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SHORT COMMUNICATION

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Adsorption of a new amphoteric cellulosic copolymer onto bentonite

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Abstract The adsorption of a new amphoteric cellulosic copolymer onto bentonite from aqueous solutions was studied at different salt concentrations and temperatures. The adsorption kinetics included a fast step and a slow step. The rate of initial rapid adsorption was reduced by the addition of NaCl. An increase in the concentration of added NaCl or increasing temperature decreased the amounts adsorbed. The influence of sodium dodecylsulfate and hexadecyl trimethylammonium chloride was also studied.

Key words Amphoteric cellulose – Bentonite – Adsorption – Surfactants

Introduction

Amphoteric polymers containing functional groups of acidic and basic character are now widely used in numerous industrial processes such as well drilling and completion [1–5], water purification [6], sewage treatment [7], scale inhibition [8], flocculation [9, 10] and dye decolorization [11]. In many of these processes, the performance is greatly governed by the nature and extent of adsorption of the polymers on the minerals. Over the last 40 years or so, a considerable amount of work on the adsorption of nonionic or ionic polymers at surfaces has been published in the scientific literature. To our knowledge, however, there is no information available on the adsorption of amphoteric polymers except for two previous publications [12, 13], which described the adsorption of a synthetic amphoteric polymer on silica and $BaSO_4$ crystals. In this paper, we report the adsorption of a new amphoteric cellulosic copolymer on bentonite. The new cellulose derivatives were synthesized recently in our laboratory [14].

Experimental

Materials

The amphoteric cellulosic copolymer (CGAD) was prepared by grafting dimethylaminoethyl methacrylate (DMAEMA) and acrylamide (AM) onto sodium carboxymethyl cellulose (NaCMC) in an aqueous solution using ammonium persulfate and *N*,*N*,*N′*,*N′*-tetramethylethylene as the redox initiator [14]. The weight percentages of NaCMC, AM and DMAEMA in CGAD were 32.46, 58.77 and 8.84, respectively. The bentonite, containing 96 wt% calcium montmorillonite, was provided by China National Oil & Gas Exploration & Development Corporation and its cation exchange capacity, determined by the methylene blue method [15], was 82.3 mEq/100 g. The CdI_2– starch coloring agent [16] was prepared by first dissolving 1 g soluble starch in 100 ml boiling water and then dissolving 1 g CdI_2. Other reagents were of analytical grade.

Adsorption measurement

For an adsorption test, a dispersion of 20 g bentonite in 1 l water was first prepared. Then a certain amount of an aqueous CGAD solution was introduced keeping pH and ionic strength constant and the mixture was stirred for a certain period. All the tests were conducted in a thermostatic incubator. After centrifugation, the polymer concentration in the supernatant was determined by a CdI_2–starch coloring/spectrophotometric method [16]. The amount of CGAD adsorbed was calculated from the difference between the initial and the equilibrium concentrations. As an illustration, a typical standard curve is shown in Fig. 1.

Viscometric measurements

Viscometric measurements were carried out using an Ubbelohde viscometer at 30 ± 0.05 °C. CGAD samples were dissolved in salt solutions of varying concentration. The viscosity data were calculated according to the Huggins equation [17]

$$\eta_{sp}/C = [\eta] + k'[\eta]^2 C \ ,$$

where η_{sp} is the specific viscosity, C is the concentration of polymer, $[\eta]$ is the intrinsic viscosity, and k' is the Huggins constant. The values of $[\eta]$ and k' are listed in Table 1.

Results and discussion

The adsorption kinetics of amphoteric CGAD polymer onto bentonite is illustrated in Fig. 2 in the presence and in the absence of salt. Adsorption increases rapidly in the first minutes, then the equilibrium adsorption is attained. It appears that there are at least two processes controlling adsorption in this case, diffusion-controlled adsorption resulting in initial rapid uptake followed by a slower rearrangement of CGAD molecules already adsorbed on the bentonite permitting adsorption of additional CGAD molecules onto its surface. In contrast to the adsorption of partially hydrolyzed polyacrylamide (HPAM) on bentonite [18], the macroions of CGAD will be attached by many negative surface charges of bentonite at pH 6.0 [19] due to the stronger electrostatic attractive forces, which may increase the adsorption rate. Addition of salt increases the time required to reach equilibrium (Fig. 2). The result implies that it is likely that the cations (Na^+) of salt compete with the cationic group [-$N^+H(CH_3)_2$] of CGAD for the surface sites of bentonite, which may reduce the adsorption rate. From the adsorption kinetic curves, an equilibrium time of 2 h was chosen for further studies.

