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THE EFFECT OF MONTMORILLONITE MODIFICATION BY Cr(III)-COMPOUNDS ON ITS MICROCRYSTALLINE STRUCTURE AND ELECTROSURFACE PROPERTIES

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Abstract: Modification of clay minerals by nanoclusters of hydroxycations Cr(III) opens the perspectives for development of a new materials (catalysts, adsorbents, pigment concentrates, leather fillings) and nanocomposites. In order to examine the effect of montmorillonite modification by Cr(III)-compounds with different basicity on its electrosurface properties the dependences of ζ -potential and the stability of MMT dispersions on pH medium and concentration of chromium nitrate have been studied. For pH 2-12, three zones of stability are observed, which alternate with three zones of coagulation. The triple change of MMT charge sign in $Cr(NO_3)_3$ solutions and alternation of stability and coagulation zones of dispersions are explained by hydrolysis, complex formation of Cr^{3+}-ions and ionization of hard phase groups. Charge reversal of MMT surface and appearance of the second zone of stability of positively charged sol are conditioned by excess adsorption) of polymerized cationic species of chromium. The adsorption of polymeric hydroxychromium cations depends upon the basicity of $Cr(NO_3)_3$ solution exceeds the CEC of MMT by 2-5 times. Hydroxychromium-montmorillonite (Hydroxy-Cr-MMT) has high positive charge (tens or hundreds $\mu C/cm^2$) and highly developed accessible specific surface area (95-260 m^2/g). Modification of MMT by hydroxychromium cations was accompanied by increase of the interlayer space along *c-axis* up to d_{001} = 1.68 nm and appearance of highly developed micro- and mesoporous turbo-stratified (disordered) structure.

Keywords: Cr-pillared montmorillonite, Cherkassky deposit, Ukraine, X-ray diffraction, microelectrophoresis, surface charge, ζ-potential, dispersion stability.

1. Introduction

Modification of clay minerals by nanoclusters of Cr(III)-hydroxycations may yield new applications such as modern leather materials and nanocomposites.

Fixation of anionic dyestuffs or vegetable tannins on modified mineral particles the can assist in obtaining dye leather fillers with multifunctional properties. It would allow combining the processes of filling, fat-liquoring and dyeing in a single process and to increase, in such a way, the effectiveness and productivity of final leather finishing. Clay minerals are cation exchangers (Grim, 1953; Tarasevich and Ovcharenko, 1975; Van Olphen, 1977), i.e. the particles are negatively charged and their adsorption capacity concerning anionic substances is negligible. In order to increase the affinity for anionic substances it is necessary to change the sign of particle charge into positive one and to elevate its density on the mineral surface. This can be achieved by means of excess-equivalent adsorption of hydroxycomplexes of multivalent metal (Al^{3+}, Fe^{3+}, Cr^{3+}, Zr^{4+}, Ti^{4+} and others) (Van Olphen, 1977; Moraru and Ovcharenko, 1986; Bottero and Cases, 1996). On the other hand this is known as pillaring clays by different types of poly(hydroxo metal)cations.

Cr(III)-compounds are widely used as leather tannins because they strongly form complexes. The mechanisms of tanning action of basic chrome salts have been studied thoroughly (Strahov et al., 1985). However the interaction mechanisms of Cr(III)-compounds with clay minerals - namely with montmorillonite (MMT), have not been adequately interpreted (Brindley and Yamanaka, 1979; Melville Carr, 1985; Bornholdt et al.,1991; Maireles-Torres et al., 1991; Jimenez-Lopez et al., 1993). The purpose of this study is to examine the effect of montmorillonite modification by Cr(III)-compounds with different basicity on its microcrystalline structure and electrosurface properties to determine optimal conditions for obtaining leather fillers and pigment concentrates.

2. Materials and Methods

Montmorillonite from the Cherkassky deposit (Ukraine), after thorough purification, washing and exchange into Na^+-form, became the object of this investigation.

