

Adsorption of Polyethylene Glycol at the Interface of Dicalcium Silicate – Sodium aluminate solution

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Abstract

Surfactants, such as polyethylene glycol (PEG), are widely used to inhibit the secondary reaction of dicalcium silicate (β -CaO-SiO₂) in sodium aluminate solution. The adsorption isotherm of PEG on β -CaO-SiO₂ in sodium aluminate solution at 80 °C was researched in this paper. It was found that the type of surface adsorption of PEG is saturated adsorption, and the adsorption behavior belongs to "S"-type, according with the multi-molecular layer adsorption model of the Freundlich Equation. The surface coverage of PEG close to saturated adsorption derived from the specific surface area of β -CaO-SiO₂ is 0.723 mol/ μ m². The relation curves between the surface pressure and the molecular area of adsorption film were obtained according to the adsorption results at the solid-liquid interface by Gibbs formula. The variation of interfacial energy caused by adsorption, as well as the relationship between the relation curves and the type of adsorption was also discussed.

Introduction

In the sintering process of alumina production, there is about 30% dicalcium silicate (β -CaO-SiO₂) in the clinker. During the leaching of clinker, as β -CaO-SiO₂ reacts with sodium aluminate solution, both Al₂O₃ and Na₂O re-enter into the red mud, resulting in the loss of Al₂O₃ and Na₂O [1]. It was found [2] that additions of surfactants, such as polyethylene glycol (PEG), can inhibit the secondary reaction of β -CaO-SiO₂ with sodium aluminate solution, which increases the leaching rate of Al₂O₃. Much of work was done on the additives for inhibiting the secondary reaction, which was mainly concerned on the selection and application of additives as well as the adsorption kinetics and

thermodynamics [3-5]. However, the basic theories, such as the models of adsorption, the laws at the interface of sodium aluminate solution and β -CaO-SiO₂, and the effect of adsorption on the solid-liquid interface were seldom studied. Consequently, according to the development of Gibbs adsorption isothermal formula on the solid-liquid interface [6-10], the adsorption laws of PEG in clinker-sodium aluminate solution systems and the mechanisms of PEG inhibiting the secondary reaction were first studied in this article.

Experimental procedures

Dicalcium silicate was prepared by pure calcium oxide and silica. Calcium oxide and silica were first mixed with the molar ratio of 2 to 1, grinded 2 hours in a mortar, and then calcined at 1350 °C followed by quenching in the air.

Sodium aluminate solution with caustic ratio (i.e. molar ratio of Na₂O to Al₂O₃) of 1.30 was prepared by the red mud lotion from the Shanxi Branch of the China Aluminum Company, industrial sodium hydroxide and aluminum hydroxide, and analytically pure sodium carbonate. The concentrations of Na₂O and Na₂CO₃ of sodium aluminate solution were 36 g/L and 15 g/L, respectively. PEG was added to sodium aluminate solution with the concentration of β -CaO-SiO₂ 75 g/L. The concentrations of PEG in sodium aluminate solution were 0, 80 mg/L, 120 mg/L, 160 mg/L, 200 mg/L, 240mg/L, respectively. The mixed solutions were stirred magnetically (600 r/min) for 1 hours in 80 °C water bath followed by centrifugal separation. 0.5 ml supernatant fluid was taken out to determine the content of PEG by the method of spectrophotometry using a 722S Spectrophotometer. The adsorbed amount per unit weight of adsorbent at equilibrium, Q_e , can be expressed as follows:

$$Q_e = (C_0 - C_e)/W_0 \quad (1)$$

where C_0 and C_e is the initial concentration and the residual concentration of additives (mg/L) in the solution, respectively, and W_0 is the concentration of adsorbent (g/L) in the solution.

Gibbs Adsorption Isothermal Formula

According to the interface Gibbs formula in the ideal solution [11], the basic form of surface tension, γ , under constant temperature and pressure is given by:

$$-d\gamma = \sum_{i=1}^k \frac{n_i}{A_s} d\mu_i = \sum_{i=1}^k \Gamma_i RT d \ln c_i \quad (2)$$

where n_i is the surface molar quantity of i component, A_s is the surface area, μ_i is the chemical potential of i component, Γ_i is the excess amount of i component per unit surface (i.e. the surface adsorbed amount or surface concentration (mol/m²)).

