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Polyelectrolyte Complexes of Potassium Humates and Poly(diallyldimethylammonium chloride) for Fixing Sand Soil

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Abstract—The preparation of electrostatic complexes between a cationic polymer, poly(diallyldimethylammonium chloride), and natural polyanions, potassium humates, is described. The polycomplexes remain stable in the aqueous solution for a long time (up to 3 months) or form precipitates that can be easily resuspended when the sample is shaken. When aqueous solutions/suspensions of polycomplexes are applied on the sand surface, polymer-sand coatings (crusts) are formed, the mechanical strength of which increases with increasing content of poly(diallyldimethylammonium chloride) in the polycomplex. The greatest resistance to water (water resistance) is exhibited by crusts with a high proportion of mutually neutralized sections of both polymers. For such crusts, sand loss during watering is in the range from 0 to 2%. The developed multicomplex formulations can be used to stabilize soil and ground against water and wind erosion.

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INTRODUCTION

Land degradation processes are taking place all over the world. These are global social, economic, and environmental problems of our time caused by climate change and anthropogenic activities [1, 2]. The main cause of degradation is the destruction of the upper fertile layer of the earth (soil layer) under the influence of water and wind, in other words, water and wind erosion [3, 4]. Various approaches are used to stabilize the soil, including mechanical [5, 6], biological [7, 8], and chemical [9, 10]. The latter are of particular interest owing to the commercial availability of the components used to obtain stabilizing formulations, their low cost, and the relatively simple technology of applying formulations on the soil surface [10].

Polymers with ionic groups (cationic, anionic, or both) that can efficiently adsorb on the surface of bulk objects often act as chemical soil stabilizers [11, 12]. The experience accumulated to date for polymer binders shows that an optimal result can be achieved if the polymers contain extended hydrophilic and hydrophobic sections [13, 14]. The former interact with hydrophilic regions on the surface of soil and ground particles and stick them together. The latter cause the same effect in relation to hydrophobic sections. This leads to a sharp increase in binding efficiency and, at the same time, ensures uniform distribution of the binder in the soil/ground layer. This condition is ideally satisfied by interpolyelectrolyte complexes

(PECs)—products of the cooperative interaction of oppositely charged polymers, cationic and anionic [14–16]. Depending on the charge-to-charge ratio of the components, two types of PEC can be obtained: water insoluble *stoichiometric polycomplexes* and *non-stoichiometric polycomplexes* bearing an excess positive or negative charge which are soluble in water and water-salt solutions [17, 18].

This work describes the formation and properties of polycomplexes formed by a cationic polymer, poly(diallyldimethylammonium chloride) (CAT), and polyanions, potassium humates (ANI). Synthetic CAT is widely used as a flocculant for wastewater treatment [19]; natural ANI is used as fertilizers for soils with a low content of organic substances and immunostimulants for plants [20, 21]. The macromolecule of quaternized polyamine CAT is positively charged at all pH values of the aqueous solution. ANIs contain several types of functional groups, including carboxyl (the main component), phenolic, and primary/secondary amino groups; the total charge of the ANI depends on the pH of the solution and becomes more and more negative upon transition from the acidic to neutral and then to alkaline region [21, 22]. Particular attention is paid to the use of CAT–ANI polycomplexes of various compositions for creating protective (anti-erosion) coatings on unstructured loose ground, quartz sand. Varying the composition of the polycomplex allowed one to optimize the ratio of the polymer components

of the formulation for fixing the soil. In earlier works [12, 14], the authors were limited, as a rule, to stoichiometric complexes; only the chemical nature of the polymers forming the complex changed.

EXPERIMENTAL

CAT with $M_w = (400–500) \times 10^3$ (Sigma-Aldrich), ANI with $M_w = 9.9 \times 10^3$ [23] (Humintech, Germany), and crystal hydrates of sodium hydrogen phosphate and dihydrogen phosphate (Himmed, Russia) were used without preliminary purification. The concentration of CAT was expressed in terms of the number of moles of cationic groups per liter of solution [CAT]. The molar concentration of anionic groups of potassium humates was previously determined [23] and corresponded to $[COO^-] = 2.6 \times 10^{-4}$ mol/L in a 0.01% aqueous solution of ANI (pH 7). Quartz sand with a rounded grain size of 0.1–0.2 mm was purified from impurities by numerous washes in double-distilled water.

