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Application of Interpolymer Complexes of Novel Poly(ampholyte-electrolyte) as Soil Structuring Agents and for Extraction of Radioactive Strontium

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Abstract

Novel linear copolymer exhibiting poly(ampholyte-electrolyte) behavior was involved into complexation reaction with anionic, cationic and nonionic polymers. Interpolymer complexes were prepared by mixing of aqueous solutions of individual polymers with concentration varying from 10^{-1}-10^{-4} mol·L^{-1}. The formed interpolymer complexes showed the soil structuring effect and the ability to extract the radioactive strontium from the polluted topsoil of Semipalatinsk Test Site. The mechanism of soil stabilization or aggregation was explained by the fact that the soil particles bearing negative charges interact with positively charged "loops" of interpolymer complexes resulting in the formation of so called "cobweb" (or protective crust) on the soil surface. The effective capturing of radioactive strontium by interpolymer complexes may be connected with formation of more stable ternary polymer-metal complexes. It was demonstrated that: i) interpolymer complexes are the most effective soil structuring agents than that of individual components; ii) the optimal concentration of interpolymer complexes for soil aggregation is 10^{-2} mol·L^{-1}; iii) pouring of soil surface by interpolymer complexes is more effective than the splashing; iv) the treatment of the soil by already pre-existing interpolymer complexes is most effective than the successive treatment of the soil by individual components; v) the best soil structuring properties were shown for interpolymer complexes stabilized by H–bonds and intra salt bonds.

Introduction

It is well known that the territory (70 sq. km) of the Semipalatinsk Test Site (STS) has been polluted by radionuclides mainly as a result of more than 400 atmospheric, underground and above-ground nuclear explosions over a period of 40 years. Survey of residual radioactivity in the soil at ten STS areas showed that a great number of the long-lived radionuclides Plutonium-239, 240, Strontuim-90 and Cesium-137 are concentrated in the depth of soil layer 0-8 cm [1,2]. Yamamoto *et al.* [3] presented some evidence that the residual radioactivity within the STS is tightly bound to the soil as a result of extreme heating and melting of the soils during the tests. According to [1] the maximal amount of radionuclides is accumulated on the fine soil particles having 0.05-1.0 mm size. Wind erosion is responsible for suspension of polluted soil particles in the air and further spreading of contamination far away causing the secondary pollution. In this connection the development of innovative materials and technology that are able to prevent the wind migration of polluted soils is very important to protect the population, flora and fauna of SNTS from the harmful effects.

One of the effective ways to fight against the spreading of radioactive matters is coating of polluted soil particles by polycomplexes – the products of cooperative interactions of functional macromolecules [4-6]. Polycomplexes are water-insoluble, moisture and gas permeable substances leading to formation of protective crust [7,8]. Polycomplexes are also able to accumulate radioactive and heavy metal ions via formation of ternary polymer-metal complexes [9]. Soil layer treated by polycomplex binders can easily be assembled mechanically and then decontaminated by special treatment [10].

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Interpolyelectrolyte complexes (IPEC) of hydrolyzed polyacrylonitrile and poly-N,N-dimethyldiallylammonium chloride were used for sedimentation and cementation of radioactive dusts of Chernobyl disaster [11]. Authors [12,13] investigated the sorption of strontium and cesium from the soil by polyacrylic acid-poly-N,N-dimethyldiallylammonium chloride complexes. It was found that the treatment of the soil by IPEC's solutions leads to aggregation of soil particles but the distribution coefficient of radioactive cesium in the soil is independent on the presence of structuring agents.

Earlier [14-17] we have carried out model and real field experiments on applicability of polycomplexes for structuring of STS soil particles in order to prevent the wind and water migration of radionuclides. Both water soluble polymers – polyacrylic acid (PAA), polyethylene glycol (PEG), poly-N,N-dimethyldiallylammonium chloride (PDMDAACl) – and H–bonded interpolymer complexes based on PAA-PEG and IPEC based on PAA-PDMDAACl were used as soil structuring agents.

