ISSN 1070-4272, Russian Journal of Applied Chemistry, 2009, Vol. 82, No. 2, pp. 328−332. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © V.F. Kurenkov, I.N. Nadezhdin, H.-G. Hartan, F.I. Lobanov, 2009, published in Zhurnal Prikladnoi Khimii, 2009, Vol. 82, No. 2, pp. 334−338.

MACROMOLECULAR COMPOUNDS AND POLYMERIC MATERIALS

Clarification of a Dilute Suspension of Calcium Carbonate in the Presence of Praestol Flocculants and Aluminum Sulfate Coagulant

V. F. Kurenkov, I. N. Nadezhdin, H.-G. Hartan, and F. I. Lobanov

Kazan State University of Technology, Kazan, Tatarstan, Russia
Stockhausen GmbH, Krefeld, Germany
Ashland Eurasia Limited Liability Company, Moscow, Russia

Received September 18, 2008

Abstract—Kinetic features of clarification of 1% suspension of calcium carbonate under the action of coagulants (aluminum sulfate, hydroxoaluminum chloride) and flocculants (nonionic, anionic, and cationic Praestols) were studied in relation to the dispersed phase concentration, nature of the coagulant and flocculants, sequence and time of their introduction into the suspension, and also molecular weight, chemical composition, and conformation of macromolecules of anionic Praestol in solution.

DOI: 10.1134/S107042720902030X

Water-soluble polymeric flocculants [1, 2] and their mixtures with coagulants [3, 4] are successfully used for efficient dehydration and concentration of mineral suspensions and for treatment of industrial wastewaters. The most widely used are polyacrylamide flocculants [5, 6], in particular, nonionic, anionic, and cationic Praestols, and also coagulants: aluminum sulfate and hydroxoaluminum chloride. For clarification of calcium carbonate suspensions used in production of paper, plastics, ceramics, and paints, it is advisable to use Praestol flocculants in combination with coagulants. However, these processes are studied insufficiently. Previously we examined the effect of cationic [7, 8] and anionic [9] Praestols on the sedimentation stability of dilute [7] and concentrated [8, 9] suspensions of calcium carbonate. Here we report on a comparative study of the performance of nonionic, anionic, and cationic Praestols as flocculants and of aluminum sulfate and hydroxoaluminum chloride as coagulants in clarification of a 1% suspension of calcium carbonate.

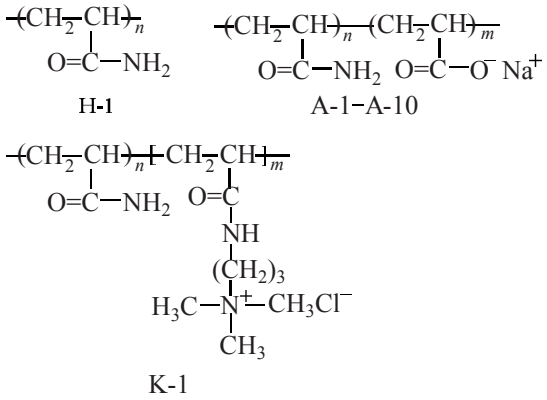
EXPERIMENTAL

Experiments were performed with Praestols produced by Ashland MSP Private Company: polyacrylamide (PAA, nonionic), copolymers of acrylamide (AA) with sodium acrylate (SA) (anionic), and copolymers of AA with *N*-acrylamidopropyl-*N,N,N*-trimethylammonium chloride (APTMAC) (cationic). The characteristics of the Praestols are given in the table. Copolymer samples with different molecular weights but the same molecular composition (A-2–A-7) were prepared by radical degradation of A-1 sample in aqueous solutions, following the procedure described in [10]. We used technical grade (purified) aluminum sulfate $Al_2(SO_4)_3 \cdot 18H_2O$ (Al_2O_3 content 16.35 wt %), hydroxoaluminum chloride [Akva-aurat 30, TU (Technical Specification) 6-09-05-1456–96, Al_2O_3 content 30 wt %], pure grade calcium carbonate with the particle size $\overline{d}$ = 0.1 mm, and other chemicals of chemically pure grade. All solutions were prepared in distilled water. Sedimentation was performed in a 150 cm^3 volumetric cylinder at 20°C. Clarification of the suspension in the cylinder was monitored continuously by the photosedimentation method following the procedure similar to that described in [9]. The content of ionic units in the AA–SA copolymer was determined by potentiometric titration [11], and that in the AA–APTMAC copolymer, mercurimetrically from the content of chlorides [12]. The molecular weight

