

Project ID: **65351**

Project Title: **Solution Effects on Cesium Complexation with Calixarene - Crown Ethers from Liquid to Supercritical Fluids**

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DOE-EMSP Project Annual Report

Project Title: Solvation Effects on Cesium Complexation with Calixarene-Crown Ethers from Liquid to Supercritical Fluids

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I. Introduction

Supercritical fluid CO₂ is an alternative solvent for extraction of metals.¹ The solubility parameter of supercritical CO₂ varies with density resembling that of liquid hexane at moderate pressures in the supercritical region to those of chlorinated solvents at very high pressures.² By changing density of supercritical CO₂, the solvation environment of a metal chelate system can vary continuously and resembles over a wide range of solvents. Thus, supercritical CO₂ provides a unique system for studying solvation effects on metal chelation.

This project is designed to investigate the solvation effects on cesium complexation with macrocyclic compounds including crown ethers and calixarene-crown ethers in CO₂ from liquid to supercritical region at high pressures. A powerful spectroscopic technique for studying cesium chelation is nuclear magnetic resonance (NMR). Cesium has only one isotope, ¹³³Cs, with a nuclear spin $I = 7/2$. Popov et al. used NMR to study cesium complexation with crown ethers and cryptand.^{3,4} Variation of the ¹³³Cs chemical shift as a function of the 18-crown-6/Cs⁺ mole ratio in different solvents indicates that the solvent plays an extremely important role in the

complexation process. The magnitude of the chemical shift upon cesium complexation with cryptand 222 (which has a tridimensional cavity) is much larger than with the flexible 18-crown-6. The NMR chemical shift for Cs^+ inside a cavity may be correlated to the configuration of the complex and the tightness of the fit.

Our collaborator, Clem Yonker at Pacific Northwest National Lab (PNNL), recently developed simple techniques for NMR studies in supercritical fluids.^{5,6} In Yonker's method, a hand pump is used to deliver the desired high pressure and to transport the dissolved solute in a fused-silica tubing placed in the NMR probe. Because capillary tubing can stand very high pressures, this technique is safe and capable of performing NMR experiments up to several kilobars. Yonker's technique will be used to start our NMR experiments (proton, ^{19}F and ^{133}Cs) for studying cesium-crown ether complexation in supercritical fluids.

The solubility of crown ethers such as dicyclohexano-18-crown-6 is reasonably high in supercritical CO_2 , $>1 \times 10^{-2}$ mol/L according to our preliminary data. The solubility of calixarene-crowns in supercritical CO_2 is much smaller, $<1 \times 10^{-3}$ mol/L. It is known that fluorination of ligand can significantly increase the solubility of metal chelates in supercritical CO_2 .^{7,8} To enhance the solubility of calixarene-crowns in supercritical CO_2 , synthesis of fluorinated calixarene-crowns are currently underway in our laboratory. For simplicity, in the beginning of this project we chose to compare the complexation of cesium with crown ethers in conventional solvent systems and in supercritical CO_2 systems.

II. Experimental Results

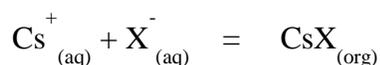
1. First extraction experiments

As a preliminary step, we began to investigate extraction of Cs^+ from an aqueous solution

into chloroform using crown ethers as the extracting agent. The choice of chloroform lays in its low dielectric constant (4.8 at 20°C), similar to that of supercritical CO₂. Publications dealing with extraction of alkali metals (including cesium) into organic solvents of higher dielectric constant, generally >10, have appeared.⁹ However, there is no such study involving an organic phase of low dielectric constant.

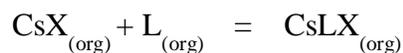
In chloroform the solubility of Cs salts is very slight. This is in contrast to studies involving more polar solvents for which easily measurable concentrations of Cs salt in the organic phase could be obtained. Our studies so far have employed Cs picrate, which will subsequently be called CsX.

When an aqueous solution of CsX is equilibrated with chloroform containing an extracting ligand L, a series of equilibria will occur. First, the salt will be distributed between the two phases:

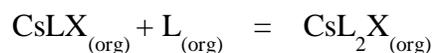


Because of the low dielectric constant of chloroform, ionization of CsX in the organic phase is negligible; the species should be considered to be an ion pair. This equilibrium will of course lie heavily on the aqueous side.

