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The Effect of Montmorillonite Modification by Cr(III)-Compounds on the Electrokinetic Properties of its Aqueous Dispersions

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Abstract: **In this paper for to elucidate the mechanism of montmorillonite recharging in the solutions of $Cr(NO_3)_3$ and setting up the zones of stability and coagulation of dispersions the dependences of ξ-potential and stability of MMT dispersions in mentioned solutions on pH medium and concentration of chrome compounds have been studied. With the increase of pH, in the interval of pH meanings 2-12, three zones of stability are observed, which alternate with three zones of coagulation. Within the limits of these zones ξ-potential change its sign three times. It has been stated that the recharging of MMT surface cannot be caused by simple adsorption of Cr^{3+} ions, but by the products of their hydrolysis.**

Keywords: **Clay minerals, montmorillonite, modification, Cr(III)compounds, ζ –potential**

I INTRODUCTION

Modification of clay minerals by nanoclusters of hydroxocations of Cr (III) suggests perspectives of creation a number of leather modern materials and nanotechnologies on their basis.

The following fixation of anionic dyestuffs or vegetable tannins on modified mineral particles can assist in obtaining dyed leather fillers with multifunctional properties. It would allow to combine 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. As it is known [1-2], the clay minerals are cation exchangers, i.e., the particles are negatively charged and their adsorption capacity concerning anionic substances is very negligible. In order to raise 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. It can be achieved by means of superequivalent adsorption of hydroxyl complexes of multicharged metals (Al^{3+}, Fe^{3+}, Cr^{3+}, Zr^{4+}, Ti^{4+} and others) [2-4].

Cr (III) compounds are widely used as leather tannins because they are able to form complexes. The mechanisms of tanning action of basic chrome salts have been studied thoroughly enough [5]. But as to the interaction of chrome compounds with clay minerals - namely with montmorillonite (MMT) – the fact is that until the present time little attention has been paid to this problem [6, 7, 8-10].

II OBJECTS AND METHODS OF INVESTIGATION

Montmorillonite of *Cherkassky* deposit (Ukraine), after thorough purification, washing and transformation into Na-form, became the object of a given investigation. In experiments twice re-crystallized $Cr(NO)_3 \times 6\ H_2O$ was used.

For comparison chlorides of single charged metals (NaCl) and double charged metals ($CaCl_2$) were also used. The change of pH in the systems (in the range of 2-12) was reached by the introduction of 0.02 M solutions of HCl and NaOH. In order to support constant ionizing power, 0.02 M solution of NaCl was used.

The experiments were carried out at constant relationship of solid and liquid phases 1:1000. Aggregative stability and position of coagulation zones were estimated according to the change of optical density of suspension measured by photocolorimeter - nephelometer *LMF – 69* at the length of wave light- 450 nm in the dishes of 3 mm thickness, and also according to sedimental volumes of precipitates.

Electrokinetic potential was determined by microelectrophoresis method [11] by the use of closed cell of rectangular section with width-height relation (a/H) = 20. In order to exclude undesirable effects, connected with water electrolysis and formation of gas bubbles, electrode chambers were separated from measuring capillary by the thin semipenetrable membranes made of cellophane.

The particles movement was observed in light field of microscope vision A*mplival* (K.-Z. Jena) supplied by objective lens ×16, condenser ×1.5 and ocular ×20 with meshy scale.

The measurements of electro-phoresis speed were performed on stationery levels where the speed of electroosmotic flow of liquid was $v_{eo}=0$.

The value of $\chi \times a$ ($1/\chi$ – *Debye* radius of screening, a – effective radius of particle) over the range of investigated concentrations of electrolyte constituted not less than 100, but dimensionless parameter of polarization $R_{el} \approx exp(\psi_D/2\text{-}l\ )/\ \chi a << 1$. Under such conditions as shown in the work [11], then one can neglect the influence of double layer polarization on the speed of electrophoresis particles and ζ -potential is calculated according to *Smolukhovskogo* equation:

$$\zeta = 4\pi\ \eta_0\ \upsilon_{ef}\ /\ \varepsilon\ E, \qquad (1)$$

where υ_{ef} - is electrophoresis speed of particles, η_0 - viscosity of medium, ε - dielectric permeability of medium, E- electric field strength which was defined by us as:

$$E = i\ /\ KS, \qquad (2)$$

where ***i*** – quantity of electric current, ***K***- specific electric conductance of suspension, ***S*** - area of cross-section of measuring chamber.

