

The Acid-Basic Properties of Carboxy-Containing Macroporous Cation Exchange Resins

Las propiedades ácido-básicas de las resinas de intercambio de cationes macroporosas que contienen carboxi

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ABSTRACT:

The authors have conducted potentiometric titration of carboxylic cation exchanger (degree of crosslinking 12-16%) in a wide range of changes in solution pH (2-12) and concentration NaCl (0.01; 0.1; 0.5; 1 M). The maximum ion exchange capacity of the ion exchanger on Na⁺ (10.100.088 mmol/g of dry weight) was determined, and it did not depend on ionic strength of the solution. It is shown that in the studied range of NaCl concentrations and pH the process of acid-base balance can be adequately described by the equation of Gregor. The values of the parameters of this equation are calculated, according to which analyzed the behavior of the carboxylic cation exchanger depending on pH and concentration of background electrolyte. The acidic properties of cation exchanger increased with increasing concentration of NaCl from 0.01 to 0.5 M, but further increase in salt concentration did not affect the ionization constant of carboxyl groups.

Keywords: Ionic strength; Ion exchange; Ionization

RESUMEN:

Los autores han llevado a cabo la titulación potenciométrica del intercambiador catiónico carboxílico (grado de reticulación del 12-16%) en una amplia gama de cambios en el pH de la solución (2-12) y concentración de NaCl (0,01; 0,1; 0,5; 1 M). Se determinó la capacidad máxima de intercambio iónico del intercambiador de iones sobre Na⁺ (10.10-0.088 mmol / g de peso seco) y no dependió de la fuerza iónica de la solución. Se demuestra que en el rango estudiado de concentraciones de NaCl y pH el proceso de equilibrio ácido-base puede ser adecuadamente descrito por la ecuación de Gregor. Se calculan los valores de los parámetros de esta ecuación, según los cuales se analizó el comportamiento del intercambiador catiónico carboxílico dependiendo del pH y la concentración del electrólito de fondo. Las propiedades ácidas del intercambiador de cationes aumentaron con una concentración creciente de NaCl de 0,01 a 0,5 M, pero un aumento adicional en la concentración de sal no afectó a la constante de ionización de los grupos

1. Introduction

The study of acid-base properties of ion exchangers with different structure of functional groups is an important step in the study of these polymers (Zharkova, 2016; Tanaka, 2015; Bulat, Volkov & Ilyina, 2016), because, on the one hand, these results serve to confirm the chemical structure of functional groups of the ion exchanger, and on the other, determine the pH range in which these groups are ionized and capable of participating in reactions of ion exchange (Inczédy, 2013; Liang et al., 2013; Nachod & J. Schubert, 2013). Widely used ion exchangers for desalination of water, in analytical chemistry for separation of substances by chromatography method⁴, chemical engineering (Tanaka, 2015; Rieman & Walton, 2013).

Information about the processes of acid-base balance in the carboxy-containing resins is limited (Zharkova, 2016; Chugunov, 2015). In the famous works of potentiometric curves analyzed in the coordinates $\text{pH}=\text{f}(\text{volume of titrant})$, and calculate the ionization constants (pK_a) – using the equation of Henderson-Hasselbach. On the basis of these studies, the authors of the famous papers (Zharkova, 2016; Chugunov, 2015) consider that the pK_a of the functional groups of carboxy-containing ion exchangers in the process of titration changes, and in the ion exchanger there are two types of carboxyl groups, characterized by different values of pK_a . However, in the above-mentioned papers did not verify the adequacy of the calculated and experimental curves of potentiometric titration that has been made by the authors the conclusions are clear.

Recently, we developed a new method of synthesis of carboxy-containing high-capacity macroporous cation exchange resin based on acrylate matrix with a high content of functional groups⁹. In these cation-exchangers when changing the degree of neutralization of the groups and the ionic strength of the surrounding solution is slow to change the conformation of polymer chains and has remained virtually unchanged the degree of swelling during ionization or protonation of carboxyl groups. However, the acid-base properties of these cation exchangers was not determined.

The aim of the present work was the experimental determination of the ionization constants of the carboxyl groups of a new cation exchanger based on a copolymer of acrylonitrile, methyl methacrylate and divinylbenzene by the potentiometric method and assessing the adequacy of calculated and experimental data, determining the dependence of the ionization degree of functional groups from pH and concentration of NaCl.

