

## Acid–Base Properties of Macroporous Weak Base Anionite Based on Aminated Acrylonitrile/Divinylbenzene Copolymer

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**Abstract**—Potentiometric titration of weak base anionite (the degree of crosslinking was 12–16%) was performed within the pH range of 2–12 and NaCl concentration range of 0.1–1.0 mol/L. The maximum ion-exchange ability against HCl does not depend on the solution ionic strength and is  $6.50 \pm 0.12$  mmol/g of dry solid matter. It was shown that the process of acid–base equilibrium can be adequately described by the Gregor equation within the studied stock electrolyte concentration and pH ranges. Two type of groups were discovered in anionite. The ionization constants of these groups differ by three orders of magnitude. The existence of amino groups of different nature was proved by the data obtained by functional analysis; it was estimated that the acidity of these groups decreases as NaCl concentration increases.

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The investigation of acid–base properties of ionites characterized by different structure of functional groups is an urgent stage of investigation of the mentioned polymers. On one hand, these results prove the chemical structure of functional groups of ion-exchange polymer; on the other hand, they allow determining the pH range which provides the ionized state required for the participation in ion-exchange reactions to these groups.

The data on the processes of acid–base equilibrium in anionites are limited [1–3]. In the known studies, potentiometric curves are analyzed within  $\text{pH} = f$  (titrant volume) coordinates; the Henderson–Hasselbalch equation is used for the calculation of ionization constants. However, the fact that weak base anionites contain primary, secondary, and tertiary amino groups is not taken into account in the aforementioned studies (see, for example, [1]).

A novel approach toward synthesis of macroporous anionite characterized by a high content of amino groups [4] was developed; this method is characterized by insignificant change in the conformation of polymer chains and the degree of swelling at ionization of amino groups under the change in the degree of neutralization of groups and ionic strength of the surrounding solution. However, acid–base properties of recently synthesized anionite were not determined.

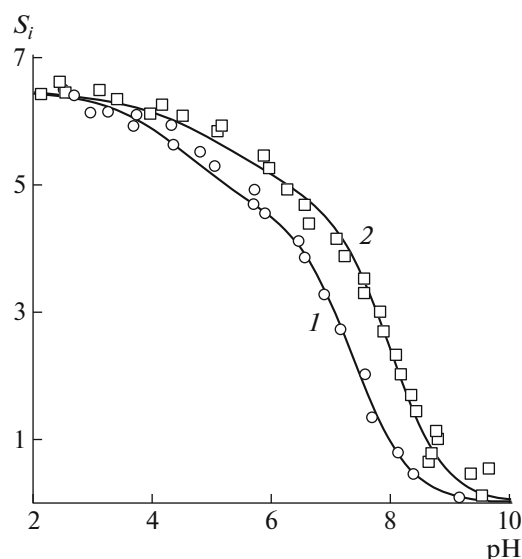
The goal of the present research was to potentiometrically determine the ionization constants of amino groups in the structure of a novel anionite based on aminated acrylonitrile/divinylbenzene copolymer.

### EXPERIMENTAL

Anionite was obtained by amination of acrylic acid nitrile/divinylbenzene (12%) copolymer by diethylenetriamine at OOO Redkozemel'nye Elementy—RKhtU according to the technique given in [4].

Anionite was standardized under dynamic conditions at cyclic washing with 3% HCl–H<sub>2</sub>O–10% NH<sub>4</sub>OH–H<sub>2</sub>O before the investigations. Washing with water at the final stage was performed until NH<sub>4</sub><sup>+</sup> ions were removed from the eluate of the column. Anionite was dried before usage at 65°C until a constant weight was obtained.