The average particle size of initial Na^+-MMT, using laser diffraction ("Zetasizer-3", Malvern Instrument), was 50-100 nm. The CEC of Na^+-MMT was E = 0,72 meq/g and specific surface area after adsorption of methylene blue was 520 m^2/g. The electrokinetic potential (ζ) of the MMT in 0.005 M NaCl solution and pH 9.5 was -30mV. Modification of MMT was performed according to Brindley and Yamanaka (1979) as follows: 0.1 M solution of chromium nitrate of variable basicity (OH/Cr = 0÷2.0) was used at a solid : liquid ratio of 1:60. The required basicity of $Cr(NO_3)_3$ solution was attained gradual addition of 0.1 M solution NaOH to the necessary molar relationship of OH/Cr.

The quantitative evaluation of the surface charge of hydroxychromium-montmorillonite (Hydroxy-Cr-MMT) was determined by the amounts of chrome adsorbed from solutions of different basicity. The adsorption of polymeric chrome on the MMT was determined by comparing the intensity of optical absorption spectra of initial and equilibrium solutions in the wavelength range 570-585 nm, using a Specord-UV-vis spectrometer.

The structural changes of MMT after modification by chromium (III)-compounds were studied with X-ray diffraction (DRON-3 with filterted CoKα -radiation). Specific surface areas of Hydroxy-Cr-MMT were determined by nitrogen adsorption at liquid nitrogen temperature using a gravimetric procedure (BET method). Samples were degassed at 200°C under high vacuum prior to the sorption measurements.

In electrokinetic experiments solutions of twice recrystallized $Cr(NO_3)_3 \times 9\ H_2O$ was used. For terms of comparison solutions of NaCl and $CaCl_2$ were also used. The pH in the systems was adjusted in the range 2-12 using 0.03 M HCl and NaOH solutions. In order to support constant ionic strength 0.03 M solution of NaCl was used. The experiments were carried out at solid: liquid ratio of 1:1000. Aggregate stability and location of coagulation zones were estimated from the change of optical density of suspension measured by photocolorimeter- nephelometer LMF-69 at wavelength 450 nm using 3 mm thick dishes, and from the sedimentation volumes of precipitates.

The electrokinetic potential was determined by the microelectrophoresis method (Dukhin and Deryaguin, 1976) using a closed rectangular cell with width-height ratio (a/H) = 20. In order to exclude undesirable effects, associated with electrolysis of water and formation of gas bubbles, electrode chambers were separated from measuring capillary by thin semipenetrable cellophane membranes.

The particle movement was observed in the light field of microscope vision A*mplival* (K.-Z. Iena), equipped with objective lens ×16, condenser ×1.5 and ocular ×20 with mesh scale. The measurements of electrophoretic velocity were performed on stationary levels where the speed of electroosmotic flow of liquid was $v_{eo}=0$. The value of χa ($1/\chi$ - Debye screening length, a - effective radius of particle) over the range of investigated concentrations of electrolyte was not less than 100, but the dimensionless parameter of polarization $Rel \approx exp(\psi_D/2-1)/\chi a$ was $<< 1$. Under such conditions the influence of double layer polarization on the electrophoresis of particles can be ignored (Dukhin and Deryaguin, 1976) and ζ -potential is calculated according to Smolukhovsky equation:

$$\zeta = 4\pi\, \eta_0\, \upsilon_{ef} / \varepsilon E,$$

where υ_{ef} – is electrophoretic velocity of particles, η_0 and ε - is viscosity and dielectric permittivity of medium respectively and, E the electric field strength defined by us as:

$$E = i / KS_0\ ,$$

where i – is current intensity, K- specific electric conductance of the suspension and S_0 is the area of cross-section of measuring chamber.

The electrical conductivity of suspensions was determined in cylinder glass cell by platinum electrodes with an alternating-current bridge P-5021, at the frequency of 1000 Hz, at 20 °C. The current intensity was recorded by microammeter M-194.

3. Results and Discussion

The interaction of clay minerals with Cr(III)-compounds is accompanied by sharp reversal of surface charge. Therefore it exerts strong influence on the electrokinetic properties and aggregative stability of mineral dispersions, what allows disclosing the mechanism of modification.

