

Binary and Ternary Polymer–Strontium Complexes and the Capture of Radioactive Strontium-90 from the Polluted Soil of the Semipalatinsk Nuclear Test Site

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ABSTRACT: The interaction of poly(acrylic acid) (PAA) and poly(ethylene glycol) (PEG) with strontium ions and the binding of strontium ions by equimolar interpolymer complexes (IPCs) of PAA and PEG were studied. The stability constants of binary polymer–metal complexes were determined. Aqueous solutions of IPCs of PAA and PEG were applied as soil structuring agents in model and real experi-

ments. The ability of IPCs to capture radioactive strontium ions from the polluted soil of the Semipalatinsk Nuclear Test Site was established. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 759–764, 2003

Key words: water soluble polymers; association; composites

INTRODUCTION

Interpolymer^{1–4} and polymer–metal^{5–8} complexes are widely known and have been studied in different aspects. The application of interpolymer complexes (IPCs) for environmental protection has at least two important applications. One of them is to combat against the wind and water migration of radionuclides from polluted soils. The second one is to accumulate radioactive elements contained in the soil within IPCs. Earlier, Kabanov and Zezin⁹ successfully used aqueous solutions of polyelectrolyte complexes for the sedimentation and cementation of radioactive dusts of the Chernobyl disaster. Researchers^{10,11} have investigated the sorption of strontium and cesium from the soil by polyelectrolyte complexes based on poly(acrylic acid) (PAA) and poly(*N,N*-dimethyldiallylammonium chloride).

This study was devoted to an investigation of the interaction of PAA and poly(ethylene glycol) (PEG) with strontium ions and the ability of IPCs stabilized by a cooperative system of hydrogen bonds to aggregate soil particles and capture radioactive strontium-90. The effectiveness of IPCs was studied in model and real conditions.

EXPERIMENTAL

Materials

PAA with a weight-average molecular weight (M_w) of 250×10^3 and PEG with a M_w of 600×10^3 were purchased from Polysciences, Inc. (Warrington, PA) and were used without purification. Reagent-grade $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ was used without additional purification. Reagent-grade solvents were used.

Instrumentation

Potentiometric and conductimetric titration was carried out on a pH/conductivity meter (Mettler Toledo MPS 227, Schwerzenbach, Switzerland) at room temperature. The viscosity of the polymer solutions was measured with an Ubbelohde viscometer (Institute of Chemical Sciences, Alma-Ata, Kazakhstan). The concentration of strontium ions in soil was determined with an atomic absorption spectrophotometer (Quant Zeta of Kortek, Moscow, Russia). The polymer–metal complexes and IPCs were obtained by mixing aqueous solutions of interacting components.

Preparation of the soil sample for analysis^{12,13}

Soil samples were taken from the different places in the Semipalatinsk region. All of the samples were mixed carefully, and for further investigation, 1 kg of sample was taken. This sample was placed as a thin layer on the paper sheet and was dried in a box containing the filtered air. After drying, the sample was weighed, placed on the paper sheet, and divided

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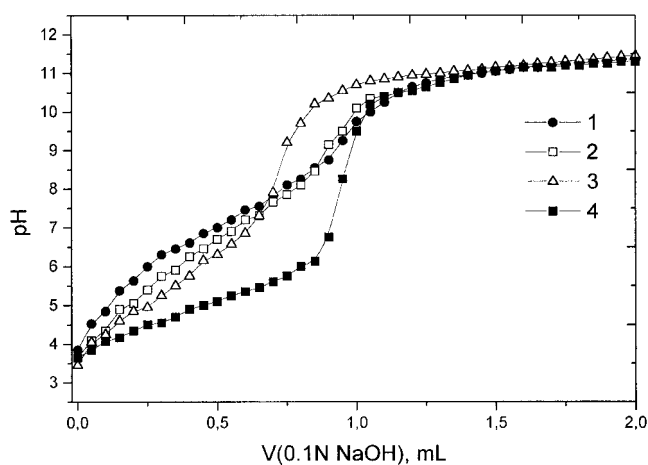


Figure 1 Potentiometric titration curves of (1) PAA and $[PAA]:[Sr^{2+}] =$ (2) 10 : 1, (3) 6 : 1, and (4) 1 : 1.

into four portions diagonally. Two opposite portions were placed in the box and kept in an unmilled state. The remaining portions were accurately mixed, and 25–30 g of soil was taken from different parts of the sample.

