

化学

# 梳形聚羧酸超塑化剂在水泥颗粒表面的吸附行为

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**摘要** 研究了吸附溶液体系温度、pH值和电解质浓度等对甲基丙烯酸-甲氧基聚乙二醇甲基丙烯酸酯(MAA-MPEGMA)梳形聚羧酸共聚物在水泥颗粒表面的吸附行为的影响。聚羧酸共聚物在水泥颗粒表面的吸附呈Langmuir等温吸附模型。吸附量随着温度的升高而降低,表明聚羧酸共聚物在水泥颗粒表面的吸附是一个放热反应。根据Clausius-Clapeyron方程计算吸附热为17.4 kJ/mol。聚羧酸共聚物在水泥颗粒表面的标准吸附自由能 $<0$ ,吸附是自发的。吸附量随着体系pH值的增大、电解质浓度的增大而减小。红外光谱分析表明,聚羧酸共聚物在水泥颗粒表面的吸附是通过分子结构上羧基与 $\text{Ca}^{2+}$ 间的配合作用实现的,说明这种吸附是一种化学吸附。

**关键词** 吸附 聚羧酸 超塑化剂 水泥

**中图法分类号** O648.125; **文献标志码** B

For high performance concrete with good workability, the cement suspensions should have good dispersion stability. The flocculation or coagulation of cement particle in suspensions due to interparticle forces generated by Van der Waals attraction leads to decrease of fluidity of concrete. Superplasticizer is commonly used to improve fluidity of concrete by dispersing cement particles in paste<sup>[1]</sup>. Polycarboxylate superplasticizer (PCE) primarily composed of comb-type copolymers with a graft chain of polyethylene oxide (PEO) provides excellent dispersibility of cement particles and significantly improves the fluidity and fluidity-retaining performance of concrete<sup>[2]</sup>. The dominant dispersing and stabilizing mechanism of PCEs in cement suspension system seems to be the steric hindrance stabilization effect that results from the exten-

sion of their graft chains away from the surfaces of cement particles in solution<sup>[1,3,4]</sup>.

Adsorption of PCE on cement particle is a necessity for PCE to exhibit its dispersibility of cement. It is reported that the adsorption amount of PCE varied with the chemical structures of PCE<sup>[4-6]</sup>, cement component minerals<sup>[4]</sup> and chemical surroundings of cement suspensions<sup>[7,8]</sup>. But it has been rarely reported in regard to thermodynamics of PCE adsorption behavior on cement and chemical interaction mechanism between PCE and cement particle.

In this study, the thermodynamics of PCE adsorption behavior on cement is investigated. The adsorption amount, equilibrium constant and adsorption free energy at different temperature as well as adsorption heat are obtained by calculation. The impacts of pH value and sulfate ion concentration on adsorption equilibrium are also studied. The chemical interaction mechanism between PCE and cement particle is examined via Fourier transform infrared (FTIR) spectroscopy.

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## 1 Experimental

### 1.1 Raw Materials

The copolymer from methacrylic acid and ( $\omega$ -methoxypolyethylene glycol) monomethacrylate (MPEGMA) was synthesized by aqueous radical polymerization procedures described before [9]. The copolymer contains two different methoxypolyethylene glycol with side chain lengths of 9 and 22 ethylene oxide units (PEO,  $n$ ). The mol ratio of MAA, MPEGMA( $n=9$ ) and MPEGMA( $n=22$ ) was chosen as 4:0.5:0.5. After copolymerization, the aqueous polymer solutions were neutralized with NaOH, producing a solution of the sodium salts of PCEs. The chemical composition is shown in fig. 1. Polymer characterization was done by high performance liquid chromatography (Waters 1515

HPLC SYSTEM, solvent 0.1 mol/L NaNO<sub>3</sub>, PCE concentration 1.0—1.5 mg/mL).

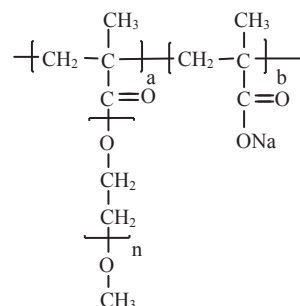


Fig. 1 Chemical structure of methacrylic acid and ( $\omega$ -methoxypolyethylene glycol) monomethacrylate copolymer

As cement, low alkali, low heat Portland cement (Beijing Building Material Research Institute, Beijing) with surface area of 322 m<sup>2</sup>/kg was chosen. Its chemical composition is given in table 1.