PEC compositions for sand processing were prepared by simple mixing of the corresponding volumes of 1% CAT and ANI in weakly saline buffer solutions with pH 7. The composition of the polycomplexes Q was expressed in terms of the ratio of the molar concentrations of the blocking polyelectrolyte ionized at pH 7 taken in deficiency to the ionized groups of the lyophilizing polyelectrolyte taken in excess.

The hydrodynamic diameter of particles was measured by dynamic light scattering on a ZetaPlus instrument (Brookhaven, United States), and their electrophoretic mobility (EPM) was studied by laser microelectrophoresis on a ZetaPlus instrument (Brookhaven, United States). To process the results, software provided by the manufacturer of the device was used.

X-ray diffraction studies were performed on an URD-6 diffractometer (Germany) using nickel-filtered CuK_α radiation. Microphotographs were taken on a JEOL JSM-6380LA scanning analytical electron microscope, Japan) at an accelerating voltage of 20 kV at the Interfaculty Laboratory of Electron Microscopy, Faculty of Biology, Moscow State University.

The strength characteristics of the polymer-sand crust were measured by the penetration method (cone immersion) using a Rehbinder conical plastometer, Russia [24]. Sandy soil samples with a protective layer on the surface were prepared as follows. Quartz sand (60 g) was placed in plastic containers, the height of the soil layer was 5 cm, and the surface area was $\sim 16 \text{ cm}^2$. Using a spray gun, a 1% solution/suspension of the polycomplex with a flow rate of 3 L/m² was applied on the surface. The samples were dried to a constant weight in air.

All the results presented are average values obtained by three repetitions of each experiment.

RESULTS AND DISCUSSION

The formation of polycomplexes was monitored by recording the charge of particles in the system. The experiments were carried out in phosphate buffer with pH 7. Under these conditions, the size (hydrodynamic diameter) of the ANI particles was 130 nm with an electron phase transition (EPT) of $-3.9 \times 10^8 \text{ m}^2/\text{Vs}$. The addition of the KAT solution to the ANI solution led to the neutralization of the polyanion, and the EPT equal to zero was achieved at $[CAT] : [ANI] = 1$ (Fig. 1, curve 1), that is, upon the mutual neutralization of all charged groups of CAT and ANI in solution. A subsequent increase in the concentration of CAT gave the particles of the complex a positive charge; the limiting value of EFT = $+4 \times 10^8 \text{ m}^2/\text{Vs}$ was achieved at $[CAT] : [ANI] = 2.1$; pH 7.

Curve 2 (Fig. 1) reflects a change in the EPT of PEC particles during back titration, when the ANI solution is added to the CAT solution. When $[ANI] : [CAT] < 1$, particles of the polycomplex carried a negative charge, the neutralization of the complex was achieved at $[ANI] : [CAT] = 1$, and the region of $[ANI] : [CAT] > 1$ corresponded to a polycomplex with an excess negative charge. Thus, the formation of an electrically neutral stoichiometric polycomplex with $[ANI] : [CAT] = 1$ did not depend on the mixing order of the initial components of the complex.

The electrostatic nature of the interaction was confirmed by scanning electron microscopy and X-ray phase analysis. Figure 2a shows a micrograph of the film obtained by applying a suspension of stoichiometric PEC with $Q = 1$ on the glass plate, followed by drying for 3 days. The photograph clearly shows numerous micro-sized objects that are removed when the resulting film is washed with water (Fig. 2b).

On the diffraction pattern of the sample PEC with $Q = 1$ (Fig. 3, curve 1), along with the amorphous halo of the polycomplex, narrow reflections are present at $2\Theta = 28.4$ and 40.6° . The same reflections are observed on the diffraction pattern of KCl salt crystals (Fig. 3, curve 2).

Thus, the formation of polycomplexes of potassium humates and poly(diallyldimethylammonium chloride) is accompanied by the release of a significant amount of small counterions into the solution (K^+ and Cl^-) and the formation of potassium chloride crystals during drying of the sample. These crystals easily dissolve in water and are removed from the surface of the polymer film when it is washed with water.

