

Flocculation of Montmorillonite by Some Hydrophobically Modified Polycations Containing Quaternary Ammonium Salt Groups in the Backbone

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ABSTRACT: The flocculating efficiency of some hydrophilic/hydrophobic cationic polyelectrolytes on montmorillonite suspension in water was investigated as a function of both the polycation structure and the flocculation parameters: polycation/montmorillonite contact time, suspension pH, polycation dose, and temperature. Cationic polyelectrolytes with quaternary ammonium salt groups in the backbone and hydrophobic side chains (hexyloxypropyl, PCA₅H₁ and PCA₅H₂; and decyloxypropyl, PCA₅D₁, respectively) were used as flocculants. The flocculation was time dependent. A negative influence of the stirring time and of the abrupt variation of pH from basic to acidic on the separation efficiency was evidenced. The increase of the polycation dose from 0.58 mg polycation/g montmorillonite up to 1.74 mg/g montmorillonite showed a positive influence on the sedimentation of montmorillonite particles for all the polycations taken into account. The influence of the polycation structure was reflected in the lower turbidity found in the case of the polycation PCA₅D₁ compared with that of PCA₅H₁, at the same concentration; this reflects the positive influence of the hydrophobicity increase on the suspension separation. A common characteristic for all the polycations is that, for more than about 60 min of settling, the lowest turbidity was found at 25°C and the highest at 5°C. The turbidity found at 15°C was in between, both before and after 60 min of settling time. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 871–876, 2002; DOI 10.1002/app.10371

Key words: montmorillonite; flocculation; cationic polyelectrolytes; turbidity/temperature dependency

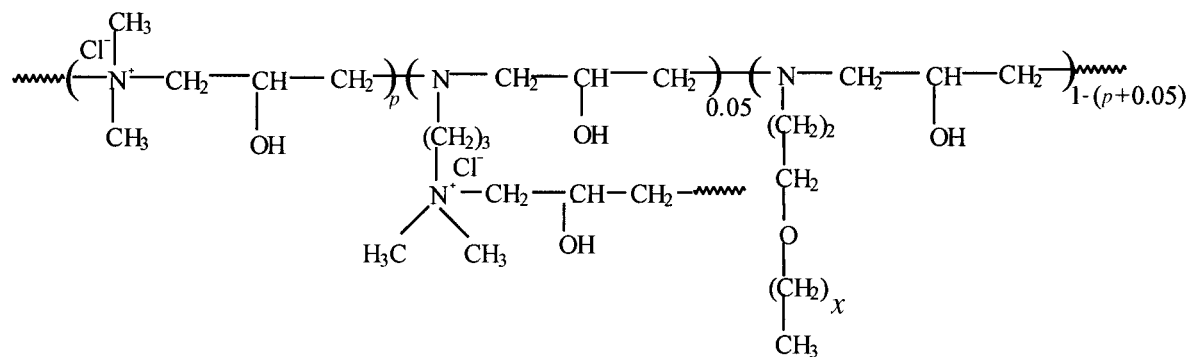
INTRODUCTION

Synthetic polyelectrolytes are widely used in the removal of matter from both surface and wastewaters. The efficiency of this process is very much dependent on the polyelectrolyte structure, on the nature and sizes of the particles in suspension, on

the environment temperature and pH, and so on. Among the synthetic flocculants, polycations primarily account for the fast rise in worldwide consumption.^{1–3} The chain flexibility, the molecular weight, and the charge density are the main factors determining the application of the cationic polymers in one of the following fields: treatment of drinking water; removal of coal, biological mashes, or waste dyes from industrial wastewaters; paper processing and, related with this, the concentration or thickening of sludges.^{4–8} The combination of polycations with polyanions in dif-

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Polycation **PCA₅H₁**; $p = 0.94$, $x = 5$; polycation **PCA₅H₂**; $p = 0.93$, $x = 5$;

polycation **PCA₅D₁**: $p = 0.94$, $x = 9$.

