Colloids and Surfaces A 532 (2017) 144–149

Contents lists available at ScienceDirect

Colloids and Surfaces A

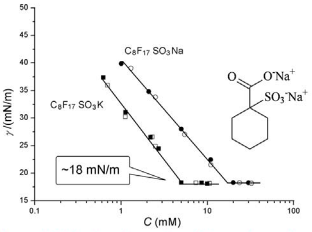
journal homepage: www.elsevier.com/locate/colsurfa

Properties of disodium salt of 1-sulfo-cyclohexanecarboxylic acid as a novel hydrotropic agent and its effects on room-temperature surface activity of perfluorooctanesulfonates with high Krafft points

Zi-Bing Xiao[a], Hang Xing[b], Jin-Xin Xiao[b,*]

[a] *College of Chemistry, Nankai University, Tianjin 300071, China*
[b] *Beijing FLUOBON Surfactant Institute, Beijing 100096, China*

GRAPHICAL ABSTRACT



The novel hydrotropic agent can enhance the room-temperature surface activity of perfluorooctane sulfonates with high Krafft points

ARTICLE INFO

Keywords:
Hydrotrope
POPs
Fluorocarbon surfactant
Environment protection
Waste utilization
Perfluorooctylsulfonate

ABSTRACT

The disodium salt of 1-sulfo-cyclohexanecarboxylic acid (SCCA) was characterized by ^1H and ^{13}C NMR. The effects of SCCA on the surface activity of two high-Krafft-point fluorinated surfactants (potassium and sodium salts of perfluorooctanesulfonic acid, KPFOS and NaPFOS) and a conventional hydrogenated surfactant (sodium dodecylbenzene sulfonate, SDBS) were studied at room temperature. When SCCA was added, the effectiveness of KPFOS and NaPFOS in surface tension reduction was both greatly enhanced and KPFOS showed higher efficiency in surface tension reduction than NaPFOS. In particular, with the assistance of SCCA the minimum surface tension of fluorinated surfactants could even be as low as ~18 mN/m at 25 °C. In contrast, the surface activity of SDBS was significantly reduced by SCCA, with the critical micelle concentation (cmc) largely increased. As a conclusion, the SCCA could act as an effective hydrotropic agent and it was able to recover the inherent character of KPFOS and NaPFOS as highly surface-active fluorinated surfactants by increasing their solubility. While for SDBS which was already soluble at room temperature, SCCA lowered the surface activity of SDBS. In addition, a preliminary study of application showed that SCCA was a qualified hydrotropic agent in formulations for industrial detergent and enhanced oil recovery.

1. Introduction

Caprolactam is an important industrial product whose annual global production has been millions of tons and remains increasing each year. The disodium salt of 1-sulfo-cyclohexanecarboxylic acid (SCCA, Scheme 1) is the major by-product during the industrial production of caprolactam from toluene [1]. It has been estimated that 60–80 kg SCCA could be generated for every ton of caprolactam produced [2]. However, such huge amount of SCCA has been abandoned each year as industrial waste because of unclear application. The disposal of SCCA,

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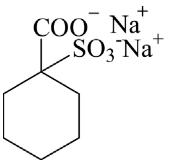
* Corresponding author.
E-mail addresses: xiaojinxin@pku.edu.cn, admin@fluobon.com (J.-X. Xiao).

http://dx.doi.org/10.1016/j.colsurfa.2017.05.072
Received 27 February 2017; Received in revised form 12 May 2017; Accepted 20 May 2017



Scheme 1. Molecular structure of SCCA.

either incineration or directly emission, could lead to great environmental pollution. Although 1-sulfo-cyclohexanecarboxylic acid could be starting material for synthesis of medical intermediates after taking off sulfonic acid group or changing it into amino group, its extraction and purification would be a great challenge [3].

Herein, according to the amphiphilic nature of SCCA (Scheme 1), our focus was whether SCCA could be applied as a hydrotropic agent.

Hydrotropic agents (or hydrotropes) are defined by their purpose to enhance the aqueous solubility of poorly soluble organic compounds. Unlike surfactants, hydrotropes lack a long hydrophobic tail and they are used at fairly high concentration [4]. Empirically, urea, short-chain aromatic sulfonates, salts of aromatic acids, etc., can all be called hydrotropic agents [5–8]. It is well known that hydrotropic agents play important roles in many application fields, e.g., to obtain concentrated detergent solutions, to solubilize insoluble or poorly soluble drugs, to accelerate two-phase chemical reactions, and to improve the rheological properties of drilling fluids in oil production [4]. If SCCA could be utilized as a qualified hydrotropic agent, industrial waste would be greatly reduced for the benefit of environment protection during the production of caprolactam.

In this work, the hydrotropy effects of SCCA had been studied from two aspects. Firstly, the effects of SCCA on the room-temperature surface activity of potassium perfluorooctane sulfonate (KPFOS) and sodium perfluorooctane sulfonate (NaPFOS) were studied. Secondly, preliminary application of SCCA in the formulations for industrial detergent and enhanced oil recovery was also studied.