The dispersion stability of the polycomplexes was monitored by dynamic light scattering. Table 1 shows the values of the hydrodynamic diameter and the values of the EPT of the PEC particles 15 min and 3 months after preparation. The composition of the polycomplexes is presented as the ratio $Q(+) = [ANI] : [CAT]$ for negatively charged polycomplexes with excess anionic ANI and $Q(-) = [CAT] : [ANI]$

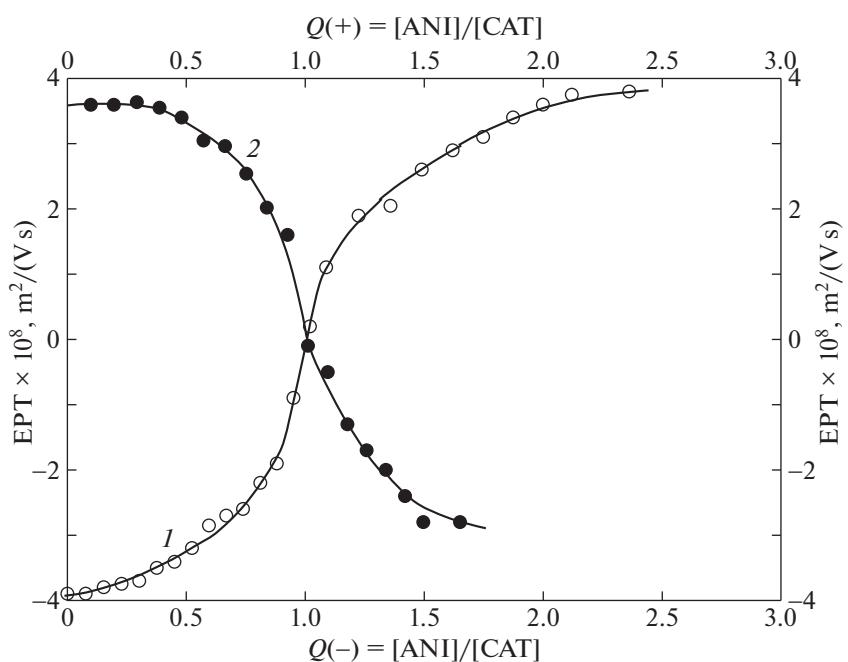


Fig. 1. Dependence of the EPT of particles in (1) 0.01% ANI solution on the ratio of functional groups $Q(-) = [\text{CAT}]/[\text{ANI}]$ and (2) in 5×10^{-3} M CAT solution on the ratio of functional groups $Q(-) = [\text{CAT}]/[\text{ANI}]$. Phosphate buffer, 2×10^{-3} M, and pH 7.

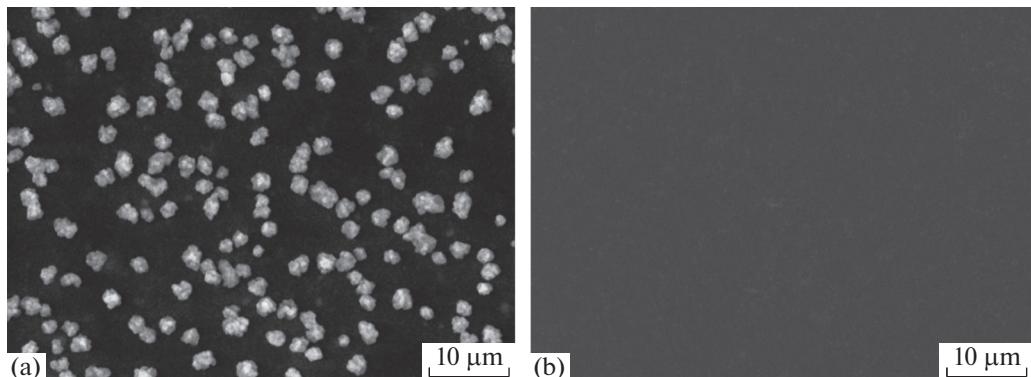


Fig. 2. Microphotographs of the films cast from 1% dispersions/suspension of (a) the equimolar mixture ANI/CAT with $Q = 1$ and (b) the equimolar mixture ANI/CAT after washing in water.

for positively charged PEC with excess cationic CAT. Composition $Q = 1$ corresponds to a stoichiometric polycomplex with an equimolar charge-to-charge ratio of components.

