



Solubilization of naphthalene and octafluoronaphthalene in ionic hydrocarbon and fluorocarbon surfactants



Keisuke Matsuoka^{a,*}, Rika Yamashita^b, Miki Ichinose^b, Maiko Kondo^b, Tomokazu Yoshimura^c

^a Faculty of Education, Laboratory of Chemistry, Saitama University, 255 Shimo-Okubo, Sakura-ku, Saitama City, Saitama 338-8570, Japan

^b Department of Physical Chemistry, Showa Pharmaceutical University, Higashi-Tamagawagakuen 3-3165, Machida City, Tokyo 194-8543, Japan

^c Research Group of Chemistry, Division of Natural Science, Nara Women's University, Kitauoyanishi-machi, Nara 630-8506, Japan

HIGHLIGHTS

- Naphthalene and octafluoronaphthalene have similar molecular structures.
- The maximum solubilities were determined in hydrocarbon/fluorocarbon surfactant.
- The gemini surfactants showed good solubilization in homogeneous systems.
- The solubilization stability can be analyzed by estimating Gibbs free energy change.
- The largest negative ΔG° is estimated to be $-34.8 \text{ kJ mol}^{-1}$ for fluorinated system.

GRAPHICAL ABSTRACT



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ABSTRACT

The solubilization abilities of various kinds of surfactants are clarified through a systematic solubilization study. Naphthalene and octafluoronaphthalene have similar molecular structures and can be used as solubilizes in hydrocarbon and fluorocarbon surfactant systems. The solubilization quantities are measured for typical anionic, cationic, and cationic gemini surfactants with different alkyl chain lengths (nine hydrocarbon and six fluorocarbon surfactants). The maximum solubilization quantities of naphthalene and octafluoronaphthalene in aqueous solutions of hydrocarbon or fluorocarbon surfactant are measured as a function of surfactant concentration at 318.2 K. There are four solubilization systems regarding hydrocarbons and fluorocarbons. Judging from the molar solubilization ratio (MSR), naphthalene is solubilized most in typical gemini surfactant solution (12–2–12), whereas hardly any naphthalene is solubilized in fluorocarbon surfactants. On the other hand, the maximum MSR of octafluoronaphthalene is found for the gemini type of fluorocarbon surfactant, whereas the minimum value is recorded in the $\text{C}_9\text{H}_{19}\text{COONa}$ system. Therefore, gemini surfactants reveal excellent solubilization abilities in homogeneous combination systems. The solubilization stability can be analyzed by estimating the Gibbs free energy change (ΔG°) for the transfer of solubilize molecules to the aggregate phase. The largest negative value of ΔG° is estimated to be $-34.8 \text{ kJ mol}^{-1}$ for the homogeneous system of octafluoronaphthalene and the

* Corresponding author. Tel.: +81 48 858 3220; fax: +81 48 858 3220.
E-mail address: matsuokakei@mail.saitama-u.ac.jp (K. Matsuoka).

gemini-type fluorocarbon surfactant, whereas smaller values are obtained for the heterogeneous systems of naphthalene and fluorocarbon surfactants. These results indicate that fluorocarbon surfactants are not generally suitable for the solubilization of naphthalene.

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1. Introduction

The key to increasing the solubility of water-insoluble materials is the appropriate selection of surfactants in the aqueous system. The solubilization phenomenon is important because there are hardly any organic solvents used as solubilizers in aqueous systems. Harmful organic solvents released through diffusion to the environment can cause pollution and may lead to human health problems [1,2]. In terms of practical applications, surfactants have been used to solubilize insoluble materials in toiletry products, drugs, and emulsifiers, in place of organic solvents. However, in contrast with the vast number of micellization reports available, there have been few studies on the solubilization abilities of water-insoluble materials associated with different kinds of surfactants [3]. In particular, it is not clear for solubilization study concerned with fluorocarbon surfactant. The few studies reported are focused on the solubilization of various fluorocarbons in fluorocarbon surfactants [4], the solubilization of octafluoronaphthalene in mixed micelles of hydrocarbon/fluorocarbon surfactants [5], the solubilization of perfluoroalkyl benzene in hydrogenated or fluorinated micelles [6], and the solubilization of 2-naphthol in fluorocarbon hybrid surfactants [7]. One of the reasons for the lack of data on the fluorocarbon surfactant solubilization system may be the immiscibility of hydrocarbons and fluorocarbons [8]. In general, useful water-insoluble organic materials are made from hydrocarbon compounds, so their materials are solubilized by suitable hydrocarbon surfactants. However, fluorinated colloidal systems are attractive for extinguishing hydrocarbon fuel fires [9], as drug delivery carriers [10], as blood substitutes [11], and as agents for ultrasound imaging. The functions are based on their oleophobic properties, oxygen affinity, and low toxicity [3]. Therefore, the fluorocarbon surfactant potential for solubilization from the viewpoint of maximum solubilization quantity with common solubilizates must be clarified. The fluorocarbon/hydrocarbon affinity for solubilization can be estimated by using the typical molecular shape of the solubilizates. Naphthalene and octafluoronaphthalene have similar molecular structures, differing only in the H or F atom, and show ultraviolet absorption. On the other hand, we prepared 15 types of surfactant with different alkyl chain lengths to determine their maximum solubilization quantities in the respective systems. The surfactants are classified as sodium alkyl carboxylate, alkyltrimethylammonium salts, and gemini surfactants. Recently, the gemini type has attracted attention as a new solubilizer or emulsifier in basic science. A few reports have shown that the novel dimeric hydrocarbon surfactants have relatively high solubilization abilities [12–15].

