

Acid-Base Properties of Macroporous Weak Base Anion Exchange Resin

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Abstract: Conducted potentiometric titration of the weakly basic anion exchange resin (degree of crosslinking 12-16%) in a wide range of changes in solution pH (2-12) and concentration of NaCl (0.1; 1 M). The maximum ion exchange capacity of the ion exchanger for HCl (6.50±0.12 mmol/g of dry weight) which does not depend on the ionic strength of the solution. It is shown that in the investigated range of concentrations of background electrolyte and pH the process of acid-base balance can be adequately described by the Gregor equation. The calculated values of the parameters of this equation, according to which analyzed the behavior of the anion exchanger depending on pH and concentration of NaCl. In the anion, there are two types of groups which ionization constants differ by three periods. The existence of the different nature of the amino groups is confirmed by the data of functional analysis and found that the acidity of the amino groups is attenuated with increasing concentration of NaCl.

Key words: Anion exchange resin, ionization constant, ionic strength, the potentiometric curves, acid-base balance, investigated

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 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 (Li *et al.*, 2013; Rahman *et al.*, 2014; Barakat and Ismat-Shah, 2013).

Due to the high performance properties of ion-exchange materials have a wide range of applications in almost all fields of science and manufacturing practices. With their help resolve one of the most pressing social and environmental problems environmental protection (Meychik *et al.*, 2009ab; Shataeva *et al.*, 1979; Sabirova and Sarbaeva, 2016).

With the help of ion exchangers can be efficient solution of the following practical tasks (Chen *et al.*, 2014; He *et al.*, 2015; Nur *et al.*, 2014):

- Water conditioning, softening or complete deionization of water

- The concentration of ions and organic substances in hydrometallurgy of nonferrous and noble metals
- The sequestration of chemically active impurities contained in gases of industrial plants
- Improving ion exchange in the soil and making the required for plant growth micronutrients and fertilizers

The use of ion-exchange resins is promising for many sectors of Applied Chemistry (Flowers and Singer, 2013; Gomes *et al.*, 2017; Ren *et al.*, 2012):

- The main inorganic synthesis (production of sulfuric, hydrochloric, nitric acids, caustic alkalis, etc.)
- production of catalysts
- Mnuufacture of pharmaceutical preparations

Information about the processes of acid-base balance anion exchangers limited (Kattaev and Ramazanov, 2016; Yergozhin *et al.*, 1983; Meychik *et al.*, 1989). In the famous works of potentiometric curves analyzed in the coordinates $pH = f(\text{volume of titrant})$ and calculate the ionization constants (pK_a) using the equation of Henderson-Hasselbach. However, these works typically

do not take into account the fact that, the weakly basic anion exchangers contain primary, secondary and tertiary amino groups (Kattaev and Ramazanov, 2016)).

Developed a new method for the synthesis of macroporous anion exchange resin with a high content of amino groups (Patent No. 2 387 673RU). In these anion exchangers in the change of 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 of amino groups. However, the acid-basic properties of a newly synthesized anion exchanger was not determined.

MATERIALS AND METHODS

The anion exchanger obtained by amination of the industrial diethylene triamine copolymer of Acrylonitrile with divinylbenzene (12-16%) in the limited liability company, rare earth elements, University of Chemical Technology of Russia according to the method described in Patent No. 2 387 673RU.

Before use, the anion exchanger was standardized under dynamic conditions in a loop: 3% HCl-H₂O-10% NH₄OH-H₂O. The washing with water in the last stage was carried out until the disappearance of NH₄⁺ ions in the eluate of the column. Then the anion exchanger was dried at 65°C to constant weight and used in the experiments.

Potentiometric titration was performed by the method of individual batches (Leikin *et al.*, 1978). A dry sample of the normalized anion 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 0.1 or 1 M. After 48 h 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 anion exchange resin in HCl at pH_i by the Eq. 1:

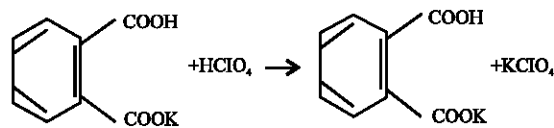


Fig. 1: Formula of Biphthalate potassium

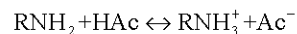
$$S_i = \frac{(C_o - C_i) \times V}{g} \quad (1)$$

