Colloids and Surfaces A: Physicochem. Eng. Aspects 446 (2014) 80–89

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

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

Synthesis of sorbital based nonionic surfactants and characterization of interfacial and adhesive properties for waterborne pressure sensitive adhesives

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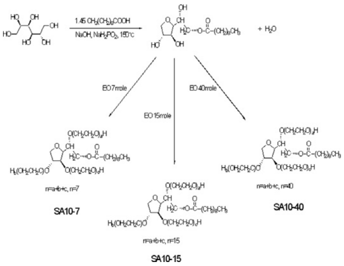
HIGHLIGHTS

- New nonionic surfactants were synthesized by the reaction of sorbitol and decanoic acid.
- The structure of a resulting product was elucidated by ^{1}H NMR, ^{13}C NMR and FT-IR.
- The interfacial and adhesive properties of the newly synthesized surfactant were measured.

GRAPHICAL ABSTRACT

New nonionic surfactants were synthesized by the reaction of sorbitol and decanoic acid followed by addition of ethylene oxide.



ARTICLE INFO

Article history:
Received 20 August 2013
Received in revised form 3 January 2014
Accepted 15 January 2014
Available online 24 January 2014

Keywords:
Nonylphenol ethoxylate
Sorbital based nonionic surfactant
Interfacial property
Adhesive property
Waterborne pressure sensitive adhesive

ABSTRACT

In this study, environmentally friendly nonionic surfactants were synthesized by the reaction of sorbitol and decanoic acid followed by addition of ethylene oxide. The structure of the product was elucidated by ^{1}H NMR, ^{13}C NMR and FT-IR and the interfacial properties such as critical micelle concentration (CMC), surface tension, interfacial tension, contact angle and foam stability were measured. These newly synthesized surfactants were used to prepare emulsion-type pressure sensitive adhesive (PSA) by emulsion polymerization and adhesive properties were measured in order to investigate the possibility of substituting a traditional nonylphenol ethoxylate surfactant NPE40. The PSA prepared by a newly synthesized surfactant SA10-40 showed better adhesive properties in peel strength and holding power than those of NPE40 and Tween40.

1. Introduction

Nonionic surfactants are known superior to ionic surfactants because nonionic surfactants are typically more hydrophobic than ionic surfactants, and tend to produce stable emulsions, less foam, and they are less toxic than most ionic surfactants. They are also less sensitive to precipitation in the presence of high electrolyte concentrations or in the presence of multivalent cations [1].

Nonylphenol ethoxylates (NPEs) have been by far the most important products within the alkylphenol ethoxylates (APEs), since they have been popular for their effectiveness, economy and easiness of handling and formulation for over 50 years. NPEs are also highly cost effective nonionic surfactants with exceptional performance and have been used in a wide range of applications such as industrial, institutional, commercial and household products such as detergents, emulsifiers, wetting and dispersing

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http://dx.doi.org/10.1016/j.colsurfa.2014.01.018

agents, antistatic agents, demulsifiers and solubilizers [2–5]. Due to the wide industrial applications of NPEs, they reach wastewater treatment facilities in substantial amounts where they are not completely degraded to nonylphenol. The derivatives formed during chemical or biological degradation of NPEs in wastewater treatment plants or in the environment have been known to be more toxic to aquatic biota than the parent substances and possess the ability to mimic natural hormones by interacting with the estrogen receptor [2,4,6,7].

NPEs have also been widely used as surfactants for adhesive preparation by acrylic emulsion polymerization and for post adding stabilization for latex applications in formulations with high filler content [8]. They aid in emulsifying monomers inside micelles, stabilize the polymer particles during nucleation and growth and promote the stability of the resulting latex [9]. Along with anionic surfactants, nonionic surfactants, including NPEs, are the most effective and widely used surfactants in emulsion polymerization, preventing coagulation by spatial or steric stabilization [10]. However, the search for environmentally friendly alternatives to NPEs has been one of the major topics because of environmental concern.

In this work, alkyl phenol-free nonionic surfactants were synthesized by the reaction of sorbitol and decanoic acid followed by addition of ethylene oxide. These newly synthesized sorbitan surfactants have been designed to meet environmental requirements while providing effective performance in emulsion polymerization. The structure of resulting products were elucidated by ^{1}H NMR, ^{13}C NMR and FT-IR and the interfacial properties such as critical micelle concentration (CMC), surface tension, interfacial tension, contact angle, and foam stability of newly synthesized surfactants were measured. Each emulsion-type pressure sensitive adhesive (PSA) was prepared by emulsion polymerization using newly synthesized surfactants, NPE40, and Tween40 respectively and their adhesive properties such as peel strength and holding power were compared with each other. Of particular interest was to test the potential applicability of newly synthesized surfactants to replace NPE40 and Tween40 in the emulsion polymerization process for preparation of waterborne PSA.

