Journal of Molecular Structure 1147 (2017) 776–785

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

Probing supramolecular complexation of cetylpyridinium chloride with crown ethers

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ARTICLE INFO

Article history:
Received 24 May 2017
Received in revised form
9 July 2017
Accepted 11 July 2017
Available online 12 July 2017

Keywords:
Cetylpyridinium chloride
Dibenzo-18-crown-6
18-Crown-6
Dicyclohexano-18-crown-6

ABSTRACT

Supramolecular complexations of cetylpyridinium chloride with three comparable cavity dimension based crown ethers, namely, dibenzo-18-crown-6, 18-crown-6 and dicyclohexano-18-crown-6 have been explored and adequately compared in acetonitrile with the help of conductivity in a series of temperatures to reveal the stoichiometry of the three host-guest complexes. Programme based mathematical treatment of the conductivity data affords association constants for complexations from which the thermodynamic parameters were derived for better comprehension about the process. The interactions at molecular level have been explained and decisively discussed by means of FT-IR and ^{1}H NMR spectroscopic studies that demonstrate H-bond type interactions as the primarily force of attraction for the investigated supramolecular complexations.

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1. Introduction

Crown ethers (CEs) are used as important hosts in supramolecular chemistry, where the host–guest interaction mimics natural systems as well as constructs various materials [1–6]. CEs are macromolecular heterocyclic compounds with essential repeating unit –CH_2CH_2O- [7]. A number of researchers are working on fabrication of crown-ether-based stimuli-responsive materials that have unique characters of ion recognize ability [8–10]. A variety of current supramolecular materials, for instance rotaxanes are made on these unique recognition properties of CEs [11,12]. Binding of CEs with cations with high selectivity and affinity has found remarkable importance in chemistry [13,14]. Formation of molecular assemblies has vast implication for the building of molecular machines having plausible use as analogous to sophisticated machines of natural systems [15,16]. Hence, fundamental investigations of the interactions between CEs and cationic species are important for their advanced applications [17,18]. In the present work cetylpyridinium chloride (CPCl) (Scheme 1) has been investigated as the cationic species, which is structurally significant because of having long lipophilic chain and pyridinium cationic head and also has medicinal applications, while three CEs, namely, dibenzo-18-crown-6 (DB-18-C-6), 18-crown-6 (18-C-6) and dicyclohexano-18-crown-6 (DCH-18-C-6) (Scheme 2) have been selected with similar cavity dimension, but having different and tailored abilities to construct supramolecular complexes [19–23]. The complexation processes have been explored in CH_3CN solution with definite host-guest type interactions in molecular level [24,25]. Pyridinium based ionic liquids (ILs) are biologically extremely significant and also have role in material chemistry for their extraordinary properties [26–28]. Here, the structure of CPCl is very important to make supramolecular materials and also has biological and medicinal functions [29,30]. In this study the three complexation processes require special attention to explore the various interactions taking place in molecular level [31,32]. Conductivity measurement and programmed mathematical treatment of the data offer quantitative idea about association constant and thermodynamic parameters, whereas FT-IR and ^{1}H NMR spectroscopic studies deliver specific information about the complexation processes for the potential applications in supramolecular host-guest chemistry.

2. Experimental section

2.1. Source and purity of samples

Cetylpyridinium chloride, dibenzo-18-crown-6, 18-crown-6 and dicyclohexano-18-crown-6 of puriss grade have been bought from Sigma-Aldrich, Germany and used as received. Purity of cetylpyridinium chloride, dibenzo-18-crown-6, 18-crown-6 and dicyclohexano-18-crown-6 were ≥98.0%, ≥98.0%, ≥99.0% and ≥98.0%