Scheme 1

ferent ways resulted in a new type of flocculation, dual flocculation.⁹⁻¹²

Rivers, the main source for drinking water, contain considerable amounts of mineral particles in suspension and humic acids originating from the decomposition of biomass and contained in soil in significant amounts. These impurities should be removed during water processing, either by coagulation or flocculation. The study of the particles in suspension in the rivers from the Republic of Moldova showed that the main inorganic component in water is montmorillonite,¹³ which has a negative charge with an electrokinetic potential of some tens of millivolts.¹⁴ Therefore, the aim of the present study was to correlate the efficiency of the montmorillonite separation from aqueous suspensions, on the one hand, with the structure of some hydrophobically modified polycations and, on the other hand, with the working conditions (polycation dose, stirring time, temperature, and pH). The presence of a low content of hydrophobic chains in the polycation structure may improve their affinity toward hydrophobic organic molecules and colloidal suspensions by the simultaneous work of the electrostatic and hydrophobic interactions.

EXPERIMENTAL

Materials

Montmorillonite Largutsa, typical for the Republic of Moldova [chemical composition (wt %): SiO₂, 61.30; Al₂O₃, 12.82; Fe₂O₃, 5.08; TiO₂, 0.91; MgO,

2.33; CaO, 4.45; K₂O, 0.60; Na₂O, 0.32; losses by calcination, 12.38], was used to prepare suspensions in water for the flocculation study with some cationic polyelectrolytes. The purification process of montmorillonite was performed by consecutive washing and separation steps with pure water until the above composition was obtained (checked by Röntgen method). The ionic-exchange capacity of the purified montmorillonite was 0.87 mequiv/g. Reagent-grade Al₂(SO₄)₃·18 H₂O was used as coagulant.

Cationic polyelectrolytes with hydrophilic/hydrophobic properties were synthesized by the condensation polymerization of epichlorohydrin with dimethylamine and *N,N*-dimethyl-1,3-diaminopropane, and two primary amines with nonpolar chains (hexyloxypropylamine-polymer type PCAH and decyloxypropylamine-polymer type PCAD), according to the method presented in detail elsewhere,^{15,16} the general structure of which is presented in **Scheme 1**. The polycations PCAH and PCAD are abbreviated as follows: PC, polycation; A, asymmetrical diamine; H and D, hydrophobic amine; the first subscript number means mol % of the polyfunctional amine and the second subscript number means mol % of the hydrophobic amine. All the polycations were carefully purified by dialysis against distilled water until the absence of Cl⁻ ions in the external water was achieved. The dilute aqueous solutions were concentrated by heating in vacuum, after which the polymer was recovered by precipitation with acetone and finally purified with methanol/acetone as solvent/nonsolvent. Polycations were dried in vacuum on

P_2O_5 at room temperature. The ionic chlorine content (Cl_i) was measured by potentiometric titration with 0.02N $AgNO_3$ and the total chlorine content (Cl_t) was performed by the combustion method (Schöniger technique). The viscometric measurements of the dilute solutions were carried out with an Ubbelohde viscometer with internal dilution at 25°C. The intrinsic viscosities were determined in 1M NaCl, in which the initial concentration of the polycation was 1 g/dL. Shear rate corrections were not necessary in these conditions.

The analytical data for the cationic polyelectrolytes used in this study were as follows: PCA_5H_1 : Cl_i , 19.82; Cl_t , 19.79; $[\eta]_{1M NaCl} = 0.395$ dL/g. PCA_5H_2 : Cl_i , 20.79; Cl_t , 21.36; $[\eta]_{1M NaCl} = 0.465$ dL/g. PCA_5D_1 : Cl_i , 20.66; Cl_t , 21.03; $[\eta]_{1M NaCl} = 0.410$ dL/g.