Table 1 Chemical composition and mineral component of Portland cement used in the study

Comp- -onent	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	Na <sub>2</sub> O <sub>eq</sub>	f-CaO	C <sub>3</sub> S
Content /(wt. %)	20.63	4.29	2.72	63.15	2.18	3.03	0.60	0.70	51.99

### 1.2 Experimental methods

#### 1.2.1 Adsorption of PCE

The adsorption test procedure was carried out as follows: 0.5 g of the Portland cement sample was mixed with 50 mL PCE solutions with different concentrations at desired pH. The suspensions were equilibrated and deagglomerated by using an ultrasonic horn for 30 minutes. Subsequently, the suspensions were centrifuged at a speed of 5 000 r/min for 10 min to obtain supernatants. The clear supernatant solution was analyzed for the residual PCE concentration by using UV adsorption spectrum at  $\lambda = 220$  nm, and then determined by using the linear calibration curve between absorbance and PCE copolymer concentrations prepared

initially. The total amount of PCE copolymer adsorbed on the Portland cement was then calculated based upon a mass balance for PCE copolymer.

#### 1.2.2 Fourier transform infrared spectroscopy (FT-IR)

Chemical characteristics of PCE copolymer and the cement hydrates powders with and without PCE copolymer were obtained by using FTIR spectroscopy. A Nicolet Magna—IR550 Fourier Transform Infrared Spectrometer operating in the (4 000 - 400) cm<sup>-1</sup> range was employed to record the IR spectra. The KBr pellet technique was utilized to prepare the powder samples for the IR studies. Approximately 3 mg of the desired sample was mixed with 300 mg spectroscopic

grade KBr and pressed into pellets to record the FTIR spectra. The PCE copolymer is initially air dried until a film was formed, which was then powdered, mixed with KBr, and pressed into pellets before recording the spectra. The cement sediments obtained after centrifugation were air dried, then the spectra of the cement hydrates powders with and without PCE copolymer were also recorded.

## 2 Results and Discussions

### 2.1 Adsorption thermodynamics of PCE copolymer on cement

The adsorption of PCE superplasticizer at different concentrations is measured to determine the amount of PCE required to have a monolayer adsorption on the Portland cement under different temperature conditions at pH = 10.9. The adsorption isotherms on cement surface at  $T=9^{\circ}\text{C}$ ,  $15^{\circ}\text{C}$ ,  $20^{\circ}\text{C}$ ,  $30^{\circ}\text{C}$  and  $40^{\circ}\text{C}$  are shown in fig. 2. The shape of adsorption isotherm varied with the temperature. For all temperature investigated, the value of adsorption increases gradually with the increase of the initial concentration of superplasticizer and then the value approaches to a constant value. The plateau displayed on the adsorption curves corresponds to the amount of PCE required for monolayer coverage. These adsorption isotherms show a typical Langmuir curve. Moreover, it is observed that the amount of PCE adsorption decreases as the temperature increases.

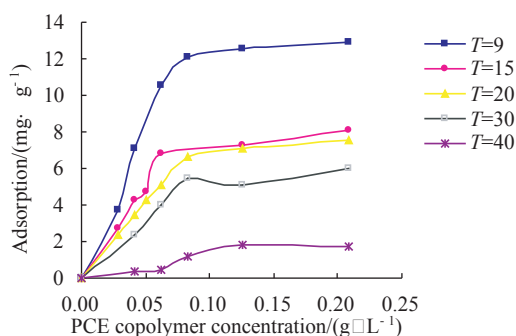


Fig. 2 Adsorption isotherm of copolymer on cement particle at different temperature

To determine the monolayer PCE adsorbance quantitatively, the data in fig. 2 are simulated using Langmuir monolayer adsorption equation<sup>[10]</sup>:

$$\frac{C_{\text{eq}}}{\Gamma} = \frac{C_{\text{eq}}}{\Gamma_{\text{max}}} + \frac{1}{K\Gamma_{\text{max}}} \quad (1)$$

The data are also plotted as  $C_{\text{eq}}/\Gamma$  vs.  $C_{\text{eq}}$  shown in fig. 3, where  $\Gamma$  refers to the adsorption amount,  $\text{mg} \cdot \text{g}^{-1}$ ;  $\Gamma_{\text{max}}$  refers to the saturated adsorption amount or the monolayer adsorbance,  $\text{mg} \cdot \text{g}^{-1}$ ;  $C_{\text{eq}}$  refers to the equilibrium concentration of PCE in solution,  $\text{mg} \cdot \text{L}^{-1}$ , and  $K$  is the adsorption equilibrium constant. The linear curves are observed, which indicates these adsorption isotherms are of Langmuir monolayer adsorption. The slopes of the linear curves represent the reciprocal of the saturated adsorption amount of PCE ( $1/\Gamma_{\text{max}}$ ). The saturated adsorption amount ( $\Gamma_{\text{max}}$ ) at each temperature can be calculated according to each slope. Moreover, the adsorption equilibrium constant ( $K$ ) at each temperature can be further calculated according to the intercept of each linear curve.