In the present communication the prevention of wind and water migration of STS topsoil polluted by radioactive strontium with the help of interpolymer complexes based on novel poly(ampholyte-electrolyte) – copolymer of carboxyethyl-3-aminocrotonate and acrylic acid (CEAC-AA) is considered.

Materials and Methods

Materials

Polyacrylic acid (PAA) with $M_w = 450 \cdot 10^3$; polyethylene glycol (PEG) with $M_w = 600 \cdot 10^3$, poly-N,N'-dimethyl-N,N'-diallylammonium chloride (PDMDAAC) with $M_w = 6300$, polystyrene sodium sulfonate (NaPSS) with $M_w = 3 \cdot 10^5$ and polyvinyl alcohol (PVA) with $M_w = 1 \cdot 10^3$ were purchased from "Polyscience" (USA) and used without purification. Poly-N-vinylpyrrolidone (PVP) with $M_w = 8.5 \cdot 10^4$ (BDH, Great Britain); polyethyleneimine (PEI) with $M_w = 1 \cdot 10^4$ (Russia) and polyhexamethylene guanidine (PHMG) ($[\eta]$ = 0.28 dl/g in 0.002N HCl) (Russia) were commercial products and used without additional purification.

Copolymer of carboxyethyl-3-aminocrotonate and acrylic acid (CEAC-AA) was synthesized by Michael addition reaction followed by radical polymerization in water-ethanol mixture (30:70 vol.%) in the presence of azobisisobutironitrile (AIBN) as initiator [18]. Ethyl-3-aminocrotonate (0.5 mol) and acrylic acid (0.5 mol) were put into the glass test-tube, then the AIBN (3 mg) and the solvent were added (the molar ratio of solvent and monomer mixtures was 1:1 mol/mol) at room temperature. The mixture was bubbled with argon for 5 min and thermostated at 70°C for 2-3 min. Polymer was washed out by acetone. The sample was dried in vacuum to constant mass. The composition of CEAC-AA determined by back potentiometric titration was equal to [CEAC]:[AA] = 38.8:61.2 mol.%.

Interpolymer complexes (IPC) were prepared by mixing of aqueous solutions of individual polymers with concentration varying from 10^{-1}-10^{-4} mol/L. Compositions of IPC were determined by potentiometric, conductimetric and viscometric methods [19].

Methods

Potentiometric and conductimetric titrations were carried out on pH/Conductivity Meter "Mettler Toledo MPS 227" (Sweden) at room temperature. Viscosity of polymer solutions was measured by Ubbelohde viscometer at 25±0.1°C. Radiological analyses were carried out at the Institute of Radiation Safety and Ecology (Kurchatov, Kazakhstan) by first counting the samples in Marinelli beakers using a coaxial, high purity Ge detector system to determine gamma-emitting radionuclide activity concentration.

Preparation of soil samples for analysis was carried out according to Refs. [21,22]. Specific for STS soil particles are loamy sand (with diameter of 0.25-0.05) and coarse dust (with diameter of 0.05-0.01). Soil samples were taken from the different zones of STS. Each sample was placed on the paper sheet as thin layer and was dried in box containing the filtered air. After drying it was weighed, placed on the paper sheet, and divided into four portions diagonally. Two opposite portions were placed into the box and kept as control sample. The rest parts were accurately mixed, then poured as thin layer and 25-30 g of soil was taken from the different parts of the sample.

Microaggregate state of soil was determined according to Savinov's "dry" method [20,21]. The sample was sifted carefully through the set of sieves with diameter of 10; 5; 3; 2; 1; 0.5 and 0.25 mm. Aggregates from the sieves were replaced into preliminary weighed porcelain cups. All sifted soil samples were divided into several fractions. Every fraction was weighed on technical balance and its content was determined in per cent.