KPFOS and NaPFOS exhibit poor surface activity at room temperature because of their high Krafft points [9]. They are typical perfluorooctanesulfonates (PFOS) of increasing environmental concerns due to their bio-accumulation and difficulty in biodegradation. It is generally known that the biodegradation of a certain chemical can be closely related to its solubility in water, i.e. the less soluble, the more difficult to biodegrade [10]. The difficulty in biodegradation of PFOS is probably a result of the relatively few naturally occurring defluorinating enzymes, but it could not be denied that their poor solubility ascribed to the highly hydrophobic fluorocarbon chain has made the situation even worse, which prevents effective contact with corresponding microorganism in water environment. It has also been reported that water can act as oxygen source for degradation products in the degradation process of fluorocarbon chains [11]. Therefore, if SCCA can do help to the solubility of PFOS, it not only made high-Krafft-point fluorinated surfactants surface active at room temperature but might also help in biodegradation of PFOS.

Our present work showed that SCCA could enhance the room-temperature surface activity of KPFOS and NaPFOS, and it was a good hydrotropic agent in formulations of detergent and flooding agent. These results are promising. Currently, one obstacle in environmental and toxicological studies of PFOS is the lack of knowledge on its physicochemical behavior with other ingredients in formulated products. The understanding of the interactions between PFOS and hydrotropes can be helpful in future studies on the degradation of PFOS, where detectable acceleration of biodegradation rate could be expected. In addition, as a novel hydrotropic agent, the utilization of SCCA separated from industrial waste can also make the waste to be useful and reduce environmental pollution.

Table 1
The product prameters of petroleum sulfonate (CN 101402592A).

Appearance	brown viscous liquid
pH (1% solution)	7.8
Aqueous solubility	9 min
Flash point	60 °C
Inorganic salt	5.2%
Unsulphonic oil	23.5%
Active ingredients	42.4%
Resistance to calcium and magnesium	135 mg/L; no obvious precipitates with interfacial tension 1×10^{-2} mN/m

2. Experimental

Disodium salt of 1-sulfo-cyclohexanecarboxylic acid (SCCA, 99%) was a gift from Hebei JIUXU Industrial Group Co., Ltd. and used as received. Potassium perfluorooctane sulfonate (KPFOS, 98%) and sodium perfluorooctane sulfonate (NaPFOS, 98%) were our products which were synthesized and purified as described in our previous work [12]. Sodium dodecylbenzene sulfonate (SDBS, AR), Na_2CO_3 (AR), dipropylene glycol methyl ether (99%) and sodium metasilicate pentahydrate were purchased from Sinopharm Chemical Reagent Co., Ltd. The petroleum sulfonate (CN 101402592A) was a product from Beijing Tianyigerun Technology Development of New Energy Co., Ltd. and the prameters of petroleum sulfonate are shown in Table 1. Crude oil was from Shengli oilfield, China.

^{1}H and ^{13}C NMR experiments were performed on a Varian Mercury Plus 300 spectrometer both with D_2O as solvent for characterizing SCCA. The chemical shifts of ^{1}H NMR were referenced to the residue peak of D_2O (δ_{HDO} 4.700 ppm). The chemical shifts of ^{13}C NMR were referenced to the external $CDCl_3$ (77 ppm), with field frequency locked.

The surface tension was measured by drop volume method on a laboratory made instrument [13] at (25.0 ± 0.1) °C. A detailed procedure as described elsewhere was followed [12] to measure the surface tension of KPFOS and NaPFOS in the presence of a hydrotrope at (25.0 ± 0.1) °C. All solutions were prepared using deionized water.

The interfacial tension between crude oil and water at (40.0 ± 0.1) °C was measured using a spinning drop tensiometer (TX-500C, Bowing Industry Co.). The equilibrium time was 2 h.

The detergency power of detergent formulations with and without SCCA were tested. Glass sheets were cleaned and dried. The clean glass sheets were then soaked in edible oil and then scrubed by tissue paper to remove the extra oil. Microsyringe was used to put a drop of 5 μL sample solution on the glass sheet. Wait until the spreading area no longer expanded. A coordinate paper (with the area of each small square equal to 1mm × 1 mm) was put under the glass sheet to obtain the length and width equal to the diameters of the spreading liquid along the directions of horizontal axis and vertical axis. The power of detergency for sample solution was compared according to its spreading area on oil-stained glass sheets.

3. Results and discussion

3.1. Characterization of SCCA by NMR

Fig. 1 shows the ^{1}H and ^{13}C NMR spectra of SCCA in the solvent of D_2O. The white powder of SCCA sample was soluble well in D_2O and almost insoluble in $CDCl_3$, indicating the feature of a salt. The style of multiple splitting for ^{1}H NMR signals probably origined from the conformation of cyclic compound. The NMR results showed that SCCA had anticipated structure and the purity was good.

3.2. The usage of SCCA as a surfactant additive

Sodium dodecylbenzene sulfonate (SDBS) is a common surfactant