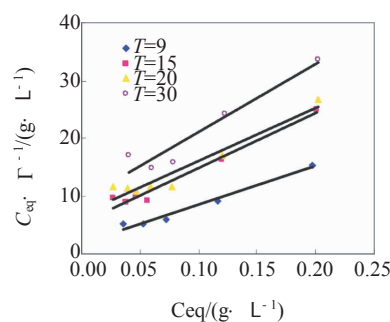


Fig. 3 Replot of fig. 2 based on the Langmuir equation

The correlation between the standard molar adsorption Gibbs free energy function ( $\Delta_{\text{ads}}G^{\circ}$ ) and the adsorption equilibrium constant ( $K$ ) can be described as following equation:<sup>[11]</sup>

$$\Delta_{\text{ads}}G^{\circ} = -RT\ln(K) \quad (2)$$

Thus, the Gibbs free energy function ( $\Delta_{\text{ads}}G^{\circ}$ ) at each temperature could be attained by equation (2), after  $K$  is already calculated to be a known parameter.

The saturated adsorption amount, the adsorption equilibrium constant and the standard molar adsorption Gibbs free energy at different temperature determined by Langmuir calibration are given in table 2.

**Table 2 Adsorption amount, equilibrium constant and free energy determined by Langmuir calibration**

$T/K$	$\Gamma_{\max}/(\text{mg} \cdot \text{g}^{-1})$	$K$	$\Delta_{\text{ads}}G^{\circ}$
282.15	14.9	36.7	-3.60 $RT$
288.15	11.2	14.2	-2.65 $RT$
293.15	10.9	13.3	-2.59 $RT$
303.15	8.5	12.7	-2.54 $RT$

From the table, it is noted that the standard molar adsorption Gibbs free energy of PCE onto cement is  $<0$ , which indicates the adsorption of PCE on cement is a spontaneous process. The Gibbs free energy decrease after PCE is adsorbed is the driving force for PCE to be adsorbed on the cement particle surface. The bigger the equilibrium constant, the larger the adsorption Gibbs free energy, and the stronger the affinity of PCE on the cement. The amount of monolayer of PCE adsorption decreases as the temperature increases, and the data are 14.9 mg per gram of cement at  $T=9^{\circ}\text{C}$ , 11.2 mg per gram of cement at  $T=15^{\circ}\text{C}$ , 10.9 mg per gram of cement at  $T=20^{\circ}\text{C}$  and 8.5 mg per gram of cement at  $T=30^{\circ}\text{C}$ . It is evidenced that the adsorption of PCE on cement particle surface is an exothermic reaction.

The correlation between the adsorption heat ( $\Delta H$ ) and the temperature is known as Clausius-Clapeyron Equation which is described as following<sup>[12,13]</sup>:

$$\frac{\Delta H}{R} = \frac{d(\ln \Gamma)}{d(1/t)} \quad (3)$$

The data are plotted as  $\ln \Gamma$  vs.  $1/T$  shown in fig. 4. The adsorption heat ( $\Delta H$ ) is calculated to be 17.4 kJ/mol by times the molar gas constant  $R$  with the slope of the linear curve.

## 2.2 Effect of pH value on adsorption properties

Figure 5 shows the adsorption of PCE on the ce-

ment particle surface at  $\text{pH} = 10.9$  and  $13.1$ . For both pH values investigated, the adsorption isotherms show a typical Langmuir curve. The critical PCE concentration to reach the adsorption plateau decreases as the pH increases, (6—8) mg per gram of cement at  $\text{pH} = 10.9$  while only around 2 mg per gram of cement at  $\text{pH} = 13.1$