Electrical conductivity of suspensions was defined in cylinder glass cell by platinum electrodes with the help of alternating current bridge *P-5021*, at the frequency of 1000 GHz, at 20 °C. The strength of current was registered by micro-ammeter – the type *M-194*.

III RESULTS AND THEIR DISCUSSION

In Fig. 1 concentration dependences of ζ -potential of *Cherkasskogo* Na^+-montmorillonite in solutions of NaCl, $CaCl_2$ and of $Cr(NO_3)_3$ have been shown. The comparative analysis of these dependences indicates the regular decrease of negative value of ζ-potential as a result of the growth of electrolyte concentration and charge of counter ion.

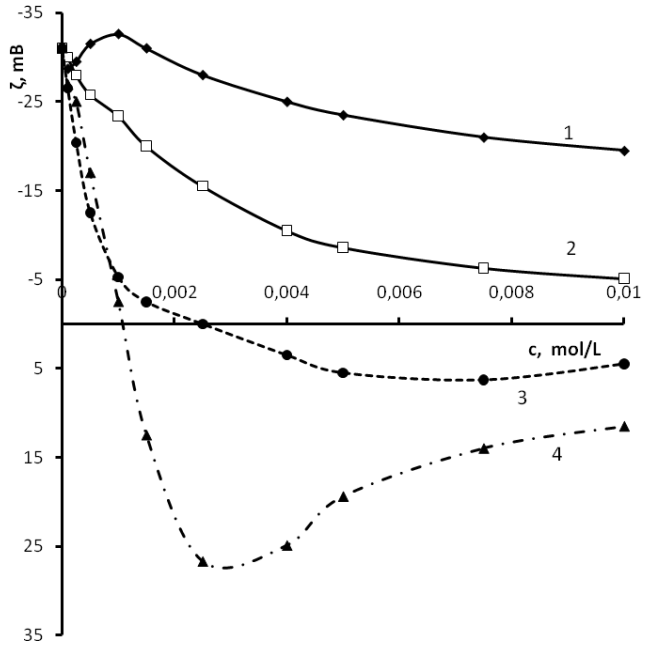


Fig. 1. The concentrational dependences of ζ –potential of Na^+-montmorillonite in solutions of NaCl (1), $CaCl_2$ (2) and $Cr(NO_3)_3$ at pH 4.2 (3) and $Cr(NO_3)_3$ at pH 5.5 (4)

This confirms the rule of *Shults-Gardi* [12]. As one can see with concentration of $Cr(NO_3)_3$ is equal to $2{,}4\times10^{-3}$ mol/L and pH ~ 4.2, |-ζ|-potential decreases to zero and, passing though isoelectrical point (IEP), changes its sign into positive. At higher pH ~ 5.5 the dependence of ζ-potential on $Cr(NO_3)_3$ concentration (curve 4) acquires more abrupt movement. The effect of recharging of montmorillonite particles abruptly intensifies. For all this, ζ-potential achieves more high positive values and then gradually decreases with the growth of $Cr(NO_3)_3$ concentration.

