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Temperature-dependent IR spectroscopic and structural study of 18-crown-6 chelating ligand in the complexation with sodium surfactant salts and potassium picrate

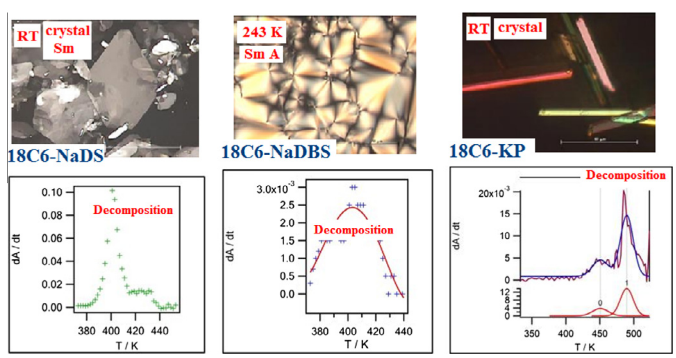
Tea Mihelj [a,*], Vlasta Tomašić [a], Nikola Biliškov [b], Feng Liu [c]

[a] Department of Physical Chemistry, Ruđer Bošković Institute, POB 180, HR-10002 Zagreb, Croatia
[b] Division of Organic Chemistry and Biochemistry, Ruđer Bošković Institute, POB 180, HR-10002 Zagreb, Croatia
[c] State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, China

HIGHLIGHTS

- Synthesis of novel 18C6 ether coordination complexes with different guests.
- Baseline analysis and temperature-dependent IR spectra obtained phase transitions.
- Temperature-dependent IR spectroscopy gave thermodynamic decomplexation parameters.
- 18C6-sodium 4-(1-pentylheptyl)benzenesulfonate is a compound with low melting point.
- 18C6-potassium picrate has a high thermal stability with the two-step distortion.

GRAPHICAL ABSTRACT



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ABSTRACT

18-crown-6 ether (18C6) complexes with the following anionic surfactants: sodium *n*-dodecylsulfate (18C6-NaDS), sodium 4-(1-pentylheptyl)benzenesulfonate (18C6-NaDBS); and potassium picrate (18C6-KP) were synthesized and studied in terms of their thermal and structural properties. Physicochemical properties of new solid 1:1 coordination complexes were characterized by infrared (IR) spectroscopy, thermogravimetry and differential thermal analysis, differential scanning calorimetry, X-ray diffraction and microscopic observations. The strength of coordination between Na^+ and oxygen atoms of 18C6 ligand does not depend on anionic part of the surfactant, as established by thermodynamical parameters obtained by temperature-dependent IR spectroscopy. Each of these complexes exhibit different kinds of endothermic transitions in heating scan. Diffraction maxima obtained by SAXS and WAXS, refer the behavior of the compounds 18C6-NaDS and 18C6-NaDBS as smectic liquid crystalline. Distortion of 18C6-NaDS and 18C6-KP complexes occurs in two steps. Temperature of the decomplexation of solid crystal complex 18C6-KP is considerably higher than of mesophase complexes, 18C6-NaDS, and 18C6-NaDBS. The structural and liquid crystalline properties of novel 18-crown-ether complexes are function of anionic molecule geometry, type of chosen cation (Na^+, K^+), as well as architecture of self-organized aggregates. A good combination of crown ether unit and amphiphile may provide a possibility for preparing new functionalized materials, opening the research field of ion complexation and of host–guest type behavior.

* Corresponding author. Address: Ruđer Bošković Institute, Department of Physical Chemistry, Laboratory for synthesis and processes of self-assembling of organic molecules, Bijenička c. 54, P.O. Box 180, HR-10002 Zagreb, Croatia. Tel.: +385 14571211; fax: +385 14680245.
E-mail address: tmihelj@irb.hr (T. Mihelj).

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Introduction

Several molecular families have been widely examined for the development of supramolecular chemistry. The group of macrocyclic polyethers, known as crown ethers, have become valuable tools in organic synthesis due to their ability to solvate alkali, alkaline-earth, transition-metal, and ammonium cations [1–4]. Their selective cation binding makes them applicable for different environmental usage [5,6], drug delivery [7,8], recovery or removal of specific species, models for biological receptors [9], reaction catalysts as well as active sites in ion selective electrodes [10] or chromatographic agents [11]. Alkali metal elements have indispensable role in many biological processes, primarily to be as bulk electrolytes that stabilize surface charges on proteins and nucleic acids [12], and also play unique structural roles in biological systems [13,14]. Their complexes with crown ligands are coordination compounds based on electrostatic interaction through ion–dipole attractions [15], with the usage for simulations of natural substances, their properties and behavior. Some new surfactants derived from crown ethers are used as templates with a particular morphology in the preparation of siliceous mesoporous molecular sieves [16].