Figure 1 shows the concentration dependence of ζ -potential of Na^+-montmorillonite in solutions of NaCl, $CaCl_2$ and of $Cr(NO_3)_3$. The ζ-potential decreases with increasing electrolyte concentration and charge of counter ions, in accordance to the Shults-Gardy rule (Kruyt 1955). At $Cr(NO_3)_3$ concentration of 2.4×10^{-3} mol/dm^3 and pH~4.2, |-ζ|-potential decreases to zero and, passing through isoelectrical point (IEP), changes its sign into positive. At pH~5.5 the dependence of ζ-potential on $Cr(NO_3)_3$ concentration is more abrupt (Fig.1, curve 4). The charge reversal of montmorillonite particles abruptly intensifies and ζ-potential becomes more positive and then gradually decreases with increase of $Cr(NO_3)_3$ concentration.

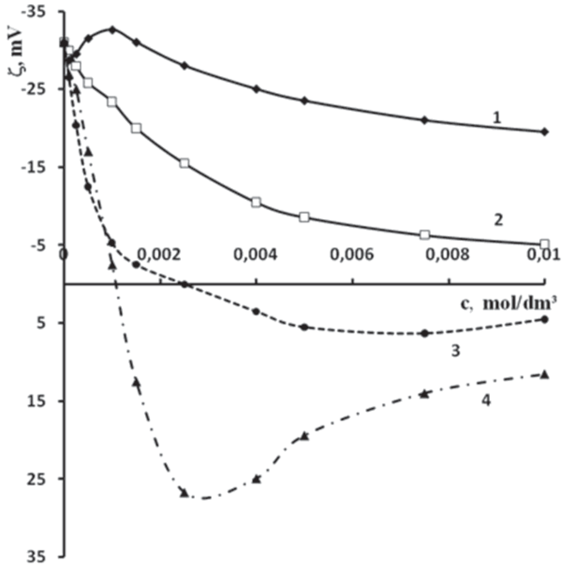

Fig. 1. The concentration dependences of ζ -potential of Na^+-montmorillonite in solutions of NaCl (1), $CaCl_2$ (2) and $Cr(NO_3)_3$ at pH 4.2 (3) and pH 5.5 (4).

Cr(III)-salts in aqueous solutions are strongly subjected to hydrolysis forming hydroxycomplex compounds (Laswick and Plane, 1959; Earley and Cannon, 1965; Baes and Mesmer, 1976). For example, the hydrolysis of chromium nitrate $[Cr(H_2O)_6]^{3+}3NO_3^-$ in aqueous solution proceeds in two stages:

$[Cr(H_2O)_6]^{3+} + H_2O \leftrightarrows Cr(H_2O)_5(OH)]^{2+} + H_3O^+$ (1)

$[Cr(H_2O)_5(OH)]^{2+}+H_2O\leftrightarrows[Cr(H_2O)_4(OH)_2]^{+}+H_3O^+$ (2)

Since $Cr(OH)_3$ precipitation for 0.1-1.0 M solutions begins at pH 4.0-4.9 (Goronovskiy et al., 1987), it can be suggested that there is a sufficient amount of hydroxycomplex chrome ions, the type $[Cr_n(OH)_m(H_2O)_x]^{(3n-m)+}$ in solution. Therefore, the charge reversal of MMT surface takes place by hydroxycomplex ions with high polarization and adsorption capacities (Brindley and Yamanaka, 1979; Matijevic, 1983; Melville Carr, 1985; Moraru and Ovcharenko, 1986).

In order to study the mechanism of montmorillonite recharging in $Cr(NO_3)_3$ solutions, the dependence of stability and ζ-potential of MMT dispersions upon the pH at constant ionic strength (0.03 M) (Fig.2) has been studied. For comparison, the dependence of ζ-potential on pH for the same dispersion in a solution containing different electrolyte (NaCl) was studied. The dependence of ζ=f (pH) is characterized by IEP at pH~3 (curve 1), but at higher pH the MMT particles become negatively charged (Fig. 2). After introducing of $Cr(NO_3)_3$ into the MMT dispersion, pH-dependence becomes more complicated (Fig.2, curve 2). With the increase of pH, three zones of stability (a, b, c) are observed, which alternate with three zones of coagulation (a′, b′, c′). In the ranges of these zones ζ-potential changes its sign three times. At pH ~ 4.0, the |-ζ|-potential of MMT abruptly decreases and becomes positive again. Alternation of coagulation zone in IEP with stability zone of positively charged dispersion corresponds to this transition (Fig. 3). At pH 4-6 rapid, gradual increase of posi-