Where:

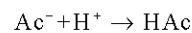
- S_i = The capacity of the anion exchange resin in HCl at the appropriate pH_i equilibrium (mmol/g of dry mass)
- C_o and C_i = Initial and the corresponding equilibrium concentration of HCl in solution (mM)
- V = Solution volume (mL)
- g = Weighed sample (g)

The determination of the primary amino groups in anion exchangers was carried out by non-aqueous titration in acetic acid (Meychik *et al.*, 2009). Sample dry samples of the anion exchange resin 20±0.001 mg was filled with 10 mL of a 10 mm solution of perchloric acid in glacial acetic acid. After 2 days, the samples were separated from the solution. Before and after contact with the anion exchange resin, the solution was titrated 10 mm solution of potassium biphthalate in glacial acetic acid in the presence of the indicator crystal violet (hexadecylpyridinium chloride). Biphthalate potassium reacts with perchloric acid in the ratio of 1-1 mol in accordance with the Fig. 1.

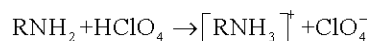
The method consists in that when a weak base (RNH₂) was dissolved in a weakly acid medium, e.g., in acetic acid (HAc), equilibrium is established:



The excess acetic acid shifts the reaction equilibrium to the right. Therefore when the solution is titrated a strong acid such as chlorine, dissolved in acetic acid, the acetate ion behaves as an acceptor of protons:



The total reaction equation of the titration of a weak base with perchloric acid can be written in the following form:



The content of primary amino groups was calculated with the Eq. 2:

$$NNH_2 = \frac{V_{initial} - V_{final} \times N_{bpt} \times V_{total}}{V_a \times g} \quad (2)$$

Where:

- NNH_2 = Content of primary amino groups (mmol/g dry weight)
- $V_{initial}$ and V_{final} = Number of biphthalate potassium required for the titration of the initial and final (after contact with the anion exchange resin) solution (mL)
- N_{bpt} = The concentration of potassium biphthalate (mM)
- V_a = Amount of solution taken for titration (mL)
- V_{total} = The total volume of the solution which flooded a portion of the sample (mL)
- g = Weighed sample of resin

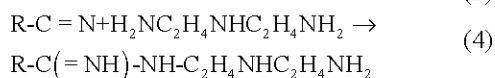
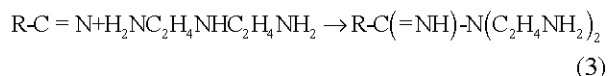
Potentiometric titration at each value of ionic strength of the solution was performed in two repetitions and for each point of the potentiometric curve 2-5 analytical replicates. Statistical processing of results was performed using Microsoft Excel and IBM SPSS Statistics.

RESULTS AND DISCUSSION

The curves of potentiometric titration of the studied anion is represented by the dependence $S_1 = f(pH_i)$ have polysigmoid character that indicates its polyfunctionality (Fig. 2).

Regardless of the concentration of the background electrolyte (C_{NaCl}) at $pH < 3.5$ the capacity of the anion exchanger in relation to the H^+ reached maximum level (S^{max}) and accounted for 6.50 ± 0.12 mmol/g of dry weight (mean \pm standard error).

In accordance with the scheme of the reaction of amination of a copolymer of acrylonitrile with divinylbenzene which can occur in two ways:



It can be assumed that in the structure of the anion exchanger can contain all types of amino groups. If the amination reaction proceeds according to reaction 3, then

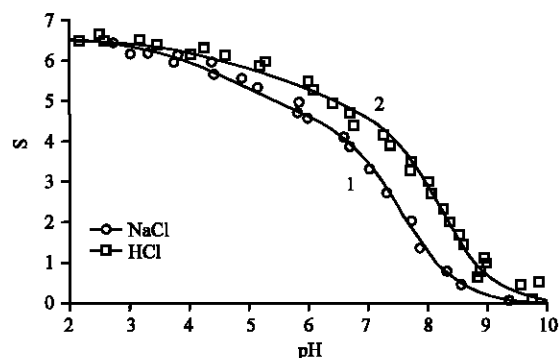


Fig. 2: Potentiometric titration curves of anion exchange resin with different concentrations of NaCl: 1-0.1 M; 2-1 M. The points experimental data, the solid lines calculated values of S_i at the experimental value pH_i with the established values of pK'_{aj} and n_j where: S_i the capacity of the anion exchange resin in HCl at the appropriate pH_i equilibrium, mmol/g of dry mass; pK'_{aj} the dissociation constant of the amino group of j-type; n_j the amino group of j-type

the ratio of the content of primary to tertiary amino groups is 2:1 and if in accordance with reaction 4, the ratio of primary to secondary amino groups is 1:2.

