ISSN 1070-4272, Russian Journal of Applied Chemistry, 2014, Vol. 87, No. 12, pp. 1836−1841. © Pleiades Publishing, Ltd., 2014.
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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Effect of Adsorption of Polyhexamethyleneguanidine Derivatives on the Formation Rate, Morphology, and Phase Composition of Carbonate Deposits

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Received December 26, 2014

Abstract—It was found that introduction of polyhexamethylguanidines modified with carboxy and phosphonic groups into a saturated solution of calcium carbonate affects the formation rate, morphology, and phase composition of the deposits being formed, with crystals in the deposit becoming coarser and rhombic structures appearing. These phenomena were manifested to a greater extent when zinc complexes of polyelectrolytes are present in solution. An analysis of the phase composition of the deposit demonstrated that the presence of polyelectrolytes and their zinc complexes in solution leads to an increase in the amount of the calcite phase. The reason why the phase composition and morphology of the deposits changes is that polyelectrolytes and their complexes are adsorbed on the surface of carbonate deposits. The adsorption of polyelectrolytes on a calcium carbonate powder is described by the Langmuir isotherm and the formation of their zinc complexes leads to an increase in the adsorption equilibrium constant by more than a factor of 2, which is due to the change in the hydrophilic-lipophilic balance of macromolecules in complexation.

DOI: 10.1134/S1070427214120076

In operation of recycling water supply systems, there occurs formation of deposits of calcium and magnesium carbonates on the surface of apparatus and its corrosion, which impairs the heat-exchange conditions, makes lower the output capacity, and leads to accidents. To protect the surface of metals from salt deposition and corrosion, special inhibitors are commonly introduced into the system, which are, in particular, hydroxyethylidenediphosphonic acid and its zinc complex [1, 2] Phosphonic groups are characterized as ligands by a large formation constant of water-soluble complexes with calcium and magnesium ions. However, these compounds lose their inhibition efficiency in media with high content of hardness salts and weakly reduce the corrosion of metals [3].

In recent years, the role of corrosion and salt-deposition inhibitors in neutral media is played by cationic polyelectrolytes based on polyhexamethylguanidine, which possess, in addition to the characteristics mentioned above, biocide properties [4–6]. To enhance the complexing capacity of polyelectrolytes with ions of alkaline-earth groups, it is advisable to introduce carboxy groups into their composition [7]. It was shown in [8] that grafting of carboxy groups to a polyhexamethylguanidine molecule improves its inhibiting capacity in salt deposition and corrosion, which is additionally enhanced when zinc complexes are formed. It has been shown that replacement of carboxy groups with phosphonic groups in salt-deposition inhibitors sharply enhances the complexing capacity of compounds [2, 9]. It is of interest to compare the formation rates, morphologies, and phase compositions of the calcium carbonate deposit in the presence of modified polyelectrolytes and their complexes, with their adsorption on the surface of the calcium carbonate powder.

EXPERIMENTAL

We used polyhexamethylguanidine hydrochloride (PH) of Metacide brand. The compounds containing carboxy (PHC) and phosphonic (PHP) groups were synthesized on its basis at the Chair of chemistry and technology of elastomer processing at the Ukrainian State University of Chemical Technology. Zinc complexes were formed upon introduction of zinc sulfate into solutions containing the corresponding polyelectrolytes.

The effect of polyelectrolytes on the amount of the calcium and magnesium carbonate deposit being formed was evaluated by the residual concentration of calcium ions in solution, determined titrimetrically in conformity with GOST (State Standard) 4151–72 [10]. We used for this purpose a supersaturated model solution (A) formed on pouring together solutions I and II. Solution I contained 1.1 g of $CaCl_2$, 0.4 g of $MgCl_2$, and 3.1 g of NaCl, dissolved in 1000 mL of twice-distilled water. Solution II: 7.5 g of NaCl, 11.0 g of $NaHCO_3$, and 1.0 g of NH_4Cl, dissolved in 1000 mL of twice-distilled water [11]. The mixture was kept for 5 h on a water bath at 75 ± 5°C, cooled to room temperature, and filtered through a "blue ribbon" paper filter. The efficiency of salt-deposition inhibition E (%) was found by the formula

$$E = \frac{(c_x - c_{x,0})}{(c_0 - c_{x,0})} \times 100, \tag{1}$$

where $c_{x,0}$ and c_x are the contents of calcium ions in a filtrate without and with inhibitor, respectively (g m^{-3}); and c_0 is the initial content of calcium ions in the model supersaturated solutions (g m^{-3}).

