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Adsorptive behavior of surfactants on surface of Portland cement

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Abstract

On the surface of Portland cement, four surfactants have different adsorptive behaviors: ethoxylated fatty alcohol sulfate (AES) belongs to the lignosulfonate (LS)-type of adsorption; cetyl piridinium chloride (CPC) is kinetically controlled; condensates of naphthalene formaldehyde (NS) have a linear relationship of adsorbance vs. concentration; and ethoxylated alkyl phenol (TX-10) is not adsorbed. All adsorbed surfactants have their hydrocarbon chain toward liquid phase and an increase in hydrophobicity of the cement surface. However, AES suffered a change of hydrophilic → hydrophobic → hydrophilic because of the formation of adsorptive micelles. Both AES and NS only increase zeta potential, but CPC changes zeta potential from negative to positive. A modified Stern double-layer model has been proposed to illustrate adsorptive characteristics of the above surfactants. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Cement; Adsorption; Modeling

1. Introduction

Various additives have been playing important roles both in improving the quality of cement and concrete and in extending their applications. In fact, many additives for cement and concrete belong to surfactants. The functions of these additives with surface activity include: as viscosity improver, as water-reducing admixture, as air-entraining admixture, as well as shrinkage-reducing admixture, etc. [1,2]. Practically, many additives with surface activity are natural or synthetic polymers such as lignosulfonate (LS), naphthalene sulfonate-formaldehyde condensate (NS), and melamine-formaldehyde condensate, etc. Typical surfactants such as alkylbenzene sulfonates and fatty alcohol derivatives have not been widely accepted by the cement and concrete industry [3,4]. In this paper, the adsorptive behaviors of four types of surfactants on Portland cement have been investigated by measuring adsorbance, contact angle, and zeta potential. The selected surfactants included: ethoxylated fatty alcohol sulfate (AES, anionic), cetyl piridinium chloride (CPC, cationic), ethoxylated alkyl phenol (TX-10, nonionic), and NS (polymeric). Based on their adsorptive characteristics, corresponding adsorptive models have been proposed.

2. Experimental

2.1. Materials

An ordinary 525# Portland cement was used in this investigation. This cement was manufactured by a local factory and consisted of C_3A, 3 ~ 4%; C_3S, 50–51%; C_2S, 10–11%; C_4AF, 12–13%; gypsum, 5%; and slag, 13%. It had an average diameter of particle size 22.7 μm and a surface area of 3 ± 0.3 m^2/g (BET, N_2 adsorption). AES, a solution containing 70% ethoxylated lauryl alcohol sulfate with 3 units of ethylene oxide, was from Hankel. TX-10 was from Condea. CPC was provided by Shanghai No. 1 Chem. Reagent Factory and NS containing 70% active matter was supported by Jiangdu Water-Reducing Admixture Factory. All chemicals were used as received without further purification.

2.2. Measurement of adsorbance

A solution of surfactant was prepared based on the ratio of water to cement (w/c) and the content of the surfactant.

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Cement was poured into the surfactant solution under agitation. After a period of adsorption (from 5 to 120 min), the paste was filtered and the obtained filtrate was used for measurement of the residue of the surfactant. To determine AES, a standard method of two-phase titration has been accepted [5]. According to this method, CPC monohydrate was used as standard reagent and a mixed indicator was prepared by dissolving 0.5 g of dimidium bromide and 0.25 g of disulfine blue in warm solution of ethanol/water (10:90). The end point was indicated by a color change from pink to blue in organic phase. Determination of CPC, TX-10, and NS were based on the spectrophotometry as they had maximum absorption at $\lambda = 214$, 277, and 230 nm, respectively.

In experiments of later addition, cement and water were mixed first. After a preset time (from 5 to 330 s), surfactant solution was added.

2.3. Contact angle

Accurately weighted cement was put into a cone flask. Then a solution with the required content of surfactant was added under agitation. After adsorption for 120 min, the cement paste was filtered and the obtained cake was dried at 50°C for at least 3 h. Meanwhile, the cake was stirred gently to avoid aggregation. The dried cake was pressed by a pelletizor at 240 kN for 20 min. The measurement of contact angles against water or liquid paraffin was conducted by a special instrument from Erma, Japan.