2. Methods

High-capacity carboxylic cation exchange resin based on acrylate adhesive matrix obtained by radical suspension copolymerization of Acrylonitrile and methyl methacrylate with divinylbenzene (12-16 %) in The limited liability company "Rare earth elements - University of Chemical Technology of Russia according to the method described in (An, Ledovskikh & Balanovskiy, 2008).

Before using cation standardized under dynamic conditions in a cycle of 3% NaOH – H₂O – 3% HCl – H₂O. The washing with water in the last stage was carried out until the disappearance of Cl⁻ - in the eluate of the column.

Potentiometric titration was performed by the method of individual batches (Leykin, Meychik & Solovyov, 1978). A dry sample of the normalized cation exchanger at 0.05 ± 0.001 g were placed in glass flasks (volume 50 ml) with glass stopper and poured 20 ml of the NaOH or HCl of various concentrations, but constant ionic strength, which was created by adding the appropriate sodium chloride (background electrolyte). The range of concentrations of acid or

alkali in the initial solutions was 0 ÷ 10 or 0.1 ÷ 0.5 mm, respectively, and the NaCl concentration was 0.01 or 0.1 or 0.5 or 1 M. After 48 hours the samples were separated from the equilibrium solutions in which the pH was determined with an accuracy of ±0.01 (pH Meter, Model 3320, the firm "Jenway" UK), and the concentration of acid or alkali by titration with indicator bromothymol blue. Similarly set the concentration of acid or alkali in the initial solutions. The change in the concentration of H⁺ or OH⁻ in initial and equilibrium solutions was calculated capacity of the cation exchange resin at pH_i by the formula:

$$S_i = \frac{(C_o - C_i) \times V}{g}, \quad (1)$$

where: S_i – the capacity of the cation exchange resin in NaOH at the appropriate pH_i equilibrium, mmol/g of dry mass; C_o and C_i – initial and the corresponding equilibrium concentration of NaOH in solution, mM; V – solution volume, ml; g – weighed sample, g.

Potentiometric titration at each value of ionic strength of the solution was performed in two repetitions, and for each point of the potentiometric curve – 2-5 analytical replicates. Statistical processing of results was performed using Microsoft Excel and IBM SPSS Statistics.

3. Data, Analysis, and Results

The curves of potentiometric titration of the studied cation exchange resin are represented by the dependence $S_i = f(\text{pH}_i)$, have monosigmoid character and are characterized by one flexibility point at the coordinates $dS_i = f(d\text{pH}_i)$, that indicates its monofunctionality (Figure 1, an example of a titration at the concentration of NaCl 0.1 M). Regardless of the concentration of the background electrolyte (C_{NaCl}) at pH > 10, the capacity of the cation exchanger in relation to the Na⁺ reached maximum level (S_{max}), and accounted for 10.10 ± 0.088 mmol/g of dry weight (mean ± standard error).

