Journal of Molecular Liquids 216 (2016) 185–191

Contents lists available at ScienceDirect

Journal of Molecular Liquids

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

Surface and interfacial tension of nonylphenol polyethylene oxides sulfonate

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ARTICLE INFO

Article history:
Received 5 November 2015
Received in revised form 8 December 2015
Accepted 3 January 2016
Available online 15 January 2016

Keywords:
Adsorption
Surface tension
Interfacial tension
Electrolytes

ABSTRACT

The equilibrium and dynamic surface tension of nonylphenol polyethylene oxides sulfonate (NPE_nS, n = 3, 5 and 7) were investigated; and, the effect of electrolytes (NaCl, $MgCl_2$ and $CaCl_2$) on the interfacial tension between NPE_nS solution and dodecane was discussed. It was found that the critical micelle concentration (cmc) of NPE_nS is almost the same. The surface tension at cmc and minimum area per molecule increase with increasing the EO number. The time required to attain the equilibrium surface tension decreases with increasing surfactant concentration and the EO number. Adsorption process for NPE_nS concentration above cmc is a mixed diffusion-kinetic adsorption mechanism. Interfacial tension between NPE_nS solution and dodecane increases with the increase of EO number at studied electrolyte concentrations (NaCl concentration from 10 to 210 g/L, $CaCl_2$ and $MgCl_2$ concentration from 0.1 to 10 g/L). Most of IFT measured keeps in the order of 10^{-1} mN/m magnitudes in a wide range of electrolytes concentrations, which indicates that NPE_nS is insensitive to electrolyte and suitable for co-surfactant in high salinity reservoirs.

1. Introduction

Petroleum is one of the world's major sources of energy. About two-thirds of the crude oil remains in oil reservoir after primary and secondary oil recovery [1]. With the development of oil fields, more and more enhanced oil recovery (EOR) technologies have carried out. Surfactant flooding is an important EOR method because the residual oil is mobilized through decreasing oil/water interfacial tension (IFT) to overcome the capillary force [2–10]. During surfactant EOR process, anionic surfactants such as alkylbenzene sulfonate and petroleum sulfonate with lower cost and extensive source have been extensively employed for common reservoirs [11–15]. While the connate water in some petroleum reservoirs contains lots of divalent ions (such as Ca^{2+} or Mg^{2+}), and small amounts of which could make these surfactants precipitate. Therefore, it is important to develop and study the surfactants applying to high salinity reservoirs.

Anion–nonionic surfactants show better performance at high salinity and high temperature reservoirs. This kind of surfactants has two hydrophilic groups: nonionic hydrophilic group (polyethylene oxides group) and anionic hydrophilic group (sulfonic group, sulfate group and carboxylate group) [6]. The alkyl polyethylene oxides sulfate used commonly in oilfield has a good resistance to electrolytes, but the terminal group of C–O–SO_3 will hydrolyze in aqueous solution at high temperature. The alkyl polyethylene oxides sulfonate has a higher resistance to electrolytes and chemical stability due to the sulfur atom that is directly connected to carbon atom. These excellent properties for ethoxylated sulfonate surfactants have attracted wide interest [16–20].

The purpose of this paper is to study the adsorption behavior of nonylphenol polyethylene oxides sulfonate (NPE_nS, n = 3, 5 and 7) with different EO number at air/water and oil/water interface. The influence of EO chain length on the surface properties and adsorption behavior of NPE_nS was studied systematically. The effect of both EO number and electrolytes (NaCl, $CaCl_2$ and $MgCl_2$) on IFT between NPE_nS solutions and dodecane was investigated in detail.

2. Experimental sections

2.1. Materials

Nonylphenol polyethylene oxides (NPE_{n-1}, n = 3, 5, and 7) were kindly supplied by Sinolight Chemicals Co., Ltd., China. The number n stands for average degree of ethoxylation. The sodium isethionate was purchased from Huanggang Yongan Pharmaceutical Co., Ltd., China. Potassium hydroxide, ethyl acetate, ethanol, calcium chloride and alkanes

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http://dx.doi.org/10.1016/j.molliq.2016.01.009
0167-7322/

were obtained from Tianjin Kemiou Chemical Reagent Co., Ltd., China. All materials were used without further purification.

2.2. Synthesis

A flask was charged with 0.3 mol NPE_{n-1} and 0.03 mol KOH. The mixture was heated under mechanical stirring at 120 °C and 20 mm Hg pressure for 2 h to remove H_2O. Then 0.25 mol sodium isethionate was added to the mixture and reaction was carried out at 180 °C and 20 mm Hg pressure over 90 min. The synthesis route of NPE_nS is shown in Scheme 1.

About 5.0 g crude products were dissolved with alcohol–water solution containing 100 ml aqueous solution and 50 ml ethanol. Then the mixed solution was extracted with 50 mL ethyl acetate in a separatory funnel. The top layer was removed, and the bottom layer was extracted successively five times with 50 mL ethyl acetate. The bottom layer was distilled to remove water and ethyl alcohol, and then the remaining was filleted and washed with ethanol to desalt. The purity of product was determined by high-performance liquid chromatography (HPLC) using a C_8 stainless steel column (4.6 × 250 mm) and an UV detector (232 nm) at 30 °C. The mobile phase was 100% methanol with a flow rate of 1.0 mL/min. The purity of obtained NPE_nS (n = 3, 5 and 7) was 95.6%, 96.8% and 95.8%, respectively.