2.4. Zeta potential

Cement (0.2 g) and a solution (50 ml) with known content of surfactant were mixed in a 100-ml beaker. After an ultrasonic treatment for 5 min, 2–4 ml of suspension was transferred into a measuring cell. Zeta potential was measured by a JS94F Eletrophoresis apparatus from Shanghai Jiecheng Instrument. The measurement was run at $V = 10$ V, $T = 25$°C with switch time at $t = 50$ s.

3. Results and discussion

3.1. Adsorbance

3.1.1. Adsorptive rate

Fig. 1 depicted the relationship between relative adsorbance and adsorptive period for AES, CPC, and NS at various concentrations. For AES, as seen from Fig. 1a, all curves were almost horizontal, indicating a fast and equilibrized adsorption. On the contrary, curves for CPC were sloped and no adsorptive equilibrium was reached (Fig. 1b). CPC also had less relative adsorbance than AES. Therefore, it seems that CPC is more difficult to be adsorbed. As to NS, a polymeric anionic surfactant, its adsorptive behavior was similar to AES but the adsorptive rate was slower when the content of surfactant was higher (Fig. 1c). TX-10 could not be adsorbed on cement (Table 1).

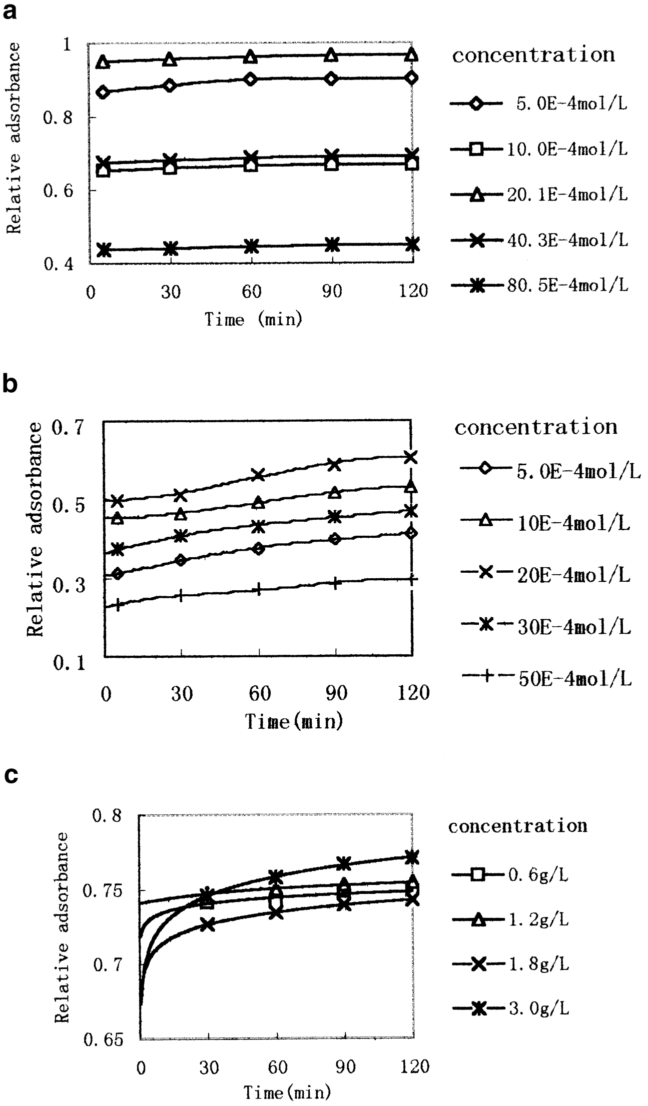

Fig. 1. Relationship between relative adsorbance and adsorptive period (w/c = 5, $T = 25$°C). (a) AES, (b) CPC, (c) NS.

3.1.2. Absolute adsorbance vs. concentration

Fig. 2 showed the dependence of absolute adsorbance vs. the concentration of surfactant at various adsorptive periods. As seen from Fig. 2a, AES showed a typical LS adsorption characterized by the appearance of double-plateau, indicating the formation of adsorptive micelles at higher concentration. The concept of adsorptive micelles was first proposed by Grandin and Fuerstenau in 1955 [6]. Based on a model of two steps of adsorption, Zhu and Gu [7] had deduced a universal isothermal equation in which the appearance of adsorptive micelles could be predicted quantitatively. On the other hand, CPC showed an S-shape of adsorptive curve (Fig. 2b). However, because of slow adsorption, the