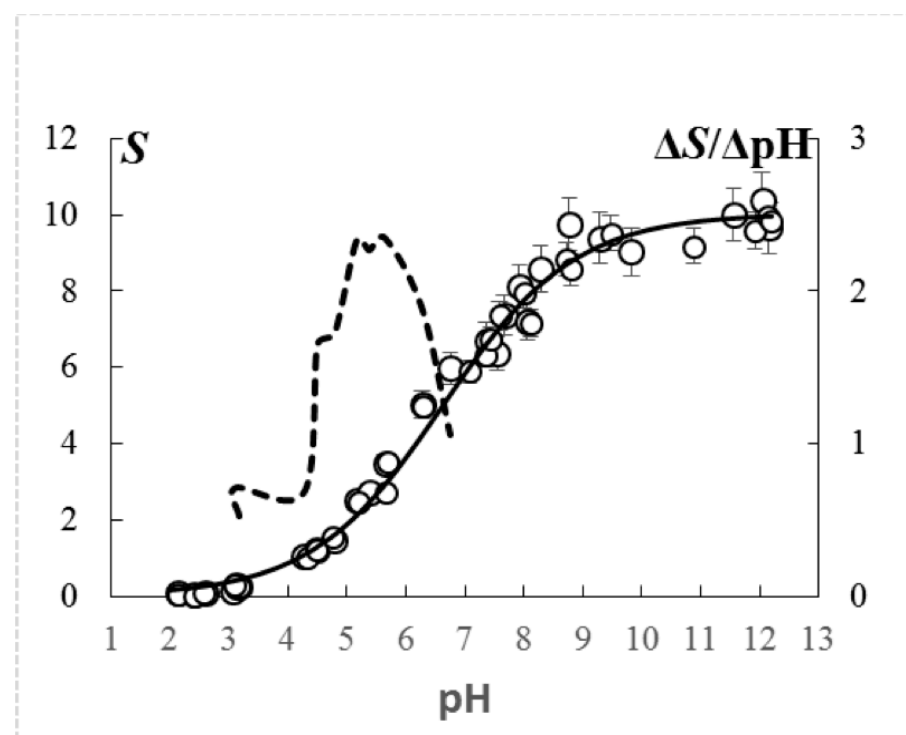


Figure 1. Curve of potentiometric titration of carboxylic cation exchange resin in the background of 0.1 M NaCl, presented in the form of the dependence $S = f(\text{pH})$. S – capacity of cation exchange resin for Na⁺, mmol/g of dry weight of cation exchanger.

The points – experimental data, the solid lines – calculated values of S_i at the experimental value pH_i with the established values of pK'_{aj} and n_j (table.1). Bars \pm SE. $\Delta S/\Delta \text{pH}$ (dashed line) – derivative curve (second y-axis), calculated by the formula: $\Delta S_i/\Delta \text{pH}_i = (S_{i+1} - S_{i-1}) / (\text{pH}_{i+1} - \text{pH}_{i-1})$. On the basis of the found values of S^{max} , we determined the degree of dissociation of a carboxyl group (α_i) for the corresponding values pH_i by the formula:

$$\alpha_i = S_i / S^{\text{max}}, \quad (2)$$

where: S_i – ion-exchange capacity of the carboxyl group at the respective equilibrium of pH_i .

To calculate values for constants of ionization of a carboxyl group (pK'_a), we used the equation proposed by Gregor for the description of potentiometric titration of polyelectrolytes, which is based on equation of Henderson-Hasselbach (Leykin, Meychik & Solovyov, 1978) having the following form:

$$\text{pH}_i = \text{pK}'_a + n \lg(\alpha_i / (1 - \alpha_i)), \quad (3)$$

where: pK'_a – the apparent ionization constants, for weakly basic cation exchangers its value depends on the ion concentration in solution (Gelferich, 1962) ; n – constant that depends on the structure of the polymer matrix and the nature of counter-ion (Shataeva & Kuznetsova, 1979).

The calculations showed that regardless of the concentration of the background electrolyte the experimental curves with high correlation coefficients linearized in the coordinates of equation 3 (Table. 1), it should be emphasized that the number of points on each straight was 11 or more.

Table 1

The effect of the concentration of the background electrolyte (CNaCl, M) on the values of the apparent ionization constants (pK'_a) and the constant n with the potentiometric titration of the carboxy-containing cation exchange resin

	C_{NaCl}			
	0.01	0.1	0.5	1
pK'_a	8,08 \pm 0,02	6.62 \pm 0,02	5.72 \pm 0,02	5.85 \pm 0,04
n	1.48 \pm 0,15	2.54 \pm 0,03	2.60 \pm 0,09	3.12 \pm 0,07
r	0.965	0.991	0.997	0.979

Footnote. Calculations of pK'_a and n were conducted in accordance with the equation $\text{pH}_i = \text{pK}'_a + n \lg(\alpha_i / (1 - \alpha_i))$, α_i is the degree of dissociation of the carboxyl group with appropriate value of pH_i . r – coefficient of dependency correlation $\text{pH}_i = f(\lg(\alpha_i / (1 - \alpha_i)))$. We gave the average values \pm standard deviation.

For each concentration of NaCl with found values of pK'_a and n , we have calculated values of the capacity of the cation exchange resin under appropriate pH_i according to the equation:

$$S_i^{cal} = \frac{S^{max}}{1+10^{(pK'_a-pH_i)/n}}, \quad (4)$$

Translation of elements: $pac\check{y}$ – calculated.

where S_i^{cal} – calculated ion-exchange capacity of the carboxyl group at pH_i , mmol/g of dry weight; S^{max} – the maximum capacity of the ion exchanger, mmol/g of dry weight; pK'_a and n parameters of the equation 3 (Table. 1), and we have developed and calculated potentiometric titration curves (Figure 1, an example of a titration at the concentration of NaCl 0.1 M).

