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Non-stoichiometric interpolyelectrolyte complexes: Promising candidates for protection of soils

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ABSTRACT

This paper describes electrostatic interaction (complexation) of two oppositely charged linear polyelectrolytes, an anionic poly(acrylic acid) and a cationic poly(diallyldimethylammonium chloride). In the excess of the anionic polymer, the complexation results in formation of non-stoichiometric interpolyelectrolyte complex (NIPEC) which is actually a block copolymer with hydrophilic regions represented by free (unbound) anionic units and hydrophobic fragments of mutually neutralized anionic and cationic units. A negative charge renders the colloidal stability to NIPEC species in aqueous solutions while ensuring their binding to heavy metal ions and positive dispersed particles. In the lab test, a NIPEC formulation (a NIPEC species aqueous solution), being deposited over a top of sod-podzolic soil with the aggregate size of 0.2 mm and less, ensures a protective NIPEC-soil layer (crust) via electrostatic and hydrophobic interactions of NIPEC species with the soil aggregates. The hardness of the NIPEC-soil crust is as more as 40 times higher than the hardness of the initial (untreated) soil, while the crust does not prevent water infiltration. These findings make NIPEC formulations promising binders for stabilization of the soil at a wind speed of 10–12 m/s. The crust seems to sustain water erosion as well. Additionally, NIPECs show a great capacity to heavy metal ions.

1. Introduction

Erosion is an intensively developing process in soil induced both by natural factors and imprudent human activities (Iturri et al., 2016; Lal, 2001; Ochoa-Cueva et al., 2013; Toy et al., 2002; Vanwalleghem et al., 2017; Yang et al., 2003). It is one of the most critical forms of soil degradation (Cerdà et al., 2010; McBratney et al., 2014; Mengistu et al., 2015). By erosion, soil loses small particles that results in removal of the key nutrient components: humus, nitrogen, phosphorus, potassium, etc., from eroded soils (Brevik et al., 2015; Mchunu and Chaplot, 2012; Withers et al., 2015; Zhang et al., 2015; Zuazo and Pleguezuelo, 2008). This problem is most remarkable in developing countries; however the soil degradation processes take place all over the world. Among various methods for stabilizing soil and ground, polymeric formulations are of particular interest (Inbar et al., 2015; Iyengar et al., 2013; Lee et al., 2013; Movahedan et al., 2012; Orts et al., 2000; Rabiee, 2010; Sadeghi et al., 2016; Sepaskhah and Shahabizad, 2010; Sojka et al., 2007; Zezin et al., 2015). They are relatively cheap, large-tonnage, and easy to use (Puoci et al., 2008; Zezin et al., 2015). However, traditional approaches do not provide a long-term protective effect. Water-soluble polymeric binders are quickly removed from soil with rainwater that leads to the loss of the stabilizing effect even at mild precipitation (Chang et al., 2016). Hydrophobic binders cannot be uniformly distributed in soil, shortly concentrate on the soil surface and form a fragile coating.

Both the fundamental research data and practical application of polymeric binders show that an optimal result for protection towards wind erosion can be achieved when the binder consists of both hydrophilic and hydrophobic fragments (blocks) (Izumrudov and Sybachin, 2006; Zezin et al., 2015). The former interact with hydrophilic regions on the surface of soil particles and bind (glue) them. The latter cause the same effect, but towards hydrophobic soil particle regions (Volikov et al., 2016). This leads, first, to a sharp increase in the binding efficiency and a reduction of binder discharge, and, second, to a uniform distribution of the binder in soil and, at the same time, its lower solubility in water.

These requirements are ideally satisfied by using interpolyelectrolyte complexes (IPECs) which can be prepared by mixing aqueous solutions of oppositely charged polyelectrolytes (Izumrudov et al., 2011; Muller, 2014). IPECs actually represent block copolymers with more or less extended (a)hydrophilic, separated cationic or

separated anionic, blocks and (b)hydrophobic, mutually neutralized cationic and anionic blocks; their hydrophobic-hydrophilic balance can be easily varied within wide limits by changing polycation/polyanion ratio (Izumrudov and Sybachin, 2006). It is this feature that determines the ability of such constructs to effectively adsorb on different surfaces (Schwarz and Dragan, 2004; Stoll and Chodanowski, 2002). Two approaches have been described for preparing IPEC formulations: a "two-solution" method with sequential deposition of aqueous solutions of oppositely charged polyelectrolytes on the surface (Mikheykin, 2004) and a "single-solution" method when a mixture of two non-interacting polymeric components in 2–5 wt% aqueous-salt solution is applied (Yamada et al., 2015; Zezin et al., 2015). However, it is difficult to cover the surface uniformly with both polymers using the "two-solution" method; therefore adhesive (mechanical) properties of an IPEC composition can hardly be controlled. The "one-solution" method favors salinization of soil that suppresses plant growth. The latter is immaterial when treating territories not currently in use but becomes a key factor when treating agricultural lands.

In the present article, we describe a novel polymeric formulation, a non-stoichiometric interpolyelctrolyte complex (NIPEC) with an excess of an anionic polymer. NIPECs are formed in the presence of minimum salt concentration that practically has no effect on the water-salt balance of soil (Dubin et al., 2012; Izumrudov and Sybachin, 2006; Muller, 2014; Ortega-Ortiz et al., 2010) We show that negatively charged NIPEC is able to bind to cationic colloidal particles and keep the binding even being electrostatically pre-complexed with heavy metal cations. Finally, we give some examples of the use of NIPEC formulation for soil stabilization and discuss the mechanism of the NIPEC stabilizing effect. Taking together, these results make the NIPEC formulations promising for suppressing erosion of soil and ground contaminated by high toxic metals.

