidity function in sulfuric acid solutions and in ion exchangers and the corresponding concentrations of H-ions. Variation of the concentration of H-counterions of the resin was achieved by replacing part of the resin capacity with sodium counterions. Within the accuracy of the measurements, identical concentrations of H-ions correspond to the same values of the acidity function both in solution and in the ion exchanger.

Dependence of the reaction-rate constant on the acidity function. Having determined a series of values for $\overline{H}_0$ and H_0, we were able to compare the catalytic activity of H-ions in the ion exchanger and in solution. For this purpose the kinetics of the dehydration of tetracycline (T) was studied in sulfuric acid solutions and in the ion-exchanger phase, in which tetracycline is the counterion. In both cases the tetracycline cation passes into the active form, which decomposes with formation of the anhydrotetracycline cation and water.

As in solution, so also in the ionite phase, the reaction rate obeys a first-order

Fig. 3. Dependence of the acidity function in acid solutions and in an ionite (H_0 and $\overline{H}_0$) on the concentration of H ions ($C_{\mathrm{H}+}$): a—H_2SO_4; b—ionite

Figure 3: Fig. 3. Dependence of the acidity function in acid solutions and in an ionite (H_0 and $\overline{H}_0$) on the concentration of H ions ($C_{\mathrm{H}+}$): a—H_2SO_4; b—ionite

Fig. 4. Dependence of the logarithm of the rate constant for dehydration of tetracycline on the acidity function: a—sulfuric acid; ionites in the form: b—Na—H—T; c—H—T; d—T—H, dried in vacuum to a definite H_2O content

Figure 4: Fig. 4. Dependence of the logarithm of the rate constant for dehydration of tetracycline on the acidity function: a—sulfuric acid; ionites in the form: b—Na—H—T; c—H—T; d—T—H, dried in vacuum to a definite H_2O content

equation. In studying the dehydration reaction of tetracycline in the ionite phase, the concentration of H counterions was varied in different ways: by changing the fraction of tetracycline in the ionite, by introducing a third counterion (Na), by decreasing the water content in mixed (H—T) forms of ionites by removing it under high vacuum, and by carrying out the dehydration of tetracycline in ionites having different maximum swelling (different divinylbenzene content in the ionites).

Fig. 3. Dependence of the acidity function in acid solutions and in an ionite (H_0 and $\overline{H}_0$) on the concentration of H ions ($C_{\mathrm{H}+}$): a—H_2SO_4; b—ionite.

Fig. 4. Dependence of the logarithm of the rate constant for dehydration of tetracycline on the acidity function: a—sulfuric acid; ionites in the form: b—Na—H—T; c—H—T; d—T—H, dried in vacuum to a definite H_2O content.

Such methods made it possible to study the dehydration of tetracycline at various concentrations of H counterions (from 0.2 to 5 N). In all cases the rate of dehydration of tetracycline was determined by the value of the acidity function in the ionite and did not depend on the presence of a third ion or on the content of cross-linking agent in the resin.

Figure 4 summarizes the data obtained for the rate constants of dehydration of tetracycline in ionites and in solution.

The same quantitative dependence exists between H_0 and the logarithm of the rate constant for dehydration of tetracycline in solution, and between $\overline{H}_0$ and the logarithm of the rate constant of the same reaction in the ionite phase. The presence of such a dependence makes it possible to conclude that the catalytic activity of H ions in an acid solution is equal to the catalytic activity of H counterions of a strongly acidic cationite.

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