The influence of salt concentration on the adsorption of CGAD on bentonite is shown in Fig. 3. Opposite to the effects of NaCl on the adsorption of anionic HPAM [20] or cationic quaternary polyamine [21] on bentonite, the amount of CGAD adsorbed (plateau value) decreas-

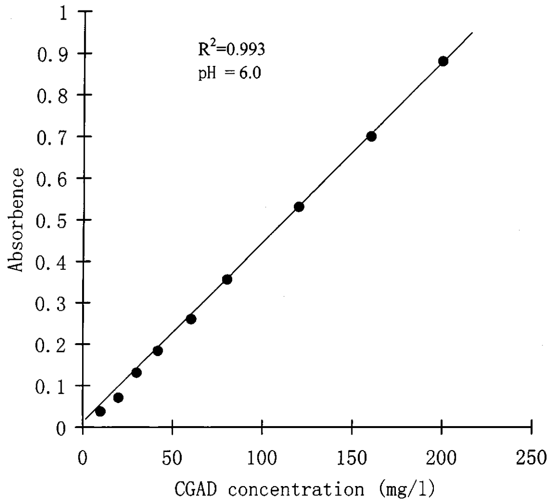

Fig. 1 Standard curve for determination of CGAD concentration (absorption at 580 nm, model 721 spectrophometer)

Table 1 Intrinsic viscosity ($[\eta]$) and Huggins constant (k′) for CGAD molecules at various salt concentrations (30 ± 0.05 °C)

Salt concentration (mol/l)	$[\eta]$ (dl/g)	k′
0	1.21	0.73
0.3	1.52	0.54
0.6	1.64	0.39
0.8	1.70	0.35
1.2	1.86	0.27

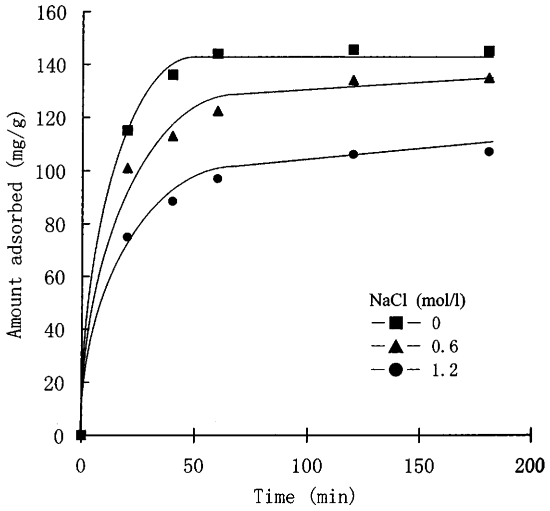

Fig. 2 Adsorption of CGAD on bentonite as a function of time in the absence and in the presence of NaCl. Initial concentration of CGAD: 3 g/l, 25 °C, pH = 6

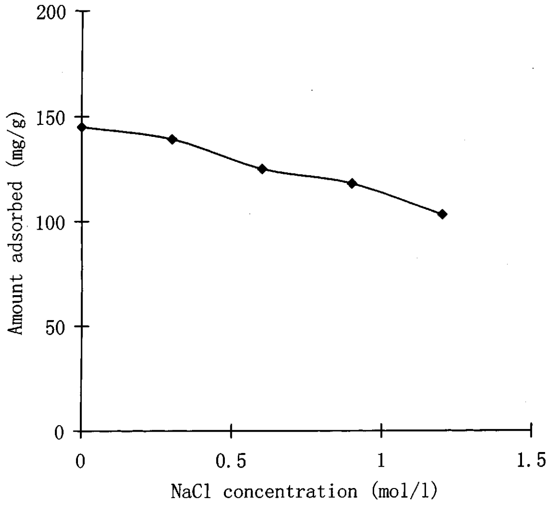

Fig. 3 Adsorption of CGAD on bentonite as a function of salt concentration. Initial concentration of CGAD: 3 g/l, equilibrium time: 2 h, 25 °C, pH = 6

es with increasing NaCl concentration. For HPAM or quarternary polyamine, adding salt to the system will promote adsorption in two ways:

(1) The salting-out effect, which worsens the solvent quality for the polymer, increases the adsorbed amount.
(2) A diminishing of long-range electrostatic interactions reduces the penalty for close approach of chains.

For amphoteric CGAD, however, the trends in $[\eta]$ and k' with salt concentration (Table 2) suggest that increasing salt concentration corresponds to improving the solvency power of aqueous solutions because NaCl screens opposite charges on the polymer chains and the attractive forces are smaller than in pure water. This induces the salting-in effect and therefore decreases the amount adsorbed [22]. Besides, over-expanded conformation of CGAD in aqueous salt solution may result in the polymer not being adsorbed compactly on the bentonite, which may also result in a lower amount adsorbed [23].

