Electronic supplementary materials *Mendeleev Commun.*, 2025, **35**, 205–207

Migration of cationic polymer between anionic polymer microspheres

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Materials

A. Poly(diallyldimethylammonium chloride) (PDADMAC) with an average molecular weight $M_w < 100$ kDa and a degree of polymerization DP < 620 (Sigma-Aldrich), poly-L-lysine hydrobromide (PL) with $M_w = 15.7$ kDa and DP = 75 (Sigma-Aldrich), poly-L-lysine with covalently attached N-fluorescein isothiocyanate (poly-L-lysine-FITC, PL*) with M_w 15-30 kDa and DP = 71-143 (Sigma-Aldrich) were used as cationic polymers (polycations). Polycations were dissolved in Tris-NaCl buffer. Concentrations of polycations were expressed in moles of either amino or ammonium groups per liter [N+].

B. Polystyrene microspheres with carboxylic surface groups (PSMs) were used as a model microplastics. PSMs were synthesized as described elsewhere.[S1] Their size (hydrodynamic diameter, D_h) was estimated by DLS. The surface charge of PSMs was quantified by polycation (PDADMAC and PL) titration of a PSM suspension in Tris-NaCl buffer (pH 7) using laser microelectrophoresis. The quantity of polycation $[N^+]$ at the point of zero of EMP was taken as the quantity of carboxylic groups of PSMs involved in complexation with polycations at pH 7. This quantity was equal to 3.2×10^{-5} moles of COO^- per g of PSMs and was used to calculate a required volume of PSMs for mixing a suspension of necessary concentration expressed in moles of carboxylic groups per liter $[COO^-]$ in Tris-NaCl buffer (pH 7).

Methods

C. Dynamic light scattering measurements (DLS) at a fixed scattering angle (90°) in a thermostatic cell (25 °C) with a Brookhaven Zeta Plus instrument (Brookhaven, USA) were used for characterizing size of PSMs and their complexes with cationic polymers. Electrophoretic mobility (EPM) of PSMs and their complexes was performed in a thermostatic cell (25 °C) by laser microelectrophoresis by using Brookhaven Zeta Plus instrument (Brookhaven, USA). D_h and EPM values were calculated with software provided by the manufacturer.

D. Fluorescent fluorimetry was carried out by using spectrofluorometer F-4000 (Hitachi, Japan) at emission wavelength $\lambda_{em} = 525$ nm and excitation wavelength $\lambda_{ex} = 490$ nm.

All experiments were performed in a 10^{-3} M Tris aqueous buffer solution with pH 7 contained 5×10^{-3} M NaCl (Tris-NaCl buffer). Experiments were implemented in triplicate repetition.

Experimental procedures

E. *Complex formation*

To form complexes of polycations with PSMs an appropriate amount of polycation solution were added to a definite amount of PSM suspension so that the molar ratio (Z = $[N^+]/[COO^-]$) of components was in the range from 0 to 2.

F. *Degree of binding of polycation with PSMs*

To estimate the degree of binding of polycation with model microplastics PL*-PSM complexes were prepared as stated above. The complexes were hold for an hour and centrifuged by Centrifuge 5430 (Eppendorf, Germany) for 11 min at 17500 rpm. Then supernatants were analyzed by fluorescent spectrofluorometer relatively a control sample. The solution of PL*with a quantity, which was formed in prepared PL*-PSM complexes, was taken as the control sample.

G. *Migration of polycations between PSMs*

To study the migration of cationic polymers between PSMs the experiment was performed as follows. Positively charged polycation-PSM complexes, which contained no free polycation in solution, were mixed with initial negatively charged PSMs without adsorbed polycation in definite proportions so that the eventual ratio Z was less than 1.0. In this case an excess of negatively charged particles in relation to polycations was formed. D_h and EPM were controlled during the experiment. According to curves of dependence of EPM on ratio Z for polycation-PSM complexes EPM of the system with a uniform redistribution of macromolecules between all PSMs should be equal to the value, which is waited at a whole distribution of polycations after mixing. Additionally, the final size of complex particles should be close to the size of the initial PSMs. The ratios of complexes before and after mixing, waited at the whole redistribution of polycations, and the proportions of suspension volumes of complexes and initial PSMs for mixing are presented in Table S1.

Table S1 Compositions of complexes before and after mixing and volumes of suspensions of positively charged complexes and initial PSMs

Migration experiment	ME-1, ME-3	ME-2	ME-4
Composition before mixing/Z	1.4	1.2	1.4
Composition after mixing/Z	0.7	0.6	0.47
Volume of complex suspension/ml	3	3	3
Volume of initial PSM suspension/ml	3	3	6

References

S1 A. Yu. Menshikova, B. M. Shabsels, N. N. Shevchenko, A. G. Bazhenova, A. B. Pevtsov, A. V. Sel'kin and A. Yu. Bilibin, *Colloids Surf., A*, 2007, **298**, 27.