Luo Chih-hsiang, E. M. Savitskaya, and B. P. Bruns

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Luo Chih-hsiang, E. M. Savitskaya, and B. P. Bruns

ON THE INFLUENCE OF AN ORGANIC SOLVENT ON THE PROPERTIES OF A CARBOXYLIC CATION EXCHANGER

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The regularities of ion exchange occurring on various ion exchangers change substantially in the transition from an aqueous solution to mixed or organic media.

One of the main factors causing changes in the kinetics and statics of ion exchange is the change in the properties of the ion exchanger itself when it is immersed in one or another solvent. Cation exchangers in the hydrogen form may be regarded as insoluble concentrated polybasic acids under a certain swelling pressure. Therefore, different solvents or their mixtures must inevitably affect the strength of these peculiar acids.

As the object of our investigation we selected a polymerization cation exchanger containing in its structure only carboxylic ionogenic groups. The external solution consisted of water-methanol mixtures of variable composition. The choice of such a system was prompted by the practical importance of studies of this kind. Aqueous-methanolic acid solutions have already found practical application for the elution of a number of complex organic ions from carboxylic resins; moreover, in a number of cases the optimum process conditions were selected empirically. The study of the indicated systems is also of independent theoretical interest for elucidating the similarities and differences between high-molecular acids and ordinary monocarboxylic acids in identical media.

To investigate the nature of the dependence of the strength of this ion exchanger on the composition of the medium, the method of potentiometric titration was used.

Experimental Part

As the object of study we used a cation exchanger obtained by alkaline saponification of a copolymer of methyl methacrylate and divinylbenzene (DVB). The preliminary preparation of the resin and the methods for measuring pH in aqueous-methanolic media were described in detail in a previous communication (^{1}).

Fig. 1. Titration curves of the cation exchanger. $C_{\mathrm{LiCl}} = 0.5\,N$; 1—in H_2O; 2—in 40% CH_3OH; 3—in 60% CH_3OH; 4—in 95% CH_3OH

Figure 1: Fig. 1. Titration curves of the cation exchanger. $C_{\mathrm{LiCl}} = 0.5\,N$; 1—in H_2O; 2—in 40% CH_3OH; 3—in 60% CH_3OH; 4—in 95% CH_3OH

The pH value in aqueous-methanolic mixtures was standardized with respect to an infinitely dilute solution of hydrogen chloride in the corresponding medium.

All data on the amount of sorbed ions were referred to 1 g of dry resin in the hydrogen form. The specific volume of the resin in the H-form in water is 2.5 ml/g.

The experimental data were obtained using three different titration methods. One of the methods was Kunin' s method (^{2}), the second was the method of direct titration of the initial external solution in the presence and in the absence of a weighed portion of resin. The results of determining the dependence of the resin capacity on the pH of the external solution, obtained by both methods, are identical at any of the investigated methanol contents in the external ···

solution. The titration curves of the cation exchanger in different media are presented in Fig. 1.

The H—Me exchange on carboxyl resins is a slow process in aqueous solution. We have shown that, as the concentration of methanol in the external solution increases, the rate of exchange decreases more and more (^{3}).

To give convincing proof that the measured pH values are equilibrium values, for each of the water-methanol mixtures we recorded titration curves starting from the hydrogen and from the salt forms of the resin. For each water-methanol solution these curves are mirror images of one another.

Fig. 1. Titration curves of the cation exchanger. $C_{\mathrm{LiCl}} = 0.5\,N$;
1—in H_2O; 2—in 40% CH_3OH; 3—in 60% CH_3OH; 4—in 95% CH_3OH.

