ISSN 1070-4272, Russian Journal of Applied Chemistry, 2009, Vol. 82, No. 2, pp. 333−336. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © V.F. Kurenkov, I.N. Nadezhdin, A.R. Sadykov, H.-G. Hartan, F.I. Lobanov, 2009, published in Zhurnal Prikladnoi Khimii, 2009, Vol. 82, No. 2, pp. 339−342.

MACROMOLECULAR COMPOUNDS AND POLYMERIC MATERIALS

Stabilization of a Concentrated Suspension of Calcium Carbonate with Cationic Praestol

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

Kazan State University of Technology, Kazan, Tatarstan, Russia
Ashland Eurasia Limited Liability Company, Moscow, Russia

Received February 14, 2008

Abstract—The sedimentation stability of a 60% suspension of calcium carbonate in the presence of various commercial samples of cationic Praestol was studied, using a torsion balance, in relation to the concentration and molecular weight of the polymer, concentrations of NaCl and $CaCl_2$, and particle size of calcium carbonate.

DOI: 10.1134/S1070427209020311

It is well known [1–3] that the character of interaction of dispersed phase particles, determining the stability of mineral suspensions, strongly depends on characteristics of polymers and disperse systems. Among various mineral suspensions, calcium carbonate suspensions are of much importance, as they are used in production of paper, ceramics, sodium carbonate, and sugar. The behavior of $CaCO_3$ suspensions has been characterized in reviews [4–6]. The effect of polymers on their stability is studied inadequately, and the available data are contradictory.

Cationic Praestols, which are water-soluble copolymers, show promise for controlling the stability of $CaCO_3$ suspensions. The effect of cationic Praestols on the sedimentation stability of dilute [7] and concentrated [8] $CaCO_3$ suspensions was studied previously. However, in [8] the polymer concentration was varied within narrow limits, $(1–5)\times10^{-3}$%, and the influence of the $CaCO_3$ particle size on the sedimentation was not taken into account.

In this study we evaluated the sedimentation stability of a 60% $CaCO_3$ suspension in the presence of various commercial samples of cationic Praestol in a wide range of its concentrations, 0.003–0.06%, in relation to the molecular weight of the polymer, NaCl and $CaCl_2$ concentrations, and $CaCO_3$ particle size.

EXPERIMENTAL

Studies were performed with cationic Praestols [copolymers of acrylamide (AA) with *N*-acrylamidopropyl-*N,N,N*-trimethylammonium chloride (APTMAC)] (Russia–Germany). The characteristics of the copolymers are given in the table. $CaCO_3$ was of pure grade [GOST (State Standard) 4530–76], with the mean particle size $\bar{d}$ = 0.1 mm. NaCl, $CaCl_2$, and $K_2S_2O_8$ were of chemically pure grade. All solutions were prepared in distilled water.

Samples C-2 and C-3 were prepared by degradation of cationic Praestol 650 VS (C-1) in a 1% solution at 50°C in the presence of potassium persulfate. The degradation procedure was similar to that described previously [9]. By this procedure we obtained copolymer samples with different intrinsic viscosity [η] and the same chemical composition of the macromolecules (see table).

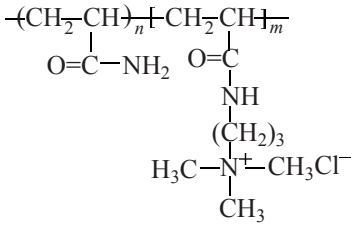
The content of ionic units in the cationic Praestol was evaluated from the chloride content determined mercurimetrically [10]. The [η] values were found from the results of viscometric measurements (VPZh-3 viscometer, capillary diameter d = 0.56 mm) in 0.5 M NaCl at 25°C, from the linear concentration dependence of the reduced viscosity η_{sp}/c_p:

$$[\eta] = \lim(\eta_{sp}/c_p) \text{ at } c_p \to 0.$$

From [η] we estimated on the molecular weight of the polymer M taking into account the Mark–Kuhn–Houwink relationship.

$CaCO_3$ particles were fractionated with a VEB MLW multilevel vibrating screen (Germany).

Characteristics of cationic Praestols



Sample	Grade	[η], $cm^3\ g^{-1}$	Content of units, mol %		
			AA	SA	APTMAC
C-1	650 BC	690	80	–	20
C-2		179	80	–	20
C-3		23	80	–	20
C-4	644 BC	620	73	–	27
C-5	655 BC	555	67	–	33

The ζ-potential of $CaCO_3$ particles was determined by electrophoresis and calculated by the Smoluchowski equation.