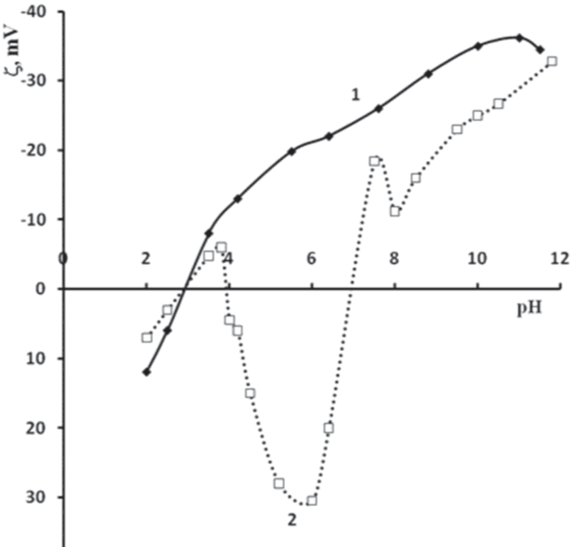

Fig. 2. The pH-dependences of ζ-potential of Na^+-montmorillonite in solutions of NaCl (1) and of $Cr(NO_3)_3$ (2) at constant ionic strength (j=0.03).

tive ζ-potential and stability of dispersions is observed. The IEP coincides with the pH of the beginning of chromium hydroxide precipitation and the stability zone of positively charged particles which extends to the pH of total precipitation of $Cr(OH)_3$ (pH 6.8). This coincidence is not accidental, as at pH ~ 4.-6., as a result of hydrolysis proceeding and complex formation, the state of chromium ions in solution abruptly changes. By "the state of chromium ions" means that after hydrolysis there is changing of their chemical valency, polarizability, hydration ability, ability to ligand's coordination. Besides hydrolysis, complex formation and condensation and polymerization take place in the solutions of Cr(III) salts (Laswick and Plane, 1959; Earley and Cannon, 1965; Baes and Mesmer, 1976; Matijevic, 1983) yielding multinuclear chromium compounds. Such processes are accompanied not only by the change of hydroxycromium ions charge and solution colouring, but by the increase of their molecular mass. This question is opened in great variety of special literature regarding Cr (III) aqueous chemistry (see eg., Laswick and Plane, 1959; Earley and Cannon, 1965; Baes and Mesmer, 1976). Data obtained by Laswick and Plane (1959) indicate that about 50% of the available Cr in the heated to 80°C solution (as in our experiments) could have been polymeric.

Reference data (Balanyi, 1939) shows that molecular mass of basic chromic nitrate, which is calculated according to the diffusion rate methods, is on the increase together with growth of basicity and amounts to 346, 442, 758 and 4080 with the meaning OH/Cr^{3+} which are 0.0, 1.0, 1.5 and 2.0 respectively.

Dimerization of hydropentaqua chrome ions takes place according to the following reaction (Laswick and Plane, 1959):

$$2[Cr(H_2O)_5OH]^{2+} \leftrightarrows [Cr_2(H_2O)_8(OH)_2]^{4+} + 2H_2O \quad (3)$$

with the hydrolysis constant $K_2=10^4$ mol/dm^3. Further polymerization and hydrolysis are also possible but they proceed very slowly at room temperature:

$$5[Cr(H_2O)_6{}^{3+}] \rightarrow [Cr_2(H_2O)_8(OH)_2]^{4+} + [Cr_3(H_2O)_9(OH)_4]^{5+} + 6H_3O^{+} + H_2O \quad (4)$$

The replacement of water molecules in the inner coordination sphere of hydrated metal ion by hydroxyl ions abruptly raises the adsorption of this ion on the surface of different chemical composition because of the increase of polarization of complex ions and the decrease of their hydration (Matijevic, 1983),. It was shown in the work of Matijevic (1983), that ion exchange of polymeric complex ions, such as chromic ions (Brindley and Yamanaka, 1979; Melville Carr, 1985; Jimenez-Lopez et al.,1993), supplemented by specific adsorption, may exceed by several times the CEC of a mineral.