In addition to the two titration methods described above, we developed a new rapid method for obtaining a series of potentiometric titration curves of a carboxyl cation exchanger in mixed and nonaqueous solvents. This method is based on determining the equilibrium pH values of the external solution in systems consisting of cation exchangers, previously neutralized to different degrees, subsequently immersed in aqueous-organic solutions of a definite ionic strength. First, calculated amounts of an aqueous base are added to identical initial weighed portions of resins in the H-form in order to obtain different degrees of replacement of the resin hydrogen ions by metal ions. After completion of the exchange, which takes 1-2 days, the water over the weighed portions of ion exchanger is removed, and they are poured over with specified volumes of mixed solvent containing a neutral salt at a definite concentration. The pH is determined several times at intervals of 1 day in order to make sure the measured values are constant. From the pH values found and the known degrees of neutralization of the cation exchanger, a titration curve is constructed. To avoid a shift in pH under the action of carbon dioxide from the air, the experiment should be carried out in a nitrogen atmosphere. When the first two methods were used, the work was likewise carried out under conditions excluding carbon dioxide from the air.

By successively transferring the same partially neutralized weighed portions of cation exchanger from a mixture of one composition to a mixture of another composition and measuring the equilibrium pH in each mixture, it is possible to obtain, in a very short time, a complete picture of the change in the properties of the acid—the cation exchanger—as the composition of the medium changes. Application of this method is especially expedient in those cases where the exchange process in the medium proceeds very slowly. Comparison of this method with Kunin’ s method gave identical results.

Results of the study

The typical form of the relationship between the degree of neutralization of the cation exchanger and the pH of the external solution is shown in Fig. 2. Comparing this curve with the neutralization curve of a monocarboxylic acid when the latter is titrated in the same medium, we observe that the neutralization curve of the ion exchanger is considerably steeper than the corresponding curve of the soluble monocarboxylic acid. The steeper slope of the curve of a three-dimensional weak polyelectrolyte is due to the fact that, as the ion exchanger is neutralized, the negative field that forms diminishes the possibility of detachment of a proton from the carboxyl group. As a consequence of this electrostatic field effect, the neutralization curve of the ion exchanger is shifted into the region of higher pH values in comparison with the monomer curve. The higher the degree of neutralization of the cation exchanger, the greater the influence of the electrostatic field.

This effect is expressed in the progressive weakening of the insoluble polyacid as hydrogen in the resin is replaced by metal ions. This phenomenon is analogous to the decrease in the dissociation constants of polybasic acids with each subsequent stage of dissociation. A similar decrease in the exchange constant of silicic-acid macromolecules as hydrogen is replaced by metal was described by N. A. Izmailov (4, 5). In the works of Kachalsky and his coworkers, on the basis of titration curves for carboxyl-containing soluble polyacids and very strongly swelling gels, a theory of this process was developed (6–8). However, the results of these studies cannot be used directly to predict the behavior of real carboxyl cation exchangers, since this theory was created for such gels as can be regarded as dilute polyelectrolytes. All the factors taken into account in the theory developed for very strongly swelling gels consisting of methacrylic-acid chains and containing divinylbenzene as cross-linking agent undoubtedly also play a role in the titration of real carboxyl cation exchangers. However, the transition to ordinary resins greatly complicates the interpretation of the titration process. Up to the present time, all investigators working in this field have operated only

Fig. 2. Dependence of the pH of the solution on the degree of neutralization α; C_LiCl = 0.1 N. 60% CH3OH: 1 –for the cation exchanger, 2 –for CH3COOH

Figure 2: Fig. 2. Dependence of the pH of the solution on the degree of neutralization α; C_LiCl = 0.1 N. 60% CH3OH: 1 –for the cation exchanger, 2 –for CH3COOH

Fig. 3. Results of titration of the cation exchanger, expressed by the Henderson equation. C_LiCl = 0.5 N; 1 –in H2O; 2 –in 40% CH3OH; 3 –in 60% CH3OH; 4 –in 95% CH3OH

Figure 3: Fig. 3. Results of titration of the cation exchanger, expressed by the Henderson equation. C_LiCl = 0.5 N; 1 –in H2O; 2 –in 40% CH3OH; 3 –in 60% CH3OH; 4 –in 95% CH3OH

with experimental data (9, 10). And as a characteristic of the strength of a cation exchanger as an acid, the concept of the mean or apparent dissociation constant of the ion exchanger is widely used.