Determination of the aggregate state of the soil according to N. I. Savvinov's method^{13,14}

The microaggregate composition of soil was determined by the dry method of aggregate analysis. The sample was sifted carefully through a set of sieves with diameters of 10, 5, 3, 2, 1, 0.5, and 0.25 mm. Aggregates from the sieves were placed into preliminarily weighed porcelain cups. All sifted soil samples were divided into several fractions. Every fraction was weighed on a technical balance, and its content was determined in percentages.

Treatment of the soil by aqueous solutions of IPCs

Samples with known fractional contents (aggregate composition) were treated with aqueous solutions of IPC with concentrations of 10^{-2} , 10^{-3} , and 10^{-4} mol/L. The treatment of the soil particles was realized by two methods: the first method (I) was a uniform splash of polymer solution; the second one (II) was the pouring onto the soil surface of the IPC solution. After treatment, the soil samples were dried in air for 3 days, and then the aggregate composition of treated soil was determined by the dry sifting method.^{13,14}

Determination of hygroscopic humidity

Hygroscopic humidity was determined by drying of the soil sample to a constant mass in drying stove at 110–150°C for 5 h. Then, the soil sample was cooled

and weighed on an analytical balance. Hygroscopic humidity (W) was calculated as

$$W = \frac{a100}{b}, \%$$

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

Determination of capillary moisture capacity

The maximum quantity of water that can be contained in the soil is called the capillary moisture capacity. A capillary tube with two open ends, 10 cm in length and 1 cm in diameter and filled with soil, was placed into the cup. The tube bottom was placed on the filter paper. The ends of filter paper were dipped into water. Water passed through the paper pores into the soil, and the capillary saturation took place. Every 10 min, the tube was weighed on a technical balance. The full capillary saturation was reached when its mass did not change. Capillary moisture capacity (CMC) was determined with the following formula:

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

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 and W is hygroscopic humidity (%).

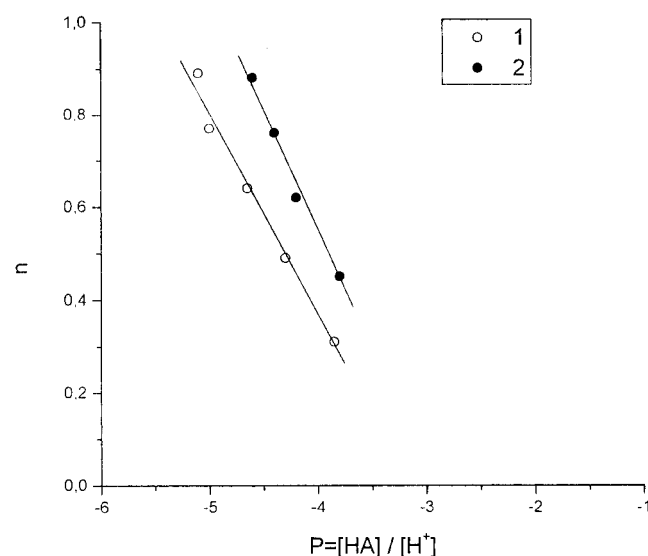


Figure 2 Curves of formation for $[PAA]:[Sr^{2+}] =$ (1) 6 : 1 and (2) 1 : 1 systems.