Methods

A stable aqueous suspension of montmorillonite was prepared by the addition of 1 L deionized water to 0.69 g dry montmorillonite. After 48 h hydration at 20°C, the suspension was stirred at 400 rpm for 4 h. Volumes of 250 mL montmorillonite suspension in water were stirred at 400 rpm in Berzelius glasses and then a volume of 0.1, 0.2, or 0.3 mL polycation solution with a concentration of 0.1 wt % (that is 0.4, 0.8, and 1.2 mg polycation/L of montmorillonite suspension, respectively) was added and the stirring was continued with the same revolution frequency for about 1 min or more. The suspension was then poured into some graduated cylinders. After settling times of 5, 10, 15 min, and more the reading of the supernatant turbidity was performed. Turbidity measurements were carried out with a spectrophotometer KFK-2, at a wavelength of 440 nm, close to the absorption maximum of the $\nu(Al-O)$ and $\delta(Si-O)$ of montmorillonite.

RESULTS AND DISCUSSION

According to **Scheme 1**, the hydrophobically modified polycations used in this study were different by both the charge density induced by the presence of various amounts of *N,N*-dimethyl-2-hydroxypropylammonium chloride units in the backbone and the hydrophilic/hydrophobic properties induced by the presence of hexyloxypropyl or decyloxypropyl as pendent substituents in their structure. Their specific polyelectro-

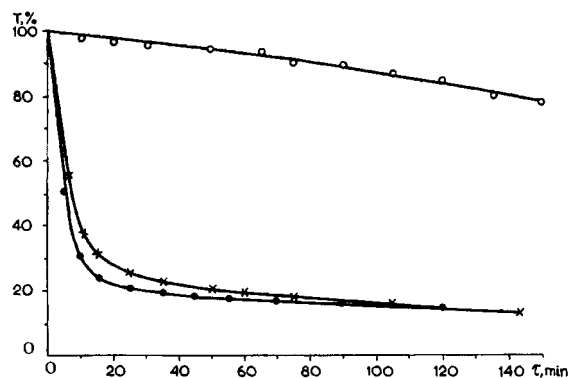


Figure 1 Turbidity variation as a function of the settling time for the montmorillonite suspension after treatment with polycation PCA_5H_2 (polycation dose was 1.16 mg/g montmorillonite, at 25°C): (○) free sedimentation; (×) 30 min of stirring; (●) 1 min of stirring.

lyte behavior in aqueous solutions was previously shown in an earlier work,¹⁷ in which their reduced viscosity was shown to continuously increase with the decrease of the polycation concentration. The flocculation of montmorillonite with all the polycations used in this investigation was time dependent. This characteristic allowed us to study the flocculation kinetic in different conditions. Figure 1 shows the turbidity variation as a function of the settling time for two values of the stirring time (1 and 30 min, respectively), when the polycation PCA_5H_2 was used as a flocculant compared against free sedimentation (without polycation).

As one can see in Figure 1 the increase of the stirring time has a negative effect on the separation velocity, mainly for the first 60 min of settling. According to the flocculation mechanism, the first step after the polycation addition to the suspension should be the adsorption of the polycation chains on the surface of montmorillonite and the second step, the bridging between more colloidal particles. The final result is the formation of flocs, the efficiency of which depends on the conformation of the polyion in solution. The adsorption process is very fast and, at an adequate rate of stirring, takes place in the first minute of the contact between the suspension and polycation¹⁸⁻²⁰ (30–40 s in our experiments). The conformation of the polycation adsorbed is not identical with that of the polycation in the bulk solution; in addition the number of loops and tails changes by the reformation of the adsorbed chains. Increased stirring time could favor more reconformations, thus reducing extension of the