Method of nonaqueous titration is determined that the anion exchanger contains 4.5 ± 0.2 mmol/g primary amino groups (S_{NH_2}). On the basis of the obtained values (S_{NH_2}) and S^{max} can be assumed that in the anion the ratio of the amount of primary to secondary and tertiary amino groups is approximately 2:1, wherein the first content is equal to 4.5 mmol/g and the content of second 2 mmol/g (difference $S^{max} - S_{NH_2}$). In addition, it can be assumed that in the amination of the copolymer occurs mainly reaction 3, since, otherwise the contents of secondary amino groups would be 2 times more than primary. Thus, based on the foregoing, we assumed that in the investigated anion exchange resin are primary and tertiary amino groups in the ratio 2:1.

It should also be emphasized that industrial diethylene triamine used in the synthesis of the investigated anion exchanger and having two primary and one secondary amino group, has the property that distinguishes it from other amines. Generally, the basicity of amines increases in the order: primary < secondary < tertiary but diethylenetriamine secondary amino group has a lower basicity and nucleophilicity ($pK_{a3} = 4.889$) than primary ($pK_{a2} = 9.386$ $pK_{a1} = 10.101$, chemist's handbook).

All the above allows to divide the potentiometric curve $S_i = f(pH_i)$ on y-axis (Fig. 2) into two sections (from

0-4.5 and 4.5-6.5 mmol/g of dry weight; Fig. 2) which will correspond to the ionization of different types of amino groups and on the x-axis to define the corresponding intervals of pH in which one or the other amino group is ionized.

On the basis of found values ΔS^j (number of amino groups of each type, mmol/g of dry weight) determined the degree of dissociation (α_j^i , j-group type) of each amino group with the appropriate values pH_i by the Eq. 5:

$$\alpha_{i1} = S_i / 4.5 \quad (5)$$

for primary amino group and according to the Eq. 6:

$$\alpha_{i2} = (S_i - 4.5) / 2 \quad (6)$$

for tertiary amino group, where S_i is the ion exchange capacity of the anion exchanger in HCl with a corresponding equilibrium pH_i .

To calculate values for constants of ionization of each of the amino groups (pK'_{aj}) used the equation proposed by Gregor for the description of potentiometric titration of polyelectrolytes which is based on:

$$pH_i = pK'_a - n \lg(i / (1 - \alpha_i)) \quad (7)$$

Where pK'_a the apparent ionization constants as weakly basic anion exchangers its value depends on the concentration present in solution ions (Gelferich, 1962) n-constant that depends on the structure of the polymer matrix and the nature of counter-ion (Shataeva *et al.*, 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 Eq. 3 (Table 1) for both types of amino groups.

With the found values of pK'_{aj} and n_j , we calculated values of capacity of the anion exchange resin in HCl (S_i^{calc}) in appropriate HCl_i according to the equation (Meychik and Yermakov, 2001). Translation of elements: data calculated (Table 1 and Fig. 2):

$$S_i^{calc} = \frac{\sum \Delta S^j}{1 + 10^{\frac{pK'_{aj} - pH_i}{n_j}}} \quad (8)$$

Where:

- S_i = The ion exchange capacity of the anion exchanger at pH_i (mmol/g of dry weight)
- ΔS^j = The number of amino groups of j-type in the ion exchanger (mmol/g of dry weight)
- pK'_{aj} and n_j = The parameters of Eq. 9 for the amino group of j-type

Table 1: The effect of the concentration of the background electrolyte (C_{NaCl} , M) on the values of the apparent ionization constants (pK'_{aj}) of different amines and the parameter n_j with the potentiometric titration of the anion exchanger

Variables	0.1		1	
	-NH ₂	-N=	-NH ₂	-N=
ΔS_j	4.5±0.2	2.0±0.2	4.5±0.2	2.0±0.2
pK'_{aj}	7.39±0.02	4.53±0.05	8.08±0.08	5.68±0.09
n_j	1.13±0.03	1.45±0.18	0.95±0.07	1.48±0.28
r	0.998	0.980	0.996	0.979