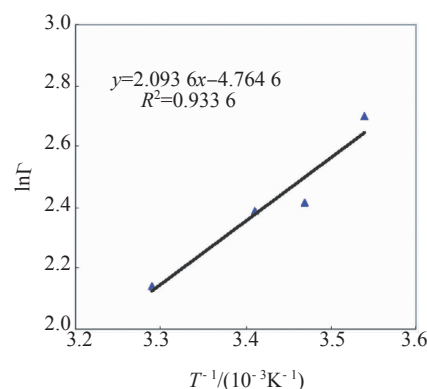


Fig. 4 The correlation between  $\ln \Gamma$  and  $1/T$

With dispersion of cement into water, and due to the hydration of cement with water, the pH value of the cement suspension increases, and the Zeta potential of cement particle surface turns from positive to negative. The higher pH of the suspension, the more negative charges of  $\text{OH}^-$  ions on the particle surface. A competitive adsorption exists between negatively charged PCE and  $\text{OH}^-$  ions onto limited number of positive sites on the cement particle surface. Moreover, the fully stretched configuration of polymer chain which is fully dissociated and a greater hydrodynamic radius at higher pH ( $\text{pH} = 13.1$ ) could lead to compacting and horizontal adsorption that reduce the amount of associated PCE adsorbed onto the cement surface and decrease the thickness of the adsorption layer. Hence, these two factors likely to explain the observed trend of decreasing amount of PCE adsorption with increasing pH.

## 2.3 Effect of Sulfate Ion Concentration on Adsorption Equilibrium

Figure 6 shows the adsorption of PCE on the ce-

ment particle surface without addition of  $\text{Na}_2\text{SO}_4$  concentration and with 0.01 mol/L concentration in the solution. With sulfate ion concentration, the adsorption isotherm still shows a typical Langmuir curve. The adsorption amount of PCE decreases significantly with 0.01 mol/L sulfate ion concentration. This behavior indicates that the competitive adsorption equilibrium of PCE copolymer with sulfate ions. In addition to that, ion strength increase by the addition of sulfates shrinks the steric size of PCE copolymer<sup>[14-16]</sup>, which could lead to wrap type adsorption conformation that compacts the adsorption layer thickness to reduce the adsorption amount.

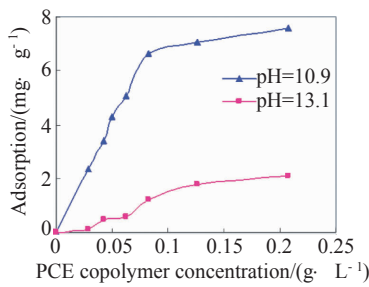


Fig. 5 The adsorption isothermal curve of copolymer on cement particle at 20 °C at different pH value

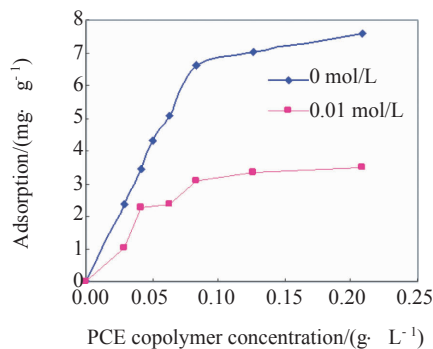


Fig. 6 The adsorption isotherm of the copolymer on cement particle with different  $\text{Na}_2\text{SO}_4$  concentrations at 20 °C

## 2.4 Surface Complexation and Chemical Interaction-FTIR Spectroscopic Studies

FTIR spectroscopic studies were carried out on the cement hydrate and polymer samples as well those obtained after adsorption. The FTIR spectrum of PCE copolymer is shown in fig. 7 (a). The medium broad bands at  $3400\text{ cm}^{-1}$  and  $2900\text{ cm}^{-1}$  are due to O—H stretching and the presence of hydrogen bonding. Strong band at  $1710\text{ cm}^{-1}$  is due to—C = O stretching vibration for methacrylate ester. Strong band at  $1580\text{ cm}^{-1}$  is due to asymmetrical  $\text{CO}_2^-$  stretching. Bands at  $1400$  and  $1350\text{ cm}^{-1}$  indicate symmetrical  $\text{CO}_2^-$  stretching. The peak at  $1450\text{ cm}^{-1}$  is due to O—H deformation vibration. The band at  $1243\text{ cm}^{-1}$  can be attributed to— $\text{CH}_2$ —deformation. Strong band at  $1105\text{ cm}^{-1}$  indicates C—O stretching.

