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Synthesis of anionic carboxylate dimeric surfactants and their interactions with electrolytes

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Abstract

The present work was a systematic study of the carboxylate anionic dimerics (CAD) *N*-methyldodecylamine and ethylene diaminetetraacetic acid dianhydride to investigate their synthesis, characterization, surface and salt behaviour. CAD were synthesized with two solvents at various temperatures. Fourier transform infrared spectroscopy was used to identify the functional groups of CAD, and ^{1}H and ^{13}C nuclear magnetic resonance were used to determine the type of proton and for carbon atom confirmation in the synthesized moiety, respectively. The effects of inorganic (NaCl, KCl) and organic salts (sodium salicylate and sodium benzoate) on surface activity were estimated by tensiometric methods. All the salts lowered the critical micelle concentration of the synthesized dimeric surfactant, the organic salts to a greater extent than the inorganic salts, in the sequence sodium salicylate > sodium benzoate > KCl > NaCl.

Keywords: Carboxylate anionic dimeric surfactant; Surface activity; Salt

1. Introduction

Dimeric surfactants have been the subject of much research. They usually comprise two amphiphilic moieties chemically linked to or near the head groups by a spacer [1,2]. The spacers are instrumental for the performance of dimeric surfactants, as they lower surface tension and form micelles at a very low critical micelle concentration(CMC). The surfactants also possess unusual wetting, aggregation and rheological properties [3]. Dimeric surfactants are therefore widely used in many fields, including the production of detergents and cleaning agents, pharmaceuticals, cosmetics and toiletries, gene transfection, genetics, corrosion inhibition, environmental protection and emulsion polymerization [4–7]. Carboxylate anionic dimerics (CADs) are modern members of the dimeric surfactants category. Anionic dimeric surfactants have been widely studied [8–10], but there have been few studies of anionic dimeric surfactants with carboxylate head groups [11,12].

In the present study, CADs were prepared as described previously [11], with small modifications. CADs based on ethylene diaminetetraacetic acid (EDTA) dianhydride and the secondary fatty amine *N*-methyldodecylamine were prepared with two solvents, methanol and ethanol, to obtain a higher yield of end-product. We also optimized the temperature of the reac-

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tion. The effects of solvent and temperature on the yield of CADs were studied at a constant molar ratio of reactants (2:1) for a constant reaction duration of 20 h. The reactants were *N*-methyldodecylamine and EDTA dianhydride, respectively. The surface properties of CADs in water and in the presence of inorganic and organic salts were determined. The parameters studied include CMC, surface tension (γ_{cmc}), efficiency in reducing surface tension (C_{20}), maximum surface excess (Γ_{cmc}) and the occupied area per molecule (A_{cmc}) at the CMC.

2. Experimental

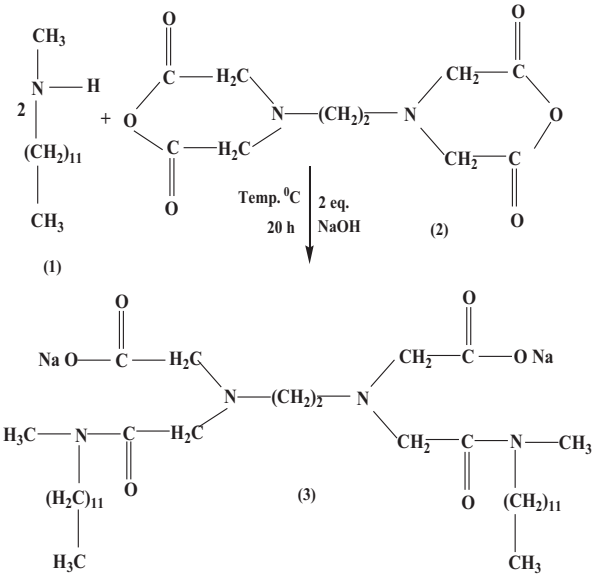
2.1. Materials and methods

EDTA dianhydride and *N*-methyldodecylamine were obtained from Sigma–Aldrich. Sodium dodecylsulfate (SDS) was purchased from Merck. NaOH, NaCl, KCl, sodium salicylate (NaSal) and sodium benzoate (NaBenz) were supplied by S.D. Fine Chemicals, Mumbai, and used as received. All the solvents were of analytical grade. Deionized water was treated with $KMnO_4$ and redistilled. All chemicals were used without further purification.

The functional group of synthesized compounds was determined by Fourier transform infrared (FT-IR) spectroscopy (Perkin Elmer, United Kingdom) before neutralization of the compound, and the spectra confirmed formation of the amide group. The chemical structure of compounds was determined by ^{1}H and ^{13}C nuclear magnetic resonance (NMR) (Bruker Avance-III 300 MHz).

Surface tension was measured with a du Noüytensiometer (Jencon, India) by the platinum ring detachment technique [13]. The tensiometer was calibrated against double-distilled water, and the platinum ring was completely cleaned and dried before each observation. The observations were carried out in such a way that the vertically hung ring was plunged into the solution to measure its surface tension and was then hauled out; the maximum force required to drag the ring through the interface was then expressed as the surface tension. The CMC and the surface tension at the CMC (γ_{cmc}) were determined by plotting the breakpoint of the surface tension against the logarithm of the concentration curve. The results were accurate within ±0.1 dyn/cm. All measurements were carried out at 25 °C.

The performance of synthesized dimerics in hard water were studied by the foaming method [14,15], in which foaming properties were evaluated by the height of foam after shaking the solution of dimeric in hard water (hardness, 160 mg/L). To assess the performance of the



Scheme 1. Synthesis pathway of CAD, 3 by N-methyldodecylamine 1 and EDTA dianhydride 2.

synthesized dimerics in hard water, the foaming power was measured for three solutions: one in 1% sodium stearate (soap) solution in hard water (A), one a 1% soap solution in double-distilled water and the third a 1% soap solution in hard water with 2.8×10^{-6} mol/L of CAD.

2.2. Synthesis and characterization of carboxylate anionic dimerics

CADs were prepared with EDTA dianhydride (10 mmol, 2.56 g) and *N*-methyldodecylamine (20 mmol, 3.98 g) in methanol and ethanol, with refluxing and constant stirred for 20 h at temperatures of 40 °C, 50 °C and 60 °C (Scheme 1). After the solvent had evaporated, the residue was purified with chloroform, and a white powder was obtained. Data on the synthesized compounds are reported in Table 1.

The FT-IR spectra of CADs prepared in methanol at 50 °C (MCAD2) (Nujol mulls, selected bands in

Table 1
Effect of solvent and varying temperatures on yield of synthesized dimerics (CADs).[a]

Surfactants (CAD)	Temperature (°C)	Solvent	Yield (%)
ECAD1	40	EtOH	64.0
MCAD1	40	MeOH	67.6
ECAD2	50	EtOH	66.1
MCAD2	50	MeOH	80.0
ECAD3	60	EtOH	61.7
MCAD3	60	MeOH	76.6

[a] Reaction conditions: reactants – *N*-methyldodecylamine and EDTA dianhydride, molar ratio – 2:1, duration of reaction – 20 h.