Assessment of compliance of the calculated and experimental values of the capacity of the cation exchanger was carried out by regression analysis $S_i^{calc}=f(S_i^{exper})$ according to the equation:

$$S_i^{calc}=AS_i^{exper}+B, \quad (5)$$

Translation of elements: $calc$ – calculated; $exper$ – experimental.

where S_i^{calc} and S_i^{exper} – calculated according to the equation 4 and the experimental values of the capacity of the ion exchanger in the ratio of sodium ions with the appropriate values of pH_i , A and B – regression coefficients.

The calculations showed that the experimental and calculated values of S_i are fully consistent among themselves, as evidenced by the values of the coefficients A and B ($A \rightarrow 1$; $B \rightarrow 0$ and do not exceed the error of the method of titration) and the values of correlation coefficients (Table 2, Figure 1).

Table 2

The adequacy of the experimental and calculated potentiometric titration of the carboxyl-containing cation exchange resin with different concentrations of NaCl in the solution (C_{NaCl} , M). A and B – regression parameters of the equation $S_{i^{calc}}=AS_{i^{exper}}+B$, where $S_{i^{calc}}$ and $S_{i^{exper}}$ – calculated according to the equation 4 and the experimental values of the capacity of the ion exchanger at the appropriate values of pH_i . r – correlation coefficient of relation of $S_{i^{calc}}=f(S_{i^{exper}})$

	C_{NaCl}			
	0.01	0.1	0.5	1
A	0.983	1.018	1.018	0.991
B	0.216	0.005	0.114	0.112
r	0.987	0.986	0.994	0.981

In accordance with the results, the increase in the concentration of background electrolyte from 0.01 to 0.5 M leads to a decrease in pK'_a values of carboxyl groups in the ion exchanger, i.e.

increase their acidic properties, which is characteristic of carboxylic cation exchangers. However, a further increase of C_{NaCl} up to 1 M does not affect this parameter (Table. 1). For carboxylic cation-exchangers with a low degree of cross-linking (less than 2%) it is known that the value of $pK'a$ depends on the concentration of background electrolyte, and at 1 M concentration of the latter is approximately equal to $pK'a$ of linear polyacid (Gelferich, 1962; Meychik & Yermakov, 2001) but for carboxylic ion exchangers with a high degree of crosslinking (more than 5%) such dependence was found for the first time. The difference is that in the studied carboxylic cation, the change in the values of $pK'a$ with the concentration background less in compared with weakly crosslinking ion exchangers, and the resulting value of $pK'a$ 5.85 in 1M of NaCl (Table. 1) is higher than the value of this indicator for polyacrylic acid (Inczédy, 2013; Leykin, Meychik & Solovyov, 1978; Shataeva, Kuznetsova & Elkin, 2001).

4. Discussion

In works (Zharkova, 2016; Chugunov, 2015), the study of acid-base equilibrium of the carboxyl ion exchangers was carried out with different salts ($NaNO_3$, NaCl), but at their fixed concentration in solution. Obtained in the present work, the values of $pK'a$ for the carboxylic cation exchanger (6.62 in 0.1 M of NaCl and 5.85 in 1 M of NaCl, Table 1) at respective concentrations of background electrolyte are close to those described in the literature. Therefore, in 0.1 M of $NaNO_3$ for cation Tokem-250, the value of $pK'a$ totaled 6.591 and KB-2E – 5.92 in 1M of NaCl.

Noteworthy is a significant effect of concentration of salt in the solution that changes the constant n of equation 3 (Table. 1). Changes in the value of this index appear at lowering the amount of C_{NaCl} from 0.1 to 0.01 and increasing from 0.5 to 1 M, while at the concentration range of 0.1-0.5 M, the values of n were not significantly different ($p < 0.05$) and equal to 3.12. In accordance with existing conceptions, n is a constant depending on the structure of the polymer matrix and the nature of counter ion (Shataeva et al., 1979), but in our experiment, these two variables remained unchanged. It can be assumed that changes in the parameter n were associated with different trends in the change in free energy of the macromolecule in its neutralization in solutions with $C_{NaCl} < 0,1$ and $C_{NaCl} > 0,5$ M. In one case, it decreases and in the other – increases.