One of the most relevant crown ethers, 18-crown-6 (18C6) features a flexible six-oxygen cyclic backbone and uncomplexed does not exhibit any liquid crystalline behavior. However, these phenomena are caused by one or more mesogenic groups attached to the molecules containing crown ether, aza, thia crown ethers, or crown ethers with several different heteroatoms [17–22]. Synthesis and properties of cholesteryl moiety bearing 16-membered crown ethers show cholesteric [23] and nematic [24] liquid crystalline behavior. Thermochemical properties of 18C6 ether complexes with aralkylammonium perchlorates show higher melting points than of both the host and the guest compound, the decomposition begins immediately after melting is completed, and each of the examined complexes is characterized by its individual properties [25]. The study of stable complexes formed between crown ether compounds and surfactants is less explored area, especially in terms of thermochemical and structural studies. So far, most studies on metal ion–crown ether complexes were focused on the determination of relative affinities and stoichiometries of the complexes in solution, rather than on their solid structures. Thus, in the present study we report the formation of defined complexes between 18C6 and different guest constituent. Two amphiphiles are chosen; one conventional known as sodium *n*-dodecylsulfate and one commercial known as sodium 4-(1-pentylheptyl)benzenesulfonate. The third chosen guest is potassium picrate that possesses hydrophilic-hydrophobic balanced properties, but is not a real amphiphile. The purpose of the present study is to provide an insight into thermal and structural behavior of 18C6 chelating ligand in the complexation with sodium surfactant salts and potassium picrate. Temperature-dependent IR spectroscopy was used in order to detect and characterize phase transitions at molecular level, as well as to determine thermodynamic parameters of the decomplexation process. The present study provides the relationship between molecular structure and physico-chemical properties by combining the properties of complex formation and supramolecular arrangements provided by liquid crystals. This ensures a guideline for further design and fine-tuning of the properties of new materials with a specific structure, allowed by an appropriate choice of cation and crown ether size, and by varying the nature of anionic constituent.

Experimental

Materials and sample preparation

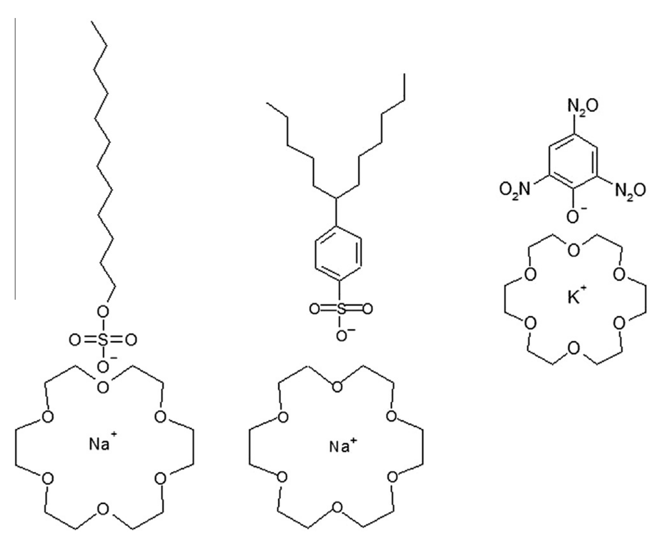
18-Crown-6 ether, *i.e.* 1,4,7,10,13,16-hexaoxacyclooctadecane ($C_{12}H_{24}O_6$, M_w/g mol^{-1} = 264.32; Sigma–Aldrich) was used without further purification. Sodium *n*-dodecylsulfate ($C_{12}H_{25}SO_4Na$, M_w/g mol^{-1} = 288.38) was obtained from Merck and recrystallized several times from ethanol. Sodium 4-(1-pentylheptyl)benzenesulfonate ($C_{12}H_{25}C_6H_4SO_3Na$, M_w/g mol^{-1} = 348.48) was analyzed and determined previously [26]. Potassium picrate, *i.e.* potassium 2,4,6-trinitrofenolate ($C_6H_2N_3O_7K$, M_w/g mol^{-1} = 267.20) was prepared and purified according the procedure described earlier [27,28].

18C6 ether complexes with different anionic constituent were prepared by high temperature mixing of equimolar aqueous solutions of both, 18C6 ether and sodium surfactant salt/potassium picrate. The complex formation equilibrium is defined as $M^+. X^- + L \leftrightarrow ML^+. X^-$, where M^+, X^- and L refer to metal ion (Na^+ or K^+), counter anion (*n*-dodecylsulfate, 4-(1-pentylheptyl)benzenesulfonate or picrate), and crown ether as neutral, endopolarophilic ligand. Samples were left aging for few days at room temperature, during which water spontaneously evaporated. 18-crown-6 ether complex with potassium picrate, formed yellow crystals that were filtered and vacuum dried till constant mass was obtained, while other two samples were waxy and after vacuum dried, glassy, colorless and transparent. The samples were stored protected from moisture and light before use.

Measurements

The complexes are shown in Scheme 1. *Elemental analysis* (Perkin–Elmer Analyzer PE 2400 Series 2) confirmed that the complexes were 1:1 charge ratio adducts. 18C6-sodium *n*-dodecylsulfate (compound **1**, $C_{24}H_{49}SO_{10}Na$, M_w/g mol^{-1} = 552.70) found: C, 52.18; H, 9.00% (calc. C, 52.16; H, 8.94%). 18C6- sodium 4-(1-pentylheptyl)benzenesulfonate (compound **2**, $C_{30}H_{53}SO_9Na$, M_w/g mol^{-1} = 612.80) found: C, 58.78%; H, 8.70 (calc. C, 58.80; H, 8.72%). 18C6-potassium picrate (compound **3,** $C_{18}H_{26}N_3O_{13}K$, M_w/g mol^{-1} = 531.52) found: C, 40.60; H, 4.90; N, 7.82% (calc. C, 40.68; H, 4.93; N, 7.91%).

TG and differential thermal analysis, DTA, were obtained on a Shimatzu DTG-60H. Samples were heated from room temperature to 573 K at the heating rate of 5 K min^{-1} in synthetic airflow of 50 mL min^{-1}. *Differential scanning calorimetry*, DSC, was carried out with a Perkin Elmer Pyris Diamond DSC calorimeter in N_2 atmosphere equipped with a model Perkin Elmer 2P intra-cooler



1 2 3

Scheme 1. The scheme of the examined complexes: 18C6-sodium *n*-dodecylsulfate (compound **1**), 18C6-sodium 4-(1-pentylheptyl)benzenesulfonate (**2**), and 18C6-potassium picrate (**3**) complex.