We evaluated the effect of polyelectrolytes on the phase composition of carbonate deposits by using the model supersaturated solution (B) [12]. To a conical flask containing 45 mL of a 1 M $CaCl_2$ solution and 10 mL of a 0.1 M $MgCl_2$ solution was added 1 mL of a polyelectrolyte solution with a concentration of 10^{-4} M and 45 mL of a 1 M $NaHCO_3$ solution. The solutions were agitated and kept at 80°C for 1 h. Then the mixture was cooled to room temperature and filtered with a "blue ribbon" filter. The precipitate was dried at room temperature, weighed, and analyzed with a DRON-3 diffractometer with monochromatized CuK_α radiation (40 kV, 20 mA, recording rate 1 deg min^{-1}). Scanning-electron-microscopic (SEM) images of the deposits were obtained with a REM-106I scanning electron microscope in the secondary-electron mode.

The adsorption of the polyelectrolytes on the $CaCO_3$ powder (Γ) was found from the loss of the adsorbate content in solution upon its contact with the adsorbent for 60 min:

$$\Gamma = \frac{c_1 - c_2}{S_{sp} m} V, \tag{2}$$

where c_1 and c_2 are the concentrations of the polyelectrolytes before and after their adsorption on calcium carbonate (mol m^{-3}); m, mass of the sorbent (g); V, solution volume taken for adsorption (m^3); and S_{sp}, specific surface area of calcium carbonate (m^2 g^{-1}).

Portions (1 g) of a $CaCO_3$ powder of chemically pure grade with a specific surface area of 0.21 m^2 g^{-1} were placed in dry flasks and poured over with 25 mL of solutions containing various concentrations of the polyelectrolytes. The residual concentrations of the polyelectrolytes upon adsorption were determined using a linearized isotherm of the surface tension at the interface between a solution under study and air as the calibration dependence. The surface tension was determined by the plate method with a Vibra HT-120 digital balance and a 59.7 × 0.3 × 7.4 mm platinum plate. The plate was degassed and burned with a burner [13].

The specific surface area of the $CaCO_3$ powder was determined in a trivial experiment [13], with isoamyl alcohol as adsorbate, and calculated by the equation

$$S_{sp} = A_\infty S_0 N_A, \tag{3}$$

where S_0 is the projection area of an isoamyl alcohol molecule in the Briegleb–Stuart model, 0.3×10^{-8} m^2 [14]; A_∞, experimental value of the specific adsorption of the alcohol on the adsorbent surface, 1.2×10^{-6} mol g^{-1}; and N_A, Avogadro's number.

The reagents used in the study were of analytically pure grade. The solutions were prepared from twice-distilled water.

RESULTS AND DISCUSSION

The introduction of the polyelectrolytes in to model solution (A) led to ac decrease in the formation rate of the crystalline phase, with this occurring to a greater extent in the case of PHP (Fig. 1). In the presence of Zn^{2+} ions,

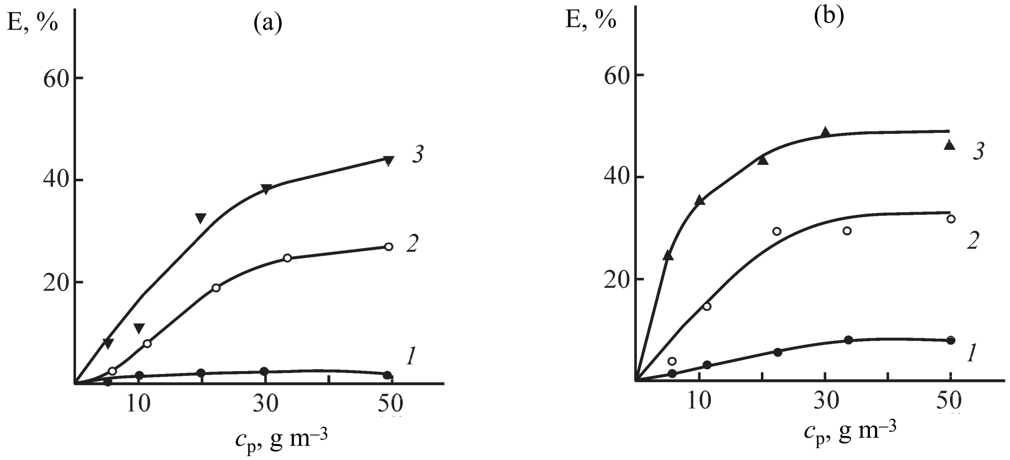

Fig. 1. Salt-deposition inhibition efficiency E in solution A vs. the concentration c_p of (a) polyelectrolytes and (b) their zinc complexes. (a) (*1*) PH, (*2*) PHC, and (*3*) PHP; (b) (*1*) Zn^{2+}PH, (*2*) Zn^{2+}PHC, and (*3*) Zn^{2+}PHP.

the polyelectrolytes reduced the salt deposition more effectively.