Table 1. Physicochemical properties of the compounds studied [3]

Sample	Copolymer grade	[η], $cm^3\ g^{-1}$	Content of units, mol %		
			AA	SA	APTMAC
N-1	2500	990	97	3	–
A-1	2530	1800	80	20	
A-2		1500	80	20	
A-3		1200	80	20	
A-4		900	80	20	
A-5		750	80	20	
A-6		200	80	20	
A-7		50	80	20	
A-8	2510	1080	92	8	
A-9	2515	1500	89	11	
A-10	2540	1600	72	28	
C-1	650	690	80	–	20

* Structure of units in macromolecule:



M of (co)polymers was determined from the intrinsic viscosity [η] using the Mark–Kuhn–Houwink equation relating *M* to [η]. The intrinsic viscosity was measured with a VPZh-3 viscometer with a capillary diameter d_c = 0.56 mm in 0.5 M NaCl at 30°C.

To determine the effective size of macromolecular globulas in solution $(\overline{r}^2)^{1/2}$, we took into account the [η]– $(\overline{r}^2)^{3/2}$, relationship described by the Flory–Fox equation [13]:

$$[\eta] = 2.17 \times 10^{21} \frac{(\overline{r}^2)^{3/2}}{M}.$$

In this study, at low copolymer concentrations c_p, we determined instead of [η] the reduced viscosity η_{sp}/c_p and, from this quantity, we indirectly evaluated trends in variation of $(\overline{r}^2)^{1/2}$ for the macromolecules of the copolymers studied.

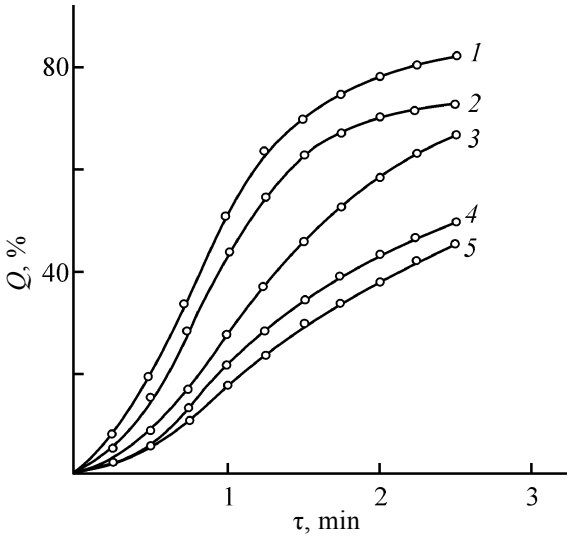


Fig. 1. Degree of suspension clarification *Q* as a function of time τ at various concentrations of the dispersed phase c_d. c_d, %: (*1*) 0.25, (*2*) 0.5, (*3*) 1, (*4*) 3, and (*5*) 5.

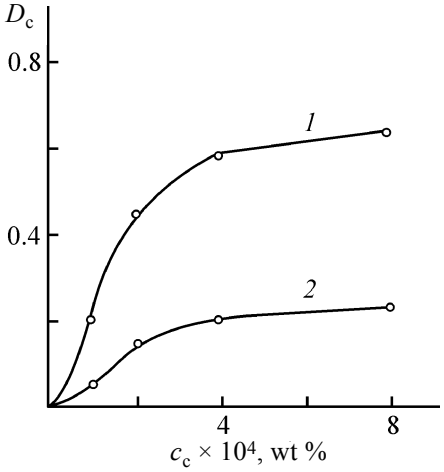


Fig. 2. Coagulating effect D_c as a function of the concentration c_c (counted on Al_2O_3) of (*1*) aluminum sulfate and (*2*) aluminum hydroxochloride.