Sedimentation of 60% $CaCO_3$ suspension was performed in a volumetric cylinder with VT-500 torsion balance. After adding the required amounts of the reagents, the contents were mixed by forward motion of a perforated stirrer for 1 min (10 runs), after which a pan of a torsion balance was immersed in the suspension to a depth of 30 mm. Variation of the precipitate weight on the balance pan was recorded at regular intervals (Fig. 1). The suspension sedimentation rate was determined from the slope of the tangent to the kinetic curve in Fig. 1. The polymer performance was quantitatively characterized by the parameter D defined as follows:

$$D = (V - V_0)/V_0,$$

where V and V_0 are the sedimentation rates of the $CaCO_3$ suspension in the presence of a polymer and without it, respectively.

Positive values of D are indicative of the flocculating activity of a polymer, and negative values, of its stabilizing effect on the sedimentation stability of the suspension.

Initially we evaluated the effect of $CaCO_3$ particle size on the rate of suspension sedimentation in the presence of polymers and without them. The results of this series of experiments are shown in Fig. 2. It can be seen that, in the presence of cationic Praestol ($c_p = 0.03 \times 10^{-3}$%), the parameter D decreases with increasing $CaCO_3$ particle size. This is apparently due to an increase in the surface area of $CaCO_3$ particles and hence in their charge, which enhances the electrostatic repulsion of particles with the adsorbed polymer and hence stabilizes the suspension. To eliminate the possible effect of $CaCO_3$ particle size on the sedimentation, the subsequent experiments were

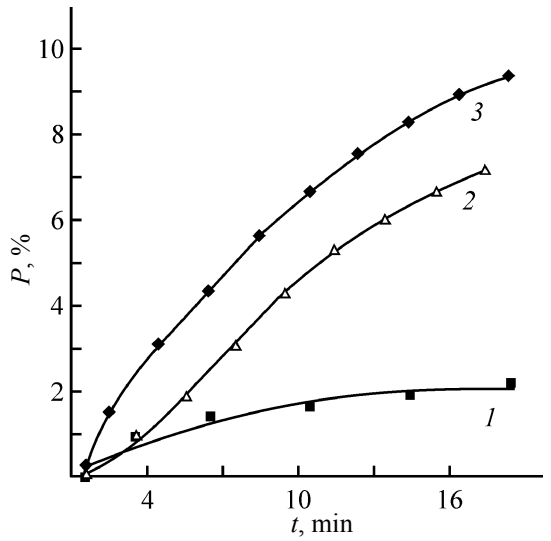


Fig. 1. Relative weight of the precipitate on the pan of the torsion balance P as a function of time t of $CaCO_3$ sedimentation (*1, 2*) in the presence of cationic Praestol (sample C-1) and (*3*) without it. c_p, %: (*1*) 0.031 and (*2*) 0.006.

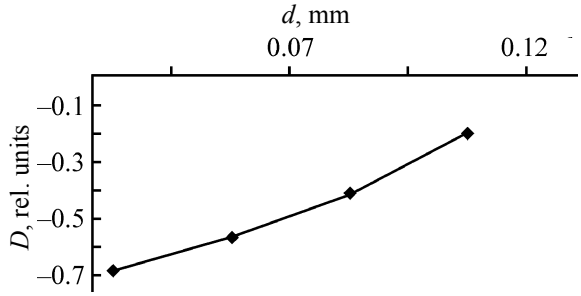


Fig. 2. Flocculating effect D of cationic Praestol (sample C-1) with $c_p = 0.03 \times 10^{-3}$% as a function of the diameter d of $CaCO_3$ particles.

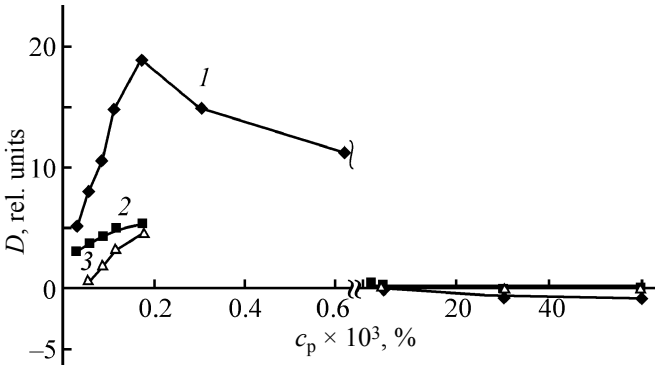


Fig. 3. Flocculating effect D as a function of the concentration c_p of cationic Praestols with [η] (*1*) 690, (*2*) 179, and (*3*) 23 $cm^3\ g^{-1}$ (d = 0.063 mm).

performed with the $CaCO_3$ fraction with the particle size $d = 0.063$ mm.