Next, interaction of CsX with the ligand L leads to a complex:



Most of our work so far has employed the crown ether dicyclohexano-18-crown-6. With this ligand an additional equilibrium occurs:



These equilibria have been studied separately.

2. NMR measurements

Measurement of solution concentrations has been carried out by nuclear magnet resonance (NMR) using a Bruker DRX500 spectrometer available in the chemistry department, University of Idaho. Proton measurements were conducted at 500.13 MHz, and ^{133}Cs measurements were taken at 65.60 MHz. A high pressure system utilizing a hand pump and capillary tubing for NMR measurements in supercritical CO_2 is currently in construction.

3. The equilibrium $\text{Cs}_{(\text{aq})}^+ + \text{X}_{(\text{aq})}^- = \text{CsX}_{(\text{org})}$

Distribution experiments have been carried out using pure deuterated chloroform and aqueous CsX solutions with concentrations 0.01 M and lower. The two-phase system is agitated for 4 hours. Then the phases are separated by centrifugation for 2 hours. The proton NMR spectrum of the resulting organic phase is shown in Fig. 1. The features shown are a very small peak at 9.19 ppm representing the picrate ion and the residual CHCl_3 peak at 7.26 ppm. It turns out that the concentration of the picrate is most conveniently measured by comparison with the CHCl_3 peak. The latter is measured separately by adding a known amount of cyclohexane to the deuterated chloroform. $[\text{CHCl}_3]$ must be measured separately for each bottle of deuterated chloroform; it generally falls in the range 0.02-0.04 M. The areas of the picrate and CHCl_3 peaks are determined by Lorentzian deconvolution.

Results obtained so far indicate a linear relation between $[\text{CsX}_{(\text{org})}]$ and $[\text{CsX}_{(\text{aq})}]$ for low $[\text{CsX}_{(\text{aq})}]$ (Fig. 2). The apparent falloff of $[\text{CsX}_{(\text{org})}]$ at higher $[\text{CsX}_{(\text{aq})}]$ requires further confirmation.

4. The equilibrium $\text{CsX}_{(\text{org})} + \text{L}_{(\text{org})} = \text{CsLX}_{(\text{org})}$

The distribution experiment now includes the ligand L = dicyclohexano-18-crown-6.

The tendency for complexation of CsX with this ligand is so strong that small amounts of the ligand must be used to study this equilibrium. The experiments conducted so far have used $[\text{CsX}_{(\text{aq})}] = 0.01\text{M}$ and $[\text{L}]$ in the range 0.008-0.0025 M. A portion of the proton NMR spectrum of one of these experiments is shown in Fig. 3. It shows a peak at 9.19 ppm representing CsX and a peak at 8.97 ppm representing CsXL. (It is possible that these species are hydrated to some degree; this issue has not been resolved.) Also shown is the residual CHCl_3 peak of the solvent. Again the relative concentrations of the Cs species are determined by Lorentzian deconvolution. The ratio of these to $[\text{L}]$ is discussed below.

From this spectrum the equilibrium constant $K_1 = [\text{CsLX}]/\{[\text{CsX}][\text{L}]\}$ can be determined.

Three measurements which we have made so far are in good agreement, giving $K_1 = 4.6 \times 10^5$.

However, there is an inconsistency between these data and the results for the CsX partition experiments: namely, the concentrations $[\text{CsX}]$ determined in the presence of the ligand should agree with those predicted from the partition experiments, but they do not. This difficulty remains to be resolved.

5. The equilibrium $\text{CsLX}_{(\text{org})} + \text{L}_{(\text{org})} = \text{CsL}_2\text{X}_{(\text{org})}$

For higher concentrations of the ligand the quantity $[\text{CsX}_{(\text{org})}]$ becomes negligible compared to the complexed forms. A typical proton NMR spectrum (with $[\text{L}] = 0.2\text{M}$) is shown in Fig. 4. The ligand resonances fall into two groups: a group of 20 protons centered at 3.7 ppm, and a group of 16 protons (present as 4 peaks of 4 protons each) centered at 1.5 ppm. The water peak, located at 2.83 ppm in this spectrum, shifts to higher field (lower ppm) at lower ligand concentrations. For the lowest concentrations, the water peak overlaps with the higher field resonances of the ligand. There is only one peak for the Cs species, indicating rapid

exchange between CsLX and CsL₂X. Also shown on the figure are the areas of the spectral regions, determined by the normal area measurement routine in the NMR software. The ligand concentration is based on the low field ligand peaks, which are free of interferences.