The adsorption Γ of copolymers on calcium carbonate particles was determined from the difference between the copolymer concentrations before (c_p^0) and after (c_p) the contact with the suspension:

$$\Gamma = \frac{c_p - c_p^0}{c_p^0}.$$

The copolymer concentration was found photocolorimetrically from the optical density of the suspension after adding the copolymer [14].

Initially we examined how the dispersed phase concentration c_d varied in the range 0.25–5% affects the

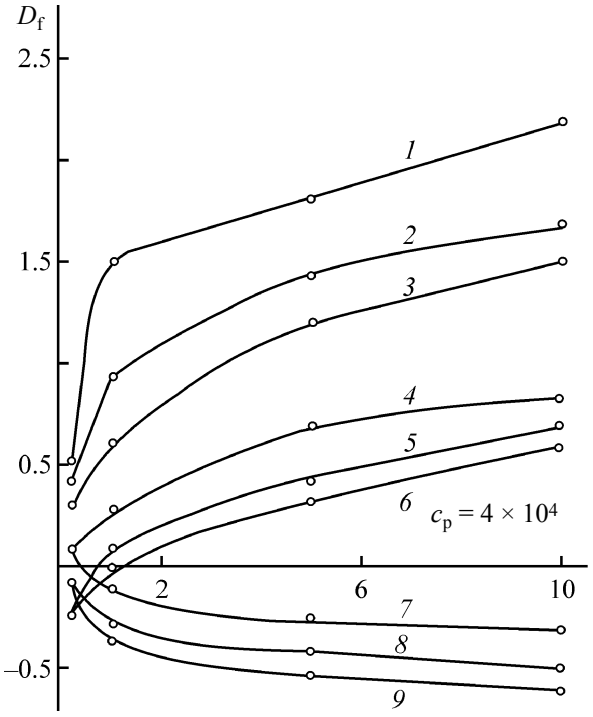


Fig. 3. Flocculating effect D_f as a function of concentration c_c of (*1–3*) AA–SA copolymer (sample A-1), (*4–6*) PAA (sample N-1), and (*7–9*) AA–APTMAC copolymer (sample C-1). c_c = 4 × 10–4%. Addition sequence: (*1, 4, 7*) first coagulant, then flocculant (C + F); (*2, 5, 8*) first flocculant, then coagulant (F + C); and (*3, 6, 9*) C and F simultaneously.

sedimentation of calcium carbonate without coagulant and flocculant. The sedimentation kinetic curves (Fig. 1) show that, with increasing c_d, the rate of the suspension sedimentation increases. This is caused by an increase in the electrostatic repulsion between the negatively charged calcium carbonate particles (ζ-potential –20 mV [9]), and also by enhancement of the hindered sedimentation effect.

Figure 2 shows how the coagulating effect D_c depends on the aluminum sulfate concentration (curve *2*) in 1% suspension of calcium carbonate. For correct comparison of the data, the coagulant concentrations are given counting on Al_2O_3. The coagulating effect D_c was calculated by the formula:

$$D_c = \frac{V - V_0}{V_0},$$

where V and V_0 are the suspension sedimentation rates in the presence of a coagulant and without it, respectively. As seen from Fig. 2, the suspension clarification efficiency increases with an increase in the coagulant concentration. Addition of coagulants results in formation of positively charged aluminum hydroxide particles insoluble in water [4], whose adsorption on negatively charged calcium carbonate particles results, owing to the charge neutralization, in formation of aggregates and their subsequent sedimentation. Fig. 3. Flocculating effect D_f as a function of concentration c_c of (*1–3*) AA–SA copolymer (sample A-1), (*4–6*) PAA (sample N-1), and (*7–9*) AA–APTMAC copolymer (sample C-1). c_c = 4 × 10–4%. Addition sequence: (*1, 4, 7*) first coagulant, then flocculant (C + F); (*2, 5, 8*) first flocculant, then coagulant (F + C); and (*3, 6, 9*) C and F simultaneously. D_f c_p × 10^4, wt % Comparison of data in Fig. 2 at a fixed coagulant concentration (counting on Al_2O_3) shows that the suspension clarification with aluminum sulfate (curve *1*) is more efficient than with hydroxoaluminum chloride (curve *2*). Therefore, in the subsequent experiments we used aluminum sulfate as coagulant. The influence of flocculant concentration c_p on the suspension clarification was evaluated in the c_p range (0.2–1.0) × 10–4%, in combination with aluminum sulfate (c_c = const). A quantitative characteristic of the flocculating effect is the parameter D_f defined as follows:

$$D_f = \frac{V' - V_0'}{V_0'},$$

where V' and V_0' is the suspension sedimentation rate in the presence of a flocculant and without it, respectively. Figure 3 shows the dependence $D_f = f(c_p)$ for PAA (curves *4–6*), AA–SA copolymer (curves *1–3*), and AA–APTMAC copolymer (curves *7–9*) at various sequences of adding coagulant (C) and flocculant (F): first C, then, 1 min later, F (C + F); first F, then, 1 min later, C (F + C); and C and F simultaneously. Figure 3 shows that, with increasing c_p for the anionic and nonionic flocculants (at any addition sequence), the sedimentation rate and D_f increase. This is due to an increase in the amount of polymeric bridges formed by adsorption of macromolecules between calcium carbonate particles and aggregates of calcium carbonate with aluminum hydroxide. As a result, the size of floccules and the rate of their sedimentation increase. Adsorption of PAA on suspension particles may be caused by formation of H bonds between amide groups of the polymer and carbonate groups of $CaCO_3$, and also by complexation between the carbonyl groups of the macromolecules and calcium. In the case of the AA–SA copolymer, adsorption of negatively charged macromolecules on

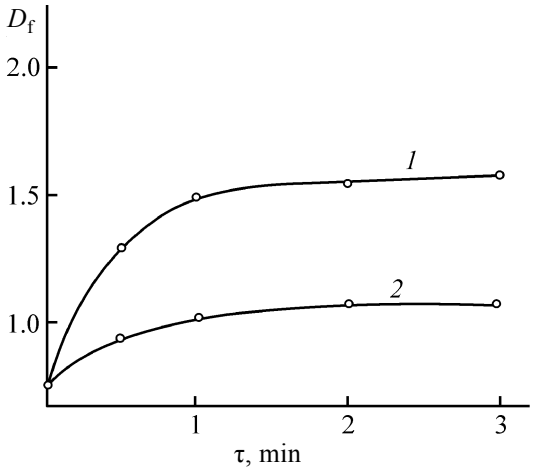


Fig. 4. Flocculating effect D_f of AA–SA copolymer (sample A-1) as a function of the time τ of adding the second component of the C–F mixture. $c_p = 1 \times 10^{-4}$, $c_c = 4 \times 10^{-4}$ wt %. Addition sequence: (*1*) C + F and (*2*) F + C.

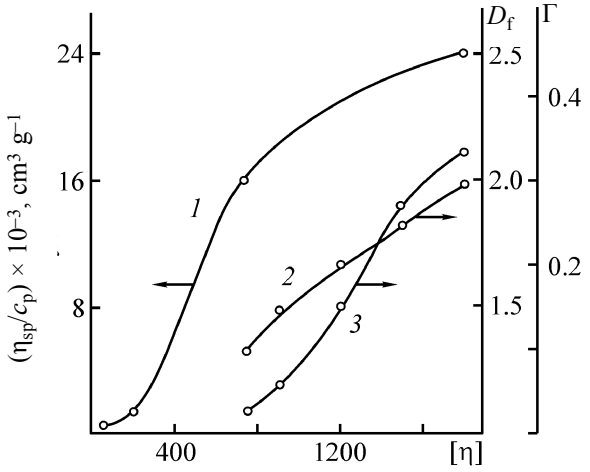


Fig. 5. (*1*) $\eta_{sp/cp}$ (in water), (*2*) adsorption Γ, and (*3*) flocculating effect D_f as functions of [η] of AA–SA copolymer. $c_p = 5 \times 10–4$, $c_c = 4 \times 10–4$ wt %; addition sequence: C + F, τ = 1 min.