The influence of the concentration of cationic Praestol (c_p) on the sedimentation of the $CaCO_3$ suspension was estimated in the interval $c_p = (0.03–31) \times 10^{-3}$%. Figure 3 shows the dependence of D on cp for cationic Praestol (sample C-1) (curve 1). The plot of D vs. c_p passes through a maximum, which is well consistent with the corresponding relationship for clarification of carbonate slime under the action of polyethylene oxide [11]. The dependence shown in Fig. 3 is accounted for as follows: As cp is increased, the flocculating effect D is initially enhanced (left part of the curve), which is due to adsorption of the positively charged polymer on negatively charged $CaCO_3$ particles. The polymer adsorption leads to recharging of the $CaCO_3$ particles, which is confirmed by measurements of the ζ-potential of $CaCO_3$ particles (Fig. 4). Enhancement of the polymer adsorption on the particles with increasing c_p increases the particle binding with macromolecular bridges, leads to floccule coarsening, and promotes their sedimentation. In the region of the maximum of the $D = f(c_p)$ curve (at $c_p = 0.2 \times 10^{-3}$%), the surface of $CaCO_3$ particles becomes saturated with the polymer.

Further increase in cp leads to multipoint adsorption of the polymer on particles with the formation of a shell of adsorbed segments of macromolecules. An increase in the charge of the $CaCO_3$ particles due to the adsorbed polymer and in the steric hindrance to mobility leads to stabilization of the $CaCO_3$ particles (right part of Fig. 3). At high concentrations of the polymer, the suspension becomes stabilized with the polymer.

Figure 3 also illustrates the influence of M of the polymer on D. Experiments were performed with cationic Praestol samples C-1–C-3 of similar chemical composition (see table). In the region of $c_p = (0.05–0.5) \times 10^{-3}$%, the parameter D increases with an increase in [η] and hence in M (Fig. 3, passing from curve *3* to curve *1*). With an increase in M, macromolecular bridges involve a larger number of $CaCO_3$ particles. As a result, the floccules consisting of $CaCO_3$ particles and the polymer grow in size and undergo sedimentation. In the region of $c_p = (6.3–31) \times 10^{-3}$%, M of the polymer has virtually no effect on D, and in all the cases the $CaCO_3$ suspension gets stabilized. Therefore, the subsequent experiments were performed at high c_p.

Figure 5 shows the effect of various commercial samples of cationic Praestol (C-1, C-4, C-5) on stabilization of $CaCO_3$ suspensions. All the polymers

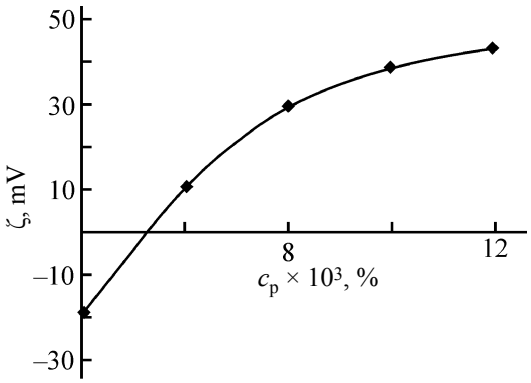


Fig. 4. Plot of the ζ-potential of $CaCO_3$ particles vs. concentration c_p of cationic Praestol (sample C-1).

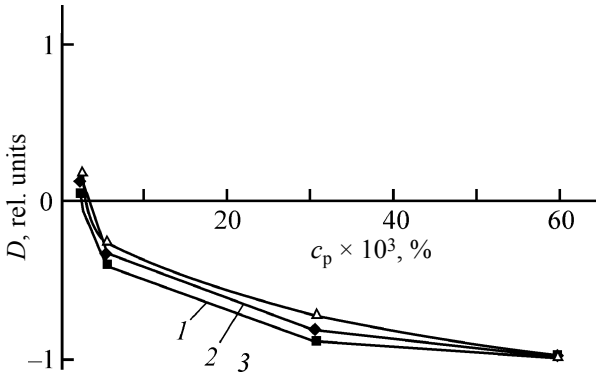


Fig. 5. Parameter D as a function of concentration c_p of cationic Praestols. Sample: (*1*) C-5, (*2*) C-4, and (*3*) C-1.