The modification of PH with carboxy and phosphonic groups strongly enhanced its salt-deposition inhibiting capacity, which was observed to a greater extent for PHP. The significant rise in the salt-deposition inhibiting capacity in the case of PH modification with carboxy and phosphonic groups may be due to the formation of soluble complexes with calcium ions. The increase in the inhibiting capacity of PHP, compared with PHC, is partly due to the fact that the formation constant of soluble complexes of calcium and magnesium cations with phosphonic groups substantially exceeds that for carboxy groups. The formation of zinc complexes enhanced the effect of the polyelectrolytes, especially at low concentrations (5–25 mg L^{-1}). It follows from the E–c_p isotherms in Fig. 1 that the limiting value of the salt-deposition inhibition efficiency is reached at high concentrations of the polyelectrolytes and their complexes, which may be due to the adsorption effects. In this case, the observed run of the isotherms may be associated with the blocking of the possible crystal growth centers, which changes the formation rate and the structure of the deposit.

Using the model supersaturated solution B, we obtained deposits of calcium and magnesium carbonates in the presence of various polyelectrolytes and their zinc complexes. An analysis of SEM micrographs of these deposits (Fig. 2) demonstrated that the presence of PH in solution led to a decrease in the size of the crystals. Upon introduction of PHP and PHC, the crystals became coarser and rhombic structures appeared in their composition. These tendencies were particularly clearly demonstrated in the case of zinc complexes of the polyelectrolytes.

The presence of crystals with needle-like and rhombic structure in the deposits pointed to their polymorphism. The phase composition of the substances was determined from the set of interplanar spacings and the corresponding intensities, found from their X-ray diffraction patterns [15, 16] (Fig. 3).

In the presence of the polyelectrolytes and their zinc complexes, the intensity of the lines related to the calcite phase increases, and that for the aragonite phase, decreases. The quantitative relationship between the phases in the presence of the polyelectrolytes (Table 1) was estimated by the intensity of the corresponding lines of calcite (I_c) and aragonite (I_a) in accordance with the following approach:

$$W_c + W_a = 100\%, \tag{4}$$

$$W_c = \frac{I_c}{I_c + I_a}, \tag{5}$$

where W_c and W_a are the contents of the calcite and aragonite phases (%).

An analysis of the data in Table 1 demonstrated that the presence of the polyelectrolytes and their zinc complexes in solution led to a higher content of the calcite phase in the deposit. The increase in the amount of the calcite phase was the most pronounced in the presence of PHP in solution: the content of calcite increased by 28.5%; whereas in the case of Zn^{2+}PHP, the increase was by 21.0%.

