Colloids and Surfaces A: Physicochem. Eng. Aspects 500 (2016) 32–39

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

The effect of functional groups on the sphere-to-wormlike micellar transition in quaternary ammonium surfactant solutions

Caili Dai[a], Weitao Li[a], Ya Cui[b,*], Yongpeng Sun[a], Wenjun Wu[a], Zhongliang Xu[a], Yifei Liu[a], Zhe Yang[a], Xuepeng Wu[a,*]

[a] School of Petroleum Engineering, State Key Laboratory of Heavy Oil Processing, China University of Petroleum (East China), Qingdao, Shandong, 266580, China

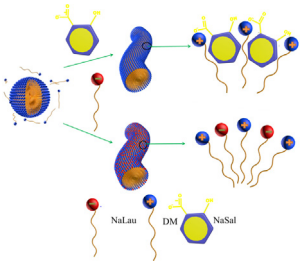
[b] Oilfield Development Department, Northwest Branch of Sinopec, Urumqi 830011, China

HIGHLIGHTS

- The intermolecular and intramolecular hydrogen bonds produced by hydroxyl group can promote the formation of wormlike micelles.
- The long hydrophobic chain has stronger ability formation the wormlike micelles than aromatic ring.
- Different mechanism of interactions could result different transition mechanism.

GRAPHICAL ABSTRACT

Different functions of NaSal and NaLau when mixed with DM aqueous solutions were investigated. Both of them can induce the shape of micellar transition from spherical to wormlike due to the strong hydrophobic interactions.



ARTICLE INFO

Article history:
Received 5 February 2016
Received in revised form 22 March 2016
Accepted 8 April 2016
Available online 8 April 2016

Keywords:
Function group
Rheology
Hydrophobic interaction

ABSTRACT

To investigate the effects of functional groups on the formation of wormlike micelles, a cationic surfactant, *N-tetradecyl-N-(2-hydroxyethyl)dimethylammonium bromide* (DM), was synthesized in this work. The viscoelastic behaviors of DM aqueous solution mixed with *sodium salicylate* (NaSal), *sodium benzoate* (NaBen) and *sodium laurate* (NaLau), respectively, have been studied with rheological measurements. Cryogenic transmission electron microscopy (cryo-TEM) and ^{1}H NMR technology have been employed to investigate the morphology and arrangement of wormlike micelles. The results show that the effects of NaSal and NaLau on wormlike micellar growth are significantly higher than that of NaBen. Superficially, such a great difference in the rheology properties arises from the effect of hydroxyl group in NaSal because this is the sole difference between the NaSal and NaBen. By comparing with NaBen in DM solution, the long hydrocarbon chain of NaLau induces greater hydrophobic interactions between Lau^- anions and DM surfactants than aromatic phenyl group of NaBen, and hydrophobic interactions play an important role in the growth of micelles.

1. Introduction

Ionic surfactant can self-assemble into various aggregates in aqueous solution, such as micelles, bicelles, microemulsions, liquid crystals and vesicles [1–4]. Due to the good prospects in application, the wormlike micelles have been studied in detail in recent years.

* Corresponding authors.
E-mail addresses: cuiy.xbsj@sinopec.com (Y. Cui), wuxuepeng@163.com (X. Wu).

