The Complexation of Na^+ by 18-Crown-6 Studied via Nuclear Magnetic Resonance
(MS #2002-0843)

Supplemental Material for Online Publication (Lab Documentation)

Directions and Experimental Procedures: A 0.1 M solution of sodium chloride in water is injected into seven capillary (melting point) tubes. Each capillary should be filled to a height of 6 cm with this solution. The ends of the capillary tubes are then sealed with a hand torch, and one capillary tube is placed into each of 7 empty NMR tubes. The signal for Na^+ in water represents the NMR standard for sodium (assigned 0.0 ppm) just as the TMS resonance is the standard for ^1H-NMR.

A 10 mL sample of a 0.1 M sodium chloride solution in deuteriated water (D_2O) is made. Varying amounts of 18-crown-6 are placed into 1 mL volumetric flasks. Students should wear gloves when handling 18-crown-6. Each of these flasks is then filled with the NaCl- D_2O solution in order to produce solutions varying from 0.0 to about 1 M in 18-crown-6. Now each of the NMR tubes containing a capillary tube is filled to a height of 5 cm with the different D_2O solutions (see Figure 1). It is necessary to use D_2O as opposed to ordinary water, as the NMR system uses the deuterium resonance as a lock signal.

The rate at which the sodium ion "jumps" in and out of the crown is so fast that the NMR cannot "see" both forms, but rather a mole fraction weighted average of the two forms of sodium ion is detected. A nice demonstration of the case where both resonances can be simultaneously observed is obtained when the experiment is carried out with [2.2.2]cryptand in place of the crown ether. There is no need for the capillary tubes containing NaCl in water for these experiments, and the concentration of crypt should be kept smaller than the concentration of Na^+. The down field resonance is due to the free solvated Na^+ ($Na^+_{(free)}$) and the high field resonance is due to the Na^+ encapsulated by the cryptand. Note the rate at which the sodium cation jumps in and out of the cryptand is slow on the NMR time scale, and the NMR can "see" both forms of the sodium ion.

