Preparation of Fe/Al Intercalated Adsorbents and Determination of Zero Charge Point Using the Mass Titration Method

Juraeva F.N., Mamataliev N.N., Kalbaev A.M., Abdikamalova A.B., Eshmetov I.D.

Doctoral student, Institute of General and Inorganic Chemistry, Tashkent, Uzbekistan;
Senior Researcher, Institute of General and Inorganic Chemistry, Tashkent, Uzbekistan;
National University of Uzbekistan, Tashkent, Uzbekistan;
Junior Researcher, Institute of General and Inorganic Chemistry, Tashkent, Uzbekistan;
Leading researcher, Institute of General and Inorganic Chemistry, Tashkent, Uzbekistan
Chief Researcher, Institute of General and Inorganic Chemistry, Tashkent, Uzbekistan

ABSTRACT: The article presents the results of determining the point of zero charge of samples synthesized on the basis of enriched Krantau, Navbakhor alkaline bentonites and polyhydroxy cations. When objects are mass titrated in solutions with different ionic strength (I=0,1; 0,01 and 0,001), their curves do not intersect. The results of the study showed that the system pH was 8,5 (I=0,1) to 9,2 (I=0,001) for Krantau bentonite, 7,2 (I=0,1) to 7,9 (I=0,001) for NIB. and in KR-Fe/Al, NIB-Fe/Al samples from 4,8 (I=0,1) to 4,5 (I=0,001) and from 4,7 (I=0,1) to 4, respectively. showed a change up to 3 (I=0,001). Solvent ions affect the recharging of the system, dissociation of the solid phase. As the ionic strength of the solution increases, the point of zero charge of bentonite samples decreases. When the ionic strength is the same (I=0,01) and pH values are different, their curves cross asymptotically and the point of zero charge is 4,5 for NIB-Fe/Al and 4,6 for KR-Fe/Al.

KEYWORDS: pH environment, point of zero charge, bentonite, montmorillonite, ionic strength, adsorptive, polyhydroxycation.

I. INTRODUCTION

The fields of application of adsorbents are extremely wide and diverse, and there are many ways of their synthesis and introduction. The value of an adsorbent depends not only on its developed specific surface, but also on its selectivity and the electrokinetic potential and charge of the surface area. Therefore, currently layered aluminosilicates (montmorillonite, kaolinite) matrix $[FeAl_{12}O_4(OH)_{24}(OH)_{12}]^{7+}$, $[Al_{13}O_4(OH)_{24}(OH)_{12}]^{7+}$, $[Cr_{13}O_4(OH)_{24}(OH)_{12}$ Special attention is being paid to the synthesis of sorbents with a stable surface charge based on the introduction of large polyoxocations such as [1-3].

The surface charge value of adsorbents predetermines the particles adsorbed on it. The so-called point of zero charge (NZN) refers to the situation where the pH value of the same medium is equal to zero. If the pH value of the system exceeds NZN, then the mineral has the ability to absorb mainly cations, if the pH value of the solution is lower than NZN, the mineral mainly absorbs anions. Adsorption and desorption of chemical elements present in cationic and anionic forms in sorbent solutions significantly affect [9]. This parameter allows for a complete interpretation of the adsorption mechanism of sorbents and the adsorbent that can be sorbed in certain pH environments..

II. SIGNIFICANCE OF THE SYSTEM

The article presents the results of determining the point of zero charge of samples synthesized on the basis of enriched Krantau, Navbakhor alkaline bentonites and polyhydroxy cations. The study of methodology is explained in

section III, section IV covers the experimental results of the study, and section V discusses the future study and conclusion.

III. METHODOLOGY

In order to synthesize adsorbents based on intercalated systems, Navbahor alkaline bentonite (NIB) of Krantau (KR), Navoi region was selected as raw material. Initially, the samples were enriched according to certain methods [5]. Changes in the mineralogical composition and structure of the enriched sample were studied by X-ray, electron microscopic and chemical composition determination methods [6].