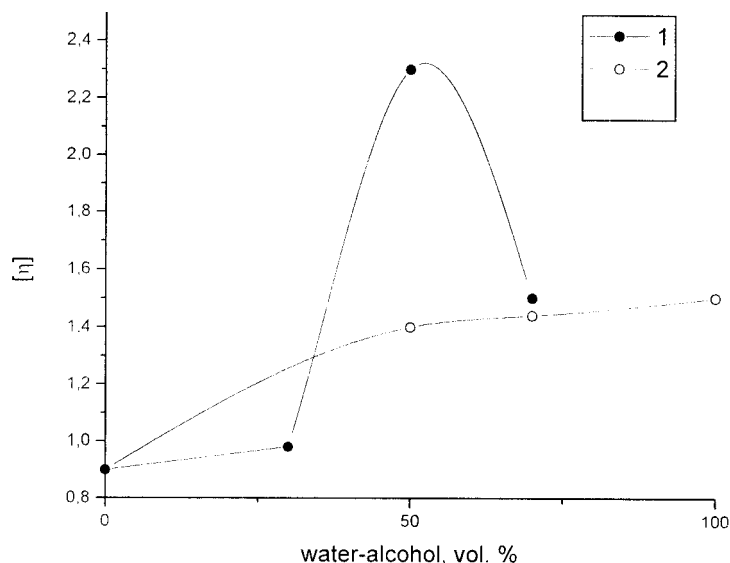


Figure 3 Dependencies of the intrinsic viscosity of PAA-Sr²⁺ complexes on the composition of mixed solvents: (1) water-C₂H₅OH and (2) water-CH₃OH.

Capillary movement of water in structured soil

Soils structured by IPCs (0.1 and 0.05% from soil weight) and untreated samples were placed into glass tubes with a diameter of 1 cm and a length of 10 cm. The ends of the tubes were placed on filter paper. The corners of the filter paper were put in contact with water, and the saturation of soil by water was carried out. The time that was necessary for the raising of the water from the bottom to the top up to the 10-mm mark was fixed.

Soil aggregates were transferred 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, and then the aggregates were washed off to preliminarily weighed small cups, dried on a water bath up to the air-dried state, and weighed. The weight of the fraction gave the content of water-stable aggregates of certain size.

Determination of the water stability of aggregates

The quantity of water-stable aggregates was determined by N. I. Savvinov's method of wet sifting.^{13,14}

RESULTS AND DISCUSSION

The potentiometric titration curves of pure PAA and PAA-Sr²⁺ at the molar ratio of [PAA]:[Sr²⁺] = 1 : 1, 6 : 1, and 10 : 1 are shown in Figure 1. The titration

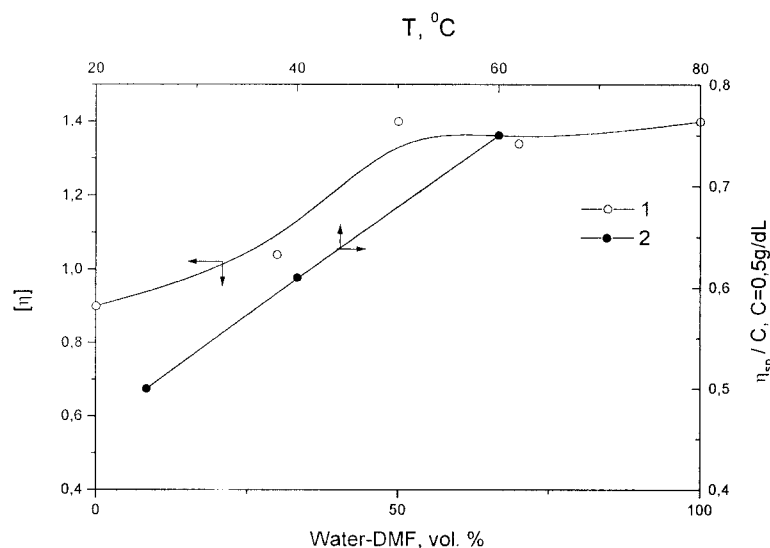


Figure 4 Dependencies of the (1) intrinsic viscosity and (2) reduced viscosity of PAA-Sr²⁺ complexes on the composition of water-DMF mixed solvent and on temperature.

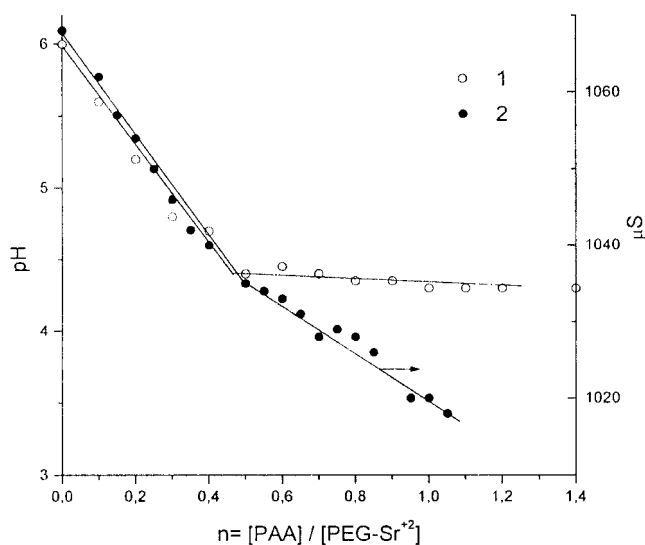


Figure 5 (1) Potentiometric and (2) conductimetric titration curves of the $[\text{PEG}] : [\text{Sr}^{2+}] = 1 : 1$ complex by PAA solution.