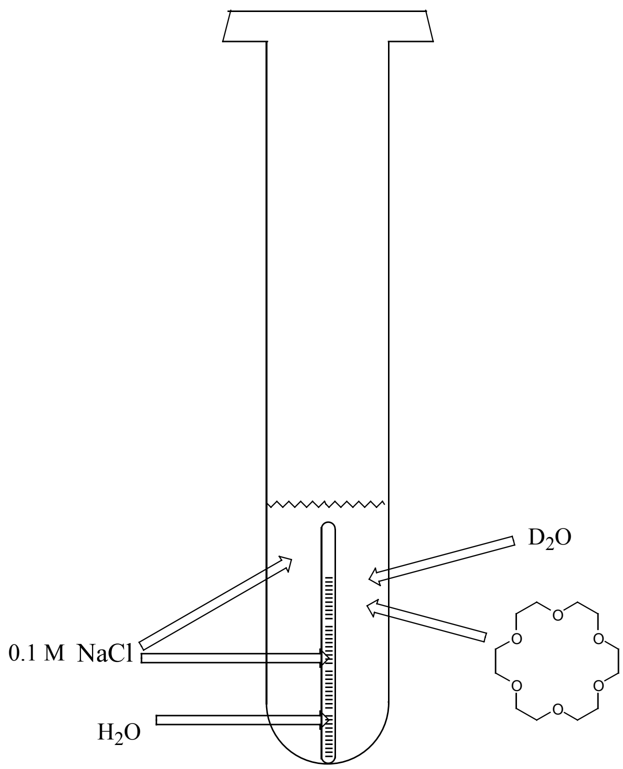


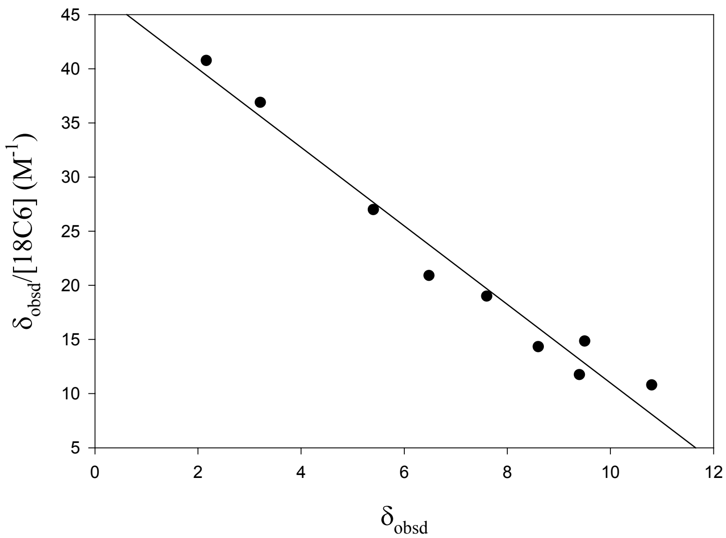
Figure 1. Schematic of an NMR tube (diameter is five millimeters) charged with a solution of 18C6 in D_2O and sodium chloride. Inside of the NMR tube is a sealed capillary tube containing sodium chloride in water.

Instructor Notes:

1. The experiments described here can be carried out successfully with any FT NMR spectrometer from 100 to 600 MHz.
2. The NMR spectrometer needs to be tuned to the ^{23}Na resonance frequency (79.38 MHz on a 300 MHz ^{1}H-NMR spectrometer) prior to the laboratory period. This can provide a little lesson on gyromagnetic ratios. The experiments described here were carried out on a Varian 300 MHz ^{1}H NMR equipped with a broad band probe and a Sun Microsystems console. The software is VNMR version 6.1b. 150 transients were collected with a sweep width of 20,000 Hz, a pulse width of 7.0 μsec (31.5 degrees), an acquisition time of 0.25 sec and a relaxation delay (d1) of 1.0 sec. The FIDs were processed using a line broadening (lb) = 1.0.

3. The resonance for the sodium cations inside of the capillary tubes remain relatively sharp, as this Na^+ does not have access to the crown ether.

4. Below is a plot of δ_{obsd}/[18C6] vs. δ_{obsd} obtained by two of our Junior physical chemistry students. From this plot they obtained a K_s of 3.63 ± 0.24 M^{-1}. The linear regression analysis of this data was done using the 95 % confidence interval, and the table below gives the error analysis for the slope and intercept. The R^2 value for this plot is 0.97.



Summary of Regression Analysis

	t	F	P
Slope	-14.9		<0.0001
Intercept	25.7		<0.0001
Regression		222	<0.0001

5. Both resonances for Na^+ in the cryptand experiment remain relatively sharp. This is because the exchange between the free and encapsulated forms is very slow. Students may also observe that the linewidth for the complexed Na^+ resonance is broader than that for the free Na^+. The quadrupole moment for both the complexed and free Na^+ nuclei interact with a surrounding nonuniform electric field gradient which will cause line broadening in the NMR spectrum. However, since the bound Na^+

experiences a larger nonuniform electric field gradient generated by the surrounding cryptand a larger linewidth is expected.

If the temperature of the solution were raised substantially, reaction 2 would become fast on the NMR time scale, and the two resonances would broaden and coalesce. Under these conditions, cryptand data could be collected and analyzed in a manner that is analogous to the 18C6 data. However, this experiment is not recommended since the cap on the NMR tubes would likely be blown off due to the high vapor pressure generated from heating the D_2O solutions, and the contents of the tubes would likely spray the inside of the NMR probe.

CAS Registry Numbers:

18-Crown-6	17455-13-9
[2.2.2]-Cryptand	23978-09-8
Deuterium oxide	7789-20-0
Sodium chloride	7647-14-5

Safety and Hazards:

18-crown-6 and [2.2.2]cryptand may cause skin and eye irritation, and may be harmful if absorbed through the skin. Both compounds target the nervous system. Consequently, students should wear gloves while handling them. The rest of the materials (i.e. NaCl and water) are innocuous.

