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The improvement of the cationic/anionic surfactant interfacial activity via the selective host-guest recognition

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ABSTRACT

Supramolecular chemistry proposed a controllable and convenient approach to construct the desired complexes used in various fields, including chemical enhanced oil recovery. β cyclodextrin (β-CD) can effectively enclose the surfactants to fabricate the stable inclusion complexes via the host-guest recognition. In the present report, the β CD effects on the interfacial activities of the mixed surfactant system consisting of *N* dodecyl *N* methylpyrrolidinium bromide (L12) and sodium dodecyl sulfate (SDS) were systematically evaluated. Interestingly, the additional β-CD molecules greatly reduced the interfacial tension (IFT) between the L12/SDS aqueous solution and model oil (toluene and n-decane, v/v = 1:1). Due to the electrostatic attraction of L12/SDS, the β-CD molecules could selectively enclose the majority surfactants to improve the intensive arrangements of mixed surfactants at the interface. In general, the host-guest recognition facilitates the fabrications of β-CD/surfactant inclusions and decrease surfactant interfacial concentrations. The competition between the host-guest recognition and the electrostatic attraction dominates the IFT variations. Then we changed the molar ratio of L12/SDS, the dissolved order of chemicals and explored the variations of the mixed surfactants hydrophile-lipophile balance to further confirm the proposed mechanism. Moreover, the salinity and temperature effects on the IFT were systematically investigated.

1. Introduction

During the past decades, surfactant flooding was widely employed in chemical enhanced oil recovery (EOR), adding huge economic benefits [1]. The surfactant largely improves the recovery of residual oil via the reduction of the oil/water interfacial tension (IFT) and the modification of the formation wettability [2–4]. To achieve the higher recovery, many groups focused on the investigations and developments of the novel high-performance surfactants, such as Gemini surfactants [5–8], double-chain surfactants [9,10], surface active ionic liquids [11–14], zwitterionic surfactants [15–18], and other types [19–21]. Cui's group demonstrated the increased hydrophobicity of surfactants with two alkyl chains could enhance the ability to reduce the IFT [9,10]. Ali Zeinolabedini Hezave et al. investigated the high interfacial activities of imidazolium and pyridinium surface active ionic liquids [11–13]. Zhang et al. found the good salt and temperature tolerances of the zwitterionic surfactants [15–17]. In a word, the peculiar structures endow the novel surfactants with many excellent properties. However, the complex synthetic steps and correspondingly high price may impose serious restrictions on their applications.

The mixed surfactants, including anionic/nonionic, nonionic/nonionic, and cationic/nonionic surfactants, may be the promising and facile systems to greatly enhance oil recovery [21–26]. In our previous report, the mixed cationic/anionic surfactants consisting of *N* dodecyl *N* methylpyrrolidinium bromide (L12) and sodium dodecyl sulfate (SDS) showed the satisfactory ability to reduce the water/oil IFT at the low concentration (500 mg/L) [27]. The closer the L12/SDS molar numbers were, the lower the IFT value was. While the equal L12/SDS molar numbers could generate the precipitates. To explore the optimal molar ratio of mixed L12/SDS system, we proposed a smart method to remove the redundant surfactant molecules at the interface by the selective host-guest recognition of the cyclodextrins (CDs).

CDs and their derivatives with a hydrophobic cavity and a hydrophilic exterior can form the stable inclusion complexes with suitable surfactants, ionic liquids, polymers, alkanes, vitamins and amino acids via the host-guest recognition [28–37]. CDs and CD-based inclusions have been widely used in various fields [38–40], including the chemical EOR [41–47]. Zhang et al. demonstrated the formation of CD/alkanes inclusion could obviously decrease the IFT values at the water/alkane interface [46]. It was found that the fabricated SDS/β-CD inclusion largely reduced the adsorption loss of SDS molecules on shale, kaolin

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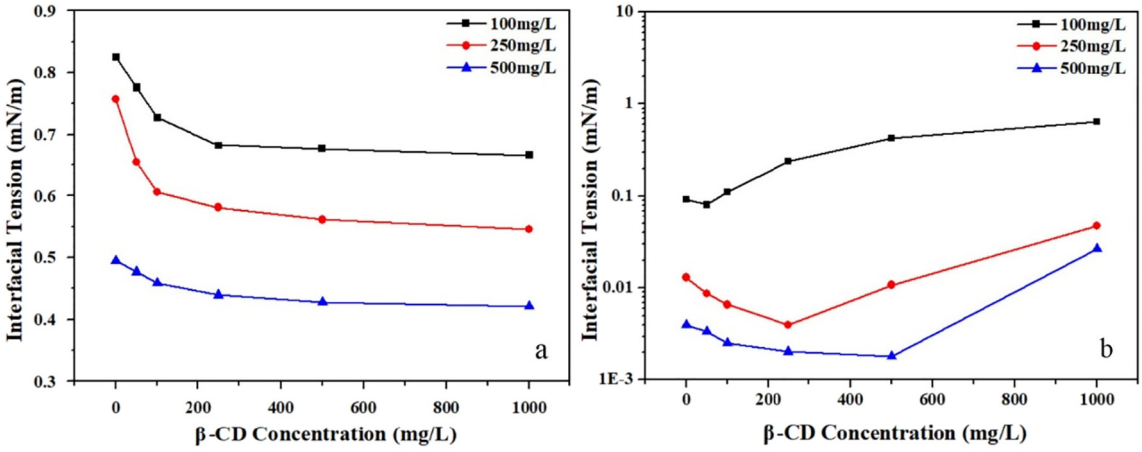