curves of PAA in the presence of Sr^{2+} were shifted to acidic region. This was connected with the replacement of the protons of PAA by strontium ions due to the formation of polymer-metal complexes. The average coordination number of metal ion (n) and the stability constants of the polymer-metal complexes (K) calculated for molar ratios $[\text{PAA}] : [\text{Sr}^{2+}] = 1 : 1$ and $6 : 1$ by Gregor method¹⁵ (Fig. 2) were equal to $n = 1$, $K = 1.25 \times 10^{-4}$ and $K = 5.62 \times 10^{-5}$, respectively.

The influence of mixed solvents [water-methanol, water-ethanol, and water-dimethylformamide (DMF)] and the temperature on the stability of $[\text{PAA}] : [\text{Sr}^{2+}] = 1 : 1$ complexes were investigated. As seen from Figures 3 and 4, the behavior of PAA- Sr^{2+} complexes in water-organic solvents was different. This was probably due to the different dielectric properties of solvents and a consequence of different degrees of ionization of the carboxylic groups of PAA. The common feature of PAA- Sr^{2+} complexes was the gradual unfolding of complex parti-

cles with increasing amounts of organic solvent content in mixed solvents and with increasing temperature.

According to potentiometric and conductimetric titrations for the PEG- Sr^{2+} system, the preferable interaction was also observed at a molar ratio of $[\text{PEG}] : [\text{Sr}^{2+}]$ of $1 : 1$. The properties of ternary polymer₁- Sr^{2+} -polymer₂ systems were also investigated. Aqueous solutions of the initial complexes $[\text{PAA}] : [\text{PEG}] = 1 : 1$, $[\text{PAA}] : [\text{Sr}^{2+}] = 1 : 1$, and $[\text{PEG}] : [\text{Sr}^{2+}] = 1 : 1$ were successively titrated by the third component, that is, Sr^{2+} , PEG, and PAA, respectively. The solution properties of an equimolar IPC composed of PAA and PEG are described in detail in refs. 1, 2, and 16–18. It was found that the titration of PAA-PEG by Sr^{2+} and PAA- Sr^{2+} by PEG led to a monotonous change of conductivity and pH values that pointed to weak (or absent) interactions. The considerable deviation from the additive properties was observed when PEG- Sr^{2+} pairs were titrated by PAA solution and indicated the formation of ternary polymer-metal complexes with the composition $n = [\text{PEG-Sr}^{2+}] / [\text{PAA}] = 2 : 1$ (Fig. 5).

Both water-soluble polymers (PAA and PEG) and IPC PAA-PEG complexes were used for the stabilization of the soil structure. This problem has enormous importance for the Semipalatinsk Nuclear Test Site due to the possibility of using polymeric reagents to protect the water and wind migration of soils polluted by radioactive strontium. It was expected that the treatment of the soil by dilute solutions of water-soluble polymers and IPC would cause the structuring of soil particles. Also, IPCs are able to form thin films on the surface of soil particles, aggregate, and considerably protect the migration.

The influence of various factors such as the concentration of the polymer and the IPC solution, soil treatment methodology, pH, the molar ratio of interacting components on the sizes of forming soil aggregates, their water stability, and other properties were investigated.

The obtained results are summarized as follows:

TABLE I
Influence of $[\text{PAA}] : [\text{PEG}] = 1 : 1$ Solution on Soil Aggregate Composition