Table 1
The absorbance of TX-10 filtrates at various adsorptive periods and later addition time (w/c = 5, T = 25°C, initial conc. of TX-10 = 20 × 10^{-4} mol/l)

Later addition time (s)	Adsorptive period (min)				
	5	30	60	90	120
0	0.561	0.562	0.561	0.561	0.560
30	0.560	0.561	0.559	0.561	0.561
90	0.562	0.561	0.560	0.561	0.562
150	0.560	0.561	0.561	0.560	0.561
210	0.561	0.560	0.561	0.559	0.560
270	0.561	0.559	0.560	0.561	0.559

adsorptive period influenced adsorbance. It was interesting that an accelerated zone appeared in a range of concentration from 10 to 20 × 10^{-4} mol/l. As to NS, a linear relationship was found for different adsorptive periods (Fig. 2c).

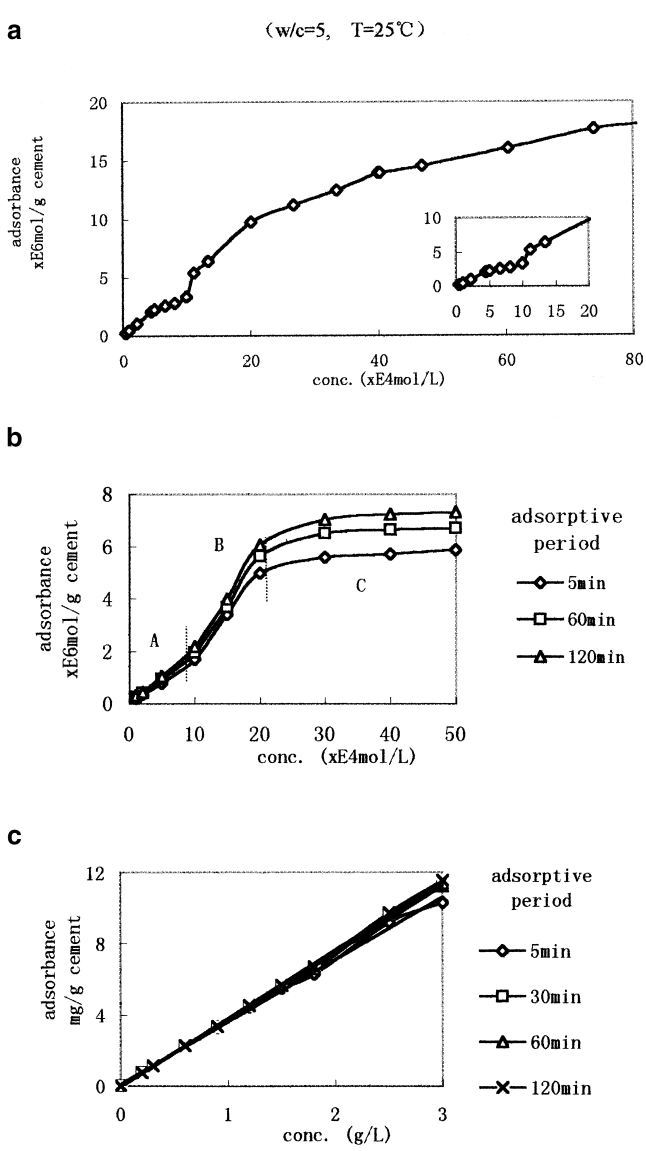

Fig. 2. Relationship between absolute adsorbance and concentration of surfactant. (a) AES (adsorptive period of 120 min), (b) CPC, (c) NS.