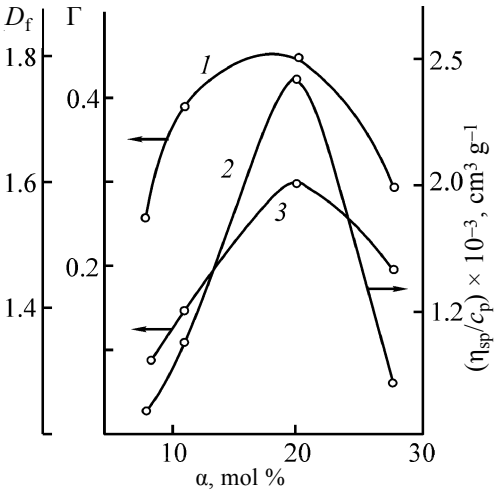


Fig. 6. (*1*) Flocculating effect D_f, (*2*) η_{sp}/c_p (in water), and (*3*) adsorption Γ as functions of the content α of ionic units in AA–SA copolymer. (*1–3*) $c_p = 5 \times 10^{-4}$, (*1*) $c_c = 4 \times 10^{-4}$ wt %; addition sequence: C + F, τ = 1 min.

positively charged particles of aluminum hydroxide, due to charge neutralization, is also possible. For the AA–APTMAC copolymer, the decisive contribution to the adsorption is made by neutralization of negatively charged calcium carbonate particles by the positively charged macromolecules. Comparison of data in Fig. 3 at c_p = const shows that, at all the sequences of introducing C and F, D_f increases in the order AA–APTMAC copolymer (C-1 sample) < PAA (N-1 sample) < AA–SA copolymer (A-1 sample). This is caused by an increase in M of (co)polymers (see table) and in $(\overline{r^2})^{1/2}$ of macromolecules in solution, which increases the probability of linking of a larger number of suspension particles with polymeric bridges. As a result, the floccules grow in size and their sedimentation accelerates. Figure 3 also demonstrates the dependence of D_f on the sequence of adding C and F. When C and F are added in succession (Fig. 3, curves *1*, *4, 7; 2, 5, 8*), D_f is higher than in the case of simultaneous addition (curve *3, 6, 9*). When C is added first (curves *1, 4, 7*), D_f is higher than when F is added first (curves *2, 5, 8*). Presumably, initial addition of C provides its complete hydrolysis with the formation of positively charged colloidal particles [4], which neutralize negatively charged calcium carbonate particles and intensify their sedimentation. Figure 4 shows how the flocculating effect of the AA–SA copolymer (sample A-1) is influenced by the time of adding the second component after the first component. It can be seen that practically the highest values of D_f are attained when F is added 1 min after adding C (Fig. 4, curve *1*), when the hydrolysis of C is complete. Therefore, this order of adding the reagents to the suspension was used in our subsequent experiments.

The effect of M on D_f was evaluated with A-1–A-7 samples having different [η] and constant chemical composition (see table), at c_p = const and c_c = const. The adsorption properties of the copolymer were studied at constant concentrations of the copolymer without coagulant. The dependence of D_f, adsorption Γ, and η_{sp}/c_p on [η] of AA–SA copolymer is shown in Fig. 5. It can be seen that, with increasing [η], D_f (Fig. 5, curve *3*) and Γ (curve *2*) both increase. This is caused by an

increase in $(\overline{r^2})^{1/2}$ (judging from η_{sp}/c_p, Fig. 5, curve *1*) and in the probability of bridge formation between calcium carbonate particles, which leads to coarsening of the floccules and accelerates their sedimentation.

The influence of the chemical composition of AA–SA macromolecules on clarification of a 1% calcium carbonate suspension was estimated with A-2 and A-8–A-10 samples having close *M* (see table). The experiments were performed at c_c = const and c_p = const; the results are shown in Fig. 6. According to these data, the dependences of D_f (Fig. 6, curve *1*) and adsorption Γ (curve 3) on the content α of SA units in AA–SA copolymer pass through a maximum at α = 20 mol %, when an optimal combination of the charge density and flexibility of the macromolecule is attained, and, as a result, the $(\overline{r^2})^{1/2}$ values are the highest. As a consequence, the larger number of suspension particles become linked by polymeric bridges, which accelerates the sedimentation.