As the interfacial tension numerically equals to the interfacial pressure (π), the relationship is $d\pi = -d\gamma$.

$$\text{Thus, } d\pi = \sum_{i=1}^k \Gamma_i RT d \ln c_i \quad (3)$$

For binary systems, if Group 1 is identified as the major component, $\Gamma_1^{(1)}=0$. The adsorbed amount of Group 2 is $\Gamma_2^{(1)}$. Then, Eq. (3) can be written as:

$$-d\gamma = RT\Gamma_2^{(1)} d \ln c_2 \quad (4)$$

For the adsorption in the dilute solution, it is reasonable to consider the surface excess amount $\Gamma_2^{(1)}$ as the actually measured amount (apparent adsorbed amount), so $\Gamma_2^{(1)}$ is replaced by Γ and c_2 is replaced by c in Eq. (3). For the solid adsorption from liquid, Eq. (3) is integrated on both sides:

$$\pi = \gamma_{S0} - \gamma_{SL} = RT \int_0^c \Gamma d \ln c \quad (5)$$

where γ_{S0} and γ_{SL} is the solid-liquid interface free energy before and after adsorbing the solute, respectively.

The value of $\int_0^c \Gamma d \ln c$ with different concentrations can be obtained by graphic integration, and then the value of π with different adsorbed amounts can be calculated. At very low concentration, the relationship between Γ and $\ln c$ is considered as a line.

Accordingly, the area of each adsorbed molecule (σ) at different amounts of Γ is given by the Avogadro constant (N_A) as:

$$\sigma = 1/(\Gamma N_A) \quad (6)$$

Results and Discussion

Adsorption isotherm

The adsorption isotherm of PEG on β -CaO-SiO₂ in sodium aluminate solution is shown in Fig. 1. The type of adsorption isotherm belongs to "S"-type, which indicates that the adsorption of PEG on 2CaO-SiO₂ accords with the Freundlich multi-layer model, and follows the Freundlich Equation as expressed in Eq. (7):

$$\ln Q_e = \ln k + \frac{\ln C_e}{n} \quad (7)$$

where k and n are constants.

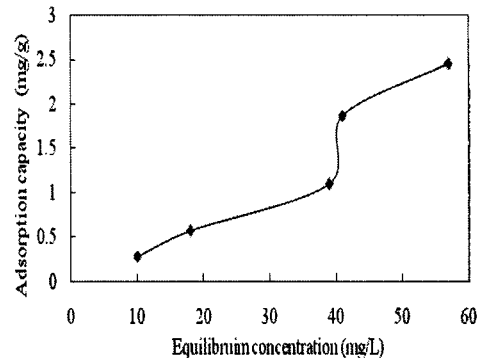


Fig. 1 Adsorption isotherm of PEG on β -CaO-SiO₂ at 80 °C

The relationship between the residual concentration (C_e) and the value of C_e/Q_e is shown in Fig. 2. The curve can be fitted by the Freundlich Equation as Eq. (8):

$$\ln Q_e = 1.242 \ln C_e - 4.184 \quad (8)$$

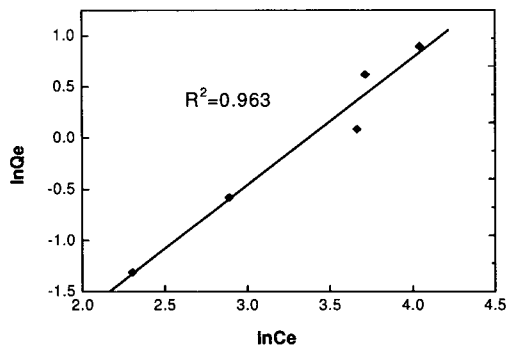


Fig. 2 Freundlich isotherm of PEG on β -CaO-SiO₂

As shown in Fig. 2, the experimental data can be well simulated by the adsorption isotherm. The adsorption of PEG at the interface of dicalcium silicate-sodium aluminate solution belongs to “S”-type, having the characteristic of multi-layer adsorption.

Adsorption film on β -CaO-SiO₂

The π - σ curve of the interfacial film on β -CaO-SiO₂ can be obtained from the adsorption results by using Eq. (5) and (6). As shown in Fig. 3, the shape of π - σ curve is similar to the adsorption of insolubles in the liquid surface [12]. Phase transitions take place at the interface of dicalcium silicate-sodium aluminate solution, which is in accordance with the formation of surface micelles. It is known that polyol compounds are typically non-ionic surfactants, with a structural formula of H-(O-CH₂-CH₂)_n-OH. When the concentration of polymer is lower, the molecules of PEG are adsorbed at the interface of the β -CaO-SiO₂ by -OH groups [13], and no significant changes of interfacial tension happen.