The adsorbent preparation process was carried out by the sol-gel method. As a modifying agent, 0,02 and 0,1 mol/l solutions of $Fe_2(SO_4)_3 \cdot 9H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ salts, respectively, were used. The solutions were titrated using 0,2 mol/L NaOH solution until the ON^-/Me^{3+} ratio was 2,5 at 70ºC. The resulting system was stirred in a magnetic stirrer at a temperature of 70ºC for 2 hours, then kept in a thermostat at a temperature of 50ºC for 1 day.

Enriched KR and NIB samples were mixed with distilled water at a mass ratio of 1:10. A polyoxocation preservative solution was mixed in the resulting suspension in the ratio of 10 mmol Me^{3+} per 1 g of bentonite. The suspension was stirred on a magnetic stirrer for 2 hours and then allowed to stand at room temperature for 5 days. The Sungra bentonite suspension system was thoroughly mixed and the solid phase was separated from the liquid phase in a vacuum filter (Diaphragm Vacuum Pump LH95D/C) and dried in a drying oven at 105±5ºC for 3 hours. After that, the samples were crushed and passed through a sieve with a diameter of 0,1 mm, and they were weighed in the amount of $0,1 \pm 0,002$ g on an analytical balance. The resulting adsorbent was tentatively named KR sample KR-Fe/Al, and NIB-Fe/Al sample for NIB.

The point of zero charge (NZN) is a crucial parameter in many chemical phenomena, adsorption, interaction of particles in colloidal suspension, coagulation, mineral dissolution, and electrochemical phenomena.

NZN is often determined classically using potentiometric and mass titration methods. However, information on potentiometric determination is very conflicting, and the values vary from 2,6 to 8,8 depending on the process conditions [7]. A mass titration method was chosen for the determination of NZN based on a number of sources.

0,1 of sodium chloride as a solvent of the guard phase in the determination of NZN; 0,01; 0,001 M solutions were prepared. The procedures were carried out on a full magnetic stirrer. First, 60 mL of pre-prepared NaCl solvent was placed in a 100 ml beaker and the pH value was measured. 0,1 g of studied samples were added to the solution. The system was stirred for 10-15 min until equilibration and the pH value was determined. Addition of successive bentonite samples to the suspension was continued until the pH value was completely unchanged. The dependence of the pH change on the ionic solvation strength was studied. The ionic index of the system was changed by using fixed solutions of NaOH and HCl.

IV. EXPERIMENTAL RESULTS

The results of determining the point of zero charge of the samples under the influence of solutions with different ionic strength are given in Table 1.

Table 1.
Dependence of the change of medium pH on the amount of solid phase.

Mass., g	KR				NIB			
	Dis. water	0,1M NaCl	0,01M NaCl	0,001M NaCl	Dis. water	0,1M NaCl	0,01M NaCl	0,001M NaCl
0	6,60	6,01	6,12	6,51	6,60	6,01	6,12	6,51
0,1	7,88	7,61	7,87	8,35	7,32	6,48	6,85	6,84
0,2	8,56	7,83	8,15	8,68	7,61	6,56	7,15	7,26
0,3	8,95	8,02	8,36	8,85	7,73	6,75	7,34	7,57
0,4	9,02	8,21	8,51	9,02	7,82	6,92	7,51	7,76
0,5	9,11	8,26	8,57	9,13	7,89	6,98	7,53	7,81
0,6	9,18	8,32	8,72	9,18	7,91	7,05	7,54	7,84
0,7	9,21	8,44	8,79	9,21	7,93	7,14	7,56	7,91
0,8	9,23	8,49	8,81	9,22	7,95	7,19	7,56	7,92
0,9	9,23	8,50	8,82	9,22	7,95	7,20	7,56	7,93
1,0	9,23	8,50	8,82	9,22	7,95	7,20	7,56	7,93

The mass titration results show that the ionic strength affects the NZN value and the electrochemical properties of the substance surface. From the table, the value of NZN for sample KR (I=0,1) is 8,50 (I=0,001) to 9,22 and for NIB (I=0,1) is 7,20 (I=0,001) to 7,93 it is stated that it has increased up to In the process, the dissociation constants of all three solutions into raw ions have approximately the same value. As the ionic strength of the solvent (ionic particles) increases, the degree of dissociation of the substance decreases, because as a result of the participation of ON^- ions in the solvent in the equilibrium of ions in the system, the dissociation and pH index of the solution with a large amount of ions is low. When the solution is carried out in a solvent with no ionic strength (distilled water) (I=0,001), it can be seen that the results are closer, which once again proves the effect of solvent ions on the dissociation constant. In general, bentonite is negatively charged, and its surface charge becomes zero due to the release of hydroxide ions into the solution under the influence of the process. It causes the concentration of hydroxide ions in the solution to increase and the environment to become alkaline.

