Adsorption characteristics of polycarboxylate-based superplasticizers on the surface of tricalcium aluminate－gypsum system

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Abstract: The adsorption characteristics of polycarboxylate-based superplasticizers (PCs) on tricalcium aluminate－gypsum (C_3A-$CaSO_4 \cdot 2H_2O$) were examined by means of gel permeation chromatography (GPC) and the thermodynamic parameters of $\triangle G$、$\triangle H$、$\triangle S$ was obtained by calculation of thermodynamic equation. The Gibbs free energy of adsorption $\triangle G^0_{ads}$, adsorption enthalpy $\triangle H^0_{ads}$ and adsorption entropy $\triangle S^0_{ads}$ were linear regression. Results clearly showed that the Gibbs free energy of the system is negative, which indicated that the adsorption behavior is a spontaneous process. As the temperature increased, the adsorption amounts of PCs on surface of C_3A-$CaSO_4 \cdot 2H_2O$ increased. The adsorption thermodynamics parameters is $\Delta H_{ad} = -18.714 \text{kJ} \cdot \text{mol}^{-1}$, $\Delta S_{ad} / = 0.072 \text{kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, $\Delta G^{\theta}_{ad} = -39.715 \text{ kJ} \cdot \text{mol}^{-1}$ (20°C). This work can be provided theoretical guidance for the application of PCs in cement and concrete.

Keywords: Polycarboxylate-based superplasticizers, adsorption, tricalcium aluminate

1 Introduction

Recently, polycarboxylate-based superplasticizers (PCs) have developed rapidly and been applied in construction projects widely. The adsorption mechanism of PCs has aroused attention of scholars both at home and abroad. In general, the dispersion effect of PCs is due to the adsorption of polymers on cement surfaces. There is large number of polar functional groups in the structure of PCs, such as carboxyl, hydroxyl. Those polar functional groups can be adsorbed on the surface of cement particles or hydration products to form a certain thickness of adsorbed layer, which can change the physicochemical property of solid-liquid interface and the interactions between particles, thus affecting the rheological properties of cement or mortar. The adsorption behaviors of PCs on cement have been investigated by many researchers. Ran et al.[1] studied the effect of molecular structure of PCs on zeta potential and adsorption amounts. Wu et al.[2] discussed the relationship between adsorption capacity of PCs and fluidity of cement at different temperature, which showed that the ambient temperature can affect dispersion and dispersing stability of PCs. The change in temperature is also an important factor affecting adsorption of the polymer molecules[3,4]. Therefore, it is very necessary to study the adsorption equilibrium and thermodynamics of PCs on the surface of the cement particles.

C_3A is one of the major components of cement minerals, which plays a very important role in the early hydration process. The dispersion and dispersing stability of PCs has much to do with the hydration behavior of C_3A. In this paper, pure C_3A was prepared and the equilibrium adsorption amount of PCs on the surface of C_3A mineral was measured. For the nonlinear fitting, Langmuir and Freundlich isotherm equilibrium data was used. The thermodynamic parameters were calculated during adsorption, such as free energy change, adsorption isotherm enthalpy and entropy. This provided a theoretical basis for the application and research of PCs.

2 Materials and methods

2.1 Materials

（1）*Preparation of PCs samples*

The PCs used in this study was synthesized based on our previous study[5]. The weight average molecular weight (M_w) and number average molecular weight (M_n) determined by GPC (Agilent Co.,USA)measurement is 9669.5 and 5816.5, respectively. The polydispersity index (PDI) is obtained by $M_w / M_n = 1.7$。

（2）*Preparation of C_3A samples*

C_3A was prepared by high-temperature calcination of analytically pure $CaCO_3$ and Al_2O_3 with molar ratio 3:1 at 1350°C for 3 h. Prior to the second burning, the prepared specimens were crushed and ground in a laboratory mill. The X-ray diffraction analysis of the sample until indicates that no other phases were present. The content of free calcium determined by means of Franke's method amounted to 0.17%，so it had no fundamental influence on the course of experiments.

2.2 Adsorption method of PC

GPC was applied to determine the adsorption amount of PCs by the solution depletion method.1.5 g of C_3A-gypsum mixture and 15 mL of 0.2wt.% PCs solution were placed in a centrifuge tube and then shaken for 1 min. The specimens

were filtered through a 0.45 μm filter by vacuum filtration. The PCs content in aqueous phases was analyzed by GPC technique after adjusting pH of the solution to less than 3 by the addition of boric acid. The amount of PCs adsorbed on the mineral phase was calculated from the differences in the initial well-known PCs concentration and the final PCs concentration after adsorption. The formula is shown below by Eq. (1) ：

$$Q_e = \frac{(C_0 - C_e)V}{m}$$
(1)

Q_e is the amount of PCs adsorbed on particles, mg.g^{-1}; C_0 is the concentration of PCs before adsorption, g/L; C_e is the equilibrium concentration of PCs after adsorption, g/L；V is the solution volume, L；m is the mass of C_3A-gypsum mixture，g.