Method	C (mol/L)	% Content of Fractions (mm)												
		5	4	3	2	1	0.5	0.25	<0.25	>0.5	$\Delta > 0.5$	>0.25	$\Delta > 0.25$	$M/C > 0.5$
Control	—	—	—	—	—	—	2.52	36.41	61.06	2.52	0	38.13	0	0
Splash	0.01	10.08	7.84	1.68	1.40	5.04	6.72	56.86	10.36	32.76	30.24	89.62	50.69	364.66
Pouring	—	11.81	8.06	2.01	2.01	8.64	9.22	49.85	8.35	41.75	38.87	91.60	27.05	468.74
Splash	0.001	7.75	6.60	1.72	1.43	4.60	5.74	61.78	10.34	27.84	24.68	89.62	48.25	297.62
Pouring	—	—	2.88	1.44	1.72	5.76	8.06	70.89	9.22	19.86	11.39	90.75	40.33	173.53
Splash	0.0001	—	3.43	2.86	4.58	5.15	4.29	71.34	10.02	20.31	16.87	91.65	50.96	203.44
Pouring	—	—	2.57	2.85	3.43	8.28	3.43	68.57	10.85	20.56	16.28	89.13	40.85	196.32

M/C = differential affectivity; M = number of fractions with particle sizes greater than 0.5 mm; C = polymer concentration (from soil weight).

TABLE II
Influence of pH on Aggregative Properties of Equimolar IPC ($C = 10^{-2}$ mol/L)

Method	pH	% Content of Fractions (mm)												
		5	4	3	2	1	0.5	0.25	<-0.25	>0.5	$\Delta > 0.5$	>0.25	$\Delta > 0.25$	M/C > 0.5
Control		—	—	—	—	—	5.71	51.43	42.86	5.71	0	57.14	0	0
Splash	8.0	—	3.14	2.29	4.57	8.86	6.29	54.57	20.29	25.15	19.44	79.72	22.58	234.43
Pouring		0.86	6.00	5.14	5.14	3.14	6.57	55.14	18.00	26.85	21.14	81.99	24.85	254.93
Splash	6.5	4.57	2.57	5.14	4.86	4.29	6.86	55.14	16.57	28.29	22.58	83.43	26.29	272.29
Pouring		4.57	2.86	4.86	5.14	5.43	7.14	55.71	14.29	30.00	24.29	85.71	28.57	292.91
Splash	4.5	4.86	2.86	5.14	5.14	4.29	7.43	56.29	14.00	29.72	24.01	86.01	28.87	289.54
Pouring		4.00	3.43	5.71	4.57	3.71	7.71	57.43	13.43	29.13	23.42	86.56	29.42	282.42
Splash	3.0	5.43	3.43	5.14	3.71	3.14	8.57	60.00	10.57	30.13	25.31	89.41	41.39	265.30
Pouring		4.57	3.71	4.57	2.86	3.43	8.86	61.43	10.57	31.20	22.29	89.43	32.29	268.79

M/C = differential affectivity; M = number of fractions with particle sizes greater than 0.5 mm; C = polymer concentration (from soil weight).

1. The optimal concentrations of polymer solutions were arranged between 10^{-4} to 10^{-2} mol/L. The best results corresponded to a concentration of 10^{-2} mol/L.
2. Pouring of the polymer solution onto the soil surface (II) was preferential in comparison to splashing the polymer solution (I).
3. Both individual polymers (PAA and PEG) and IPC (PAA-PEG) showed the structuring effect. However, the best results were observed for the IPC solution. The results of dry sifting obtained for PAA-PEG complexes are represented in Table I. The treatment of soil by PAA-PEG with a concentration of 10^{-2} mol/L increased the amount of particles greater than 0.25 mm from 38.13% (control) up to 89.62% by method I and 91.60% by method II. Fractions 5 mm in diameter were considerably increased. For low concentrations of PAA-PEG solutions, the aggregating effect was lower.
4. The treatment of soil by already preexisting IPC solution was most effective. The successive treatment of the soil at first by PAA solution then PEG solution and vice versa gave the worst results.
5. Deviation from the equimolar composition of IPC, for instance, for $[PAA] : [PEG] = 1 : 2$ and $[PAA] : [PEG] = 2 : 1$ mol/mol, led to the worst results. This may have been due to the formation of stable IPCs at the equimolar ratio of components.^{1,2,16-18}
6. The results of soil treatment by IPC solutions having different pH's (8.0, 4.5, and 3.0) are summarized in Table II. Acidification of IPC solutions caused the strengthening of the structuring effect because of the suppression of the dissociation of PAA and the formation of more stable IPCs.^{1,2,16-18}

Thus, the best structuring effect was obtained for the equimolar $[PAA] : [PEG] = 1 : 1$ complex solution with a concentration of 10^{-2} mol/L and at a pH of 3.0

when the IPC solution was poured through soil surface.