Before measuring the size and charge, the stratified samples with $Q(-) = 0.6$ and 0.8 and $Q(+) = 0.6$ and 0.8 were shaken manually for three to four minutes. After shaking, the sample with $Q = 1$ formed a suspension with a particle size beyond the technical capabilities of the photometer. Other samples were homogeneous light brown solutions that did not require additional dispersion. As follows from Table 1, the size of the PEC particles increased with decreasing absolute

value of their charge. However, in all cases (except the sample with $Q = 1$), their size did not exceed 500 nm. After 3 months, the picture was preserved: during this time, the particle size in homogeneous solutions and solutions subjected to dispersion practically hardly changed.

The following procedure was used to study the stabilizing properties of PEC. The sand (100 g) was placed in a Petri dish, and 25 mL of a 1% aqueous solution/suspension of the starting polymers, CAT or ANI, or polycomplexes of different composition was applied on top. The resulting samples were air-dried for 3 days. Figure 4 shows the initial sand and the sand

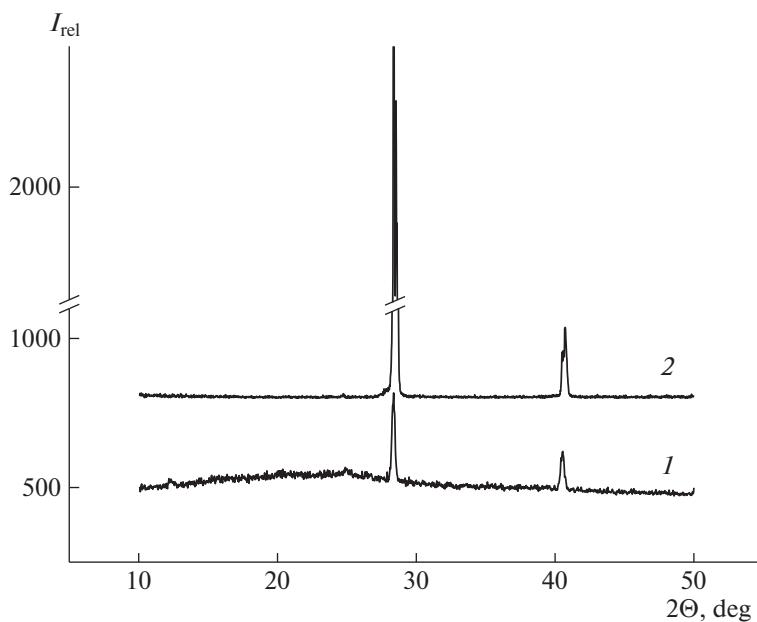


Fig. 3. X-ray diffraction patterns of (1) the dry polycomplex with $Q = 1$ and (2) potassium chloride.

treated with PEC $Q(+)$ = 0.6. After the Petri dish was lifted at one edge by an angle of 25° , the untreated sand moved to the opposite edge of the cup (Fig. 4a). The sand treated with the polymer formulation did not move and did not spill out of the cup even after it was moved to the vertical position (Fig. 4b) owing to formation of a surface polymer-sand crust. A photograph of the crust taken from the sand surface is shown in Fig. 4c.

The strength of the polymer-sand crust was measured by the penetration method using a Rehbinder

conical plastometer. It was shown that such a characteristic of composite coatings (penetration strength) reflects well the effectiveness of their use as anti-erosion screens [25, 26]. The strength of the crust composed of sand and ANI was 1.5 ± 0.3 kg/cm² (Table 2). Crusts formed from the sand and polycomplexes had a significantly higher strength, which progressively increased with an increase in the fraction of CAT in the polycomplex and reached a maximum value of 730 ± 40 kg/cm² for the crust formed from the sand and individual CAT. This behavior of the crusts is due to the fact that the surface of the sand carries a negative charge [27], and for their binding to large and strong aggregates (crusts), a polymer with a high density of cationic groups is required.

Another important parameter of crusts is water resistance, which reflects their capacity for long-term protection of the soil in the case of possible rainfall. During the experiments, Petri dishes filled with 100 g of sand and treated with ANI, CAT, or polycomplexes were tilted by 45° and poured with water for 15 min in a pulsed mode (simulating sprinkling) from a distance of 20 cm. The total amount of applied water was 200 mL per sample.

