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SHORT COMMUNICATIONS

Effect of Poly(acrylic acid-*co*-*N*-vinylpyrrolidone) on Calcium Oxalate Crystallization

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Polyelectrolyte effect on all stages of salt precipitation from solution have been extensively studied.[1-5] This research is important for the prevention of scale formation in heat exchanger, water desalination plants, bone desease, pathological desalination of artificial implants, etc. Polyelectrolyte inhibition effect on calcium oxalate CO crystallization is of special interest as the latter is a general process of the kidney stone formation.[4-7] In the present work the dependence of the induction period (τ) and CO crystallization kinetics on the composition and concentration of poly(acrylic acid-*co*-*N*-vinyl pyrrolidone) (AAVP) is studied. There are at least three reasons to choose this copolyelectrolyte: 1. Synthetic copolyelectrolytes are not used up to now as CO crystallization effectors. 2. Possibility for the realization of the combined effect of poly(vinylpyrrolidone) (PVP) and poly(acrylic acid) (PAA) on CO crystallization. The former is known as an excellent dispersing agent and the latter—as a power inhibitor of CO crystals growth. Recently[5] it was shown the combined use of different types of CO crystallization effectors is favored. 3. Possibility to check the efficiency of the new controlled CO crystallization parameter—the copolymer composition.

EXPERIMENTAL

PVP (Fluka) with $K_F = 10$ was used. AAVP with mole fractions of AA units of 0.25, 0.46, and 0.87 (CP25, CP46, and CP87, respectively) were synthesized by radical copolymerization in water or in the absence of a solvent using azobisisobutyronitrile (0.5%) as initiator at 70°C. The obtained copolymers were separated and purified by precipitation in diethyl ether. CO was obtained by mixing of equimolar solutions of calcium chloride, hexahydrate and potassium oxalate, monohydrate in a 0.3 M sodium chloride solution in bidistilled water. Sodium chloride provided the ionic strength corresponding to that of urine. The salts used were with p.a. qualification. Just before mixing both solutions were filtered through a Millipore filter with a pore size of 0.45 μm. The isothermal chemical crystallization was performed in a closed vessel without stirring. Experiments with predetermined quantities of copolymers added to the solutions were also carried out. The induction periods were determined nephelometrically by means of a Pulfrich photometer (Carl Zeiss, Jena) or by a Particle Coulter-Counter PCA 1 (England). The CO crystallization kinetics was followed complexometrically by determination of the Ca con-

centration in the filtered samples. Inhibitory efficiency (γ) was calculated using the ratio $\gamma=(\tau_I-\tau_0)/\tau_0$ where τ_I and τ_0 are induction periods in the presence or absence of the inhibitor correspondingly.

RESULTS AND DISCUSSION

τ and γ values during CO crystallization at different temperatures, in the absence or presence of PVP at different concentrations are given in Table I. It is evident that PVP behaves as an inhibitor only in the temperature range from 14°C to 37°C at concentrations up to 0.1% (w/v). But γ values at 45°C is practically zero at all PVP concentrations studied. The same holds for 0.25% (w/v) PVP and for practically all PAA concentrations in the entire temperature range.

However, the inhibitory effect of AAVP to CO crystallization differs from those of PVA and PAA. τ and γ dependences on the temperature and copolymer concentration are presented in Table II. The first considerable difference between homopolymer and copolymer inhibitory effects on CO crystallization is that AAVP keeps this effect at 50°C while homopolymers lose it at 45°C. Even so at 50°C γ for CP samples assumes its peak value. Figure 1 shows this difference more clearly.

The second differences between homo- and copolymer inhibitory effects is of practical interest because the maximal γ values achieved at 0.1% (w/v) PVP are obtained at 0.03% (w/v) CP. Data shown in Table II and Figure 1 prove also a considerable influence of the

Table I. Effect of the temperature and PVP concentration (C_{PVP}) on the induction period (τ) and inhibitory efficiency (γ) (Supersaturation 1.3)

	C_{PVP}/% (w/v)				
T/°C	0.00	0.01	0.03	0.10	0.25
	τ/min (γ)				
14.4	39.0	44.5 (0.141)	46.5 (0.192)	78.0 (1.000)	39.5 (0.013)
20.0	35.0	40.5 (0.157)	41.0 (0.171)	70.0 (1.000)	35.0 (0.000)
22.0	30.0	39.0 (0.300)	41.5 (0.383)	64.5 (1.150)	29.0 (0.033)
25.0	25.0	25.0 (0.000)	40.5 (0.620)	63.5 (1.540)	28.0 (0.000)
37.0	11.0	11.0 (0.000)	25.5 (1.318)	29.5 (1.682)	11.0 (0.000)
45.0	10.0	10.0 (0.000)	10.5 (0.050)	11.0 (0.100)	10.0 (0.000)

Table II. Effect of the temperature and copolymer concentration (C_{CP}) on the induction period (τ) and inhibitory efficiency (γ) (Supersaturation 1.3)

Copolymer	C_{CP}/% (w/v)	T/°C		
		25 τ/min (γ)	37 τ/min (γ)	50 τ/min (γ)
No	0.00	25.0	11.0	4.0
CP25	0.03	42.5 (0.700)	29.0 (1.636)	8.5 (1.125)
CP25	0.07	53.0 (1.120)	35.0 (2.182)	23.0 (4.750)
CP46	0.03	49.0 (0.960)	42.0 (2.818)	17.0 (3.250)
CP46	0.07	64.0 (1.560)	47.0 (3.272)	36.0 (8.000)
CP87	0.03	38.0 (0.520)	25.0 (1.212)	8.0 (1.000)
CP87	0.07	53.5 (1.140)	32.5 (1.954)	9.5 (1.375)