The capillary moisture capacity and water stability at optimal soil treatment conditions soils are given in Tables III and IV. The moisture capacity of the soil increased with increasing polymer concentration. The moisture capacity of untreated soil was 20.65%, whereas the same parameter of soil treated by a 0.1% complex solution was 47.13%. This means that the structured soil particles effectively preserved the moisture and prevented its evaporation.

At a concentration of IPC equal to 0.05%, the velocity of moisture movement for treated soils sharply increased in comparison with that of the untreated one. The further increasing of IPC concentration up to 0.1% led to an acceleration of capillary raising of water; then, the delay was observed. According to ref. 19, the delay of capillary water movement is connected with the break of continuity of capillaries on particle surfaces with the formation of interaggregates and a large emptiness that not possessed by capillary properties. The soil treated by a 0.1% complex solution showed the most water stability; the quantity of water-stable aggregates greater than 0.25 mm was 46.1% in comparison with control experiments (5.8%).

The soil structuring effectiveness of equimolar IPCs and water-soluble polymers at the same concentration increased in the order $PAA : PEG = 1 : 1$ (pH 3.0) $>$ $PAA : PEG = 1 : 1$ (pH 4.5) $>$ $PAA : PEG = 1 : 1$ (pH 6.5) $>$ $PAA : PEG = 1 : 1$ (pH 8.0) $>$ $PAA >$ PEG .

Because PAA, PEG, and PAA-PEG complexes were able to form polymer-metal complexes with Sr^{2+} ions,

TABLE III
Capillary Moisture Capacity of Treated and Untreated by IPC Soils

Variant	Capillary moisture capacity
Untreated soil	20.65
Soil + 0.05% IPC	28.42
Soil + 0.1% IPC	47.13

TABLE IV
Influence of PAA-PEG Complex on Water Stability of Aggregated Soils

C (% from soil weight)	Content of fractions (% size of particles, mm)						Number of water stable aggregates > 0.25 mm
	>1	1-0.25	0.5-0.25	0.25-0.005	0.005-0.001	<0.001	
Control	—	—	5.8	62.8	21.4	10	5.8
0.05	—	—	8.3	55.3	28.4	8.0	8.3
0.1	7.1	24.0	15.0	37.5	9.1	7.3	46.1

the possibility of the capture of soil radionuclides by means of binding into the complex was investigated. The quantitative analysis of strontium-90 treated by polymer solutions and untreated soils was carried out. These data are accumulated in Table V.

As shown, the Sr^{90} content increased twice in soils treated by single polymer solutions (PAA or PEG) in comparison with that of untreated soil, probably due to the formation of PAA- Sr^{2+} and PEG- Sr^{2+} complexes. The most Sr^{90} content was observed in soils treated by the [PAA] : [PEG] = 1 : 1 complex. Strontium content increased up to 9.34 $\mu\text{g/L}$ in comparison with control experiments (2.31 $\mu\text{g/L}$), which may have been due to the formation of ternary PAA- Sr^{2+} -PEG polymer-metal complexes.

The results show the possibility of the application of IPCs not only for soil structuring agents but also for the disinfection of radioactive strontium from polluted soils.

CONCLUSIONS

The formation of binary PAA- Sr^{2+} , PEG- Sr^{2+} and ternary PAA- Sr^{2+} -PEG polymer-metal complexes was shown in aqueous solution. n and the K_s were determined for PAA- Sr^{2+} complexes. The PAA- Sr^{2+} complexes were not stable to changes of the thermo-

dynamic quality of water-organic mixtures and temperature. The structuring effect of water-soluble polymers and IPCs with respect to soil particles was investigated. We found the optimal conditions for soil treatment. The best structuring effect was shown in the course of pouring the IPC solution with a concentration of 10^{-2} mol/L onto the soil surface at pH 3.0. The influence of different factors such as the size of the forming soil aggregates on water stability and capillary moisture capacity was investigated.

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TABLE V
Atomic Adsorption Determination of Strontium in Soils Treated by Polymer Solutions

Variant	C of polymer solution (mol/L)	C_{Sr} ($\mu\text{g/L}$)
Soil (control)	—	2.31
PAA	0.01	4.13
	0.0001	4.45
PEG	0.01	4.49
	0.0001	3.69
PAA-PEG = 1:1	0.01	9.34