NZN of synthesized KR-Fe/Al and NIB-Fe/Al samples was determined. The obtained results are presented in Table 2.

Table 2.
Dependence of the change of pH on the amount of solid phase in solutions with different ionic strength

№	Mass, gr	KR-Fe/Al				NIB-Fe/Al			
		Dis, water	0,1M NaCl	0,01M NaCl	0,001M NaCl	Dis, water	0,1M NaCl	0,01M NaCl	0,001M NaCl
1	0	6,60	6,01	6,12	6,51	6,60	6,01	6,12	6,51
2	0,1	5,02	5,35	5,85	5,13	4,56	5,53	5,72	5,04
3	0,2	4,91	5,29	5,08	4,84	4,44	4,91	4,87	4,91
4	0,3	4,88	5,17	4,97	4,85	4,43	4,83	4,72	4,86
5	0,4	4,82	5,04	4,85	4,75	4,42	4,82	4,69	4,75
6	0,5	4,74	4,97	4,75	4,77	4,37	4,78	4,67	4,63
7	0,6	4,67	4,92	4,71	4,66	4,36	4,76	4,56	4,56
8	0,7	4,55	4,82	4,65	4,65	4,33	4,75	4,55	4,55
9	0,8	4,56	4,83	4,67	4,58	4,32	4,74	4,53	4,36
10	0,9	4,56	4,83	4,62	4,53	4,31	4,72	4,53	4,35
11	1,0	4,56	4,83	4,62	4,53	4,31	4,72	4,53	4,35

rom the obtained results, pH NZN values in KR-Fe/Al and NIB-Fe/Al samples ranged from 4,83 (I=0,1) to 4,53 (I=0,001), from 4,72 (I=0,1), respectively. It can be seen that it varies up to 4,35 (I=0,001). This modifier indicates that the polyhydoxocation ($[FeAl_{12}O_4(OH)_{24}(OH)_{12}]^{7+}$) has been exchanged with sodium ions in the bentonite matrix. As a result of the dissociation of intercalated iron and aluminum polyhydroxycations, the increase in the amount of N^+ ions increases the level of acidity in the system.

When studying the variation of pH of the samples depending on the amount of solid phase, it was found that NZN has different numerical values in solutions with different ionic strength. This means that the ionic strength directly affects the point of zero charge. Carrying out the process at the same ionic strength (0,01M NaCl) and different pH values allows to know the exact numerical value of the point of zero charge, which is also useful in determining the adsorptive limit of synthesized adsorbent samples. The results are presented in Table 3.

Table 3.
Dependence of the change of the system pH indicator on the mass of the solid phase

№	Mass, gr	KR-Fe/Al			NIB-Fe/Al		
		NaCl 0,01M, I=0,01			NaCl 0,01M, I=0,01		
1	0	10,42	9,14	4,41	10,42	9,14	4,41
2	0,1	5,65	5,38	4,42	5,01	5,08	4,43
3	0,2	5,18	5,27	4,42	4,91	4,98	4,45
4	0,3	5,02	5,16	4,44	4,89	4,86	4,48
5	0,4	4,99	4,98	4,46	4,80	4,82	4,49
6	0,5	4,87	4,72	4,49	4,70	4,75	4,51
7	0,6	4,68	4,69	4,50	4,62	4,66	4,52

8	0,7	4,66	4,68	4,56	4,60	4,61	4,53
9	0,8	4,65	4,65	4,58	4,59	4,59	4,55
10	0,9	4,63	4,64	4,64	4,55	4,55	4,55
11	1,0	4,64	4,64	4,64	4,55	4,55	4,55

The obtained results made it possible to determine the point where the surface charge of iron-aluminum intercalated bentonites is equal to zero, i.e. NZN. pH indicators 10,4; It can be seen from Figure 1 that in the same solutions of ionic strength 9,4 and 4,4, the mass dependence curves of pH correspond to the values of 4,55 and 4,64 for NIB-Fe/Al and KR-Fe/Al samples, respectively.