2.3. Structure characterization

Fig. 1 shows the negative ion MS of NPE_nS ionized by ESI. The molecular mass of NPE_nS was calculated to be 306 + 44m. The number m was the real EO number of NPE_nS. The ESI-MS spectrum of NPE_nS shows the ions at m/z $306 + 44m^{-23}$, corresponding to the molecule [MNa]. NPE_3S is consisted of NPE_mS in which m varies from 2 to 5; for NPE_5S, m varies from 2 to 10; for NPE_7S, m varies from 2 to 12.

2.4. Measurement of static surface tension

Surface tension was measured using a KRÜSS K12 Processor Tensiometer by the Wilhelmy plate technique at 25 °C. Solutions were prepared with deionized doubly distilled water. The length and thickness of the platinum plate were 19.9 mm and 0.2 mm, respectively. The dipping distance was 2 mm.

2.5. Measurement of dynamic surface tension

The dynamic surface tension was measured using a KRŰSS bubble pressure tensiometer BP100 method that involves measuring the maximum pressure necessary to blow a bubble in a liquid from the tip of a capillary. The measurements were conducted with effective surface ages from 0.01 to 250 s.

2.6. Measurement of interfacial tensions

Interfacial tension between surfactants aqueous solution and dodecane was measured at 30 °C by the spinning-drop technique using a model TX-500C interfacial tensiometer.

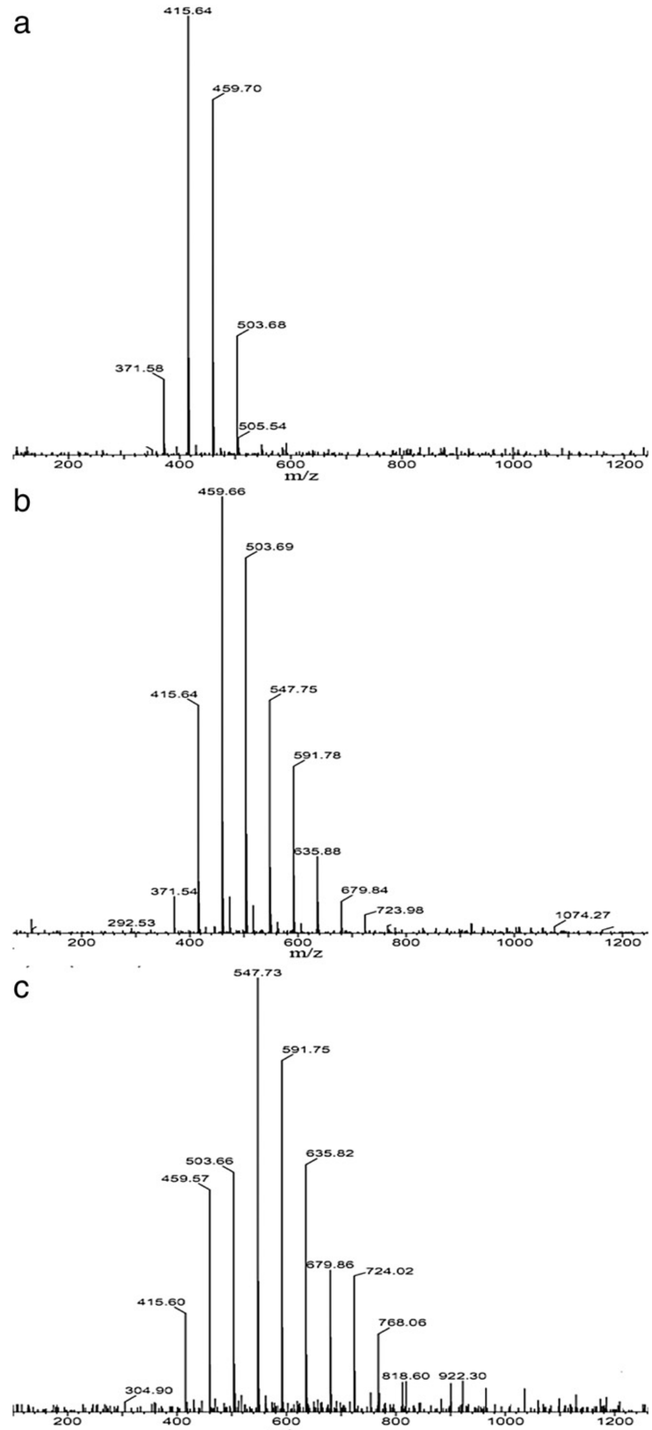
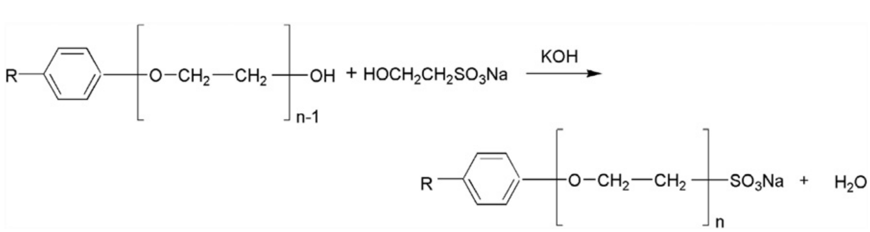


Fig. 1. ESI-MS of NPE_nS, a NPE3S, b NPE_5S, c NPE_7S.



Scheme 1. Synthetic route of NPE_nS, n = 3, 5 and 7.