The relationships that we revealed for clarification of a calcium carbonate suspension by addition of aluminum sulfate in combination with AA–SA copolymer can be used for intensification of the concentration and dehydration of calcium carbonate suspension and for treatment of industrial wastewaters containing calcium carbonate particles.

CONCLUSIONS

(1) Sedimentation of a calcium carbonate suspension is accelerated with decreasing concentration of the dispersed phase and with increasing concentration of coagulants and flocculants. The reagent effect increases in the following order: hydroxoaluminum chloride < aluminum sulfate; copolymer of acrylamide with *N*-acrylamidopropyl-*N,N,N*-trimethylammonium chloride < polyacrylamide < copolymer of acrylamide with sodium acrylate. The treatment efficiency also depends on the sequence of adding the reagents as follows: simultaneous addition < first flocculant, then coagulant < first coagulant, then flocculant.

(2) When acrylamide–sodium acrylate copolymer is taken in combination with aluminum sulfate, the flocculating effect, adsorption of macromolecules on suspension particles, and η_{sp}/c_p (at c_p = const) vary similarly with varying the molecular weight and the content of ionic units in the copolymer, which is due to a change in the effective size of macromolecules in solution. The flocculating effect is enhanced with an increase in the molecular weight and passes through a maximum (at α = 20 mol %) with increasing content α of ionic units in the copolymer.

REFERENCES

1. Aripov, E.A., Glekel', F.L., and Khamraev, S.S., *Zh. Vses. Khim. O–va. im. D.I. Mendeleeva*, 1989, vol. 34, no. 2, pp.219–223.
2. Lafuma, F., Polymery, 1998, vol. 43, no. 2, pp. 104–108.
3. Veitser, Yu.I. and Mints, D.M., *Vysokomolekulyarnye flokulyanty v protsessakh ochistki prirodnykh i stochnykh vod* (Macromolecular Flocculants in Treatment of Natural and Waste Waters), Moscow: Stroiizdat, 1984.
4. Zapol'skii, A.K. and Baran, A.A., *Koagulyanty i flokulyanty v protsessakh ochistki vody: Svoistva. Poluchenie. Primenenie* (Coagulants and Flocculants in Water Treatment: Properties, Preparation, Application), Leningrad: Khimiya, 1987.
5. Kurenkov, V.F., *Soros. Obraz. Zh.*, 1997, no. 7, pp. 57–63.
6. Myagchenkov, V.A., Baran', Sh., Bekturov, E.A., and Bulidorova, G.V., *Poliakrilamidnye flokulyanty* (Polyacrylamide Flocculants), Kazan: Kazan. Gos. Tekhnol. Univ., 1998.
7. Kurenkov, V.F., Nadezhdin, I.N., Kurenkov, A.V., et al., *Khim. Tekhnol.*, 2006, vol. 7, no. 5, pp. 12–16.
8. Kurenkov, V.F., Nadezhdin, I.N., Kurenkov, A.V., et al., *Zh. Prikl. Khim*., 2007, vol. 80, no. 5, pp. 827–831.
9. Kurenkov, V.F., Nadezhdin, I.N., Hartan, H.-G., and Lobanov, F.I., *Khim. Tekhnol.,* 2008, vol. 9, no. 2, pp. 53–57.
10. Kurenkov, V.F., Budarina, L.A., and Zaikin, A.E., *Praktikum po khimii i fizike vysokomolekulyarnykh soedinenii* (Practical Course of Chemistry and Physics of Macromolecular Compounds), Moscow: Koloss, 2008, pp. 167–168.
11. Kurenkov, V.F., Baidurov, T.A., and Stupen'kova, L.A., in *Fiziko-khimicheskie osnovy sinteza i pererabotki polimerov* (Physicochemical Principles of Polymer Synthesis and Processing), Gor'kii: Gor'k. Gos. Univ., 1985, pp. 79–86.
12. *Rukovodstvo po khimicheskomu i tekhnologicheskomu analizu vody* (Guide on Chemical and Technological Water Analysis), Moscow: Khimiya, 1982.
13. Flory, P.J. and Fox, T.G., *J. Am. Chem. Soc.*, 1951, vol. 73, pp. 1904–1908.
14. GOST (State Standard) 19355–85: Potable Water: *Methods for Determining Polyacrylamide*.