Fig. 2. Dependence of the pH of the solution on the degree of neutralization α; $C_{\mathrm{LiCl}} = 0.1\,N$. 60% CH_3OH: 1 –for the cation exchanger, 2 –for CH_3COOH.

To determine the influence of the medium on the strength of carboxyl cation exchangers, we also calculated the mean or apparent dissociation constant of the resin by the modified Henderson equation:

$$\mathrm{pH} = \overline{pK} - n \lg \frac{1-\alpha}{\alpha},$$

where pH is the hydrogen-ion exponent of the external solution, $\overline{pK}$ is the exponent of the mean dissociation constant of the cation exchanger ($\overline{K}$), α is the degree of neutralization of the ion exchanger, and n is a constant quantity.

Fig. 3. Results of titration of the cation exchanger, expressed by the Henderson equation. $C_{\mathrm{LiCl}} = 0.5\,N$; 1 –in H_2O; 2 –in 40% CH_3OH; 3 –in 60% CH_3OH; 4 –in 95% CH_3OH.

The determination of $\overline{pK}$ of the cation exchanger in aqueous-methanolic media was carried out under conditions in which the only variable in the systems was the concentration of methanol. Figure 3 shows how the experimental results satisfy the equation given above. At all investigated methanol concentrations in the solutions, the experimental data fit this equation well. The value of n is the same and is equal to ~ 1.6, independently of the methanol concentration in the system. The higher the methanol content in the medium, the greater the value of $\overline{pK}$.

At methanol concentrations in the solution equal to 0, 40, 60, and 95%, the corresponding values of $\overline{pK}$ of the cation exchanger are 5.90, 6.35, 6.75, and

Fig. 4. Dependence of $\overline{\mathrm{p}K}$ of the cation exchanger—1 and pK of CH_3COOH—2 on $1/D$; $C_{\mathrm{LiCl}} = 0.1\,N$

Figure 4: Fig. 4. Dependence of $\overline{\mathrm{p}K}$ of the cation exchanger—1 and pK of CH_3COOH—2 on $1/D$; $C_{\mathrm{LiCl}} = 0.1\,N$

7.85 (at a $0.5\,N$ concentration of lithium chloride in the solution).

These data indicate that, with increasing concentration

of alcohol, the strength of the cation exchanger acid decreases, which is analogous to the decrease in the dissociation constant of monocarboxylic acids in the same media.

Fig. 4 shows the change in the values of $\overline{\mathrm{p}K}$ of the cation exchanger and pK of acetic acid (^{11}) as a function of the dielectric constant of the medium, D. As the dielectric constant decreases, the interaction between the anion of the cation exchanger and the H-counterion is strengthened, which leads to a decrease in the dissociation constant of the ion exchanger. The $\overline{\mathrm{p}K}$ of the resin depends linearly on $1/D$ of the solution, i.e., for the resin a change in $\overline{\mathrm{p}K}$ is observed that is in agreement with the conclusions of Brønsted' s theory (^{12}). This dependence indicates that, within the investigated limits of methanol concentration, there is no change in the basicity of the solvent present in the resin phase. It is quite probable that even at a 95% alcohol concentration in the solution, preferential sorption of water by the resin is observed.

Fig. 4. Dependence of $\overline{\mathrm{p}K}$ of the cation exchanger—1 and pK of CH_3COOH—2 on $1/D$; $C_{\mathrm{LiCl}} = 0.1\,N$

As the ionic strength of the external aqueous-methanolic solution increases, the value of $\overline{\mathrm{p}K}$ of the cation exchanger decreases. If, in the absence of a neutral electrolyte, it is equal to 8.70, then in a $0.1\,N$ lithium chloride solution it becomes 7.60, and at a $0.5\,N$ salt concentration it decreases to 6.75 (methanol concentration 60%). The decrease in $\overline{\mathrm{p}K}$ of the ion exchanger is explained by shielding of the negative field in the resin owing to the increasing amount of neutral electrolyte in the resin (Donnan effect).

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Institute of Antibiotics

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