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Proton NMR probing of stoichiometry and thermodynamic data for the complexation of Na^+ and Li^+ ions with 15-Crown-5 in acetonitrile–nitrobenzene mixtures

Mohsen Irandoust [a,*], Hiua Daraei [b], Roshanak Rostamian [a]

[a] Department of Chemistry, Razi University, Kermanshah, Iran
[b] Environmental Health Research Center, Kurdistan University of Medical Sciences, Sanandaj, Iran

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ABSTRACT

Proton NMR was used to study the complexation reaction of Li^+ and Na^+ ions with 15-Crown-5 (15C5) in a number of binary acetonitrile (AN)–nitrobenzene (NB) mixtures at different temperatures. In all cases, the exchange between free and complexed 15C5 was fast on the NMR timescale and only a single population average ^1H signal was observed. The formation constants of the resulting 1:1 complexes in different solvent mixtures were determined by computer fitting of the chemical shift mole ratio data. There is an inverse relationship between the complex stability and the amount of AN in the solvent mixtures. The enthalpy and entropy values for the complexation reaction were evaluated from the temperature dependence of the formation constants. In all the solvent mixtures studied, the resulting complex is enthalpy stabilized but entropy destabilized. Finally, the experimental results were compared with theoretical ones that were obtained from molecular modeling methods. Based on our results, it is most probable that Li^+–15C5 in solvent stays in a rather nesting complex form with greater $Log K_f$ values, but Na^+–15C5 forms a complete perching complex form with lower $Log K_f$ values.

1. Introduction

One of the fundamental components of systems that exhibit molecular recognition is non-covalent interactions [1]. Such interactions involve a subtle interplay of entropic and enthalpic effects that are difficult to separate. One model system that has come under intense scrutiny is the interaction of alkali metal ions with macrocyclic ligands such as crown ethers [2–5]. Crown ethers are compounds with a number of oxygen heteroatoms (three or more) incorporated in a monocyclic carbon backbone. They were first synthesized by Pedersen [2] and their generic name originates from their molecular shape, which is reminiscent of a royal crown [4]. According to the "hard–soft" acid–base theory and owing to the nature of their binding sites and to the presence of a hydrophilic cavity delineated by a lipophilic envelope, crown ethers exhibit a strong affinity and high selectivity for ammonium, alkali and alkaline earth metal ions [5–9]. The metal ion–crown ether interaction arises principally from the electrostatic interaction between the metal ions and the electron rich ether backbone of the crown ethers. The metal ion–crown ether binding strength is primarily governed by the number of available electron donor sites within the crown ether, the donor atom basicity, the distance separating the metal ion and the ether oxygen, and the dipole orientation [3].

Earlier, the focus of attention was concentrated on matching the metal ion's diameter to the crown ether cavity [3,4]. Crown ethers can form different types of complexes with metal ions, both in solution and in the solid-state. With a close match between the ligand cavity size and the cation diameter, a nesting complex (Fig. 1) may be formed. Perching complexes are formed when the cation is too large to fit within the ligand cavity. However, in cases with a large difference between the ligand cavity size and the cation diameter, 1:2 or 2:1 (ligand: metal mole ratio) complexes can be formed (Fig. 1) [10].

In this work, we have studied the stoichiometry and thermodynamics of complexation of Li^+ and Na^+ with 15C5 in a number of binary acetonitrile–nitrobenzene (AN–NB) mixtures, using the ^1H NMR technique [11–14], and we found results similar to previous theoretical investigations [5].

2. Materials and methods

2.1. Materials

Reagent grade 15C5 (Aldrich), lithium perchlorate and sodium perchlorate (Fluka) were of the highest purity available and were

* Corresponding author. Tel./fax: +98 831 427 4559.
E-mail address: irandoust1341@yahoo.com (M. Irandoust).