Because the Cs species are represented by only a single peak, the equilibrium constant $K_2 = [\text{CsL}_2\text{X}] / \{[\text{CsLX}][\text{CsX}]\}$ cannot be determined from the proton NMR spectrum. We have attempted to estimate K_2 by making use of the Cs spectrum. For $[\text{L}] = 0.01$ to 0.2 in the presence of $[\text{CsX}_{(\text{aq})}] = 0.01\text{M}$, the Cs spectrum consists of a single peak. The chemical shift of this peak, however, shifts with ligand concentration. This is shown in Fig. 5. For the range of chemical shifts shown, the relation is linear above $[\text{L}] = 0.01\text{M}$.

There is an extensive literature on the variation of Cs chemical shifts with ligand concentration.^{3,4} However, they generally involve organic solvents with high dielectric constants, for which relatively concentrated solutions can be prepared even in the absence of complexing ligands. In these circumstances it is possible to determine the Cs chemical shift for $[\text{L}] = 0$. In the present situation, we would like to determine the chemical shifts for the pure species CsLX and CsL₂X. Then, the ratio of these species could be determined by interpolation. However, these chemical shifts are not directly available from Fig. 5. A fairly good estimate can be made for the shift of CsLX, but it is not at all clear when the trend of Fig. 5 will level off for high ligand concentrations so that the shift of CsL₂X can be determined. We are limited by the solubility of the dicyclohexano-18-crown-6 ligand.

Nonetheless, by making reasonable estimates we can guess at K_2 . The values are relatively low, somewhere in the range 1-10. There is fairly good agreement between K_2 values obtained for different ligand concentrations for constant assumptions on the chemical shifts,

indicating that this approach to measurement of K_2 is at least reasonable. At this point, however, the problem of measuring this constant is not resolved.

6. The role of water in the CsX-ligand equilibria

In an early set of experiments, we compared the introduction of CsX into a chloroform phase containing dicyclohexano-18-crown-6 by two methods: (1) equilibrating the chloroform phase with solid CsX, and (2) equilibrating the organic phase with an aqueous solution of CsX. We estimated the equilibrium constant K_2 from the proton and Cs NMR spectra, using consistent assumptions for the Cs chemical shifts of pure species. We found that K_2 differed by about an order of magnitude for the two circumstances. While differences are to be expected in general terms, we wanted to get a more detailed picture of the role of water in the equilibria.

To this end we are studying the equilibration of solutions of crown ethers in chloroform with a pure water phase, with no Cs salt present. Water has a slight but significant solubility in chloroform, about 0.05M. It turns out that the crown ether attracts water into the chloroform phase in proportion to the concentration of the crown ether, presumably by forming cryptands of the type H_2OL .

Fig. 6 shows the total water concentration $[H_2O]_{tot} = [H_2O]_{free} + [H_2OL]$ as a function of ligand concentration $[L]$ of dicyclohexano-18-crown-6 in chloroform. The data can be fit to a straight line:

$$[H_2O]_{tot} = 0.060 + 0.81[L]$$

In this equation, 0.060 represents the concentration of free water which will be constant because of the two-phase equilibrium with pure water. The figure 0.81 indicates that not all ligand molecules take up a water molecule: only 81% do.

This equilibrium is responsible for the variation of the water proton chemical shift with ligand concentration noted above. [Figure 7](#) shows the water proton NMR chemical shift as a function of the crown concentration. The chemical shift suggests a rapid exchange between free H₂O and crown bound H₂O existing in the solvent. The result shows that evaluation of the equilibria involving Cs species in the extraction experiments must take account of the interaction of water with the extracting ligand. It is also possible that water interacts with the various Cs complexes, but that is yet to be determined.

As an offshoot of this project, we will study the extraction of water into pure organic phases (including eventually supercritical carbon dioxide) using various crown ethers.