Fig. 1. Effects of additional β-CD on the IFT between mixed L12/SDS aqueous solutions (100 mg/L, 250 mg/L, and 500 mg/L) and model oil at 30 °C: (a) $R = 2.5:1$; (b) $R = 1:2.5$.

and sand [47]. Meanwhile, the interfacial activities of SDS molecules were seriously weakened with the additional β-CD. We further recovered the SDS ability to reduce the IFT by the addition of adamantanamine chloride [48].

In the previous literatures, the additional β-CD molecules could control over surfactant compositions in mixed cationic/anionic surfactant aqueous solution by the selective remove of the excess component, achieving the approximate electroneutral mixing stoichiometry in the aggregates [49,50]. Herein, we investigated the effects of the additional β-CD molecules on the mixed cationic/anionic surfactants at the water/oil interface. Both the selective bind and the electrostatic interaction could seriously affect the interfacial arrangements of mixed surfactants and the IFT variations. To verify the proposed mechanism, we explored the effects of the chemical dissolved order, the molar ratio of L12/SDS, the mixed surfactant hydrophile-lipophile balance, the additional salt and temperature in the control experiments.

2. Experimental

2.1. Chemicals

N-Dodecyl-*N*-methylpyrrolidinium bromide (L12) was synthesized according to our previous report [27]. The product purity was examined

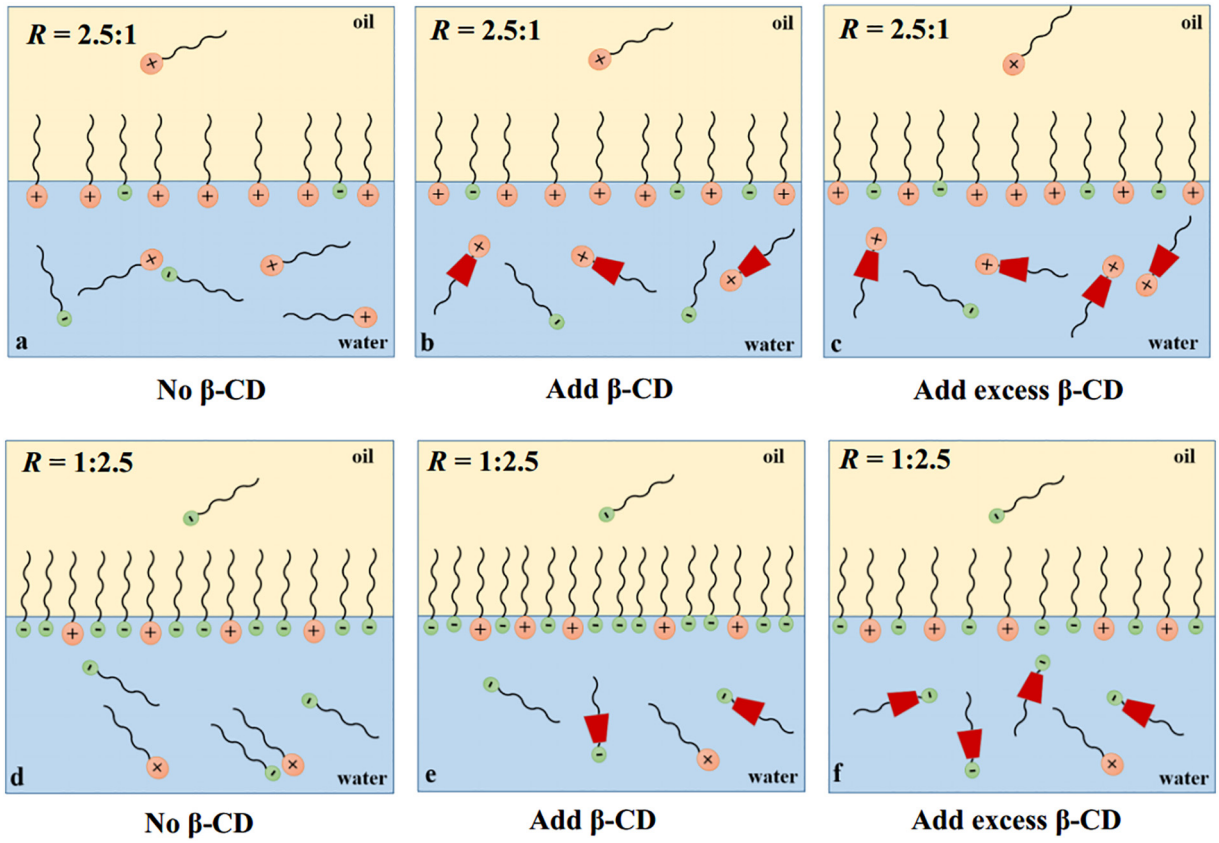

Fig. 2. Schematic illustrations of the effects of the additional β-CD.