As it is known [13-15], Cr (III) salts in aqueous solutions are strongly subjected to hydrolysis with formation of hydroxocomplex compounds. For example, the hydrolysis of nitrate chrome $[Cr(H_2O)_6]^{3+}3NO_3^-$ in aqueous solution proceeds in two stages: 1) $[Cr(H_2O)_6]^{3+} + H_2O \leftrightarrows Cr(H_2O)_5(OH)]^{2+} + H_3O^+$ and 2) $[Cr(H_2O)_5(OH)]^{2+} + H_2O \leftrightarrows [Cr(H_2O)_4(OH)_2]^+ + H_3O^+$. Taking into account that $Cr(OH)_3$ precipitation for 0.1-1.0 M solutions begins when pH is 4.0-4.9 [16], then it is possible to confirm that there is a sufficient amount of hydroxocomplex chrome ions, the type $[Cr_n(OH)_m(H_2O)_x]^{(3n-m)+}$ in solution.

Therefore, the recharging of MMT surface is conditioned not by Cr^{3+} ions but by hydroxyl complex ions which have high polarization and adsorption capabilities [6, 7, 17].

In order to study the mechanism of montmorillonite recharging in $Cr(NO_3)_3$ solutions, the dependences of stability and ζ-potential of dispersions of MMT upon pH medium at constant ion power (0.01 M) of background electrolyte (Fig.2) have been studied.

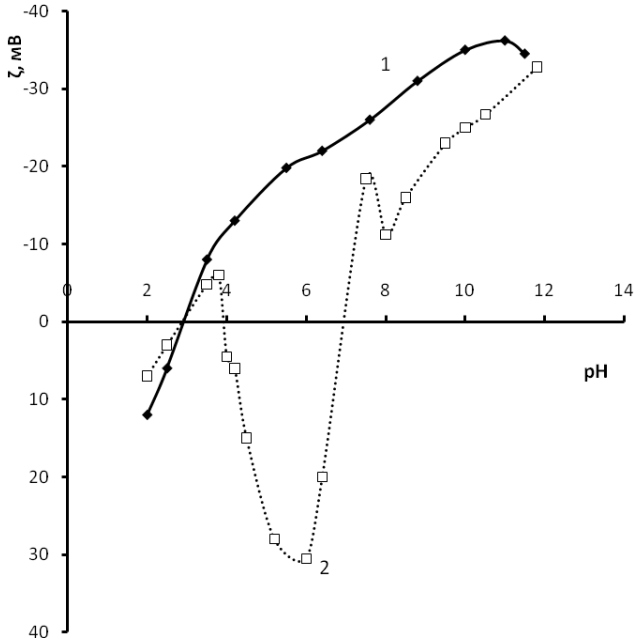
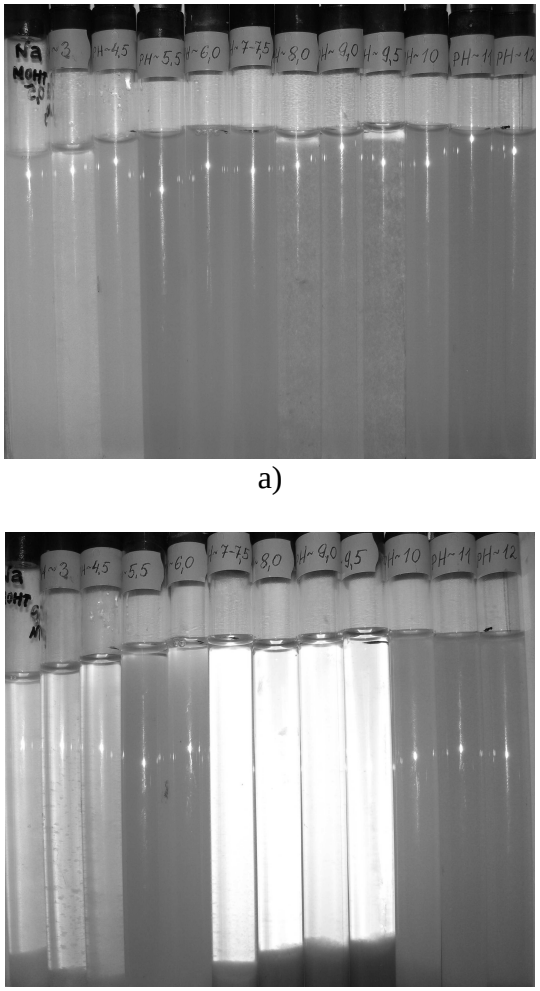


Fig. 2. The pH-dependences of ζ-potential of Na^+- montmorillonite in solutions of NaCl (1) and of $Cr(NO_3)_3$ (2)

For comparison, in Fig. 2, the dependence of ζ=f(pH) for the same dispersion in solution of electrolyte (NaCl) was adduced. The Fig.2 shows that the dependence of ζ=f(pH) is characterized by IEP at pH ~ 3 (curve 1), but when pH is higher, then MMT particles become negatively charged.