7. Extraction of cesium with crown ethers in supercritical carbon dioxide

Some preliminary extraction experiments have been carried out to investigate the feasibility of extracting Cs⁺ with supercritical CO₂ using crown ethers as extractants. The Cs⁺-crown ether complexes are not soluble in supercritical CO₂. Our idea is to use a fluorinated counteranion to neutralize the charge of the complex and to transport the Cs⁺-crown complex as an ion pair into supercritical CO₂. Because of the presence of fluorine atoms in the counteranion, the ion-pair may become soluble in supercritical CO₂. Preliminary results indicate that using pentadecafluoro-n-octanoic acid, CF₃(CF₂)₆COOH, or perfluoro-1-octanesulfonic acid tetraethylammonium salt, CF₃(CF₂)₇SO₃[N(C₂H₅)₄]⁺ as a counteranion, Cs⁺ in aqueous solutions can be extracted by supercritical CO₂ containing dicyclohexano-18-crown-6. The results will be presented at the forthcoming National ACS meeting to be held in New Orleans in August.

III. Future Studies

We will start the supercritical fluid NMR studies this summer. The first system to be examined will be the crown ether/H₂O/CO₂ system to evaluate the differences between organic solvents and supercritical CO₂ for the $[H_2O]_{tot} = [H_2O]_{free} + [H_2OL]$ equilibrium. Crown ethers of different cavity sizes will be studied. It is known that crown ethers can carry water into the organic phase during liquid-liquid extraction, but the details of equilibration between free H₂O and crown ether bound H₂O in different solvents are not known. NMR provides an opportunity for us to look into this problem in detail. Supercritical fluid NMR study of this system as a function of fluid density will provide interesting information regarding the solvation effects on the H₂O-crown ether interaction.

The Cs picrate/crown ether/H₂O/CO₂ system will be examined next. We will continue our study of the Cs picrate/crown ether/ H₂O/CDCl₃ system to understand the equilibrium relations of the various Cs species involved. The effects of H₂O on Cs complexation with crown ether will be carefully examined in solvent and in supercritical CO₂ systems. Other counteranions including the perfluorinated carboxylic acid pentadecafluoro-n-octanoic acid will also be studied instead of picrate in the systems discussed above.

Proton NMR should be sensitive enough for the proposed NMR studies using the capillary tubing technique. ¹³³Cs NMR may not be sensitive enough for supercritical CO₂ studies because of the limited solubilities of regular Cs-crown ether complexes in the fluid phase. Some fluorinated calixarene-crown ethers should be ready for our tests this summer. It is hoped that the solubilities of the fluorinated calixarene-crowns will be sufficient for the proposed ¹³³Cs NMR studies.

We have also contacted Dr. J.W. Rathke of the Chemical Technology Division, Argonne National Lab, who is a well established scientist in high pressure NMR studies. The NMR probe used by Rathke's group at ANL is based on a toroid cavity resonator that provides signal-to-noise ratios which are superior to the solenoid and Helmholtz coils that are typically used in commercial NMR spectrometers. Dr. Rathke is interested in collaborating with us on the Cs complexation studies in supercritical fluids. In case we need a high sensitivity NMR probe for the proposed Cs study, we will work with Dr. Rathke at ANL for our NMR experiments.

IV. References

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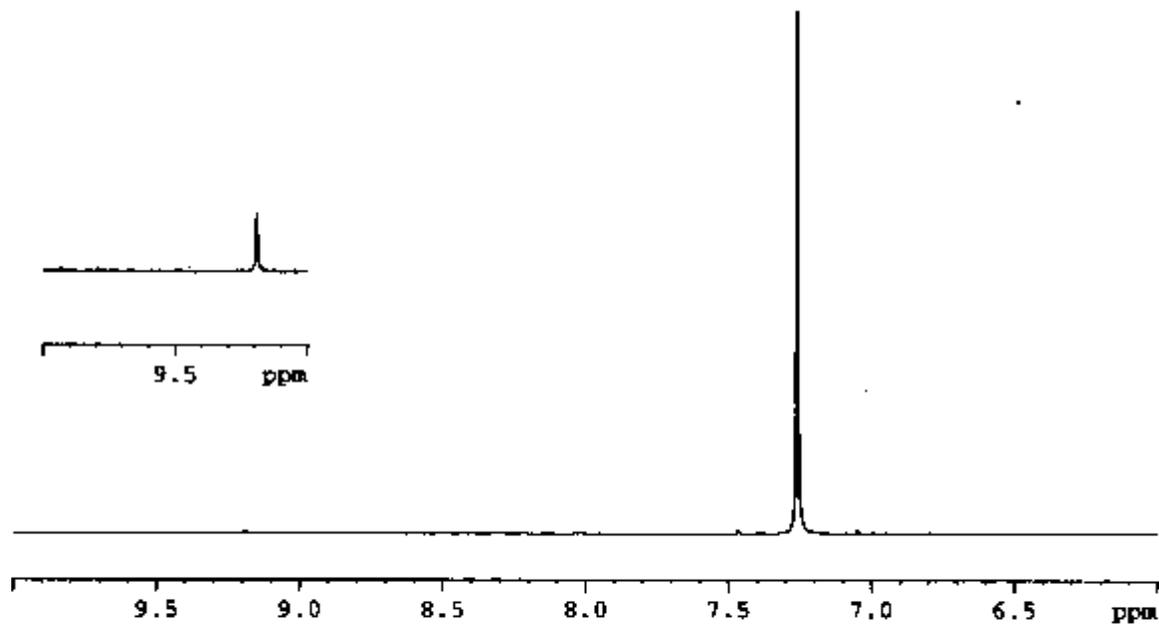