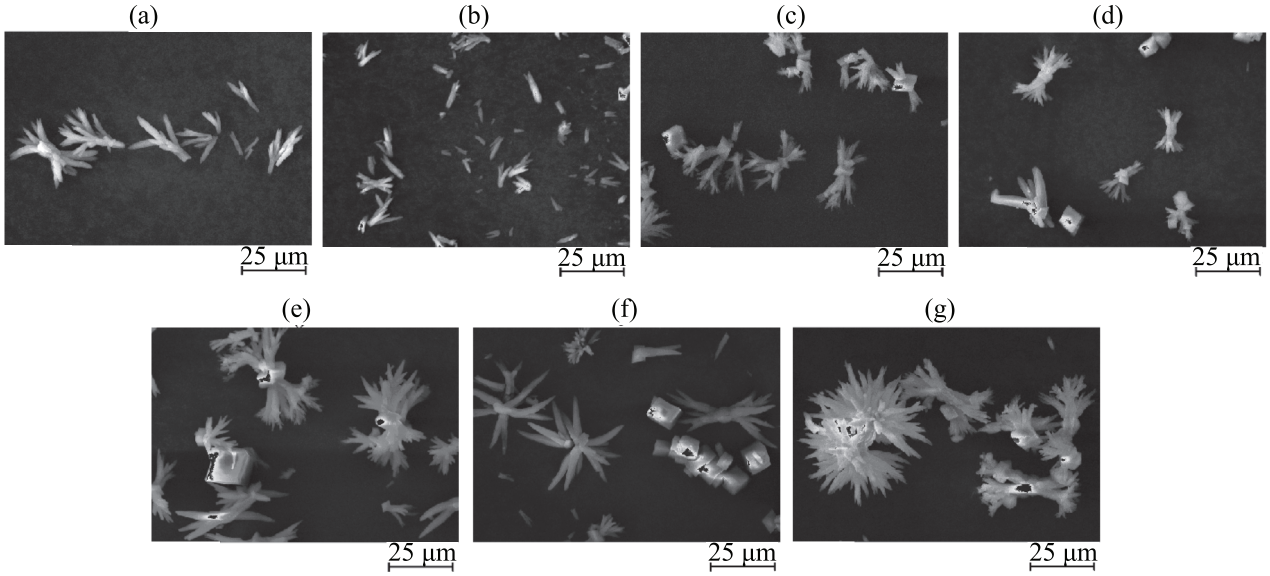

Fig. 2. SEM images of the calcium carbonate deposit (a) without additives and in the presence of (b) PH, (c) PHC, (d) PHP, (e) Zn^{2+}PH, (f) Zn^{2+}PHC, and (g) Zn^{2+}PHP. Magnification ×1000.

These effects may be due, in addition to a change in the equilibrium content of calcium ions in solution as a result of complexation, to the adsorption of the polyelectrolytes and their complexes on calcium carbonate faces. The adsorption of the polyelectrolytes and their complexes at the solution/$CaCO_3$ interface is described by the Langmuir isotherm (Fig. 4). This nature of the inhibition efficiency isotherms (Fig. 1) and the isotherms of inhibitor adsorption at the solution/$CaCO_3$ interface (Fig. 4) indicates that this assumption is justified.

Using the data in Fig. 4, we determined values of the limiting adsorption Γ_∞, adsorption equilibrium constant B, and Gibbs free energy $\Delta G°$ (Table 2).

Analysis of the data in Table 2 shows that values of the limiting adsorption of the polyelectrolytes under study remain nearly unchanged, and decrease in the presence of zinc ions by more than a factor of 2 as compared with the starting oligomers. This may be due to the coarsening of polyelectrolyte macromolecules as a result of the change of their conformation in complexation with zinc ions. The adsorption equilibrium constants slightly increased in the order PHC < PH < PHP. In the complexation of the polyelectrolytes with zinc ions, their adsorption equilibrium constants substantially increased, with the largest value observed for Zn^{2+}PHP. This effect may be due to a change in the hydrophilic-lipophilic balance of the macromolecules in complexation and to their enhanced expulsion by the solvent to the phase boundary. The rise in the hydrophobicity of the zinc complexes of the polyelectrolytes is confirmed by the increase in the distribution coefficient by factors of 1.6 for Zn^{2+}PHC, 1.2 for Zn^{2+}PHP, and 1.4 for Zn^{2+}PH, compared with the base oligomers [9].

Thus, the above experimental data demonstrate that polyelectrolytes can reduce formation of carbonate deposits both via formation of soluble complexes with calcium and magnesium ions and due to the adsorption of polyelectrolytes on the surface of crystals in a deposit. We believe that the main reason why the formulations under study affect the polymorphic forms, morphology, and size of particles is that polymers undergo a selective specific adsorption on the calcium carbonate faces being formed, with just the difference in the strength of the

Table 1. Phase composition of calcium carbonate obtained in the presence of the polyelectrolytes and their zinc complexes

Additive	W_c	W_a
	%	
Absent	60.1	39.9
PH	62.5	37.5
PHC	77.3	22.7
PHP	88.6	11.4
Zn^{2+}PH	78.4	21.6
Zn^{2+}PHC	78.8	21.2
Zn^{2+}PHP	81.1	18.9