3. Results and discussion

3.1 Adsorption thermodynamics of PCs

The adsorption isotherms of PCs on the surface of C_3A were measured at 20, 30, 40°C, as shown in Fig.1. In this experiment, the dosage of PCs was 0.15% of the mass of C_3A/$CaSO_4 \cdot 2H_2O$, the ratio of water and cement was 3.5:1, and the dosage of cement was 20 g.
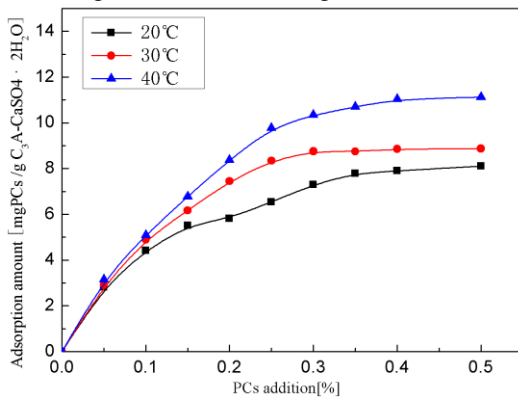
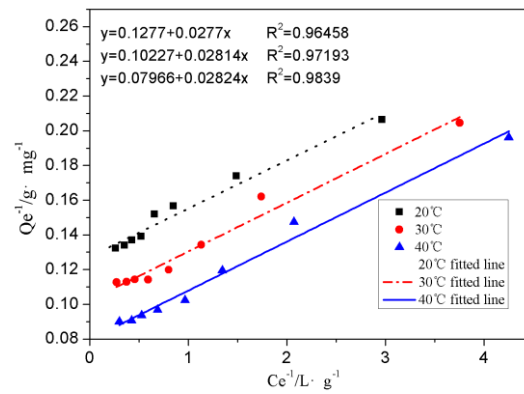

| Figure 1 The adsorption isotherms of PCs on C_3A | Figure 2 Langmuir equation fitting line |

As shown in Fig.1, the amount of PCs adsorbed on the surface of cement particles increases as the equilibrium concentration of PCs. At the same temperature, the adsorption quantity increases rapidly when the equilibrium concentration is low and the adsorption quantity increases slowly when the equilibrium concentration of PCs increases to a certain extent. Finally, the amount of PCs adsorbed on the surface of cement particles reaches a plateau. At different temperature, the influence of temperature on the adsorption quantity is small when equilibrium concentration is low and the maximum adsorption capacity increases from 7.83 mg.g^{-1} to 12.55 mg.g^{-1}as the temperature increases when the equilibrium concentration of PCs increases to a certain extent. The adsorption quantity increases significantly with increasing of temperature.

3.2. The establishment of adsorption model for PCs

To establish adsorption model of PCs on the surface of cement particles, the adsorption isotherm in Fig.2 was fitted by using Langmuir equation and Freundlich equation.

$$\text{Langmuir equation: } \frac{Q_e}{Q_{em}} = \frac{bC_e}{1+bC_e}$$

Q_e is the amount of PCs adsorbed on particles, mg.g^{-1}, Q_{em} is saturated adsorption, mg.g^{-1}, C_e is equilibrium concentration of non-adsorbed PCE, g· L^{-1},b is Langmuir constant associated with temperature, L ·g^{-1}.Langmuir equation can be varied to obtain a linear form

$$\frac{1}{Q_e} = \frac{1}{Q_{em}} + \frac{1}{bQ_{em}C_e}$$

Draw the fitting curve by $\frac{1}{Q_e}$ to $\frac{1}{C_e}$ (see Fig.3). b and Q_{em} can be obtained by the straight line of slope and intercept. Fitting parameters are shown in Table 2.

Freundlich equation can be represented as: $Q_e = K_f C_e^{1/n}$, Q_e is the amount of PCs adsorbed on particles, mg.g^{-1}, K_f is adsorption ability constant associated with the type, characteristic and the temperature of adsorbent, C_e is equilibrium concentration, g·L^{-1}, n is strength parameter of adsorption associated with temperature.

Take the logarithm on both sides of the Freundlich adsorption equation, as shown below:

$$\ln Q_e = \ln K_f + \frac{1}{n}\ln C_e$$

Draw the fitting curve by $\ln Q_e$ to $\ln C_e$ (see Fig.3, K_f and n can be obtained by the straight line of slope and intercept. Fitting results are shown in Table 2.
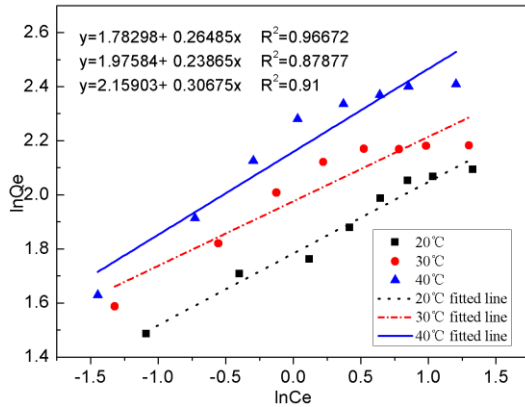