The soil sample with known fractional content (aggregate composition) was treated by aqueous solutions of IPC with concentration of 10^{-2}; 10^{-3} and 10^{-4} $mol \cdot L^{-1}$. The treatment of the soil particles was carried out by two methods: the first method (I) is uniform splash of polymer solution; the second one (II) is pouring of soil surface by IPC solution. After treatment the soil samples were dried on the air during 3 days and then the aggregate composition of treated soil was determined by "dry sifting" method [20,21].

Maximal quantity of water that contains in the soil is called the capillary moisture capacity. Capillary tube with open two ends, 10 cm of length and 1 cm in diameter filled by soil sample was placed into the cup. The tube bottom was placed on the filter paper. The ends of filter paper were dipped into water. Water passes through the paper pores into the soil and the capillary saturation takes place. Every 10 minutes the tube was weighed on technical balance. Capillary moisture capacity (*CMC*) was determined by formula:

$$\%CMC = \frac{(m_2 - m_1)}{m_1} 100$$

where m_1 and m_2 are the masses (g) of dry and wet soil in the tube respectively.

$$m_1 = \frac{100a}{100 + W}$$

where a is the mass of air-dried soil in the tube, W is hygroscopic humidity, %.

The hygroscopic humidity in its turn was determined by drying of the soil sample up to constant mass in drying-stove at 110-150°C during 5 hrs. Then the soil sample was cooled and weighed on analytical balance. Hygroscopic humidity W was calculated as

$$W = \frac{a}{b} 100\%$$

where a is the mass of evaporated water (g); b is the mass of dry soil (g).

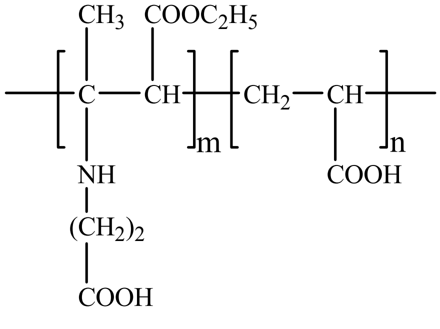
In order to determine the capillary movement of water in soil samples, an initial (untreated) and structured by interpolymer complexes (0.1 and 0.05% from soil weight) soil samples were placed into the glass tube with diameter 1 cm and length 10 cm. Ends of tubes were placed on filter paper. The corners of filter paper were contacted with water and the saturation of soil by water was carried out. The time that is necessary for raising of water from bottom to top up to 10 mm mark was fixed.

The quantity of water stable aggregates was determined by Savinov's method of "wet sifting" [20, 21]. Soil aggregates were placed on the set of sieves and sifted under the water. Sieves were shaken from time to time. The residual aggregates on the sieves were washed off into the large cups. The surplus of water was poured off, then aggregates were washed off to preliminary weighed small cups and dried on water bath up to air-dry state and were weighed. The weight of fraction gives the content of water stable aggregates of certain size.

Results and Discussion

According to chemical structure, CEAC-AA belongs to poly(ampholyte-electrolyte) type polymer because it exhibits both polyampholytic and polyelectrolytic character simultaneously (Scheme 1). The unique properties of poly(ampholyte-electrolyte)s have been outlined previously [22]. As distinct from classical polyelectrolytes and polyampholytes, poly(ampholyte- electrolyte)s have two negative and one positive charges in macromolecular chain. Due to presence carboxylic groups in the side chain CEAC-AA is able to form IPCs with PEG, PVP and PVA stabilized via hydrogen bonds (H–IPC). The potentiometric and conductimetric titration curves of aqueous solution of CEAC-AA (10^{-2} mol/L) by aqueous solution of PEG (10^{-1} mol/L) are represented in Fig. 1. The inflections corresponding to 1:1 mol/mol testify the formation of stoichiometric H–IPC.

The CEAC-AA can also be involved in complexation reactions with anionic and cationic polyelectrolytes and form so-called interpolyelectrolyte complexes (IPECs). Formation of IPECs with participation of CEAC-AA and anionic (NaPSS) and/or cationic (PDMDAAC, PEI, PHMG) polyelectrolytes proceeds through the destruction of the five-membered intraionic (or zwitterionic) bonds and formation of



$$-\left[\overset{CH_3}{\underset{NH(CH_2)_2COOH}{C}}-\overset{COOC_2H_5}{CH}\right]_m-\left[CH_2-\underset{COOH}{CH}\right]_n-$$

Scheme 1. Repeating monomeric units of CEAC-AA.