Based on the experimental data, it is possible to build the estimated dependency curves $S = f$ (pH) (Figure 2), which clearly show that the investigated carboxylic cation exchange resins are monofunctional and do not have second ionogenic groups with $pK'a \sim 1.5$, which is expected based on the study of acid-base equilibrium of the carboxylic cation exchange resin (brand Tokem-200) at the ionic strength of the solution 1.0 M. The results of this study show (Figure 2) that in the acidic area (pH 1-2), the carboxyl groups are not fully deprotonated, because at these pH, the capacity of the cation exchanger according to Na^+ ranges from 0.2 to 0.4 mmol/g of dry weight that is not due to dibasic carboxyl groups, but due to the change in electrostatic free energy of a macromolecule in a 1 M solution of NaCl. Evidence of this situation is the results of potentiometric titration of the studied carboxylic cation exchange resin in solutions of NaCl concentrations of 0.01 and 0.1 M. Under these conditions, the carboxylic groups are fully protonated, because the capacity of the cation exchanger according to Na^+ tends to 0 (Figure 2).

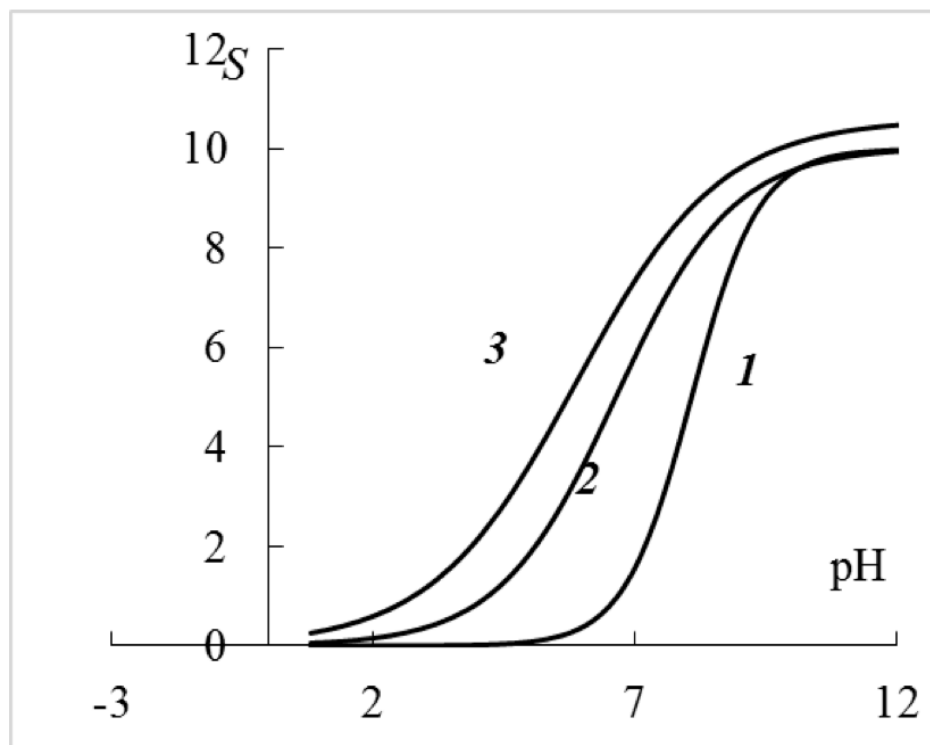


Figure 2. The calculated titration curves (equation 4 according to Table. 1) of carboxylic cation exchange resin in the background of various NaCl concentrations: 1 – 0.01 M; 2 – 0.1 M; 3 – 1 M. S – capacity of cation exchange resin for Na^+ , mmol/g of dry weight of cation exchange resin.

5. Conclusion

Thus, in the present work new data on the regularities of the processes of acid-base equilibrium occurring in the cross-linked macroporous carboxylic cation exchange resin based on acrylate matrix. For these polymers, as well as for the linear analogues, the $pK'a$ of carboxyl groups depends on the concentration of salt in the environment but its value is higher than for carboxyl linear polyacids. The parameter n in the Henderson-Hasselbach equation modified by Gregor is determined not only by the degree of crosslinking of the ion exchanger and the nature of the ion, which is filled with sorbent, but also by the concentration of the electrolyte in which the potentiometric titration of carboxylic cation exchangers is carried out.

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