Technology Based Materials:

No special software is necessary to carry out this experiment and obtain good results for a viable report. However, the use of SAS or Sigma Plot allows convenient graphing and statistical analysis. The actual NMR spectra can (if desired) be inserted into a Microsoft Word document with the use of gNMR and Sigma Plot. The FIDs can be save into the gNMR program (Cherwell Scientific Publishing) and subsequently placed into Sigma Plot or Microsoft Excel. The resulting spectra can then be copied and pasted into a word document to make an aesthetic student presentation.

Students can carry out very insightful molecular modeling in conjunction with this experiment. Simple PM3 and AM1 models of the alkali metal cations encapsulated in 18C6 and [2.2.2]cryptand can be generated with the use of a wide variety of molecular modeling software. The Titan program by Wavefunction/Scroedinger works particularly well and gives the student a three dimensional view of the complexes that they prepared in the laboratory. After the molecule is drawn in the Titan program, the PM3 geometry optimization only requires about two minutes using a 1 GHz processor. This particular program then allows the student to view the molecular system using a variety of styles including a space filling model.

Figure Captions:

Figure 1. Schematic of an NMR tube (diameter is five millimeters) charged with a solution of 18C6 in D_2O and sodium chloride. Inside of the NMR tube is a sealed capillary tube containing sodium chloride in water.

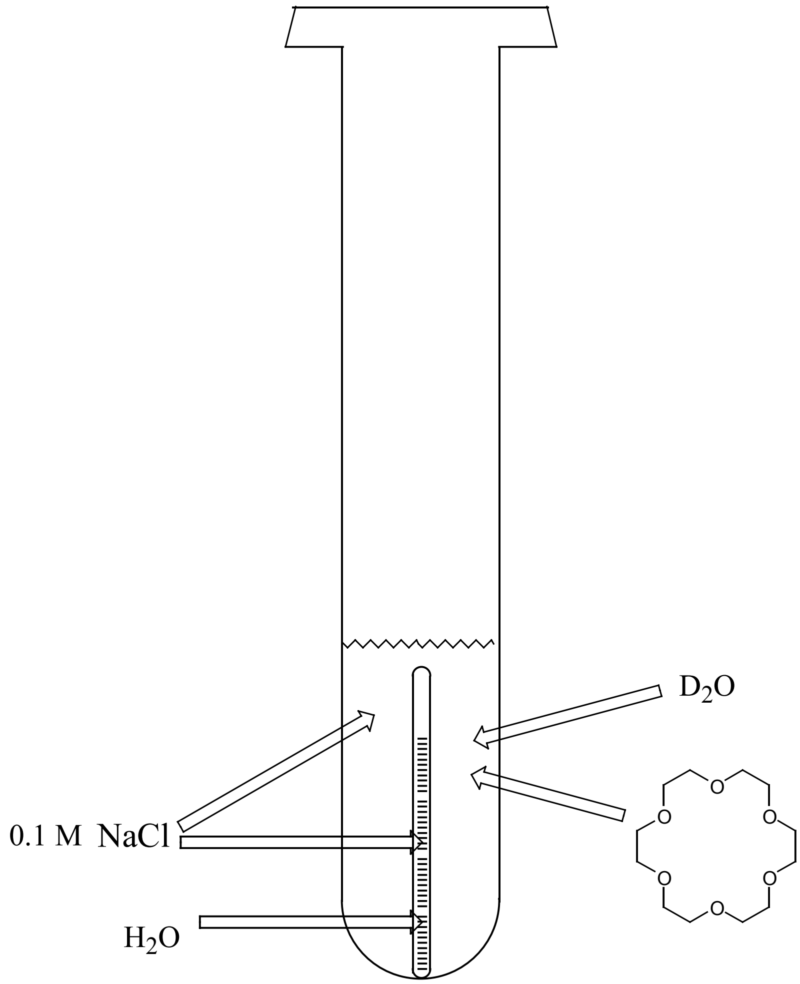


Figure 1