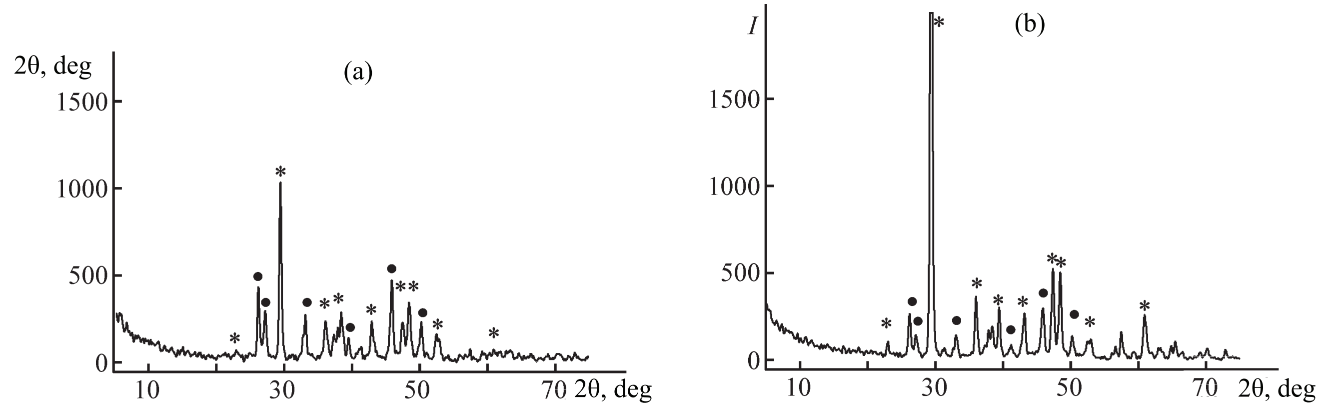

Fig. 3. X-ray diffraction patterns of calcium carbonate (a) without additives and (b) in the presence of PHP. Phase: (*I*) calcite and (*II*) aragonite.

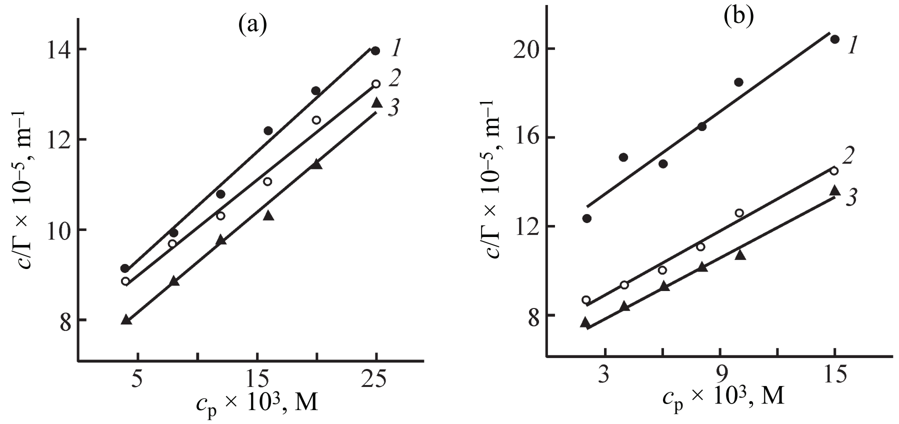

Fig. 4. Adsorption isotherms c/Γ–c_p of (a) polyelectrolytes and (b) their zinc complexes on the surface of calcium carbonate. $c_{Zn} = 1 \times 10^{-4}$ M, $T = 290$ K. (*1*) PH, (*2*) PHC, and (*3*) PHP.

adsorption interaction determined by the nature of a polyelectrolyte determining the final polymorphic form of carbonate deposits.

CONCLUSIONS

(1) Presence of polyhexamethylguanidines modified with carboxy and phosphonic groups in solution leads to a lower rate of deposit formation, change in the size and shape of crystals, and larger fraction of calcite in the deposited calcium carbonate.

(2) When zinc complexes of polyhexamethylguanidine hydrochloride and PHC are formed, the deposit becomes coarser and its content of the calcite phase grows. Introduction of PHP into the model solution raises the content of calcite by 28.5%, with this increase being 21.0% in the case of Zn^{2+}PHP.

(3) The change in the formation rate, morphology, and phase composition of the deposit is due to the adsorption of the polyelectrolytes and their complexes on the surface of calcium carbonate. Among the polyelectrolytes under study, the best adsorption properties on the surface of the

Table 2. Adsorption parameters of the polyelectrolytes and their zinc complexes on the surface of calcium carbonate

Parameter	PH	PHC	PHP	Zn^{2+}PH	Zn^{2+}PHC	Zn^{2+}PHP
$\Gamma_\infty \times 10^7$, mol m^{-2}	4.2	4.8	4.5	1.7	2.2	2.2
B, m^3 mol^{-1}	29.3	26.5	31.6	51.1	61.7	68.5
$-\Delta G°$, kJ mol^{-1}	35.4	35.2	35.6	36.8	37.3	37.5

deposit were observed for PHP. The formation of zinc complexes of the polyelectrolytes led to an increase in the adsorption equilibrium constant more than a factor of 2. The rise in the adsorption of the zinc complexes of the polyelectrolytes is due to the change of the hydrophilic-lipophilic balance of their macromolecules and their stronger expulsion by the solvent to the phase boundary.

ACKNOWLEDGMENTS

The study was carried out in the framework of budget-funded research project no. 0113U000016.

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