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http://dx.doi.org/10.1016/j.molstruc.2017.07.017
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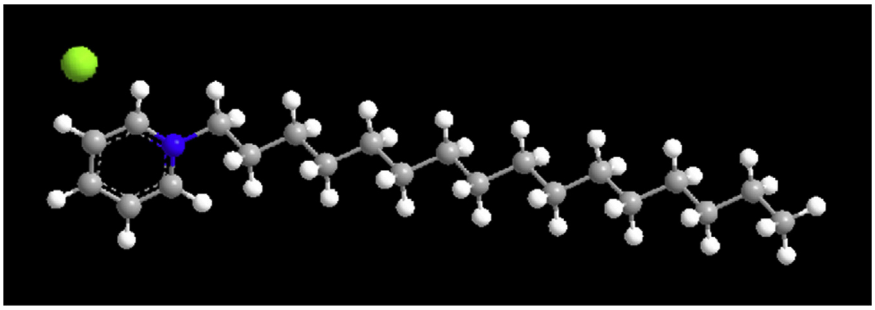
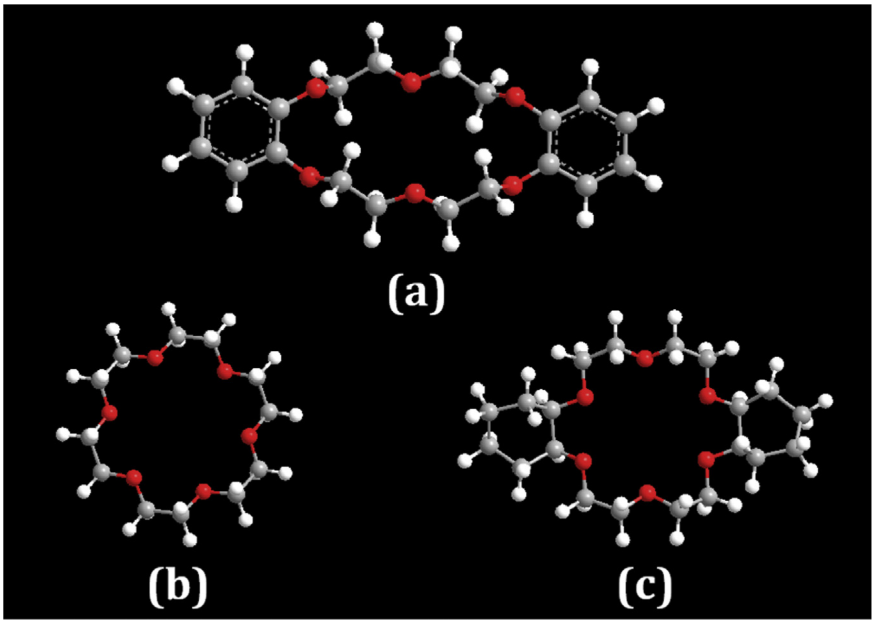


Scheme 1. Cetylpyridinium chloride (CPCl).



Scheme 2. (a) Dibenzo-18-crown-6 (DB-18-C-6), (b) 18-crown-6 (18-C-6) and (c) dicyclohexano-18-crown-6 (DCH-18-C-6).

respectively.

2.2. Apparatus and procedure

Solubilities of cetylpyridinium chloride, dibenzo-18-crown-6, 18-crown-6 and dicyclohexano-18-crown-6 have been verified in HPLC grade CH_3CN. All the stock solutions of CPCl and crown ethers were arranged by mass using Mettler Toledo AG-285 with uncertainty ±0.1 mg. Sufficient precautions were made to minimize the evaporation during mixing and working with these solutions.

Specific conductivity values of the experimental solutions were measured by Mettler Toledo Seven Multi conductivity meter with uncertainty $\pm 1.0\ \mu S\ m^{-1}$. The measurements were carried out using HPLC grade CH_3CN in an auto-thermostat water bath maintaining at ±0.1 K of the desired temperature. The cell was calibrated using standard procedure.

Fourier transform infrared (FT-IR) spectra were recorded on a Perkin Elmer FT-IR spectrometer in CH_3CN solution. The FTIR measurements were performed in the scanning range of $4000–400\ cm^{-1}$ at room temperature.

^1H NMR spectra were recorded in CD_3CN at 300 MHz using Bruker Avance 300 MHz instrument at 298 K. Signals are cited as δ values in ppm using residual protonated solvent signal as internal standard ($C\underline{H}_3CN$, δ 1.96 ppm). Data are reported as chemical shift.

3. Results and discussion

3.1. Conductivity study

Conductivity study is a convincing method for exploring complexation in solution not only because it affords information for minute alteration of concentrations of the charged particles, but also it offers data for the various interactions among the particles taking place in the solution system [33,34]. Conductivity of a solution with IL and added CE provides valuable information for the complexation process between the CE and IL in solution [35,36]. In our work complexations have been explored between CPCl and three similar CEs in CH_3CN solution. Thus to acquire data about complexation, conductivity of the CPCl solution with initial concentration of 10.0 mM have been measured with increasing concentration of the three CEs at five various temperatures from 293 K to 313 K in 5 K intervals and presented in Tables S1–S3 with increasing CE/IL mole ratio. The plots of conductance are depicted in Fig. 1–3, in which CE/IL mole ratio is shown in abscissa and conductance is shown in ordinate. A gradual decrease in conductance is observed with increasing CE/IL mole ratio for each plot, which signifies capture of the cetylpyridinium ions by the CEs respectively in CH_3CN solution, because CPCl being strong electrolyte can't form ion pair in the studied solution system [37]. So

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