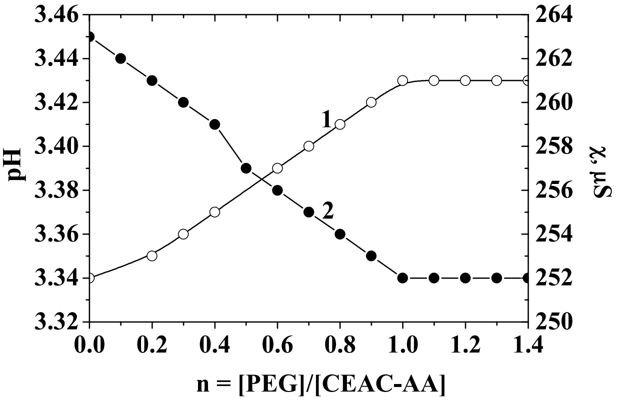


Fig. 1. Potentiometric (1) and conductimetric (2) titration curves of CEAC-AA by PEG solution. [CEAC-AA] = 10^{-2} mol·L^{-1}; [PEG] = 10^{-1} mol·L^{-1}.

interionic salt bonds. The stoichiometry of H–IPC and IPEC and their intrinsic viscosities are summarized in Table 1 together with characteristics of H–IPC and IPEC composed of PAA/PEG and PAA/PDMDAAC for comparison [15].

Table 1

The compositions and the intrinsic viscosities of H–PEC and IPEC

Interacting systems	Polycomplexes compositions	*[η]*, dL/g
CEAC-AA/PEG	1:1	0.13
CEAC-AA/PVP	2:1	0.14
CEAC-AA/PVA	1:1	-
CEAC-AA/PDMDAAC	1:1	0.11
CEAC-AA/PEI	1:1	0.08
CEAC-AA/NaPSS	2:1	0.11
CEAC-AA/PHMG	1:1	0.09
PAA/PEG	1:1	0.08
PAA/PDMDAAC	1:1	0.10