After introduction of $Cr(NO_3)_3$ into dispersion of MMT, pH-dependence becomes more complicated (Fig.2, curve 2). With the increase of pH, in the range of pH 2-12 values, three zones of stability (a, b, c) are observed. They alternate with three zones of coagulation (a′, b′, c′). In the ranges of these zones ζ-potential changes its charge. In acid medium of pH ~ 2-3, MMT particles are positively charged because of weak dissociation of its surface groups according to the principal type. For all that |+ζ|-potential is not high and co-ions of Al^{3+} subjecting to electrostatic repulsion of the surface are mainly distributed in the diffusive part of the double electric layer (DEL). In the range of pH ~ 3-3.8, |-ζ|-potential of montmorillonite changes in spite of the presence of counter ions in solution. It confirms that Cr^{3+} ions are not able to induce recharging of MMT surface and they are mainly distributed in the diffusive part of DEL. Thus, ions H^+ and OH^-

become potential determining before pH has reached 3,8. The exchange of $Cr^{3+} \leftrightarrow H^+$ and $Cr^{3+} \leftrightarrow Na^+$ only initiates the compression of DEL, the decrease of ζ-potential and stability of systems. Therefore the sign inversion of dispersion charge is conditioned by other causes.



a)

b)

Fig. 3. The zones of stability (a) and of coagulation after 4 hours (b) as result of interaction of Na-montmorillonite and $Cr(NO_3)_3$

It is interesting to note that as soon as pH approaches to 4.0, |-ζ|-potential of MMT abruptly decreases as to absolute value and again becomes positive. Interlacing of coagulation zone in DEL with stability zone of positively charged dispersion corresponds to this (see Fig. 3.).

The medium of pH 4.0-6.0 is characterized by rapid, stepped growth of positive ζ-potential and stability of dispersions. It is interesting that DEL coincides with pH of the beginning of precipitation of chrome hydroxide and the stability of positively charged dispersion extends nearly to pH full precipitation of $Cr(OH)_3$ (pH 6.8). It is evident, that this coincidence is not accidental, as at pH ~ 4.0-6.0, as a result of hydrolysis proceeding and complex formation, the state of chrome ions in solution abruptly changes.

Really, as it is seen from a number of works [17, 13-15], besides hydrolysis, in the solutions of Cr(III) salts, the phenomena of comlexformation and also the processes of condensation and polymerization (olification and ageing) take place. This results in the formation of multinuclear chrome compounds. Such processes are accompanied not only by the change of hydrocomplex ions and solution colouring but by the increase of their molecular mass.

According to [30] the process of dimerization of hydropentaqua chrome ions takes place according to the following scheme: $2[Cr(H_2O)_5OH]^{2+} \leftrightarrows [Cr_2(H_2O)_8(OH)_2]^{4+} + 2\ H_2O$, with the constant of hydrolysis $K_2=10^4$ mol/L. The further polymerization and hydrolysis are also possible but they proceed very slowly at the room temperature. For example: $5[Cr(H_2O)_6^{3+}] \rightarrow [Cr_2(H_2O)_8(OH)_2]^{4+} + [Cr_3(H_2O)_9(OH)_4]^{5+} + 6H_3O^+ + H_2O$

As it was shown in the work [17], the replacement of water molecules in the internal coordinational sphere of hydrated metal ion into hydroxyl ion abruptly raises the adsorption of this ion on the surface of different chemical compositions.