Figure 1. Proton NMR - extraction of 0.006 M Cs picrate into chloroform

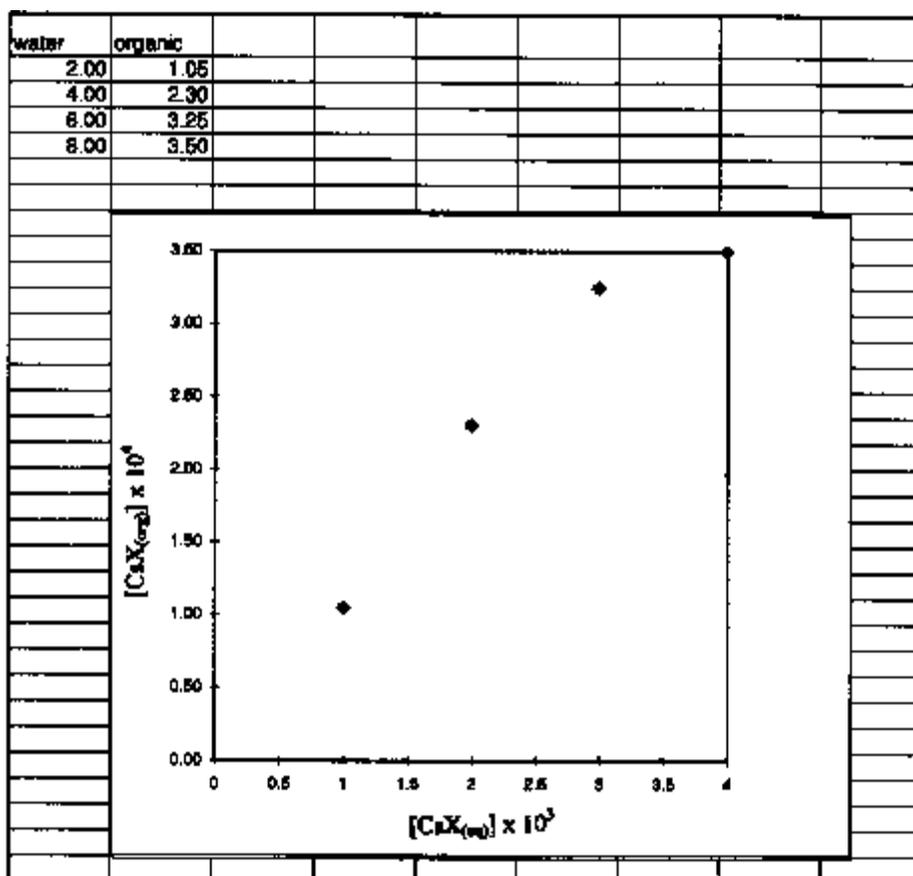


Figure 2. Partition of Cs picrate between water and chloroform phases.