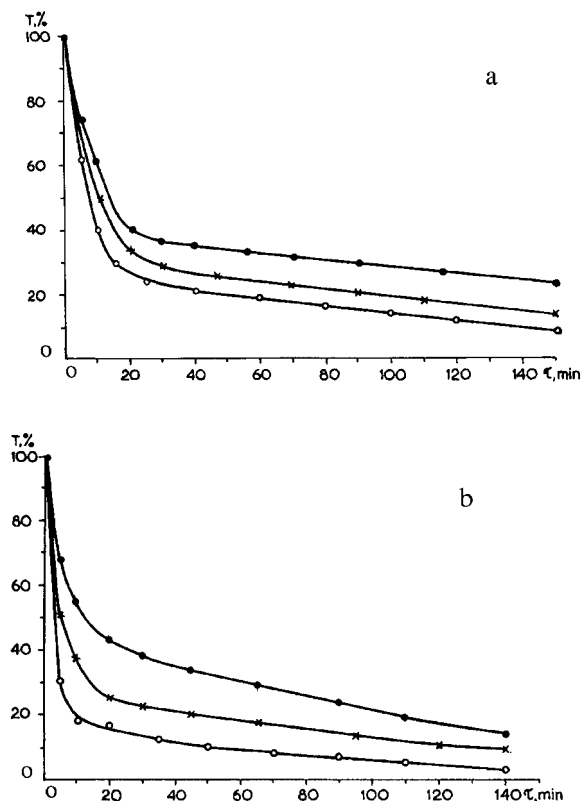


Figure 2 Turbidity variation as a function of the settling time for the montmorillonite suspension after treatment with different doses of polycation: (a) PCA_5D_1 at 15°C ; (b) PCA_5H_1 at 25°C . (●) 0.58 mg polycation/g montmorillonite; (×) 1.16 mg polycation/g montmorillonite; (○) 1.74 mg polycation/g montmorillonite.

chains; the flocs already formed could be broken, thus diminishing the flocculation efficiency (Fig. 1, stirring time of 30 min).

Figures 2(a) and 2(b) show the influence of the polycation dose on the turbidity as a function of the settling time, for two polycations with different lengths of hydrophobic side chains (PCA_5H_1 and PCA_5D_1). The increase of the polycation dose from 0.58 to 1.74 mg/g montmorillonite (calculated taking into account the amount of polycation added per liter of suspension and the concentration of montmorillonite in suspension; see Experimental section above) led to a faster floc formation and also to a faster sedimentation velocity. This result could be caused by the increase of the effective collision number between particles. A similar behavior was previously evidenced when one polycation having the backbone structure like those used in this study, but without hydrophobic side chains (PCA_5), was used to separate a ben-

tonitic clay from an aqueous suspension, the optimal dose of which was 0.6 mg polycation/L of suspension.²² The last value of the polycation dose (1.74 mg polycation/g montmorillonite) seems to be close to the optimal dose for flocculation, in the case of PCA_5H_1 at least, at 25°C [Fig. 2(b)]. Even the highest polycation dose used in this study is very low compared with the overlap concentration C^* , determined for these polycations: 0.127 g/dL for PCA_5H_1 , 0.166 g/dL for PCA_5H_2 , and 0.108 g/dL for PCA_5D_1 , respectively.¹⁷

The influence of pH on the flocculation efficiency of the montmorillonite by the polycation PCA_5H_1 is illustrated in Figure 3. As one can see, this polycation is more effective in the weak basic (8.40) and basic pH (11.15) than in acidic pH (3.15). This behavior, which is a common characteristic for all the polycations taken into account in this study, can be primarily explained by the specific and complex characteristics of the active sites of montmorillonite (Al—OH and Si—OH), which could be ionized in the basic range. The reduced influence of the pH variation on the flocculation efficiency in the basic range shows that the polycation is working not only as a salt but also as an ammonium quaternary base.