It is connected with the growth of polarization of complex ions and with the decrease of their hydration. It was shown in the work of Matievich [17] that ion exchange adsorption of such polymeric complex ions, for example, chromic [18, 6, 10], supplemented by specific one, is able to exceed in several times the capacitance of mineral exchange.

Consequently, the most possible reason of sign inversion of MMT charge and the emergence of stability zone of positively charged sol is a super equivalent specific adsorption of polymerized ionic forms of chrome from solution. At the same time, the stepped growth of positive ζ-potential of MMT particles with the increase of pH (Fig. 2) can be explained by successive adsorption of monomeric and dimeric forms of hydroxyl complex ions of chrome with the growth of their basicity. This conclusion is fully confirmed by the results of the work [19].

The further change of ζ-pH dependence of dispersions in chrome solutions is probably, determined by the character of dissociation of surface MMT groups and by the conversions (transformations) of adsorbed polymerized products of hydrolysis [13-15].

Thus, 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 next, the third recharging of MMT surface takes place. This is accompanied by the new zone of coagulation (b′) and by the zone of dispersion stability (c) with negative charge sign, in spite of the fact that the dissolution of hydroxide chrome, according to official data [16], begins at pH = 12. It can be supposed that polynuclear chrome complexes are stable in the narrow range of pH ~ 4.5-6.5. So, it is quite possible, that the recharging is connected with decomposition and desorption of polymeric chrome complexes.

The successive dissociation of Si-OH and Al-OH – groups, which increases the negative charge of MMT particles, also assists, in recharging of MMT surface. Simultaneously with this, the processes of further transformation of adsorbed product of hydrolysis are unavoidable. In the range of pH ~ 7.0-10.0 the depolymerization of $Cr_n(OH)_m$ is very likely, predominating. Leading with pH ~ 8.0, this process is very likely intensified with the formation of anions – $[Cr(OH)_6]^{3-}$ and $[CrO_4]^{2-}$. The abrupt change of |-ζ|-potential corresponds

to this. Here, the dissociation of Al-OH – groups, which finishes at pH ~ 11.0, also makes its contributions. The consequence of these processes is the emergence of maximum stable zone of negatively charged dispersion (c). On the other hand, it is known [27, 30-32], that with the increase of pH and the basicity of solution, $Cr(NO_3)_3$, OH–ions are able to introduce themselves into internal coordinate sphere of complex chrome ions with sign inversion of their charge, As a result, the adsorption of negatively charged complex chrome ions (which were formed) on positively charged MMT surface can also be one of the reason of the third recharging of particles and the growth of |-ζ|-potential up to pH ~ 11,0.

The following decrease of ζ-potential is undoubtedly connected with the growth of ionic strength of solution by hydroxyl-ion and compression of DEL. Set forth data are in good agreement with the changes of dispersion stability (Fig.3, photo).

These stable positively charged dispersions can be used for the following adsorption and strong fixation of anionic dyestuffs with the aim of obtaining dyed fillings for leather semi-finished items.

IV CONCLUSIONS

In order to elucidate the mechanism of montmorillonite recharging in the solutions of $Cr(NO_3)_3$ and setting up the zones of stability and coagulation of dispersions the dependences of ξ-potential and stability of MMT dispersions in mentioned solutions on pH medium and concentration of chrome compounds have been studied. With the increase of pH, in the interval of pH meanings 2-12, three zones of stability are observed, which alternate with three zones of coagulation. Within the limits of these zones ξ-potential change its sign three times. 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 also by the character of ionization of hard phase groups. It has been shown that recharging of MMT surface and appearance of the second zone of stability of positively charged sol are conditioned by excess-equivalent adsorption of polymerized ionic forms of chrome from solution. Convincing argument has been obtained concerning the fact that recharging of MMT surface cannot be caused by simple adsorption of Cr^{3+} ions, but by the products of their hydrolysis.