Consequently, the most possible cause of sign inversion of MMT charge and the emergence of stability zone of positively charged sol is an excess-equivalent specific adsorption of polymerized chrome cationic forms. Further change of ζ-pH dependence in dispersions of hydroxychromium solutions is probably determined by the type of dissociation of MMT surface groups and by the conversions (transformations) of adsorbed polymerized products of hydrolysis (Laswick and Plane, 1959).

The next addition of alkali and the increase of pH results in the decrease of positive ζ-potential to zero and at pH ~ 6.8-7.0 the third recharging of MMT surface takes place. This is accompanied by

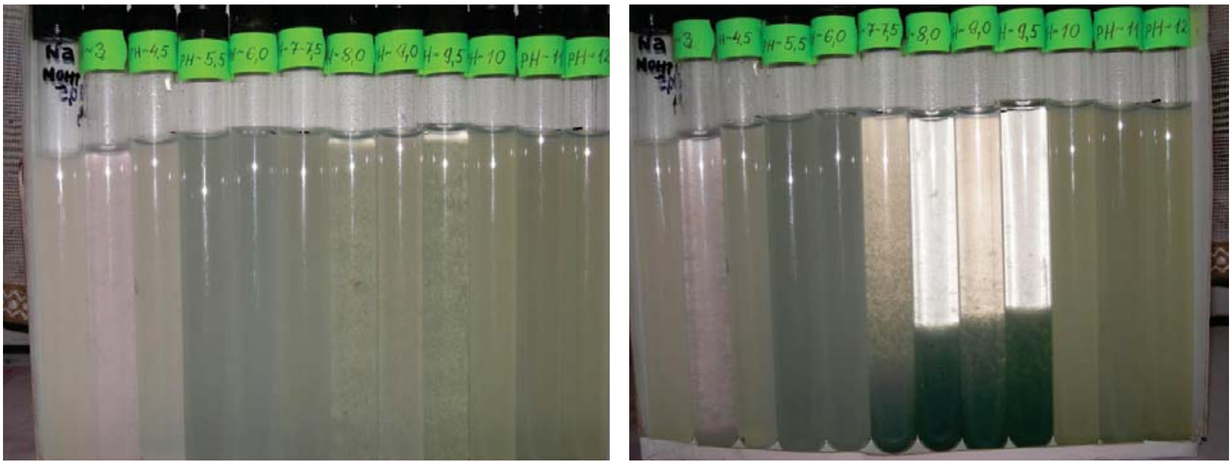

Fig. 3. The zones of stability and of coagulation as result of interaction of Na^+-montmorillonite with $Cr(NO_3)_3$ solutions at different pH: after 5 (a, left) and after 30 minutes (b, right). (pH values are indicated on test-tube).

a new coagulation zone (c′) and by a zone of dispersion stability (c) with negative charge sign, in spite of the fact that the dissolution of $Cr(OH)_3$, according to reference data (Goronovskiy et al., 1987) begins at pH 12. It can be suggested that multinuclear chromium complexes are stable in the narrow range of pH ~ 4.0-6.5 and that the third recharging is associated with decomposition (depolymerization of $[Cr_n(OH)_m(H_2O)_x]^{(3n-m)+}$) and desorption of polymeric chromium complexes. The obtained data are in good agreement with the changes of dispersion stability (Fig.3). These stable positively charged dispersions can be used for adsorption and strong fixation of anionic dyestuffs in order to obtain dyed fillings for leather semi-finished items.