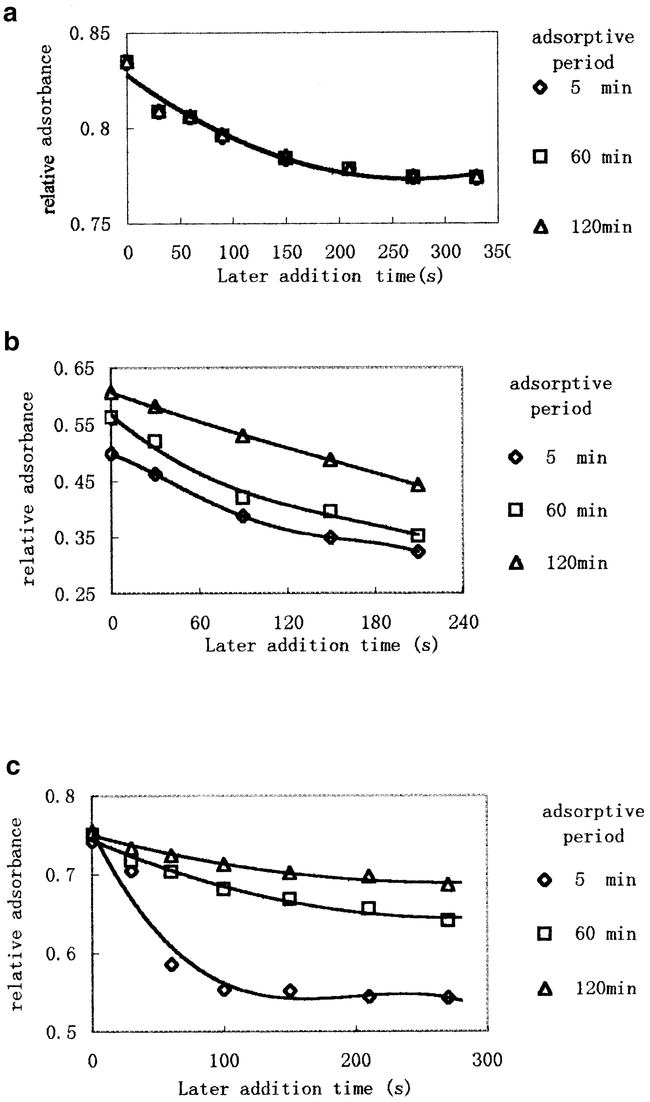

Fig. 3. Effect of later addition, T = 25°C, w/c = 5. (a) AES conc. 26.85E − 4 mol/l, (b) CPC conc. 20E − 4 mol/l, (c) NS conc. 0.6 g/l.

3.1.3. Effect of later addition

To observe the effect of later addition, the concentration of surfactant in cement paste should be fixed. The selected concentration of surfactant was around 0.6% based on the weight of cement. Fig. 3 illustrated the dependence of relative adsorbance vs. later addition time. As seen from Fig. 3a, with an extension of later addition time, the relative adsorbance of AES reduced from 0.83 to 0.77. However, for adsorptive period from 5 to 120 min, all curves overlapped each other. In the case of CPC (Fig. 3b), adsorbance depended on both the later addition time and the adsorptive period, indicating a kinetic character of adsorption. Later addition also reduced the adsorbance of NS and had significant influence on the short adsorptive period (Fig. 3c). It was attributed to the adsorptive character of the polymeric molecule.

Table 1 gave the absorbance of TX-10 filtrate at various adsorptive periods and later addition time. The initial concentration of TX-10 was 20.0×10^{-4} mol/l. As seen from the data in Table 1, in all cases, the absorbance was the same as the original. Therefore, TX-10 had little or no adsorption on the surface of cement.

Based on the above investigation, we concluded that the four selected surfactants had different adsorptive behaviors on the surface of Portland cement. Their adsorptive rates allow the following sequence: AES > NS > CPC > TX-10.

The result that both cationic and anionic surfactants could be adsorbed but nonionic failed indicated that electrostatic interaction between surfactant and Portland cement played an important role. The different adsorptive behaviors of four surfactants depend on their adsorptive mechanism and will be discussed later.

3.2. Contact angle

The relationship between contact angle and AES concentration was shown in Fig. 4. Along with an increase of AES, the contact angle against water was up, via maximum and then down. Contrarily, the contact angle against liquid paraffin was changed in the reverse direction. Both maximum and minimum contact angles located at an AES concentration of $5-10 \times 10^{-4}$ mol/l, nearby the first plateau of absolute adsorbance (Fig. 2a). Consequently, during AES adsorption, the surface of Portland cement proceeded with a change from hydrophilic → hydrophobic → hydrophilic. It indicated that during adsorption, the hydrocarbon chain of AES oriented towards the liquid phase. However, when adsorptive micelles were formed by interaction of hydrocarbon chains, the hydrophilic group of AES would expose to liquid phase again, leading to an increase of hydrophilicity (see Fig. 10).

The dependence of contact angle against water vs. concentration of four surfactants were depicted in Fig. 5. As seen from figure, the contact angles of both CPC and NS monotonically increased along with their concentrations. It was different with the case of AES. Therefore, adsorptive micelles may not be formed. AES had almost double relative adsorbance as CPC had, so that AES was more efficient in the modification of cement surface. However, NS is a polymeric surfactant; its characteristic of molecular structure makes it impossible to act as an effective modifier as those with low molecular weight. TX-10 was not adsorbed so that it had little influence on the surface properties of cement.