Potentiometric titration was performed according to the technique of individual samples [5]. Dry samples of standardized anionite ( $0.05 \pm 0.001$  g) were placed into glass flasks (50 mL) with sealing plugs; 20 mL of NaOH or HCl solution of varying concentration (but of constant ionic strength provided by the addition of corresponding solutions of stock electrolyte—sodium chloride) was poured into the flask. The range of variation of concentration of acid or alkali in



**Fig. 1.** Curves of potentiometric titration of anionite at NaCl concentration of 0.1 (1) and 1.0 mol/L (2). Points represent the experimental data; curves represent the data calculated at experimental  $\text{pH}_i$  and determined values of  $\text{p}K'_{aj}$  and  $\eta_j$  (Table 1).

the initial solution was 0–10 or 0.1–0.5 mmol/L, respectively; the NaCl concentration was 0.1 or 1.0 mol/L. The samples were separated from equilibrium solutions after 48 h. The value of pH of these solutions was measured within the accuracy of  $\pm 0.01$  (pH Meter, Model 3320, Jenway, UK); the concentration of acid or alkali was determined by titration with bromthymol blue. The concentration of acid or alkali in initial solutions was determined similarly. Anionite capacity against HCl was determined according to the change in concentration of  $\text{H}^+$  or  $\text{OH}^-$  in the initial and equilibrium solutions at  $\text{pH}_i$  using the equation

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

where  $S_i$  is the anionite capacity against HCl at corresponding equilibrium value  $\text{pH}_i$ , mmol/g of dry solid matter;  $C_o$  and  $C_i$  are the initial and corresponding equilibrium concentration of HCl in solution, mol/L;  $V$  is the volume of solution, mL; and  $g$  is the weight of the sample, g.

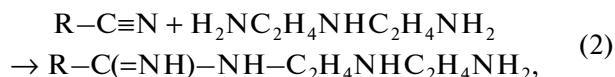
The content of primary amino groups in anionites was determined by nonaqueous titration in acetic acid [6]. Dry anionite samples ( $0.020 \pm 0.001$  g) were flooded with 10 mL of perchloric acid solution in glacial acetic acid (10 mmol/L). The samples were separated from the solution after two days. The solution was titrated by potassium biphthalate solution in glacial acetic acid (10 mmol/L) in the presence of crystal violet dye (hexamethyl pararosaniline chloride) before and after contact with anionite.

Potentiometric titration at every value of ionic strength of solution was performed twice; titration was performed 2–5 times for every point of the potentiometric curve. Statistical processing of the results was performed using the Microsoft Excel and IBM SPSS Statistics programs.

## RESULTS AND DISCUSSION

Potentiometric titration curves of the anionite under study represented by the dependence  $S_i = f(\text{pH}_i)$  exhibit polysigmoid character, indicating its polyfunctionality (Fig. 1). The values of anionite capacity against  $\text{H}^+$  achieved the maximum value ( $S^{\text{max}}$ ) at  $\text{pH} < 3.5$  irrespective of the concentration of stock electrolyte ( $C_{\text{NaCl}}$ ); the maximum capacity was  $6.50 \pm 0.12$  mmol/g of dry solid matter.

According to the scheme of reaction of amination of acrylonitrile/divinylbenzene copolymer, which can proceed in two different directions



one can suppose that all of the types of amino groups exist in the structure of anionite. If the amination reaction takes place according to reaction (1), then the ratio between primary and tertiary amino groups is 2 : 1; if the reaction takes place according to the reaction (2), then this ratio is 1 : 2.

It was determined by nonaqueous titration that anionite contains  $4.5 \pm 0.2$  mmol/g of primary amino groups  $S_{\text{NH}_2}$ . On the basis of the obtained values of  $S_{\text{NH}_2}$  and  $S^{\text{max}}$ , one can conclude that the ratio between primary amino groups and the sum of secondary and tertiary ones is approximately 2 : 1 in the anionite; in this case, the content of the ones first mentioned is 4.5 mmol/g, while the content of the second ones is 2 mmol/g (the difference  $S^{\text{max}} - S_{\text{NH}_2}$ ). Moreover, one can suppose that reaction (1) predominantly takes place at the amination of copolymer. If not, the content of secondary amino groups should be 2 times higher than the content of primary amino groups. Thus, it can be considered that primary and tertiary amino groups are present in the anionite under study in the ratio of 2 : 1.