Calculations of pK'_{aj} and n_j conducted in accordance with the equation Gregor: $pH_i = pK'_{aj} + n_j \lg(\alpha_j^i / (1 - \alpha_j^i))$. pK'_{aj} is the dissociation constant of the amino group of j-type; n_j constant equation of Gregor to the amino group of j-type; α_j^i is the degree of dissociation of the amino group of the j-type with appropriate value of pH_i . r correlation coefficient based on $pH_i = f(\lg(\alpha_j^i / (1 - \alpha_j^i)))$. We gave the average values±standard deviation

Table 2: The adequacy of the experimental and calculated potentiometric titration of the anion exchange resin with different concentrations of NaCl (C_{NaCl} , M)

C_{NaCl}	A	B	r
0.1	0.988	0.035	0.997
1	1.031	0.04	0.986

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 6 and the experimental values of the capacity of the ion exchanger in HCl at the appropriate values of pH_i . r correlation coefficient of relation of $S_i^{calc} = f(S_i^{exper})$

Assessment of compliance of the calculated and experimental values of capacity of the anion exchanger was carried out by regression analysis $S_i^{calc} = f(S_i^{exper})$ according to the Eq. 9:

$$S_i^{calc} = AS_i^{exper} + B \quad (9)$$

Where S_i^{calc} and S_i^{exper} calculated according to the Eq. 8 and the experimental values of the capacity of the ion exchanger for HCl with the appropriate values pH_i , A and B are regression coefficients.

The calculations showed that the assumption of the existence in the anion the two types of amino groups of 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→1; B→0 and do not exceed the error of the method of titration) and the values of correlation coefficients (Table 2 and Fig. 2).

Figure 3 presents the accordance of experimental and calculated values of the capacity of the anion exchange resin at different pH in the assumption that the anion is dominated by only one amino group (Fig. 3a) or there are two types of amino groups (Fig. 3b). Comparative analysis clearly shows that the investigated anion exchanger is not monofunctional as in the first case, the calculated data match the experimental unsatisfactory.

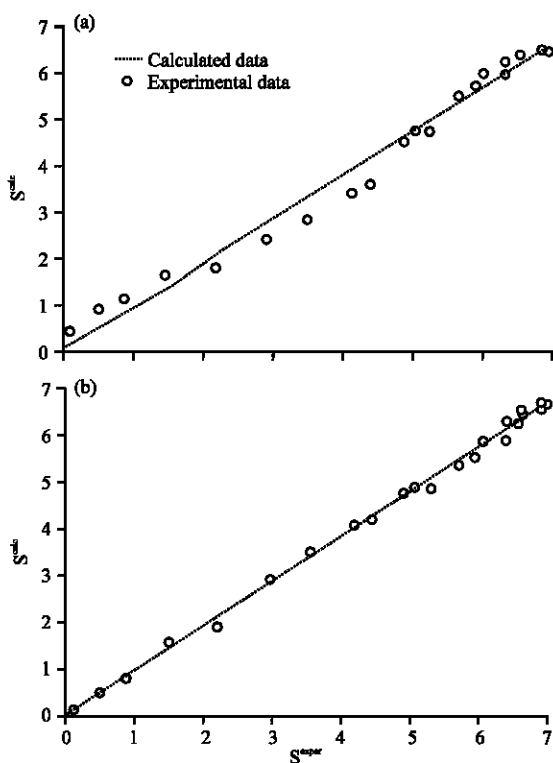


Fig. 3: The correspondence between calculated and experimental data: a) The assumption of the existence in the structure of the anion exchanger of the same type of amino groups; b) The assumption of the existence in the structure of the anion exchanger two types of amino groups

CONCLUSION

In accordance with the results, the increase in the concentration of background electrolyte from 0.1-1 M leads to an increase in pK'_a of both types of amino groups, i.e., weaken their acidic properties and the basicity increase. For weakly basic cation exchange resin it is known that the value of pK'_a depends on the concentration of background electrolyte, (Gelferich, 1962; Shataeva *et al.*, 1979) but weakly basic anion exchange resin such dependence was found for the first time. The difference in values pK'_{aj} of two different amino groups reaches three pH units which suggests that the anion exchange reactions will involve mainly primary amino groups.

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