The adsorption data for various initial concentrations of CGAD at five different temperatures are given in Fig. 4. The adsorption decreased slightly at the lower initial concentration of 1 g/l and shows a significant decrease at higher initial concentrations. Because the plot of $\ln \Gamma$ versus T^{-1} is found to be linear, the variation of the amount adsorbed (Γ) with temperature (T) may be represented by the general relation

$$\Gamma = A\,e^{E_a/RT} ,$$

where A is a pre-exponential parameter and E_a is the activation energy of adsorption. Thus the E_a, reflecting the sensitivity of the adsorption towards temperature, may be estimated from the $\ln \Gamma$ versus T^{-1} plot (Table 2). As seen, the values of E_a at higher initial concentrations of 3 and 5 g/l are bigger than the value of E_a at the lower initial concentration of 1 g/l. According to Boomgaard et al. [24], the temperature effects can be rather complex because of the simultaneous influence on several properties such as solvent power, polymer configuration, mineral solubility and electrostatic adsorption.

The effect of both anionic and cationic surfactants on the adsorption of CGAD onto bentonite is illustrated in Fig. 5. Sodium dodecylsulfate (SDS) decreased the amount of the amphoteric cellulosic copolymer adsorbed only slightly. The effect was much stronger with hexadecyl trimethylammonium chloride. The cationic surfactant is absorbed by the negative surface sites and competes with CGAD adsorption. In contrast, anionic SDS blocks only the positive edges of bentonite. Because the number of positive edge sites is very small at pH 6.0 [19], the influence of SDS addition is weak. This fact was also observed by Williams et al. [12].

Table 2 The values of E_a corresponding to various initial concentrations of CGAD

Initial concentration (g/l)	E_a (kJ/mol)	Linear regression coefficient
1	5.48	0.974
3	15.12	0.999
5	11.63	0.982

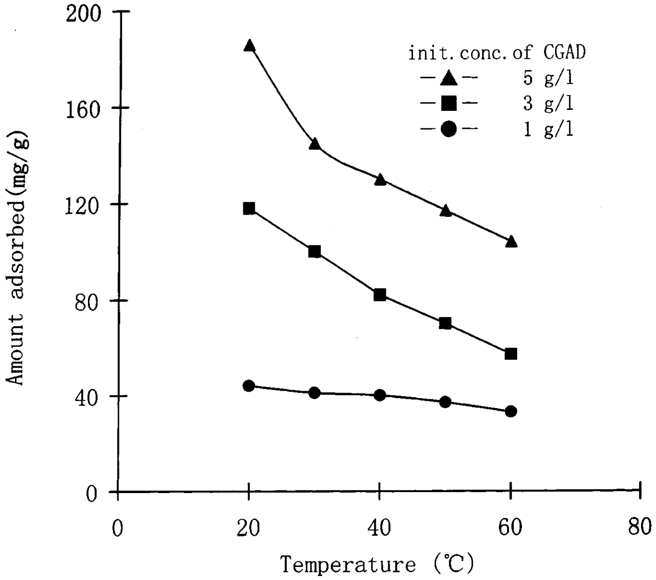

Fig. 4 Adsorption of CGAD on bentonite as a function of temperature. Equilibrium time: 2 h, pH = 6

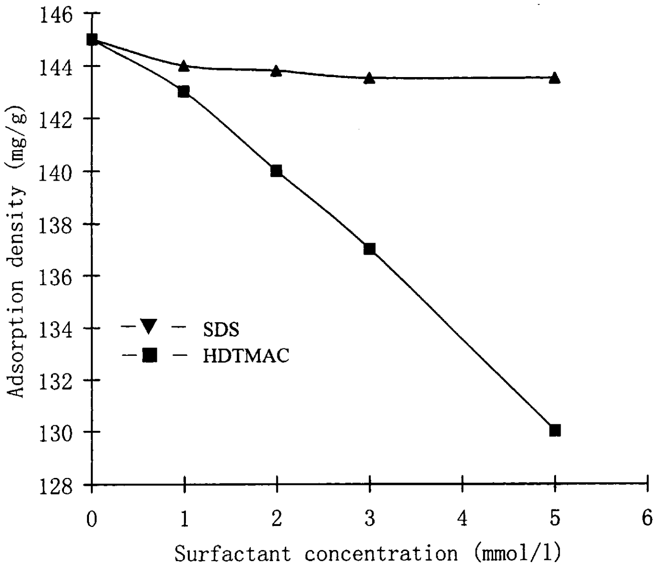

Fig. 5 Effect of anionic and cationic surfactants on the adsorption of CGAD on bentonite. Initial concentration of CGAD: 3 g/l, equilibrium time: 2 h, 25 °C

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