It should be underlined that diethylenetriamine containing two primary and one secondary amino group, which was used in the synthesis of the anionite under study, is characterized by a property which distinguishes it from other amines. Generally, the basicity of amines increases in the following series: primary–secondary–tertiary amines; however, in diethylenetriamine, the secondary amino group is characterized by

lower basicity and nucleophilicity ( $pK_{a3} = 4.889$ ) than the primary ones ( $pK_{a2} = 9.386$  and  $pK_{a1} = 10.101$  [7]).

The data given above allow splitting potentiometric curve  $S_i = f(pH_i)$  along the  $y$  axis (Fig. 1) into two regions (0–4.5 and 4.5–6.5 mmol/g of dry solid matter) which correspond to the ionization of different types of amino groups; certain pH ranges can be set along the  $x$  axis which correspond to the ionization of certain amino groups.

The degree of dissociation ( $\alpha_i^j$ , where  $j$  is the type of group) of every amino group at corresponding values of  $pH_i$  was determined on basis of the found content of all of the types of amino groups in anionite ( $S^j$ , mmol/g of dry solid matter). In the case of the primary amino group, it was determined according to the equation

$$\alpha_{i1} = S_i/4.5, \quad (3)$$

while in case of the tertiary amino group the following equation was used:

$$\alpha_{i2} = (S_i - 4.5)/2, \quad (4)$$

where  $S_i$  is the ion-exchange ability of anionite against HCl at the corresponding equilibrium value of  $pH_i$ .

The ionization constants of every amino group  $pK'_{aj}$  were calculated according to the equation introduced by Gregor for the description of potentiometric titration of polyelectrolytes (the latter is based on the Henderson–Hasselbalch equation [5]):

$$pH_i = pK'_a + n \log(\alpha_i/(1 - \alpha_i)), \quad (5)$$

where  $pK'_a$  is the apparent ionization constant (for weak base anionites, its value depends on the concentration of ions existing in the solution [8]) and  $n$  is a constant depending on the structure of polymer matrix and nature of counterion [9].

The calculations showed that experimental curves with high correlation coefficients are linearized in coordinates of Eq. (5) for both types of amino groups (Table 1) irrespective of concentration of stock electrolyte.

The values of anionite capacity against HCl ( $S_i^{\text{calc}}$ ) were calculated according to the found values of  $pK'_{aj}$  and  $n_j$  at corresponding  $pH_i$  values using the equation [10]

$$S_i^{\text{calc}} = \sum \frac{S^j}{1 + 10^{(pK'_{aj} - pH_i)n_j}}, \quad (6)$$

where  $S_i^{\text{calc}}$  is the calculated ion-exchange capacity of anionite at  $pH_i$ , mmol/g of dry solid matter;  $S^j$  is the amount of amino group of  $j$ th type in ionite, mmol/g of dry solid matter; and  $pK'_{aj}$  and  $n_j$  are the parameters of Eq. (5) for amino group of  $j$ th type (Table 1, Fig. 1).

**Table 1.** The influence of stock electrolyte concentration on the values of apparent ionization constant  $pK'_{aj}$  of different amino groups and parameter  $n_j$  at potentiometric titration of anionite

$C_{\text{NaCl}},$ mol/L	$j$	$S^j$	$pK'_{aj}$	$n_j$	$r$
0.1	NH <sub>2</sub>	$4.5 \pm 0.2$	$7.39 \pm 0.02$	$1.13 \pm 0.03$	0.998
	NH	$2.0 \pm 0.2$	$4.53 \pm 0.05$	$1.45 \pm 0.18$	0.980
1.0	NH <sub>2</sub>	$4.5 \pm 0.2$	$8.08 \pm 0.08$	$0.95 \pm 0.07$	0.996
	NH	$2.0 \pm 0.2$	$5.68 \pm 0.09$	$1.48 \pm 0.28$	0.979