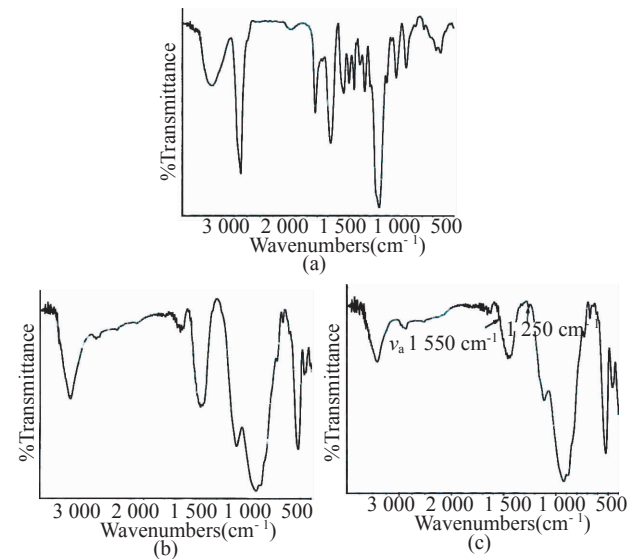


Fig. 7 IR spectra of (a) PCE copolymer (b) Cement hydrate (c) Cement hydrate with PCE copolymer

The FTIR spectra of cement hydrate without and with PCE copolymer are shown in fig. 7b and 7c. The FTIR spectrum of cement hydrate with adsorbed PCE is very similar to that of cement hydrate without PCE copolymer. Though the amount of PCE adsorbed was very

small, it is noted that the band at  $1\ 580\ \text{cm}^{-1}$  and  $1\ 243\ \text{cm}^{-1}$  observed in the case of free polymer due to asymmetrical  $\text{CO}_2^-$  stretching and  $-\text{CH}_2-$  deformation respectively is reduced in intensity and appear at  $1\ 550\ \text{cm}^{-1}$  and  $1\ 250\ \text{cm}^{-1}$  in the adsorbed sample. The wavenumber shift for  $\nu_a(\text{COO}^-)$  from  $1\ 580\ \text{cm}^{-1}$  to  $1\ 550\ \text{cm}^{-1}$  indicates that the adsorption of the polymer on cement occurs by surface reactions involving  $-\text{COO}^-$  groups of the polymer with metal ions (e. g. calcium ions) on cement hydrate surface.

### 3 Conclusions

The adsorption amount of PCE is found to decrease with an increase of temperature. The adsorption of PCE copolymer on cement particle is an exothermal reaction. The adsorption heat is calculated to be  $17.4\ \text{kJ/mol}$ , by Clausius-Clapeyron equation. The adsorption Gibbs free energy  $\Delta_{\text{ads}} G^0 < 0$ , which indicates the adsorption of PCE on cement is a spontaneous process.

The adsorption of PCE decreases as the pH increases, because the PCE is more negatively charged and stretched, which results in a compacting and horizontal adsorption conformation of PCE onto cement, and a more competitive adsorption with  $\text{OH}^-$  ions at a higher pH.

The adsorption amount of PCE decreases significantly with the presence of sulfate ion concentration, because sulfate ions compete with PCE to form competitive adsorption on cement particle, and shrinks the steric size of PCE copolymer, which leads to a wrap type adsorption conformation.

FTIR spectroscopic studies verify the surface complexation and chemical interaction formed by carboxylate functional groups  $-\text{COO}^-$  of copolymers with  $\text{Ca}^{2+}$  on particle surface.

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## Adsorption Behavior of Comb-type Polycarboxylate Superplasticizer on Cement

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**[Abstract]** The adsorption of poly (methacrylic acid-co-methoxypolyethylene glycol monomethacrylate) comb-type polycarboxylate superplasticizer (PCE) on cement particle surface has been studied as a function of temperature, pH, and electrolyte concentration. The adsorption amount of PCE is found to decrease with an increase of temperature, pH or concentration of electrolyte respectively. The adsorption isotherm of PCE exhibits Langmuirian behavior. The adsorption of PCE copolymer on cement particle is an exothermal reaction. The adsorption heat is calculated to be 17.4 kJ/mol, by Clausius-Clapeyron equation. The adsorption Gibbs free energy  $\Delta_{\text{ads}} G^{\circ} < 0$ , which indicates the adsorption of PCE on cement is a spontaneous process. FTIR spectroscopic data provide evidence in support of surface complexation and chemical interaction formed by carboxylate functional groups  $-\text{COO}^-$  of copolymers with  $\text{Ca}^{2+}$  on particle surface.

**[Key words]** adsorption polycarboxylate superplasticizer cement