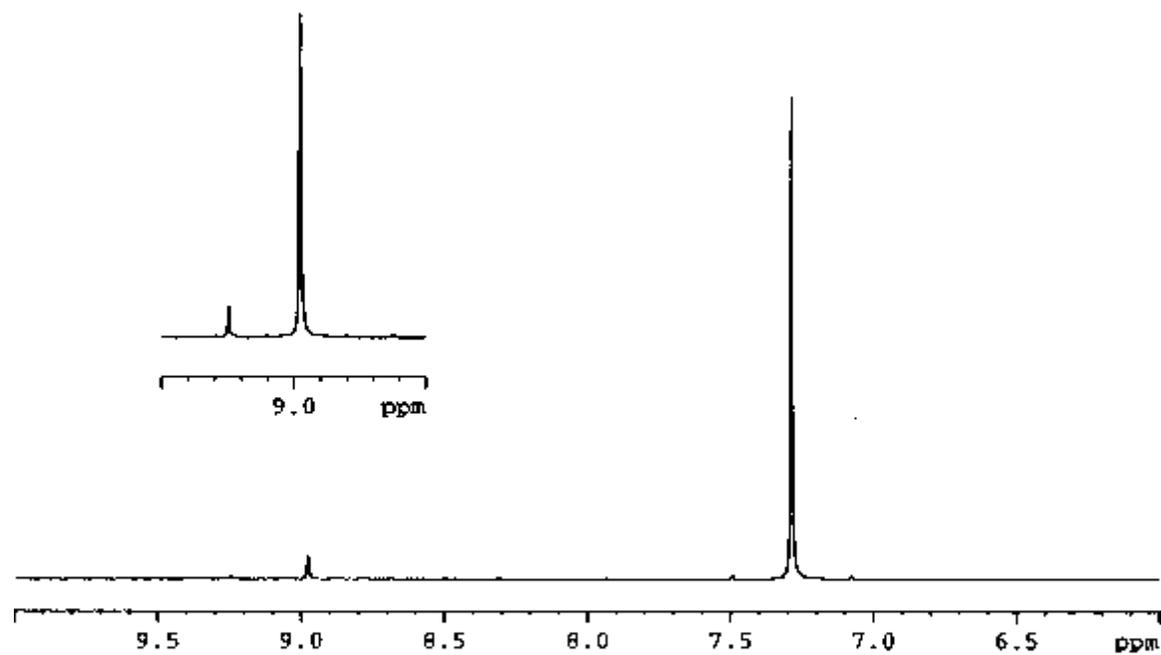


Figure 3. Proton NMR - extraction of 0.01M Cs picrate into chloroform
which is 0.001M in dicyclohexane-18-C-6