The examination of accordance between calculated and experimental values of anionite capacity was performed by the method of regression analysis of  $S_i^{\text{calc}} = f(S_i^{\text{exp}})$  according to the equation

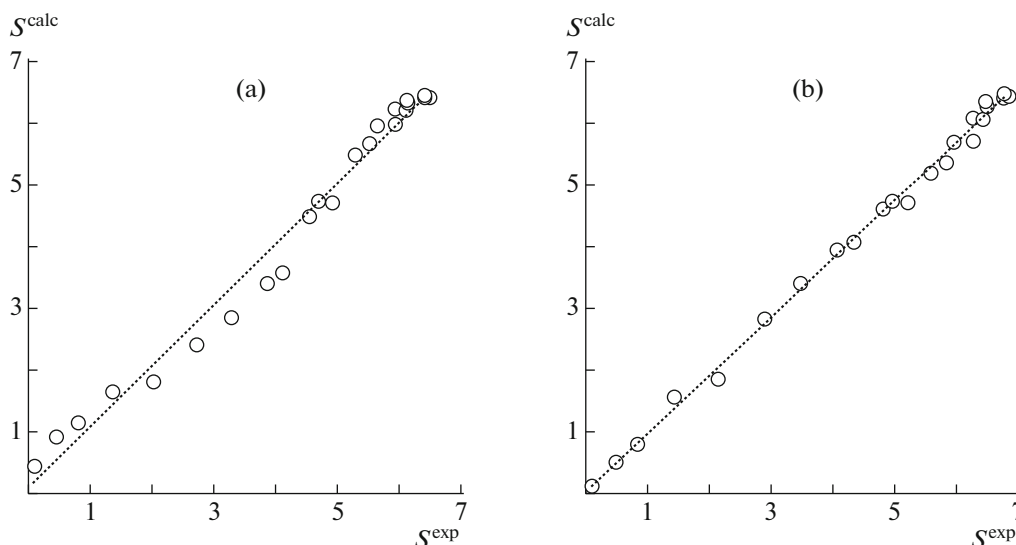
$$S_i^{\text{calc}} = AS_i^{\text{exp}} + B, \quad (7)$$

where  $S_i^{\text{exp}}$  are the experimental values of ionite capacity against HCl at corresponding  $pH_i$  values and  $A$  and  $B$  are the regression coefficients.

The calculations according to Eq. (7) showed that experimental and calculated values of  $S_i$  are in full agreement with each other in terms of the supposition that two types of amino groups exist in anionite; the values of coefficients  $A$  and  $B$  ( $A \rightarrow 1$ ;  $B \rightarrow 0$ ) and correlation coefficients  $r^2$  are evidence of this fact:  $A = 0.988$ ,  $B = 0.035$ ,  $r^2 = 0.997$  and  $A = 1.031$ ,  $B = 0.004$ ,  $r^2 = 0.986$  for NaCl concentration equal to 0.1 and 1.0 mol/L, respectively.

Data proving the accordance between experimental and calculated values of anionite capacity at different pH values are given in Fig. 2. Figure 2a represents the supposition that only one amino group predominates in anionite, while Fig. 2b demonstrates the presence of both types of amino groups. Comparative analysis shows that anionite under study is not monofunctional because there is no satisfactory accordance between calculated and experimental data in the first case.

According to the results obtained, one can conclude that the increase in concentration of stock electrolyte from 0.1 to 1.0 mol/L leads to the increase in  $pK'_a$  of both types of amino groups, i.e., their acidic properties are weakened, while their basicity increases (Table 1). It is known that the value of  $pK'_a$  of weak base cationites depends on the concentration of stock electrolyte [9, 10], but in the present research, such dependence was for the first time obtained for weak base anionites. The difference between values of  $pK'_{aj}$  of the two different amino groups reaches three units of pH (Table 1), which makes it possible to conclude



**Fig. 2.** The correlation between calculated (straight lines) and experimental (points) data plotted under the supposition that only one (a) or two (b) types of amino groups exist in the anionite.

that primary amino groups will predominantly participate in the anion-exchange reactions.

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