2. Materials and methods

2.1. Materials

Sorbitol ($C_6H_{14}O_6$), decanoic acid ($CH_3(CH_2)_8COOH$), sodium hydroxide (NaOH) and sodium phosphate monobasic anhydrous (NaH_2PO_4) were purchased from Sigma–Aldrich Co. and used without any further purification. *N*-decane ($C_{12}H_{22}$) with a purity of greater than 99% was purchased from Sigma–Aldrich Co. and used as a model nonpolar hydrocarbon oil for interfacial tension measurement. Monomers used during emulsion polymerization were 2-ethylhexyl acrylate (2-EHA, Aldrich), *n*-butyl acrylate (*n*-BA, Aldrich), and acrylic acid (AA, Aldrich). Ammonium persulfate (APS, Aldrich) and 1-dodecanethiol (Fluka) were used as an initiator and as a chain transfer agent (CTA), respectively. All the reagents were used as supplied without further purification. As an anionic surfactant, ammonium nonylphenol ether sulfate (CO-436, Rhodia Co.) was used. Two kinds of nonionic surfactants, polyoxyethylene nonylphenyl ether NPE40 ($C_9H_{19}C_6H_4(OCH_2CH_2)_{40}OH$, Dong Nam Co., Korea) and polyoxyethylenesorbitan monopalmitate Tween40 ($C_{62}H_{122}O_{26}$, Aldrich Co.), were also used to prepare emulsion-type pressure sensitive adhesive and to compare the adhesive properties. The structure of nonionic surfactants used during study is shown in Fig. 1. Water used for sample preparation was ultrapure having been double distilled and passed through a Nanopure (Sybron-Brinkman Inc.) ion exchange system.

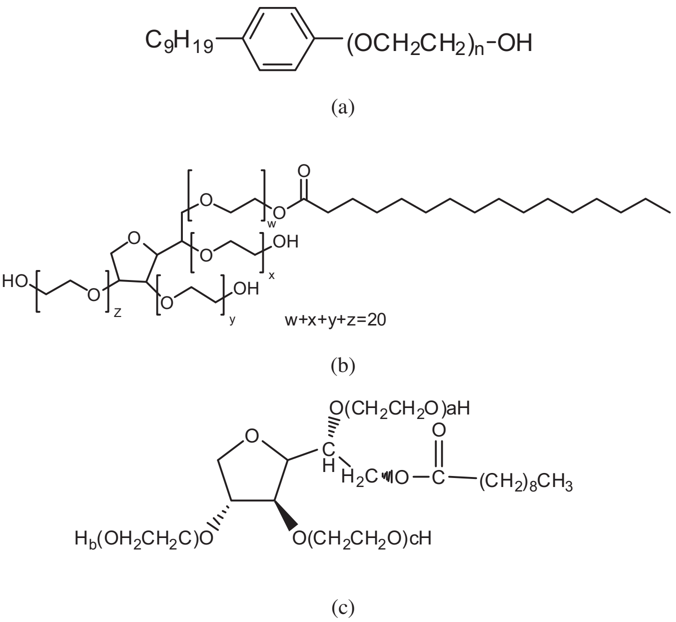

Fig. 1. Structures of nonionic surfactants used during study: (a) NPE40 where *n* is 40, (b) Tween40, (c) SA10-*n* series where $n = a + b + c$.

2.2. Methods

2.2.1. Synthesis

As shown in Scheme 1, the new nonionic surfactants were synthesized via 2 steps involving condensation and ethoxylation reactions. First, SA10 intermediate was obtained from sorbitol and decanoic acid, and then, final products such as SA10-7, SA10-15 and SA10-40 were prepared by the addition of the corresponding moles of ethylene oxide (EO). Addition of EO to the SA intermediate was carried out at Jung Woo Fine Chemical Company (Korea). During the addition of EO, a conventional alkali catalyst (KOH) was used as a catalyst.

Synthesis of SA10 intermediate [2-(3,4-dihydroxytetrahydrofuran-2-yl)-2-hydroxyethyl decanoate]

1 mole of sorbitol, 0.36 g of sodium phosphate monobasic anhydrous and 0.36 g of 50% sodium hydroxide solutions were added to the five-neck round bottom flask equipped with mechanical stirrer, heater, cooler and thermometer and stirred for 1 h at 70 °C where sodium phosphate monobasic anhydrous and sodium hydroxide were used as catalysts. Then 1.45 mole of decanoic acid was added to the flask and stirred for 5 h at 150 °C. The mixture was additionally stirred for 2 h after raising temperature to 180 °C. The yield of SA10 intermediate was 95.8%.

Synthesis of SA10-7 ($C_{30}H_{58}O_{13}$)

[2-((2-hydroxyethoxy)$_a$-2-(4-(2-hyroxyethoxy)$_b$)-3-(2-hydroxyethoxy)$_c$tetrahydrofuran-2-yl)ethyldecanoate] ($a + b + c = 7$)

SA10-7 was obtained by reacting 1 mole of SA10 intermediate and 7 moles of ethylene oxide. The reaction vessel was heated to 160 °C and ethylene oxide was added to SA10 intermediate in the reactor. The reaction mixture was stirred for 1 h. After the completion of the reaction, sulfuric acid was added to neutralize at 80 °C. The yield of SA10-7 was 94.2%.

Synthesis of SA10-15 ($C_{46}H_{90}O_{21}$)

[2-((2-hydroxyethoxy)$_a$-2-(4-(2-hyroxyethoxy)$_b$)-3-(2-hydroxyethoxy)$_c$tetrahydrofuran-2-yl)ethyldecanoate] ($a + b + c = 15$)