Influence of Temperature on Removal of Montmorillonite

The results regarding the influence of the environmental temperature on the separation kinetics of the montmorillonite particles as a function of the polycation structure, compared with the

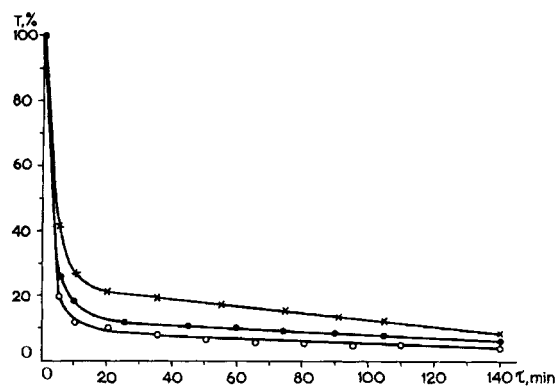


Figure 3 Turbidity variation as a function of the settling time for the montmorillonite flocculation with the polycation PCA_5H_1 at 25°C (polycation dose was 1.16 mg polycation/g montmorillonite) at different pH: (×) pH 3.15; (●) pH 11.15; (○) pH 8.4.

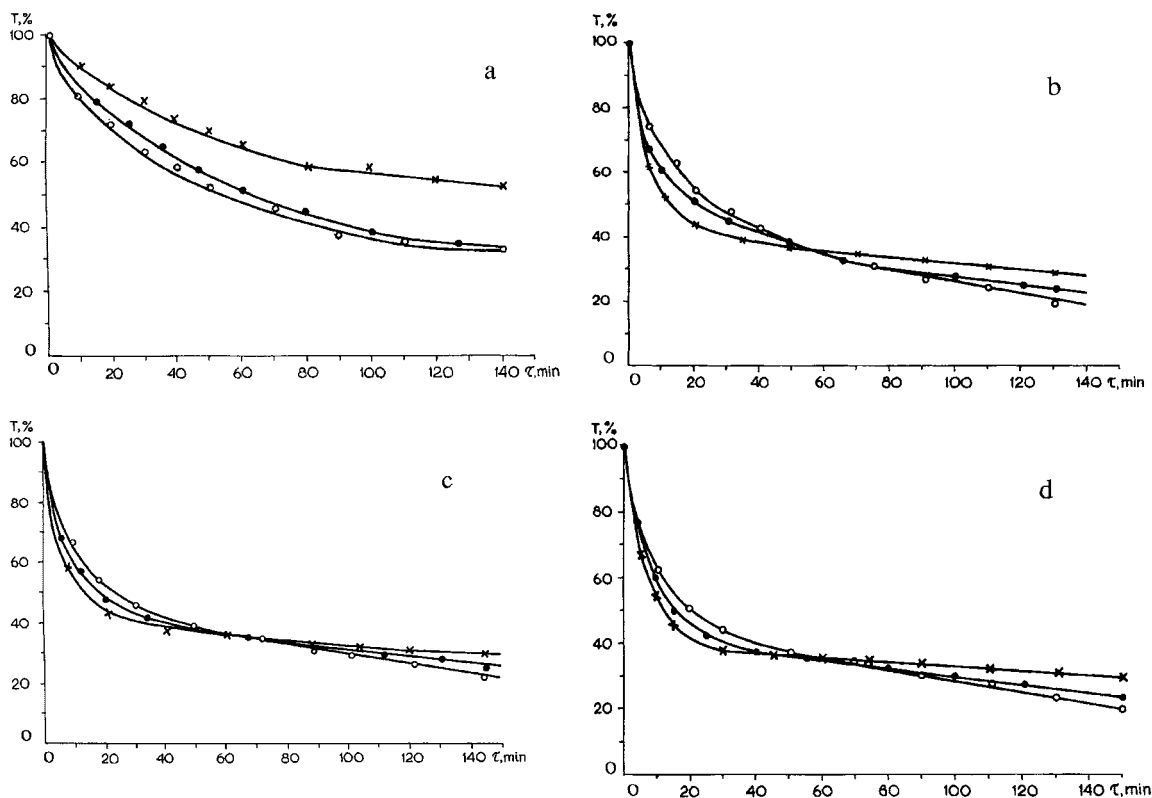


Figure 4 Turbidity variation as a function of the settling time for the montmorillonite flocculation with different polycations at different temperatures (polycation dose was 0.58 mg polycation/g montmorillonite) compared with coagulation: (a) coagulation with $\text{Al}_2(\text{SO}_4)_3$; (b) flocculation with PCA_5H_1 ; (c) flocculation with PCA_5H_2 ; (d) flocculation with PCA_5D_1 . (x) 5°C; (●) 15°C; (○) 25°C.