Therefore, the optimal conditions of montmorillonite modification by Cr(III)-compounds are realized in the pH range 4-6, whereby the surface of montmorillonite, acquires the highest possible positive charge after adsorption of hydroxychromium cations. In order to analyze the changes of electrosurface properties and the structure of montmorillonite at this pH range, the adsorption of chromium compounds depending upon the basicity of $Cr(NO_3)_3$ solutions, was investigated. X-ray diffraction measurements of Hydroxy-Cr-MMT was also carried out. The results are shown in Table 1. It is observed that the higher the solution basicity the greater the adsorption of polymeric chromium complexes on Na^+-montmorillonite. The summary adsorption can exceed the CEC by 2-5 times. Actually, stoichiometry of ionic exchange all-sufficient is maintained. However in case of such big and strongly polarized ions as chromium hydroxycomplexes, along with ionexchange saturation of CEC, additional specific adsorption of chromium polyoxycation always takes place due to van der Waals' forces. This is explained by the gradual increase of molecular mass and size of the polymeric forms of chrome in solution (dimers, trimers, tetramers etc) (Laswick and Plane 1959). However, it should be considered that at the beginning the interaction has an ion exchange, and neutralization character and positive charge on the particles surface is only created by excessively adsorbed chrome polyoxycations. It is difficult to calculate precisely this charge because the exact composition and the charge of adsorbed polycations are unknown. Nevertheless, it is certain that the surface charge formed as a result of adsorption, is of the order of tens or hundreds of $\mu C/cm^2$. Let us calculate the density of the surface charge ($+\sigma$) for Hydroxy-Cr-MMT with the basicity of 1.0 (Tab.1). We consider that excess-equivalent adsorption of chrome polycations (a) is 2.94-0.72 = 2.22 meq/g and that the specific surface of initial Na^+-montmorillonite (S) is 520 m^2/g. Considering that the minimum charge of Cr-polyoxycations (z) is +1, then $\sigma = z\ a\ F / S = 1 \times 2.22.10^{-3} \times 9.65.10^4 / 520 = 0.412\ C/m^2 = 41.2\ \mu C/cm^2$, where F is the Faraday constant (Table 1). But if we take into account that the maximum charge of chromium polyoxycations is +4, then $\sigma = 164.8\ \mu C/cm^2$. In reality such large electrical charge is spread three-dimensionally in the surface layer since polyoxychromium cations have 1-2 nm thickness .

Table 1 lists the principal characteristics of Hydroxy-Cr-MMT which were obtained at various conditions. Hydroxy-Cr-MMT obtains the high positive charge, potential and large specific surface area. Hence it is expected that considerable adsorption and strong fixation of anionic dyestuffs and surfactant detergents can take place on Hydroxy-Cr-MMT surface.

The analysis of diffractograms of Hydroxy-Cr-MMT (Fig. 4) and data of Table 1 suggest that hydroxochromium cations of various degrees of polymerization and sizes are intercalated into the interlayer space of MMT crystals increasing d_{001} to 1.68 nm (The expansion of basal spacing $\Delta d = d_{001} - 0.94 = 0.74$ nm, where 0.94 nm – is the thickness of the montmorillonite packet). The

Table 1. The principal colloid-chemical characteristics of Hydroxy-Cr-montmorillonities.

Modifier	Basicity, OH/Cr	Adsorption of Cr-complexes, a, meq/g	Surface charge, σ, C/m^2	d_{001} nm	S m^2/g	pH	$K \cdot 10^{-4}$ S/cm	ζ mV
$Cr(NO_3)_3 \cdot 9H_2O$	0.1	1.73	0.187	1.39	95	4.5	1.50	+11.0
	0.5	2.49	0.328	1.45	140	4.6	1.25	+16.4
	1.0	2.94	0.412	1.51	190	4.7	2.20	+20.5
	1.5	3.46	0.508	1.57	235	5.0	1.40	+25.9
	2.0	4.02	0.612	1.68	260	5.3	1.20	+30.3

variations in the basal spacings (Fig.4) can be attributed to differences both in the nature and the orientations of the interlayer species in accordance to other workers (Brindley and Yamanaka 1979; Melville Carr 1985). Apparently, in the process of drying bevelling of silicate layers occurs mainly along the edgy sections of packages because of non-homogeneous splitting of layered structure by hydroxychromium cations of various sizes. Hydroxy-Cr-MMT acquires highly developed micro- and mesoporous turbostratic structure. Possibly, it occurs because of the following that small monomeric cations penetrate more deeply between layers, while larger polyoxycations of chrome, because of steric hindrance, are closer to edges of lamella, forming cuneal airspaces. During drying and dehydration, obviously, it occurs packages' canting of Hydroxy-Cr-MMT.