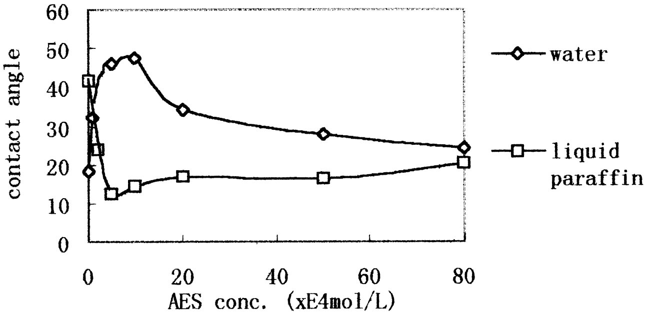

Fig. 4. Dependence of contact angles vs. concentration of AES.

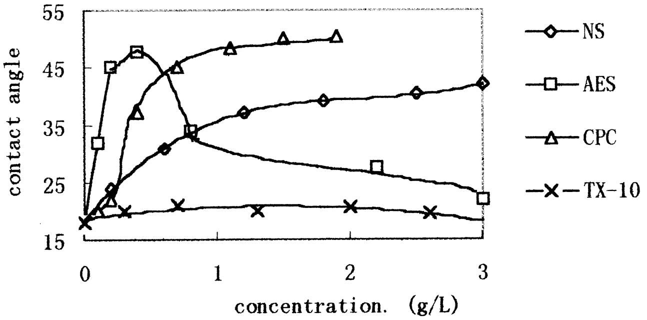

Fig. 5. Relationship between contact angle and concentration of various surfactants.

3.3. Zeta potential

In investigation of both adsorbance and contact angle, the w/c ratio was usually fixed at 5. However, for measurement of zeta potential, a higher content of cement was not suitable. Instead, a ratio of w/c = 250 was selected. Probably, adsorptive behavior of surfactants in such dilute phase was different with that in concentrated phase.

In Fig. 6, dependence of zeta potential vs. adsorptive period for various surfactants at different concentrations was depicted. As seen from Fig. 6, for all surfactants their zeta potentials vibrated during the first 20 min but became stable thereafter. It was reasonable because of faster initial hydration of cement. The measurement of both pH value and conductivity of cement paste also showed similar phenomena (not shown in this paper). It might be said that after 20 min of hydration, a quasi-stable interface could be formed. Therefore, in continuing research all data of zeta potential were measured at an adsorptive period of 40 min.

The relationship between zeta potential and concentration of surfactants was shown in Fig. 7. After hydration for 40 min, pure cement paste had a zeta potential of − 11 mV. Because of different adsorptive behaviors, every surfactant exhibited different influences on zeta potential. As seen from Fig. 7, the adsorption of AES increased the negative zeta potential on the cement surface and two maximums, − 20 and − 32 mV, appeared at concentrations of AES 0.05 and 0.8 g/l, respectively. Probably, the first maximum corresponded to monolayer adsorption of AES, and the second maximum indicated the formation of adsorptive micelles. When CPC was adsorbed, it changed the zeta potential from negative to positive and only one maximum, + 20 mV, was reached. Because of its lower relative adsor-