coagulation with $\text{Al}_2(\text{SO}_4)_3$, are presented in Figures 4(a)–4(d). These results show that the sedimentation velocity of the montmorillonite particles is more significantly influenced by temperature in the case of the coagulation process increasing concomitantly with the increase of the temperature, as expected [Fig. 4(a)]. This behavior is caused mainly by the decrease of medium viscosity and by the decrease of the electrokinetic potential of the mineral particles along with the temperature increase. The less-intensive process of coagulation at 5°C is primarily explained by the fact that in these conditions (close to 4°C) the hydration of $\text{Al}(\text{OH})_3$ [the hydrolysis product of $\text{Al}_2(\text{SO}_4)_3$] sharply increases, thus leading to the decrease in coagulation efficiency.

The temperature influence on the flocculation process by the polycations PCA_5H_1 [Fig. 4(b)], PCA_5H_2 [Fig. 4(c)], and PCA_5D_1 [Fig. 4(d)], at a polycation dose of 0.58 mg polycation/g montmorillonite, was less evident. A common characteristic for all the polycations was that, for less than about 60 min of settling, the lowest turbidity was

found at 5°C and the highest at 25°C. The turbidity found at 15°C was in between, both before and after 60 min of settling time. This different behavior could be explained by the reduced possibilities of the chain reconformations at low temperature, at which the polyelectrolyte is adsorbed from the beginning in a coiled shape, which could promote the collision of more colloidal particles. The abrupt decrease of turbidity in the first minutes of settling found at 5°C was followed by a leveling off. At higher temperatures (15 and 25°C) the flocculation process is not in an equilibrium state, given that the polycation chains have, from the beginning, greater flexibility and more possibilities for reconformations in these cases. The efficiency of hydrophobic interactions is also evident, in which the longer alkyl chain (polycation PCA_5D_1) results in a lower turbidity after about 100 min of settling.

Regarding the influence of the polycation structure on flocculation efficiency, the polycation PCA_5D_1 showed the highest efficiency on the removal of montmorillonite from the aqueous sus-

pensions at every temperature; the polycations PCA_5H_1 and PCA_5H_2 showed a comparable efficiency in this process under the same conditions, the results of which were in agreement with those found at 25°C in a previous work²³; that is, the larger the hydrophobic side chain, the higher the flocculation efficiency, the other parameters being the same.

CONCLUSIONS

The main conclusions that could be drawn from the study of the montmorillonite separation from the aqueous suspensions by polycations having quaternary ammonium salt groups in the backbone and nonpolar side chains are as follows:

1. Increased stirring time could favor more reconformations, and the extension of the chains would thus be reduced. The flocs already formed could be broken and the flocculation efficiency thus be diminished.
2. The increase of the polycation dose from 0.58 to 1.74 mg/g montmorillonite continuously decreased the turbidity of the montmorillonite aqueous suspension for all the polycations with nonpolar side chains.
3. The polycation PCA_5D_1 , having the longest hydrophobic chain, showed the highest efficiency on the removal of montmorillonite from the aqueous suspensions at every temperature, and the polycations PCA_5H_1 and PCA_5H_2 showed a comparable efficiency in this process under the same conditions.
4. The abrupt decrease of the turbidity at 5°C, in the first minute of settling, is followed by a leveling off, whereas at higher temperatures (15 and 25°C) the flocculation process continued as a result of the higher flexibility and more possibilities for reconformations of the polycation chains.

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