http://dx.doi.org/10.1016/j.colsurfa.2016.04.024
0927-7757/

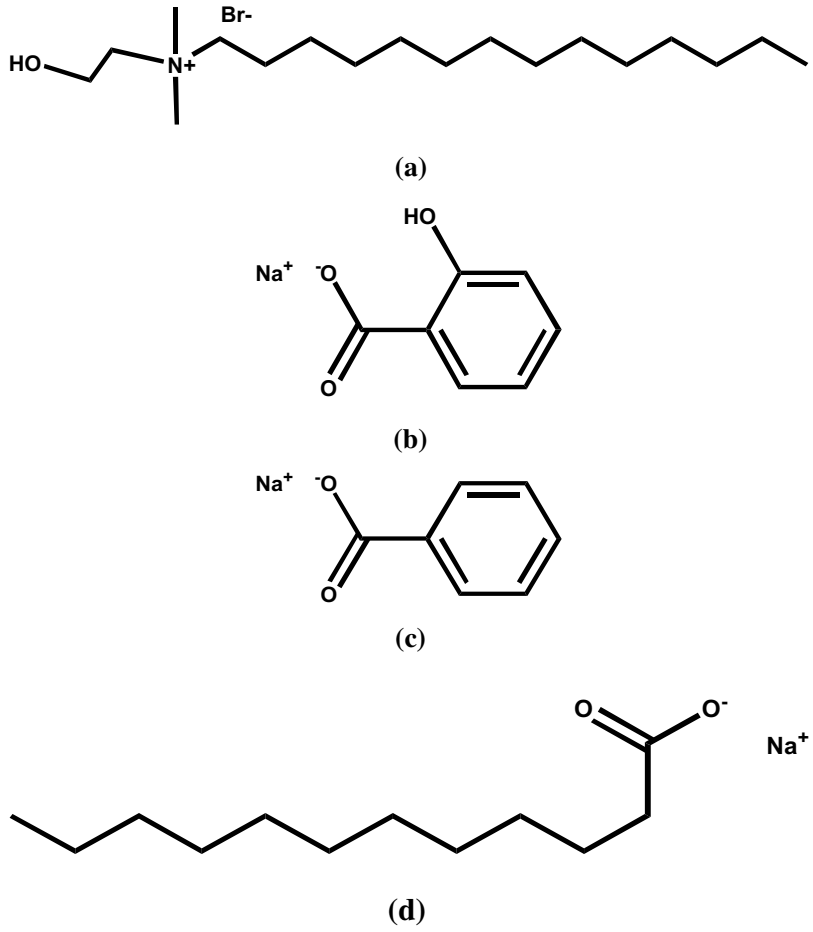


Fig. 1. Chemical structure of DM (a), NaSal (b), NaBen (c) and NaLau (d).

By changing the concentration of surfactants, temperature or with the addition of salts or cosurfactants etc., the spherical micelles formed in solution can grow along the direction of one dimension into thread-like and entangled wormlike micelles, whose viscoelastic properties are analogous to that of flexible polymers in aqueous solutions. But unlike flexible polymers, wormlike micelles keep a state of dynamic equilibrium and their structures constantly break and recombine with ionic bonding [5]. In terms of these viscoelastic behaviors, the wormlike micelles are widely applied in many areas, such as fracturing fluids for oilfield development, drag reducing fluids, personal care agents, and the templates for the synthesis of nanomaterial [6–11].

In recent years, many novel cationic surfactants have been synthesized by introducing some functional groups to investigate new self-assembly behavior under given conditions. For instance, Wei et al. have synthesized two novel cationic surfactants, *3-hexadecyloxy-2-hydroxypropyltrimethyl ammonium bromide* and *chloride*, by incorporating a 2-hydroxy-propoxy group between the headgroups and alkyl chain of the surfactant cation and this new cationic surfactant showed non-toxic and varied properties [12]. Song et al. have gained three types of long-chain quaternary ammonium surfactants through introducing different numbers of hydroxyl groups to study the effects of headgroups on solution behavior and solid phase transitions [13]. Inspired by these achievements, a novel cationic surfactants have been synthesized by introducing hydroxyl groups and prepared to investigate the effects of function groups on the formation of wormlike micelles.

It is known that the micelles of cationic surfactants (e.g., *alkyltrimethylammonium halide*) can transform into wormlike micelles from spherical micelles in the presence of salts or anionic cosurfactant. These wormlike micelles would grow rapidly and entangle each other, exhibiting striking viscoelastic behavior even at low surfactant concentrations [14,15]. Up to now, a large numbers of researches have been conducted on cationic surfactants solution in the presence of salts, including *cetyltrimethylammonium bromide* or *chloride* (CTAB or CTAC) with added NaBen or NaSal; *cetylpyridinium bromide* (CPyBr) with added KBr; *cetylpyridinium salicylate*(CPySal) with added NaSal, etc [16–21]. The addition of these salts can screen the repulsions between headgroups of cationic surfactant and arouse one dimensional micellar growth by decreasing cross-sectional area of per headgroups of the surfactant molecule [22]. On the other hand, the mixtures of cationic surfactants and anionic ones can give rise to synergistic effects to generate wormlike micelles, such as *cetyl trimethylammonium tosylate* (CTAT) and sodium *dodecylbenzene sulfonat*e (SDBS) mixture solution; *dodecyl trimethylammoniumbromide* (DTAB) and NaLau mixture solution; *cetyltrimethylammonium bromide* (CTAB) and *sodium octyl sulfate* (SOS) mixture solution [23–28]. The strong hydrophobic interaction and reduced electrostatic repulsion between the oppositely charged headgroups can facilitate micelles growth and cause micellar transition. Organic salts and cosurfactants can affect the self-assembly behaviors of surfactant solutions in different ways, and the different function groups in the counterions can result in different aggregation mechanism [21,29]. Hence, to investigate the effect of aromatic and aliphatic anions on the aggregation behavior of the novel cationic surfactant is of great importance.