2. Materials and methods

2.1. Soil samples

A sample of retisol (sod-podzolic soil) was collected in Moscow region (Russia). An upper 10 cm layer of soil was used with the following characteristics: pH 5.8, a moisture content of 3 wt%, OM $2 \pm 0.05\%$, CEC 7.9 ± 0.14 meq/100 g, EC at 25 °C 4.7 ± 0.11 mS/cm These parameters correlate with described elsewhere (Sidorova and Borisova, 2014). Then the sample was dried at 100 °C to constant weight, additionally milled and sifted through a 0.25 mm sieve. The sieved sample was fractioned by sequential passing through a set of sieves followed by weighting each fraction. The granulometric composition of the soil sample is shown in Table 1.

2.2. Polymers

An anionic polymer, poly(acrylic acid) (ANI, $M_w \sim 100,000$), a cationic polymer, poly(diallyldimethylammonium chloride) (CAT, $M_w \sim 300,000$), and tris-(hydroxymethyl)-aminomethane from Sigma-Aldrich, both low-toxic with LD50 of 2500 mg/kg for ANI and 3000 mg/kg for CAT (the data is presented by supplier), were used as received. Nickel acetate and hydrochloric acid from Reachim (Russia) were used as received. A cationic latex, 90 nm in diameter and average concentration of cationic groups 1.6×10^{-5} mol/g was kindly provided by Professor Ballauff (Sybachin et al., 2012). Polymers were weighted and dissolved in 10 mM TRIS buffer aqueous solution with pH 7.

2.3. NIPECs preparation

Interpolyelctrolyte complexes were prepared by mixing of ANI and CAT solutions with corresponding concentrations The concentrations of the polymers are given in the molar concentration of their ionic units, carboxylic ([COOH]) and quaternized ammonium ([N]).

2.4. Experimental techniques

Electrophoretic mobility (EPM) of polycomplexes and polycomplex/latex particles was measured by laser microelectrophoresis in a thermostatic cell using a Brookhaven Zeta Plus instrument. An average result of 5 measurements was used. Mean hydrodynamic diameters of ANI/CAT binary complexes and ANI/CAT/Ni complexes were determined by dynamic light scattering at the fixed scattering angle (90°) in a thermostatic cell using an ALV-5 laser light scattering photometer (Germany). Autocorrelation functions were analyzed using the software package DynaLs (Alango, Israel). All the probes were measured after 5 min after preparation. The average result of 5 measurements was used.

An aqueous solution of Ni(OAc)$_2$ was used as a source of heavy Ni cations. The capacity of the negatively charged ANI/CAT complexes for Ni-cations was estimated as follows. A series of Ni(OAc)$_2$ solutions with different Ni concentrations was prepared and mixed with a solution of ANI/CAT complexes. 30 min after the ternary complexes were separated from unbound Ni-cations by 40 min centrifugation at 20,000 rpm, and concentration of Ni-cations in the supernatants were determined spectrophotometrically by the following the procedure described elsewhere (Sousa and Korn, 2001). Briefly, 0.5 mL of Ni(2 +)-contained solution was mixed with 21.5 mL of distilled water, 2 mL of a iodine-saturated water, 0.01 mL of a 25 wt% ammonia solution and 1 mL of a 1 wt% dimethylglyoxime solution in ethanol. The system was thoroughly mixed and left to stay for 10 min at room temperature, after that an absorbance at 470 nm was measured spectrophotometrically using Shimadzu UV-mini 1240 spectrophotometer and converted to Ni(2 +) ion concentration using a corresponding calibration curve. Detection limits for Ni-ions were estimated from 1.5×10^{-5} g/L to 1.5×10^{-3} g/L. The average results of 5 measurements were used.

The NIPEC-to-latex complexation was monitored by measuring EPM of particles in the system and compared with the latex binding to free (non-complexed) ANI taken as a control.

Interaction of a cationic latex suspension with a suspension of the NIPEC/Ni ternary complex was studied by titration; a latex-to-complex binding was controlled by measuring size of particles in the system.

Scanning electron microscopy images were obtained using LEO 1550 FE SEM microscope (ZIESS, Germany).

2.5. Soil treatment

The treatment of soil samples with NIPEC formulations were made as follows. First, glass Petri dishes were filled with 35 g of soil each. The thickness of soil layer in the dishes was about 1.5 cm. Then the soil samples were treated by 20 mL of water (control) and 20 mL of a ANI/CAT NIPEC formulation (0.26 wt% aqueous solution) with a ratio between a mole concentration of cationic CAT units ([N]) and a mole concentration of anionic ANI units ([COOH]) $Q = [N]/[COOH] = 0.15$. The samples were left to dry for 3 days in the air.

The samples with NIPEC-stabilized soil were mechanically damaged using TED Pella Craft Knife with 548-3 Handle and 548-1 #11 Blade. The pieces of crust were separated from bottom layer of soil unbound

Table 1
Granulometric composition of the soil samples (wt%).

Average particle size (mm)	1.5–0.25	0.25–0.05	0.05–0.01	0.01–0.005	0.005–0.001	< 0.001
Soil	–	77.8	10.2	1.2	2.8	8