As the concentration of polymer increases, the surface micelles (or called semi-micelles) are formed between PEG molecules and adsorbed molecules by the hydrophobic effects of C-H bonds, resulting in a sharp increase of adsorption. At the same time, the interface pressure changes rapidly, while the correspondingly molecular area only changes in a cell range, which is correlative to the formation of surface micelles. The reason of the sudden rise in the adsorption capacity is the formation of hemi-micelles at the

interface [14, 15]. Therefore, the adsorption of polyethylene glycol is mainly physical adsorption, which is also confirmed by IR detection. In addition, the curve in Fig. 3 changes at the point of 1.09 mg/g, which is approximately considered as the adsorption capacity of the covered monolayer.

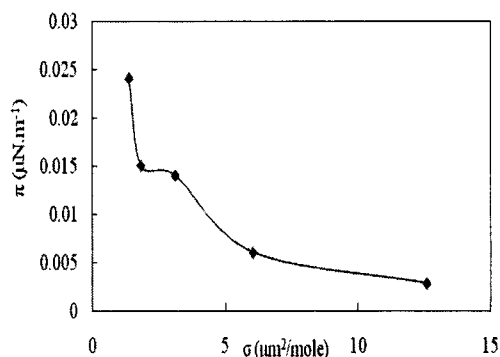


Fig. 3 Relationship between the interfacial pressure and molecular area

When the adsorption capacity is 2.45mg/g, the surface coverage is calculated to be 2.24, which is larger than 1, demonstrating that the adsorption of PEG is a multi-molecular layer. Meanwhile, the single molecular area is 1.383 $\mu\text{m}^2/\text{mol}$, and the corresponding coverage is about 0.723 mol/ μm^2 .

Conclusions

It was found in the research that the adsorption of PEG at the interface of dicalcium silicate-sodium aluminate solution is a saturated multi-layer adsorption and the type of adsorption is “S”-type in accordance with the Freundlich Equation. The adsorption of PEG on β -CaO-SiO₂ in sodium aluminate solution belongs to physical adsorption. The π - σ curve can be drawn according to the Gibbs formula, which is available to obtain useful information from the shape of the π - σ curve.

References

- [1] BI S W, YU H Y. Production technology of alumina [M]. Beijing: Chemical Industry Press, 2006: 250-251.

- [2] ZHANG C Z. Research on additive for inhibiting secondary reaction in clinker leaching process [D]. Northeastern University. 2008: 49-50.
- [3] REN G K. Technical research of secondary reaction inhibitor and sweetening process [J]. *Light Metals*, 2008(5): 16-18.
- [4] LI T C. Technical Research of Secondary Reaction Inhibitor and its Sweetening Process [J]. *Nonferrous Metals*, 2002(1): 26-28.
- [5] SHEU E Y, STORM D A, SHIELDS M B. Adsorption kinetics of asphaltenes at toluene/acid solution interface [J]. *Fuel*, 1995, 74: 1475-1479.
- [6] OLOF S, TOBIAS H, TORGNY S, THOMAS A. Adsorption of delmopinol at the solid/liquid interface – The role of the acid–base equilibrium [J]. *Journal of Colloid and Interface Science*, 2010, 350: 275-281.
- [7] PAUL J, JOHN R. The adsorption of a polysaccharide at the talc–aqueous solution interface [J]. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 1998, 139: 27-40.
- [8] WU Z S, LI C. Kinetics and thermodynamics of b-carotene and chlorophyll adsorption onto acid-activated bentonite from Xinjiang in xylene solution [J]. *Journal of Hazardous Materials*, 2009, 171: 582-587.
- [9] SOMASUNDARAN P, KRISHNAKUMAR S. Adsorption of surfactants and polymers at the solid-liquid interface [J]. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 1997, 123-124: 491-513.
- [10] WANG Y J, SONG Z F. *Spectroscopy and Chromatography* [M]. Beijing: Peking University Press, 1995: 225-239.
- [11] HU Y. *Modern Chemical and Engineering Thermodynamics* [M]. Shanghai: Shanghai Science and Technology Press, 1994: 239-240.
- [12] HARKINS W D. *The Physical Chemistry of Surface Films*[M]. New York Reinhold, 1952: Chap2.
- [13] CHEN H W, ZHOU Z K. The Analyses on the Impact of the clinker stripping conditions on the Secondary Reaction[J].*Light Metal*, 2001(8):21-24.
- [14] SCAMEHORN J F, SCHECHTER R S, WADE W H. *Journal of Colloid Interface Science*, 1982, 85:463-467.
- [15] ZHU B Y, ZHAO X L, GU T R. *Journal of Chemistry Society Faraday Transactions*, 1988, 84 (11):3951-3958.

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