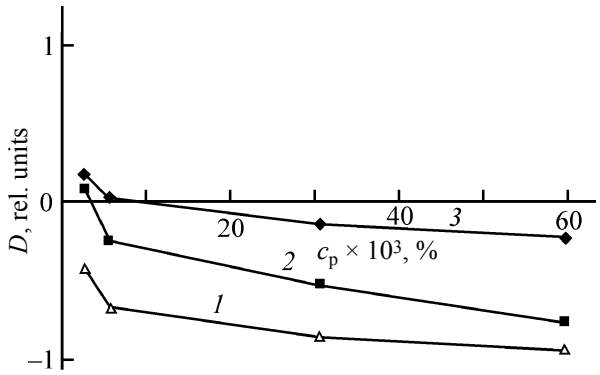


Fig. 6. Parameter D as a function of concentration c_p of cationic Praestol (sample C-1) (*1*) in the presence of 0.5 M NaCl, (*2*) without salt additions, and (*3*) in the presence of 0.5 M $CaCl_2$.

exerted a stabilizing effect on the $CaCO_3$ suspension and did not differ essentially in the D values, because they were similar in [η] and in the chemical composition (see table).

The effect of NaCl and $CaCl_2$ additions on the dependence $D = f(c_p)$ for cationic Praestol is shown in Fig.

6. As can be seen, D decreases with increasing c_p both in the presence of the salts (curves *1, 3*) and without them (curve *2*). Comparison of the curves in Fig. 6 at c_p = const shows that D increases on adding $CaCl_2$. Apparently, this is due to formation of bridges of the type $CaCO_3$ particle–macroion–Ca^{2+}–macroion–$CaCO_3$ particle, in which Ca^{2+} ions form complexes with carboxy groups of the macromolecules. Such bridges cause aggregation of floccules and their sedimentation, which leads to an increase in D. In contrast to Ca^{2+} ions, Na^+ ions do not form such complex bridges, and aggregates of particles and macromolecules, formed in their presence, are smaller. Therefore, D is lower than in the presence of $CaCl_2$. Furthermore, on adding NaCl the acrylate anions of cationic Praestol macromolecules become shielded with Cl^- counterions. As a result, the size of macromolecular globulas and the probability of bridge formation between the particles decrease. As a result, the aggregate size and D decrease (Fig. 6, passing from curve *2* to curve *1*, comparison at c_p = const).

CONCLUSIONS

(1) A study of the effect of cationic Praestol on the sedimentation stability of a 60% suspension of $CaCO_3$ with d = 0.063 mm showed that D of the polymer as a function of c_p passed through a maximum at $c_p \approx 0.2 \times 10^{-3}$%.

(2) D increases with an increase in c_p in the range (0.03–0.2)×10^{-3}% and in [η] from 79 to 690 $cm^3\ g^{-1}$, decreases with a further increase in c_p in the range (0.2–31) × 10^{-3}%, and is independent of [η] in the latter range of c_p.

(3) In the range c_p = (0.2–31) × 10^{-3}%, various commercial samples of cationic Praestols exert a stabilizing effect on the $CaCO_3$ suspension.

(4) D of cationic Praestol decreases on adding NaCl and increases on adding $CaCl_2$.

REFERENCES

1. Napper, D.H., *Polymeric Stabilization of Colloidal Dispersions,* New York: Academic, 1983.
2. Aripov, E.A., Gloeckel, F.L., and Khamraev, S.S., *Zh. Vses. Khim. O–va. im. D.I. Mendeleeva*, 1989, no. 2, pp. 219–223.
3. Lafuma, F., *Polymery*, 1998, vol. 43, no. 2, pp. 104–108.
4. Duplop-Jones, N. and Jaycock, M.J., *Paper Trade J.,* 1981, vol. 34, no. 20, pp. 169–173.
5. Siffert, B. and Fimbel, P., *Colloids Surf.*, 1984, vol. 377, nos. 3–4, pp. 11–18.
6. Huang, Y.A., Fowkes, F.M., Lloyd, T.B., and Sanders, N.D., *Langmuir*, 1991, no. 7, pp. 1742–1750.
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. 827–830.
9. Kurenkov, V.F., Len'ko, O.A., Snigirev, S.V., and Lobanov, F.I., *Zh. Prikl. Khim.*, 2002, vol. 75, no. 7, pp. 1164–1168.
10. Mel'nikova, E.A., *Rukovodstvo po khimicheskomu i tekhnologicheskomu analizu vody* (Guide on Chemical and Technological Water Analysis), Moscow: Khimiya, 1982.
11. Solomentseva, I.M., Baran, A.A., Postoronko, A.I., and Kurilenko, O.D., *Ukr. Khim. Zh.*, 1973, vol. 39, no. 8, pp. 785–789.