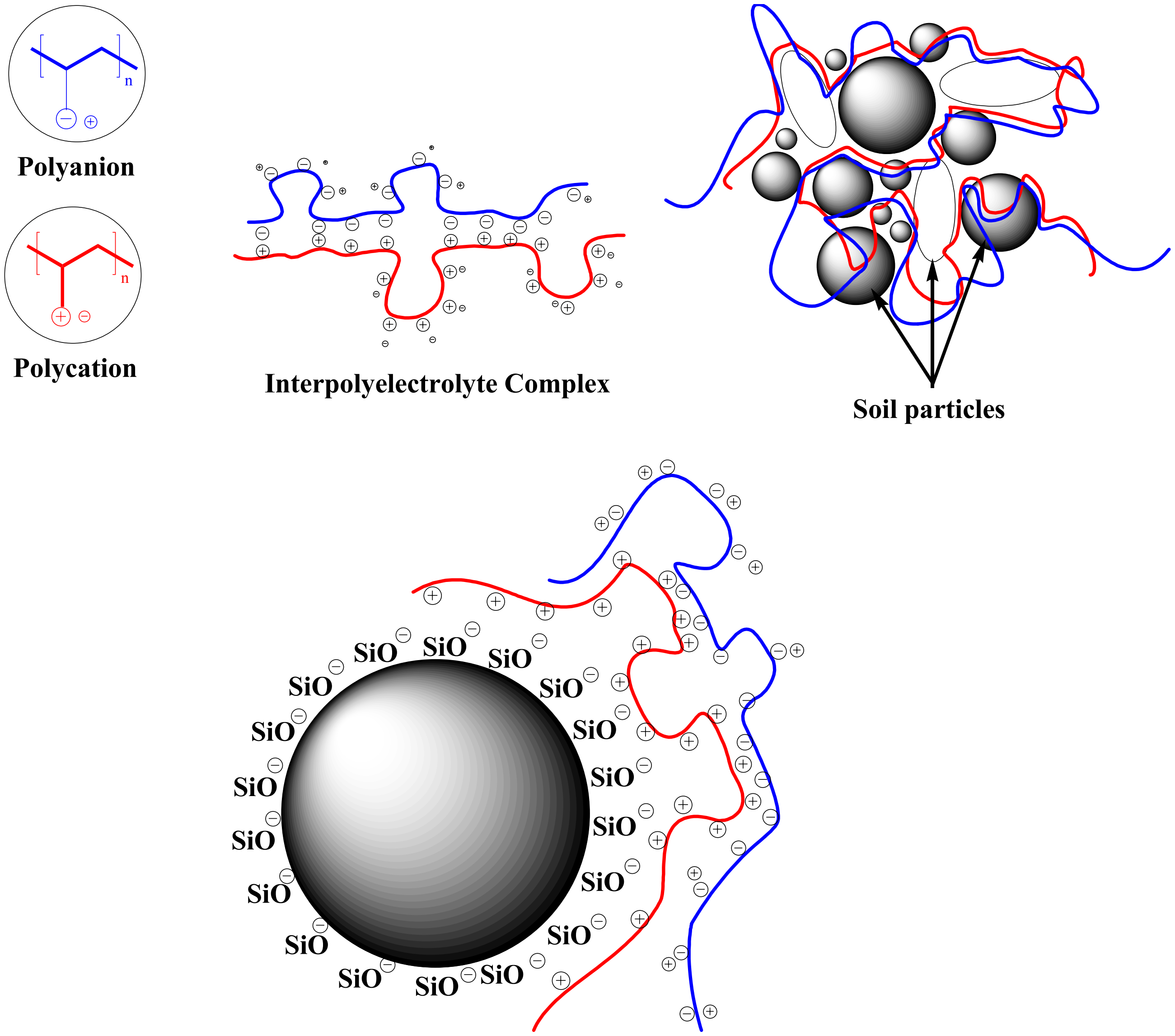
The soil structuring effectiveness of polycomplexes is arranged in the following sequence: CEAC-AA/PEG > CEAC-AA/PDMDAAC > CEAC-AA/PVP > CEAC-AA/PEI. Therefore for the further experiments two types of polycomplexes – H–IPC (CEAC-AA/PEG) and IPEC (CEAC-AA/PDMDAAC) were selected due to the best soil structuring properties. It was found that the optimal conditions for soil structuring are stoichiometric composition of polycomplex [CEAC-AA]:[PEG] = 1:1 at concentration $C = 1 \cdot 10^{-2}$ mol/L and pH = 3.0. In these conditions the soil fractions with diameter more than 0.25 mm increases from 37.3% (control) to 83.9 % when the pouring method II is used for soil treatment. While the effectiveness of uniform splash method I is only 70%. For the system consisting of [CEAC-AA]:[PDMDAAC] = 2:1 and [CEAC-AA]:[PDMDAAC] = 1:1 the average value of fractions with diameter > 0.25 mm was found to be 98.3% and 92.4% respectively (pouring method). Apparently the insufficient structural complementarity of CEAC-AA and PDMDAAC is responsible for the enrichment of complex composition by CEAC-AA component.

Thus the effectiveness of polycomplexes to aggregate the soil particles depends on the concentration of polycomplexes; the method of soil treatment (splash or pouring); molar ratio of interacting polymer components in polycomplexes; the order of soil treatment by polymer solutions. The obtained results are summarized as follows:

- Polycomplexes are the most effective soil structuring agents than that of individual components.
- The optimal concentration of polycomplexes for soil treatment is 10^{-2} mol·L^{-1}.
- Pouring of soil surface (method II) by polycomplexes is more effective than the splash method (method I).
- The treatment of the soil by already pre-existing polycomplexes is most effective than the successive treatment of the soil by individual components.
- The results of soil treatment by H–IPC solutions having different pH (8.0, 4.5 and 3.0) show that the acidification of H–IPC solutions causes the strengthening of structuring effect due to suppressing the dissociation of acidic components of poly(electrolyte-ampholyte) and formation of more stable H–IPC.