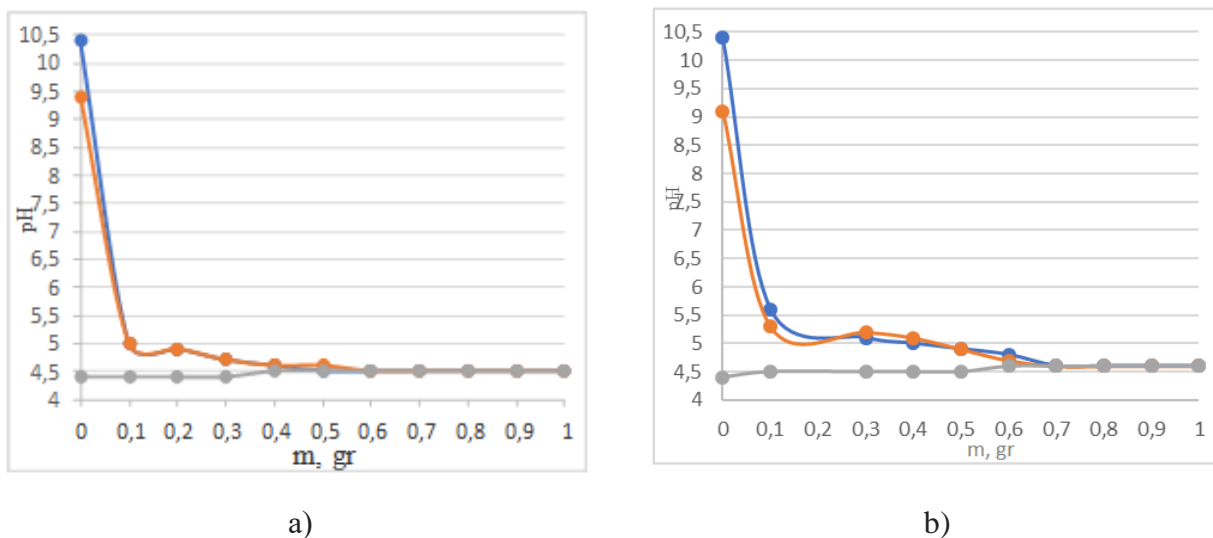a)   b)

Figure 1. a) NIB-Fe/Al and b) KR-Fe/Al samples 1)- 10.4 2)-9.4 and 3)-4.4 solutions of pH NZN solutions.
We can see that the NZN values of these junctions are significantly lower than those of the original bentonite samples.

V. CONCLUSION AND FUTURE WORK

It was found that the NZN value of the samples soaked in solutions with different ionic strength (0,1; 0,01; 0,001M) does not intersect, and this is explained by the fact that the surface of the samples has different electrochemical parameters in the solution with different ionic strength. Modified if NZN value varied from 8,50 (I=0,1) to 9,22 (I=0,001) for KR and from 7,20 (I=0,1) to 7,93 (I=0,001) for NIB 4,83 (I=0,1) to 4,53 (I=0,001), 4,72 (I=0,1) to 4,35 (I= 0,001) was found to decrease. The melting curves asymptotically approach the constant limiting point of NIB-Fe/Al 4,55 and NIB-Fe/Al 4,61 when the ionic strength of the initial samples is the same (I=0,01) and the values of pH are different, which determined the point of zero charge for the samples. As a result of the dissociation of the initial samples, forming an alkaline environment, the pH values of the suspensions correspond to 9,22 and 7,93. As a result of the modification of the original bentonite samples with Fe^{3+}/Al^{3+} polyhydroxy cations, this indicator decreased to 4,55-4,61, which proves that the amount of Na+ exchangeable cations is reduced due to the replacement with polycations.

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