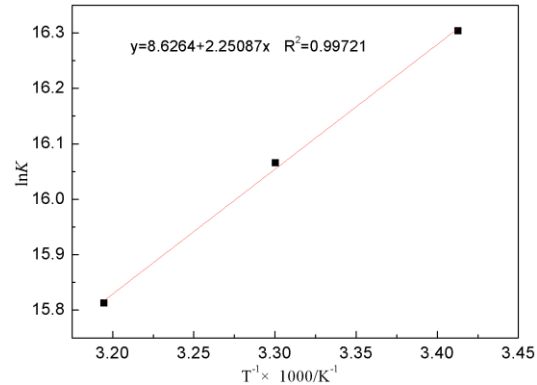**Figure 3** The Freundlich equation fitting line   **Figure 4** The results of thermodynamic measurement

Table 2. Fitting parameters of adsorption isotherm for PCs at different temperature

T/°C	Fitted values by Langmuir equation				Fitted values by Freundlich equation		
	b/ L·g⁻¹	K	Q_{em}/ mg·g⁻¹	R^2	K_f	n	R^2
20	4.610	12035857	7.83	0.96458	5.947554	3.775722	0.96672
30	3.364	9488336	9.78	0.97193	7.212676	4.190237	0.87877
40	2.821	7364470	12.55	0.9839	8.662731	3.259984	0.91

Note: K=46956×55.6b

As shown in Table 2, the adsorption isotherms of PCs on the surface of cement particles has good agreement with Langmuir equation at different temperature. The correlation coefficient r^2 is between 0.92 and 0.98, greater than the fitting correlation coefficient in the Freundlich equation. As the fitting result of Langmuir equation shown, Langmuir constant b decreases from 3.364 L·g⁻¹to 2.821 L·g⁻¹ as the rise of the temperature, which suggests that the adsorption equilibrium constant also decreases with the increasing of temperature. Thus, the temperature increasing is not conducive to adsorption originally. However, the adsorption capacity increases from7.83 mg·g⁻¹to 12.55 mg·g⁻¹with the increasing of temperature. This contradiction situation can also be seen from the fitting results of Freundlich equation. As the temperature increases, the value of indicating the adsorption intensity of PCs on the surface of cement particles decreases, but the value of K_f indicating the adsorption capacity increases. For this reason, we believe that with the temperature increasing, the hydration degree of C_3A will increase and the number of positive charge on the surface of ettringite particles will increase, so that the PCs are more easily adsorbed. At the same time, the PCs adsorbed on the surface of cement particles are more likely to participate in the hydration to be wrapped in hydration products with the increasing of temperature. Then the PCs in solution will be automatically added to the surface of cement particles, which causes apparent adsorption capacity increasing.

3.3 The analysis of adsorption thermodynamic for PCs

The study of adsorption thermodynamics is not only helpful to understand the trend, extent and driving force of the adsorption process, but also significant to explain the characteristics, regularity and mechanism of adsorption. Therefore, in order to further analyze the adsorption process, the thermodynamic parameters of the adsorption process can be calculated. The relation between the adsorption heat and temperature is shown below. The lower the temperature, the more beneficially the adsorption process happens.

$$\Delta H_{ad} - T\Delta S_{ad} = -RT\ln K$$

$$\Delta G^{\theta}_{ad} = -RT\ln K$$

Draw the curve by $\ln K$ to 1/T (see Fig.5). The calculation results are listed in Table 3.

Table 3 The calculation for adsorption thermodynamic parameters of PCs at different temperature

T/°C	ΔH_{ad}/kJ·mol⁻¹	ΔS_{ad} / kJ·mol⁻¹·K⁻¹	ΔG^{θ}_{ad} / kJ·mol⁻¹
20	-18.714	0.072	-39.715
30			-40.471
40			-41.147

As shown in Table 3, the adsorption free energy ΔG^{θ}_{ad} of PCs on the surface of cement particles is negative and the entropy in process increases. Therefore, the adsorption process is a spontaneous process. ΔH_{ad} is negative, so adsorption is an exothermic process.

4. Conclusions

The study of adsorption thermodynamics for PCs on the surface of cement particles showed with increasing of temperature, the adsorption quantity of PCs on the surface of cement particles increased. The thermodynamic parameters were obtained by the thermodynamic formula, ΔH_{ad} =-18.714 kJ·mol^{-1}, ΔS_{ad} =0.072 kJ·mol^{-1}·K^{-1}, ΔG^{θ}_{ad} =-39.715 kJ·mol^{-1}(20℃), -40.471 kJ·mol^{-1} (30℃), -41.147 kJ·mol^{-1}(40℃). It was found that the adsorption was a spontaneous, exothermic and entropy increasing process. Temperature increasing is not helpful for adsorption theoretically, but the heat released promoted the cement hydration because of the increasing of temperature, causing the PCs were easily to be wrapped in hydration products. So that more PCs molecules were adsorbed to the surface of cement particles, causing the amount of adsorption increased.

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