The mechanism of soil stabilization or aggregation by IPECs can be explained by Scheme 2. The soil particles can bear silanol groups Si–OH which are able to dissociate in dependence of soil pH. Treatment of soil particles by IPECs leads to binding of negatively charged particles with positively charged "loops" of IPECs [23]. As a result, so called "cobweb" is formed on the soil surface leading to formation of protective crust.

Capillary moisture and water stability of structured soil particles are given in Table 2. As seen from Table 2 the increase of capillary moisture capacity is larger for complexes of poly(electrolyte-ampho-



Scheme 2. Representation of formation of protective crust on the surface of soil particles.

lyte) than for complexes of homopolyelectrolytes. The same peculiarities are observed with respect to soil structuring effect, water stability of aggregated particles, content and activity of radioactive elements (Table 3). As follows from Table 3, the best soil structuring and strontium extracting properties exhibit the polycomplexes of poly(ampholyte-electrolyte) stabilized by hydrogen or salt bonds. This is probably connected with amphoteric character of CEAC-AA fragments having the pronounced affinity to soil particles. The effective capturing of radioactive strontium by polycomplexes of CEAC-AA and PEG may be connected with inclusion of strontium ions within spiral conformation of PEG and formation of more stable ternary polymer-metal complexes [15].

Table 2

Capillary moisture capacity of structured and unstructured soils

Treatment conditions of soil with diameter > 0.25 mm	Capillary moisture capacity, %
Untreated soil	20.65
Soil + 0.05% [CEAC-AA]:[PDMDAAC] = 2:1	42.17
Soil + 0.1% [CEAC-AA]:[PDMDAAC] = 2:1	70.82
Soil + 0.05% [PAA]:[PDMDAAC] = 1:1	32.13
Soil + 0.1% [PAA]:[PDMDAAC] = 1:1	54.17

Table 3

Comparison of some characteristics of soil samples before and after treatment by polycomplexes

The property	Polycomplexes	Effectiveness
		The number of water stable particles with diameter > 0.25 mm, %
Water stability of structured soil	Control	39.5
	[PAA]:[PDMDAAC] = 1:1	69.4
	Control	37.0
	[CEAC-AA]:[PDMDAAC] = 1:1	92.4
	[CEAC-AA]:[PDMDAAC] = 2:1	98.3
		The content of particles with diameter > 0.5 mm, %
Structuring effect of polycomplexes	Control	3.0
	[PAA]:[PDMDAAC] = 1:1	40.7
	[PAA]:[PDMDAAC] = 2:1	27.2
	Control	6.5
	[CEAC-AA]:[PDMDAAC] = 1:1	84.7
	[CEAC-AA]:[PDMDAAC] = 2:1	96.0
Activity of Sr-90 in soil samples after treatment by polycomplexes, Bq/kg	Control	3105
	[PAA]:[PEG] = 1:1	4567
	[CEAC-AA]:[PEG] = 1:1	6171
	Control	2822
	[PAA]:[PDMDAAC] = 1:1	3160
	[CEAC-AA]:[PDMDAAC] = 2:1	4260

Conclusions

The formation of interpolymer complexes of novel poly(ampholyte-electrolyte) with some anionic, cationic and nonionic polymers have been established. Stoichiometric complexes of CEAC-AA with polyethylene glycol (PEG) and poly-N,N'-dimethyl-N,N'-diallylammonium chloride (PDMDAAC) were found to be the most effective for structuring of radioactively polluted topsoil of Semipalatinsk Test Site. In addition the applied polycomplexes exhibit the ability to extract the radioactive strontium more effectively than the corresponding complexes of homopolyelectrolytes.

Acknowledgements

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