The initial unstructured sand (before treatment with a polymer formulation) after sprinkling lost 55 ± 3 g of sand (Table 2). After ANI treatment, the amount of washed sand increased to 58 ± 5 g; after CAT treatment, it increased to 80 ± 6 g. Probably, this behavior of the polymer-sand crust based on individual polymers is associated, on one hand, with the high solubility of ANI and CAT in water and the rapid leaching of polymers from the interparticle space and, on the other hand, with the hydrophilization of the

Table 1. The hydrodynamic diameter and electron phase transition of particles in 0.01% dispersions/suspensions of polycomplexes in 2×10^{-3} M phosphate buffer (pH 7)

PEC composition	Diameter, nm	EPT $\times 10^8$, m ² / (Vs)
$Q(-) = 0.2$	135/140	-3.5/-3.5
$Q(-) = 0.4$	140/150	-2.9/-3.0
$Q(-) = 0.6$	190 (p.s.)/200 (p.s.)	-2.2/-2.1
$Q(-) = 0.8$	480 (p.s.)/470 (p.s.)	-1.3/-1.3
$Q = 1$	p.s./p.s.	0/0
$Q(+) = 0.8$	510 (p.s.)/500 (p.s.)	0.9/1.0
$Q(+) = 0.6$	340 (p.s.)/350 (p.s.)	2.4/2.5
$Q(+) = 0.4$	220/230	3.1/3.2
$Q(+) = 0.2$	205/200	3.9/3.9

In the numerator, after 15 min; in the denominator, after 3 months. p.s. implies phase separation (particle size after shaking).

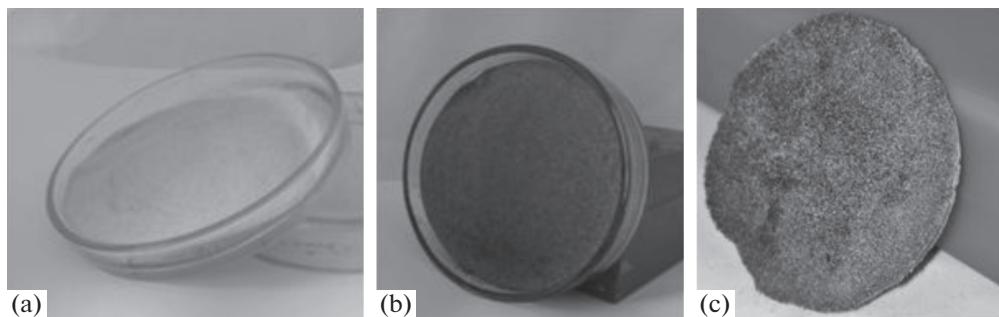


Fig. 4. Photos of (a) the initial sand, (b) the sand treated with PEC with $Q(+)$ = 0.6, and (c) the surface of the polymer-sand crust.

surface of particles by adsorbed polymers and the improved slip of modified particles relative to each other. Processing of the sand with multicomplex formulations led to the formation of protective coatings significantly reducing or completely blocking soil washout. The water resistance of the polymer-sand crust strongly depended on the composition of the polymer formulation. The crusts formed from polycomplexes with a high proportion of mutually neutralized sections of both polymers turned out to be the most resistant to sprinkling: from $Q(-)$ = 0.6 through Q = 1 and further to $Q(+)$ = 0.4. For such polymer-sand crusts, sand loss during sprinkling ranged from 0 to 2%. Polymer-sand crusts with a high proportion of uncompensated charge $Q(-) \leq 0.4$ and $Q(+) \leq 0.2$ lost noticeably more sand. Obviously, the stability of the films in the presence of water was associated with the presence of extended hydrophobic blocks in the PEC represented by sequences of mutually neutralized fragments of the chains of both polymers. Such PECs were bound to sand particles owing to ionic and hydrophobic contacts that stabilized polymer-sand crusts in an aqueous environment. Reduction in the proportion of

hydrophobic blocks in the PEC (decrease in Q) gave the polycomplexes solubility in water and led to the destruction of polymer-sand crusts upon sprinkling.

Thus, water-resistant composite coatings on the surface of bulk material, quartz sand, can be formed using a combination of water-soluble macromolecules: natural polyanions, potassium humates, and synthetic polycations, poly (diallyldimethylammonium chloride). The mechanical strength of the polymer-sand crusts reflecting the efficiency of sand binding with polymers increases with increasing polycation content in the complex. Protective coatings based on the majority of PEC, unlike individual polyelectrolytes, prevented 90–100% of the sand from being washed away from an inclined surface during heavy sprinkling. The greatest water resistance was shown by the polymer-sand crusts based on positively charged compositions with an average and high degree of charge compensation.

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