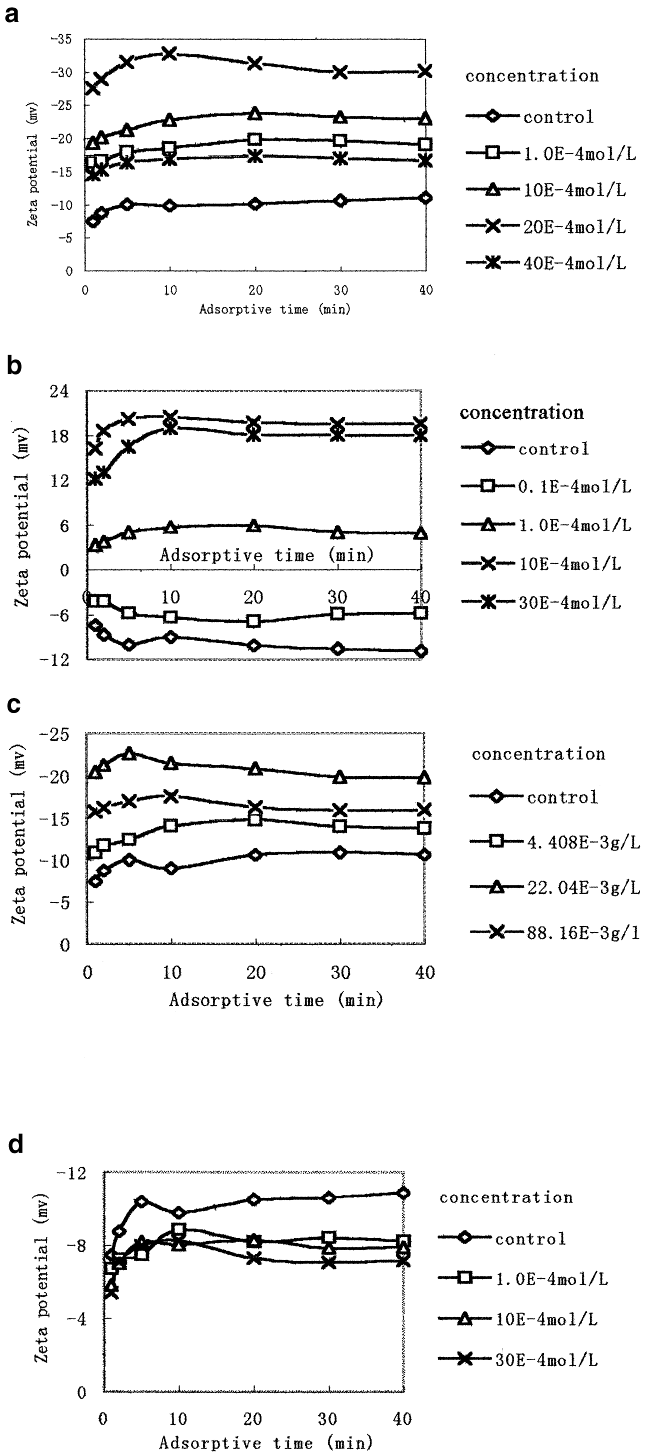

Fig. 6. Dependence of zeta potential vs. adsorptive period ($T=25°C$, w/c = 250). (a) AES, (b) CPC, (c) NS, (d) TX-10.

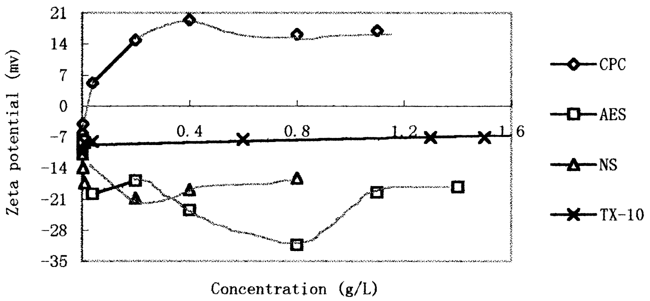

Fig. 7. Dependence of zeta potential vs. concentration of surfactants (adsorptive period 40 min; $T=25°C$, w/c = 250).

bance, a higher concentration (0.4 g/l) was required to reach maximum. NS had a maximum zeta potential of − 21 mV at a concentration of 0.2 g/l. It indicated that NS was not as effective to be adsorbed as AES. Besides, no second maximum appeared. In the case of TX-10, zeta potential had no much change during all ranges of concentration. It coincided with its measurements of both adsorbance and contact angle.

4. Proposed adsorptive models

Like other inorganic salts and oxides, Portland cement has a high surface energy so that it has strong adsorbability. When cement is mixed with water, hydration starts immediately. Hydration takes place in very thin film of water surrounding cement particles and is a complicated physico-chemical process including dissolution, reaction, formation of gel, precipitation, crystallization, etc. [8,9]. Consequently, during initial hydration, the surface of cement is in a dynamic state. When surfactant enters the paste of cement/water, competitive adsorption will happen. If the concentration of surfactant is greater than its cmc, micelles will form in the paste. Similarly, formation of adsorptive micelle has been proposed [6]. Therefore, in cement paste, molecules of surfactant may occur in four possible states, as shown in Fig. 8.