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Olena Mokrousova, Vasil Moraru. Ar Cr(III) savienojumiem realizētas montmorillonīta modificēšanas ietekme uz tā dispersiju elektrokinētiskajām īpašībām.
Lai izskaidrotu montmorillonīta (MMT) pārlādēšanās mehānismu $Cr(NO_3)_3$ šķīdumos un noteiktu dispersiju koagulācijas un stabilitātes zonas, šajā publikācijā pētīta ξ-potenciāla un MMT dispersiju stabilitātes atkarība no vides pH un hroma savienojumu koncentrācijas. Ir iegūtas Na^+ montmorillonīta koncentrācijas atkarības no ζ-potenciālu NaCl, $CaCl_2$ un $Cr(NO_3)_3$. Konstatēts, ka ζ-potenciāla ar negatīvo vērtību nepārtrauktā samazināšanās ir saistīta ar elektrolītu koncentrācijas pieaugumu un pretējo jonu lādiņa palielināšanos. Palielinot pH robežās no 2 līdz 12, novērojamas trīs stabilitātes zonas, kuras mijās ar trim koagulācijas zonām. Šo zonu robežās ξ-potenciāls trīs reizes maina savu zīmi. Noskaidrots, ka lādiņa zīmes maiņu uz MMT virsmas izraisa nevis vienkāršie Cr^{3+} joni, bet to hidrolīzes produkti. Trīskārtīga MMT ξ-potenciāla zīmes maiņa $Cr(NO_3)_3$ šķīdumā un atbilstošā dispersijas stabilitātes un koagulācijas zonu izmaiņas varētu izskaidrot ar hidrolīzi, kompleksu Cr^{3+} jonu

izveidi un cietās fāzes grupu jonizācijas mehānisma raksturu. Darbā pierādīts, ka MMT virsmas lādiņa pārlādēšana un otrās stabilitātes zonas parādīšanas pozitīvi lādētam solam ir saistītas ar polimerizētu hroma jonu ekvivalentu adsorbciju no šķīduma. Iegūtas pozitīvi lādētās stabilas dispersijas var izmantot anjonu krāsvielu adsorbcijai un stingrai fiksācijai ar turpmāku mērķi iegūt efektīvās krāsvielas ādas pusfabrikātu apstrādei.

Олена Мокроусова, Васил Морару. Влияние модификации монтмориллонита с соединениями Cr (III) на электрокинетические свойства их водных дисперсий.

В работе, с целью выяснения механизма перезарядки монтмориллонита (ММТ) в растворах $Cr(NO_3)_3$ и уставления зон устойчивости и коагуляции дисперсий, изучены зависимости ξ- потенциала и устойчивости дисперсий ММТ в указанных растворах от pH среды и концентрации соединений хрома. Зависимости ζ-потенциала от концентрации Na^+ монтмориллонита в растворах NaCl, $CaCl_2$ и $Cr(NO_3)_3$ были получены. Найдено, что непрерывное уменьшение отрицательного значения ζ-потенциала связано с концентрацией электролита и увеличением заряда противоположных ионов. С увеличением pH в интервале значений 2-12.0 наблюдаются три зоны устойчивости, которые чередуются с тремя зонами коагуляции. В пределах этих зон ξ- потенциал трижды меняет свой знак. Установлено, что перезарядку поверхности ММТ способны производить не простые ионы Cr^{3+}, а продукты их гидролиза. Трёхразовое изменение знака ξ-потенциала на поверхности ММТ в растворе $Cr(NO_3)_3$ и соответствующее изменение стабильности дисперсий и их зоны коагуляции может быть объяснено гидролизом, образованием комплексов ионов Cr^{3+} и характером механизма ионизации групп в твёрдой фазе. В работе показано, что перезарядка поверхностного заряда ММТ и появление второй зоны стабильности у положительно заряженной дисперсии может быть связано с эквивалентной адсорбцией полимеризованных ионов хрома. Полученные стабильные положительно заряженные дисперсии могут быть использованы для адсорбции и прочной фиксации анионных красителей, с целью получить эффективные красители для кожи и её полуфабрикатов.