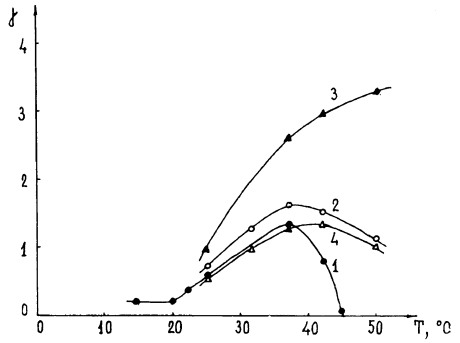

Figure 1. Inhibitory efficiency (γ) of CO crystallization affected by PVP (curve 1), CP25 (curve 2), CP46 (curve 3), and CP87 (curve 4) as a function of a temperature. Supersaturation, 1.3; $C_{pol}=0.03\%$ (w/v).

Table III. Effect of the initial salt and polymer solution fitration quality on τ and γ of CO crystallization in the absence or presence of PVP, CP25, CP46, and CP87 (Polymer concentration 0.03% (w/v); $T=14.4°C$)

Filter	Polymer	τ/min	γ
G-5	No	39.0	
	PVP	46.5	0.192
	CP25	50.5	0.294
	CP46	53.0	0.359
	CP87	42.5	0.090
Millipore 0.45 μm	No	55.0	
	PVP	55.0	0.000
	CP25	71.5	0.300
	CP46	77.0	0.400
	CP87	60.5	0.100

copolymer composition on its inhibitory effect. The obtained dependence of γ on mole fraction of AA in AAVP is extremal with maximum at CP46. The decrease of γ for CP87 could be explained with the compositional approximation of CP87 to PAA which is a good dispersing agent but not an inhibitor of CO crystallization.[5] Macromolecular linear charge density (MLCD) and conformation are obvious determining factors for the polyelectrolyte inhibitory efficiency.

Recently[5] it was proved that solution filtration quality, cleaning of apparatus, perfomance of the flow cell, etc. influence considerably on the polyelectrolyte inhibitory effect of the CO crystallization. The results included in Table III confirm this conclusion. But at the same time they demonstrate again the different relation of homo- and copolyelectrolytes to the quality of the solvent filtration. When solutions are filtered through a glass filter G5 with a pore size of 1—6 μm τ values are smaller than those obtained after filtration through Millipore with pore size of 0.45 μm. But PVP γ value after a fine filtration is zero while CP γ values in this case are just above those before this operation. These opposite effects prove principle different modes of the homo- (PVP and PAA) and copolyelectrolyte (CP25, CP46, CP87) inhibitory influence on the CO crystallization consisting of nucleation, crystal grows and aggregation process. A probable explanation of this difference is that PVP effect is a result of its interaction with the heteroseeds in salt solutions. After filtration of the latter, PVP influence on the CO crystallization ends. The ability of the carboxylic group to form complexes with calcium ions results in another way for CP and PAA to remove these ions and to retard the CO crystallization. The complex formation ability depends on the carboxylic group concentration and macromolecular flexibility.[8] Opposite change directions of this explanes the maximal τ and γ values for CP46. At low MLCD the change of the first factor predominates and it is responsible for τ and γ increase in a series PVP, CP25, and CP46. At high MLCD the change of the second factor prevails and it is responsible for the decrease of the PAA and CP87 influence on the CO crystallization.

This assumption is confirmed also by the PVP and CP influence on the CO crystallization rate. It is established that PVP and CP differ in their ability to diminish the growth rate of CO crystals in a similar way as they influence τ and γ (Figure 2). The crystallization kinetics is presented by the dependence degree of crystallization (α) *vs.* time (t). The

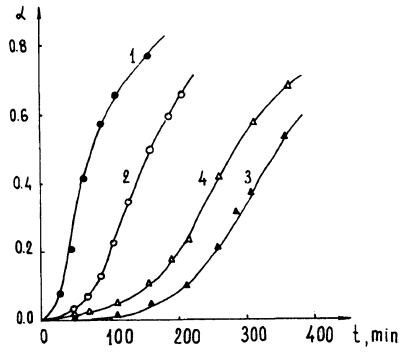

Figure 2. CO crystallization kinetics at 37°C without polymer (curve 1) and with CP25 (curve 2), CP46 (curve 3), and CP87 (curve 4). Supersaturation, 1.3; $C_{pol}=0.03\%$ (w/v); temperature, 37°C.

addition of PVP to the salt mixture hardly affects the CO crystallization rate; it remains the same as that determined in the mixtures free of additives. CP25 and CP46 decrease significantly the CO crystallization rate as it is demonstrated in Figure 2. As it should be expected, CP87 decrease the CO crystallization rate a little less than CP46. These observations are in agreement with those for the influence of the same polymers on τ and γ. So, these results prove that the copolymers used, influence both nucleation and crystals growth of the CO crystallization in opposite sense as compared to that of the PVP and PAA influence.

SUMMARY

AAVP are more effective inhibitors of the CO crystallization than PVP and PAA. They increase τ and γ values, decrease the crystals growth rate and expand temperature and concentration intervals of the CO crystallization control. It is proved the possibility to combine effects of homopolymers (influencing on the different stages of the CO crystallization) using copolymers of the corresponding monomers. The advantage of the copolymer application is the possibility to control the inhibition of the CO crystallization and crystals growth rate by the change of the copolymer composition.

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