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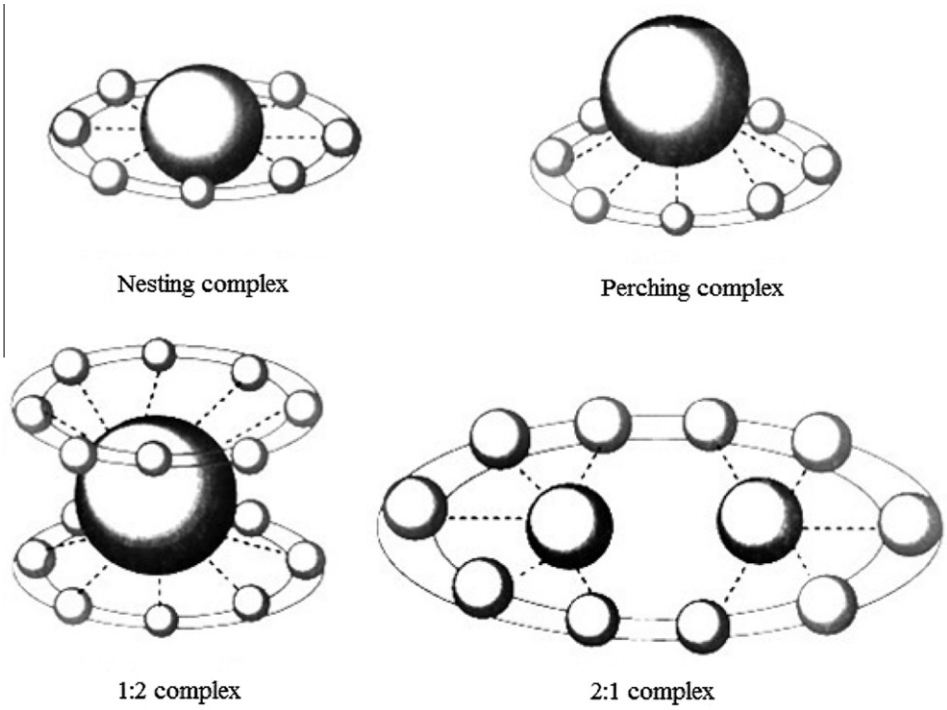

Fig. 1. Four kinds of metal ion–crown ether complexes.

used without further purification, except for vacuum drying. Reagent grade acetonitrile (Merck) and extra pure nitrobenzene (Merck) were used to prepare the solvent mixtures by weight.

2.2. Methods

All NMR measurements were made on a Bruker Avance (DPX) 200FT-NMR spectrometer with a field strength of 4.7 T (47 kG), equipped with a temperature controller. The temperature of the probe was adjusted to an accuracy of ±0.1 K using the temperature controller incorporated in the spectrometer.

In a typical experiment, 0.5 mL of the AN–NB mixtures containing 15C5 (0.018 M) was placed in the NMR tube, thermostated to the desired temperature and the ^{1}H NMR spectra of the resulting solutions were recorded and the chemical shift of the single NMR signal was measured. Then, a known amount of a concentrated metal ion solution in the same mixed solvent was added in a stepwise manner using a calibrated micropipette, thermostated to the desired temperature and the ^{1}H NMR spectra of the resulting solutions were recorded after each addition. The metal solution was continually added until the desired cation to ligand mole ratio was achieved. Then, formation of the complexes occurred in the

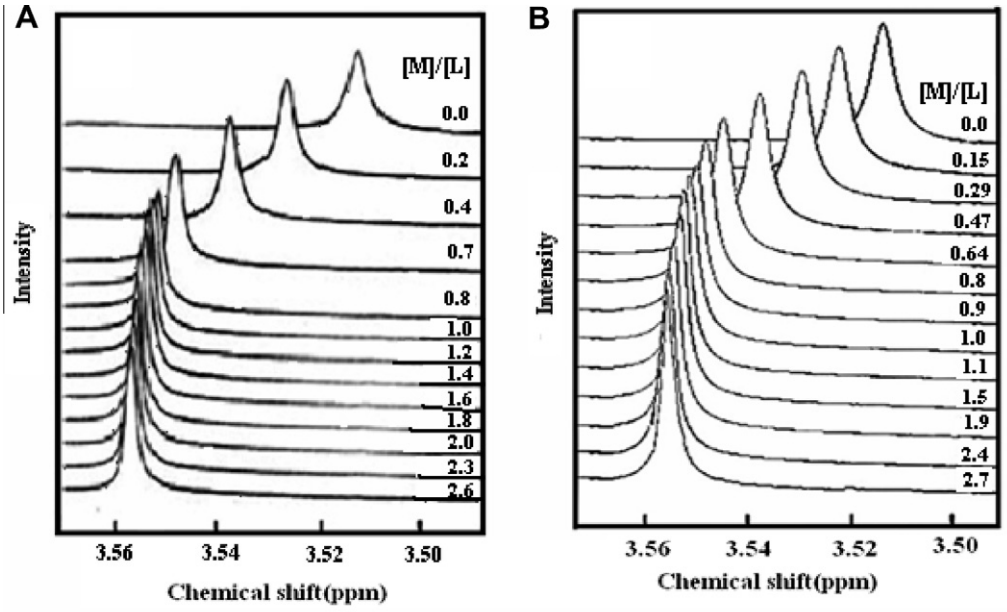

Fig. 2. Proton NMR spectra of 15C5 in 40% NB–60% AN mixture at 25 °C at (A) various [Na^+]/[15C5] mole ratios and (B) various [Li^+]/[15C5] mole ratios.