In the present study, we determine the maximum solubilities of naphthalene/octafluoronaphthalene in hydrocarbon/fluorocarbon surfactant solutions. There are four solubilization systems regarding hydrocarbons and fluorocarbons. A series of experiments is performed to determine the Gibbs free energies of solubilization in the hydrocarbon/fluorocarbon surfactants. Finally, the affinity between hydrocarbons and fluorocarbons on solubilization are estimated from the Gibbs free energy. The results obtained from this systematic solubilization study will be helpful for further studies on fluorocarbon surfactants.

2. Materials and methods

2.1. Materials

The carboxylic surfactants sodium decanoate (>99%), undecanoic acid (>98%), sodium laurate (>97%), pentadecafluorooctanoic acid (>98%), and heptadecafluorononanoic acid (>95%) were obtained from Tokyo Chemical Industry Co., Ltd. The carboxylic acids were prepared through stoichiometric neutralization by adding a sodium hydroxide solution and diluting to the required concentration.

The trimethylammonium surfactants dodecyltrimethylammonium chloride (>98%), tetradecyltrimethylammonium chloride (>98%), and hexadecyltrimethylammonium chloride (>95%) were purchased from Tokyo Chemical Industry Co., Ltd, and purified thrice by recrystallization from acetone/ethanol mixtures. The preparation procedures for *N*-(1,1-dihydroperfluorodecyl)-*N,N,N*-trimethylammonium chloride ($C_9F_{19}CH_2N(CH_3)_3Cl$) and *N*-(1,1-dihydroperfluorododecyl)-*N,N,N*-trimethylammonium chloride ($C_{11}F_{23}CH_2N(CH_3)_3Cl$) were reported in a previous study [16,17]. The purities were checked by elemental analysis and NMR measurements [18].

The cationic gemini surfactants, 1,2-bis(alkyldimethylammonio)ethane dibromide (*n*-2-*n*; *n* is hydrocarbon chain length, *n* = 10, 12, and 14) and novel partially fluorinated gemini surfactant 1,2-bis[dimethyl-(3-perfluoroalkyl-2-hydroxypropyl)ammonio]ethane bromide ($C_n^F C_3-2-C_3 C_n^F$, where *n* = 6 and 8) were prepared [19,20]. The chemical structures of the cationic gemini surfactants are shown in Fig. 1. The purities of these amphiphiles were tested by elemental analysis and 1H and ^{19}F NMR measurements, and no impurities were detected [19,20].

Naphthalene (Wako Pure Chemical Industries, Ltd., 99%) and octafluoronaphthalene (Sigma-Aldrich, 96%) were used after recrystallization from ethanol.

The water used in the experiments was distilled once after ion-exchange treatment.

2.2. Solubilization

The concentrations of surfactants were varied from below the critical micelle concentration (cmc) to 15–30 times the cmc in response to the properties of each solution. Three milliliters of each surfactant solution and excess solubilizate (crystal) was

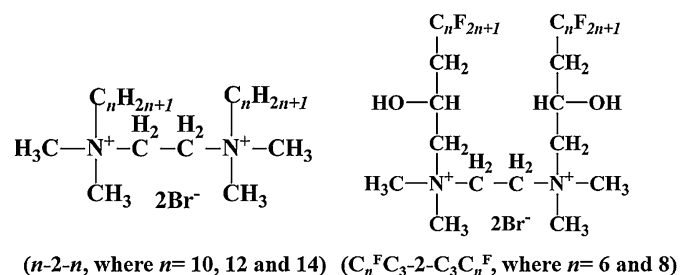


Fig. 1. Chemical structures of cationic gemini surfactants, 1,2-bis(alkyldimethylammonio)ethane dibromide (*n*-2-*n*; *n* is hydrocarbon chain length, *n* = 10, 12, and 14) and 1,2-bis[dimethyl-(3-perfluoroalkyl-2-hydroxypropyl)ammonio]ethane bromides ($C_n^F C_3-2-C_3 C_n^F$; *n* = 6 and 8).

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