This investigation is part of a project referring to cement grouting. In engineering practice, grouting has to be controlled in less than 4 h because cement paste usually starts to set and harden after this period. Therefore, only the adsorptive behavior at the early stage of hydration is concerned. As seen from measurement of the zeta potential, the surface of cement particle tends to be stable after 20 min of hydration (w/c = 250). To set forth an adsorptive model, a stable surface of Portland cement has been proposed.

To explain the adsorptive behavior of various surfactants, a model of modified double-electrical layer proposed by

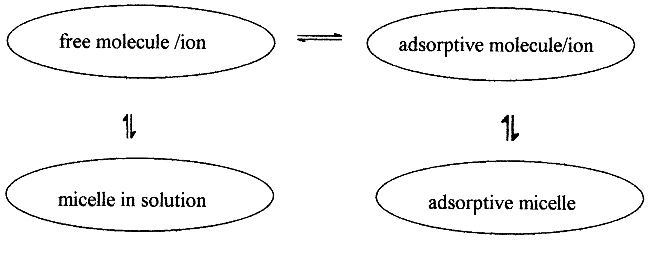

Fig. 8. Possible states of surfactant in cement paste.

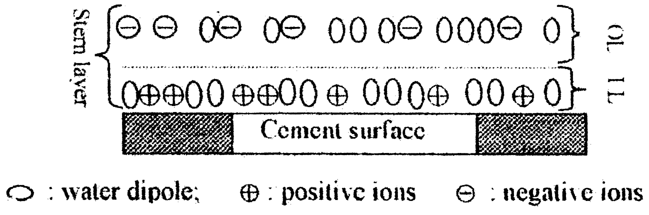

Fig. 9. Modified Stern double-layer model on cement surface.

Graham [10] has been accepted as starting point. According to this model, the Stern layer consists of two layers: an inner layer (IL) in which adsorbed molecules or ions connect with the surface of cement directly and have intimate arrangement each other; and an outer layer (OL) in which adsorbed molecules or ions have a looser arrangement. When cement is mixed with water, positive ions such as Ca^{2+}, Mg^{2+} and Na^{+} are dissolved into the solution while the frame of SiO_4^{3-}, AlO_3^{3-} remain, leading to its surface with negative charge. Therefore, its Stern IL consists of positive ions and water dipole and its Stern OL — negative ions and water dipole. When surfactant is absent, the adsorptive model of cement surface is illustrated in Fig. 9. In this model, the sum of positive charges in the IL has to be more than the sum of negative charges in the OL. Because of a strong physico-chemical interaction between cement and water, it is reasonable to think that many water dipoles are present in both Stern IL and OL. A similar modified double-layer model has been accepted by Yousuf et al. [11] to explain the adsorption of sodium lignosulphonate on the surface of C_3S.

When AES participated in competitive adsorption, AES^{-} ion could only enter the Stern OL because of its character of charge. It means no exchange of ions happens in the Stern IL. This kind of adsorption, from bulk phase to Stern OL, is faster and easier. When the water dipole in the Stern OL was replaced by AES^{-} ion, the zeta potential increased. Because of the characteristic of AES structure, adsorbed AES^{-} had to be oriented with its hydrocarbon chain toward bulk phase. Along with the increase of content, AES^{-} might form saturate adsorption on the surface and form micelles in the solution, resulting in appearance of the first plateau (Fig. 2a). When more AES was presented, adsorptive micelles formed on the surface, leading to a significant increase of both adsorbance and zeta potential. However, such adsorptive micelles were O/W type so that the hydrophobicity of cement surface decreased again. The adsorptive model of AES was depicted in Fig. 10.

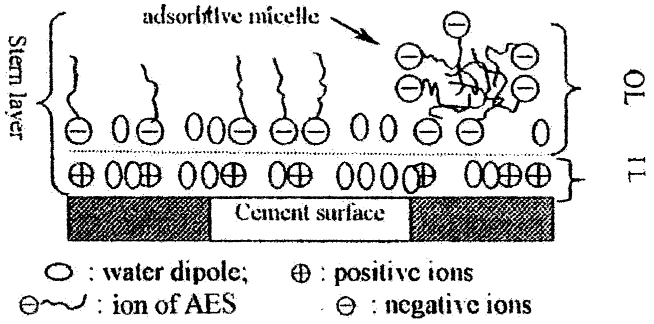

Fig. 10. Adsorptive model of AES on surface of Portland cement.