This is confirmed not only by the breadths of diffraction maxima and the practical absence of higher orders reflections (Brindley and Yamanaka, 1979; Mokrousova and Moraru, 2009) but also by the sharp increase of accessible specific surface area of Hydroxy-Cr-MMT, which ranges from 95 to 260 m^2/g.

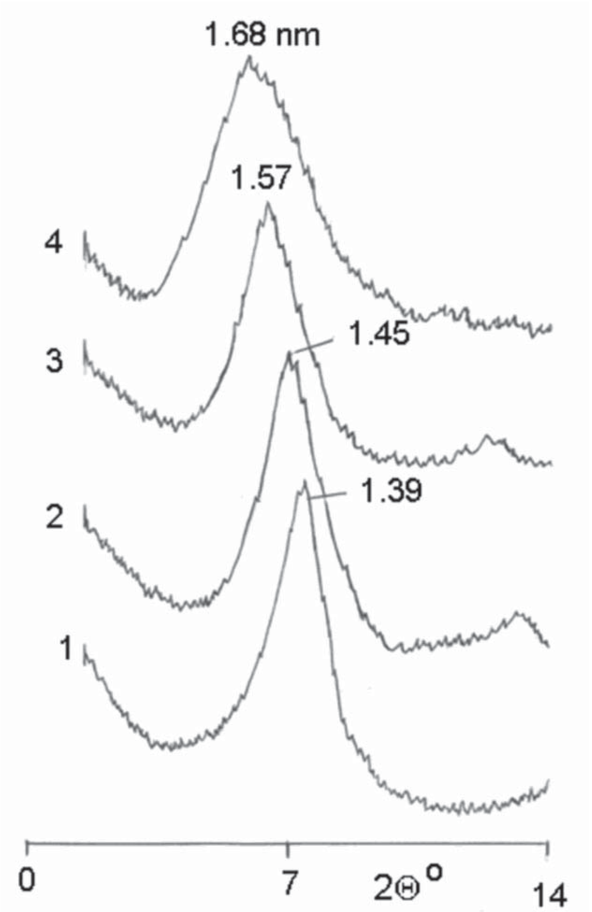

Fig. 4. The first-order basal reflections maxima of Na^+-montmorillonite modified by 0.1 M solutions of $Cr(NO_3)_3$ with different basicity: OH/Cr=0.1(1), 0.5(2), 1.5(3), 2.0(4).

4. Conclusions

In this paper we elucidated the mechanism of montmorillonite (MMT) charge reversal using solutions of $Cr(NO_3)_3$. Also we studied the zones of stability and coagulation of the dispersions, the dependence of ζ-potential and stability of MMT dispersions at variable pH and concentration of chromium nitrate. Charge reversal of the MMT surface and appearance of the second zone of stability of positively charged sol are conditioned by excess adsorption of polymerized cationic forms of chromium from solution.

With the growth of $Cr(NO_3)_3$ solution basicity, adsorption of polymeric chromium complexes on Na^+-montmorillonite increases and exceeds the CEC by 2-5 times. The calculations showed that the positive charge on Hydroxy-Cr-MMT surface reaches tens or hundreds of $\mu C/cm^2$.

Adsorption of hydroxychromium cations with different polymerization degree and size is accompanied by intercalation into the interlayer space of montmorillonite and expansion along *c* axis up to d_{001}=1.68 nm. Because of non-homogeneous splitting of layered structure, during of drying process, beveling of silicate layers is going mainly along the edgy sections of packages, and Hydroxy-Cr-MMT has micro- and mesoporous structure. It allows to obtain mineral fillers with turbostratic structure, increasing accessible surface and adsorption capacity relatively to anionic dyestuffs and surfactants.

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