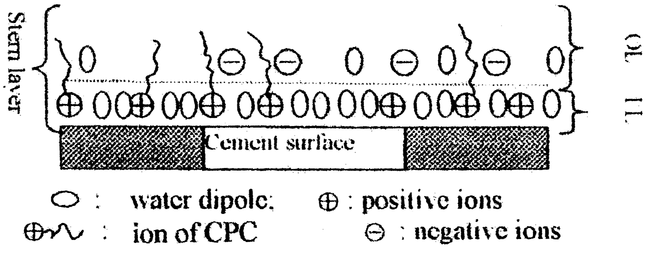

Fig. 11. Adsorptive model of CPC on surface of Portland cement.

When CPC participated in competitive adsorption, CPC^{+} ion should enter the Stern IL via the Stern OL. That means CPC^{+} ion should overcome more barriers. Therefore, CPC^{+} adsorption was slow and in lower adsorbance. As in the case of AES, CPC^{+} has its hydrocarbon chain towards the outside, resulting in an increase of hydrophobicity. Because of strong characteristic adsorption, CPC^{+} ion can replace water dipole in the Stern IL so that the zeta potential changed to positive. However, because of the following reasons, adsorptive micelles could not be formed: CPC^{+} was adsorbed tightly on the surface site so that their surface migration was more difficult; Stern OL formed a barrier. The adsorptive model of CPC was shown in Fig. 11.

When NS participated in competitive adsorption, only replacement in the Stern OL was involved. Therefore, like AES, the adsorption was faster. However, as polymer, many $-SO_3^{-}$ groups occurred in a molecule, so that multipoint adsorption was a usual way. An adsorptive model of train-formation proposed by Anderson et al. [12] was one of multipoint adsorption. When NS was adsorbed, it brought many negative charges to the surface. However, because of the character of the structure, adsorbed NS would form individual clusters on the surface. Probably, the linear relationship between adsorbance and concentration (Fig. 2c) indicated the independence of formed clusters. Consequently, neither saturated monolayer nor adsorptive micelles could be formed. Besides, formation of clusters made the

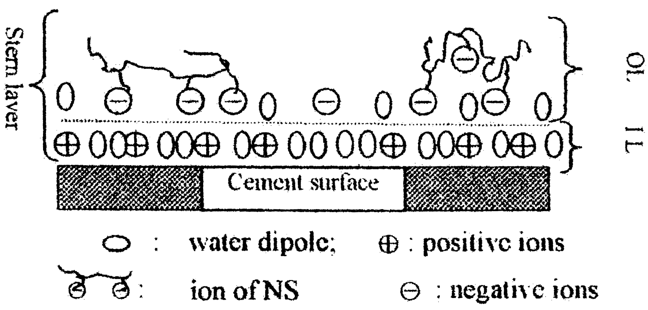

Fig. 12. Adsorptive model of NS on surface of Portland cement.

Stern OL much thicker than the case of AES adsorption. Uchikawa et al. [13] had proven that NS was unevenly adsorbed on the surface. On the polished C_3S surface, the NS adsorptive layer had a thickness of 50 nm and on interstitial phase — even 300 nm. The adsorptive model of NS was shown in Fig. 12.

The effect of later addition attributed to two reasons.

(1) Competitive adsorption: in later addition, surfactants have to substitute molecules or ions which have been adsorbed in advance. It is more difficult than simultaneous competition.

(2) Change of surface structure. A hydrated surface of cement is less active than the original one so that adsorbance may be reduced.

5. Conclusions

(1) It has been found that on the surface of Portland cement four kinds of surfactants, AES, CPC, NS, and TX-10, have different adsorptive behaviors: AES is adsorbed fast and belongs to the LS-type of adsorption; CPC is slow and kinetically controlled; NS has a linear relationship of adsorbance vs. concentration; TX-10 is not adsorbed.

(2) On the surface of Portland cement, all adsorbed surfactants have their hydrophobic chain towards the bulk phase. In the case of AES, probably because of the formation of adsorptive micelles, the surface of cement suffered a change from hydrophilic → hydrophobic → hydrophilic.

(3) Measurement of the zeta potential of Portland cement also proves that both cationic and anionic surfactants can be adsorbed on the cement surface. In the case of CPC adsorption, the zeta potential changed from negative to positive.

(4) A modified Stern double-layer model has been proposed to illustrate the adsorptive behaviors for all surfactants.

Acknowledgments

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