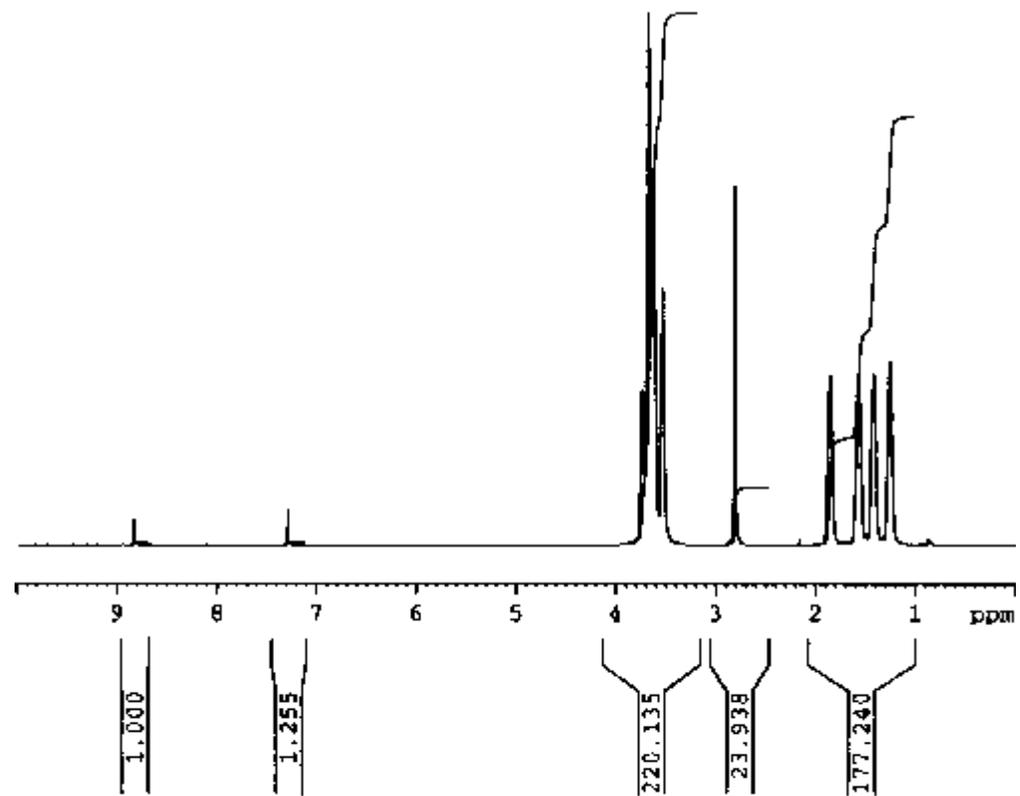


Figure 4. Proton NMR - extraction of 0.01 M Cs picrate into chloroform containing 0.2 M dicyclohexano-18-crown-6.

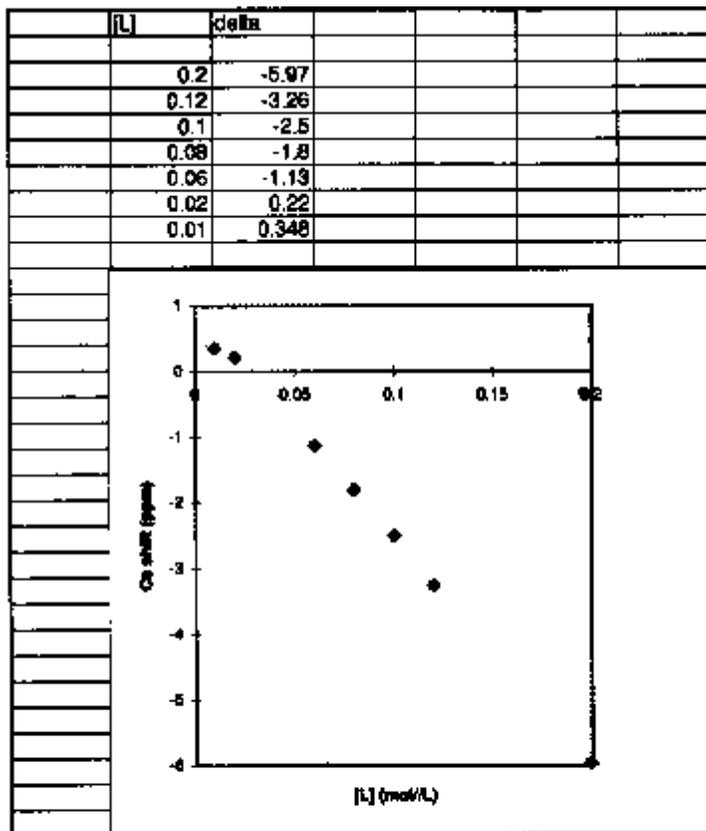


Figure 5. Relative Cs chemical shift vs. total ligand concentration for extraction of aqueous Cs picrate into chloroform containing dicyclohexano-18-crown-6.

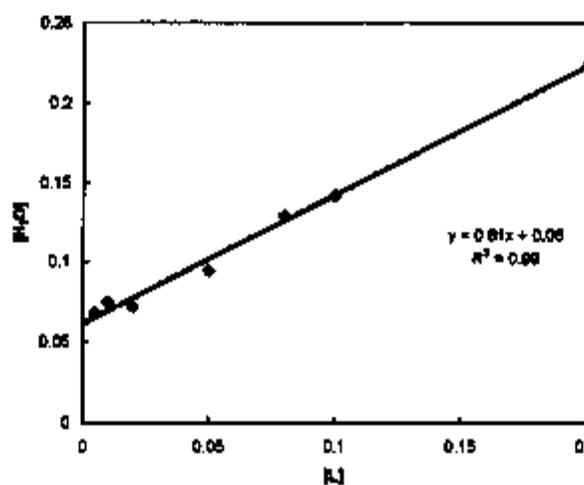


Figure 6. Total water concentration $[H_2O]_{tot}$ vs ligand concentration $[L]$ for extraction of pure water into a chloroform solution of dicyclohexano-18-crown-6.

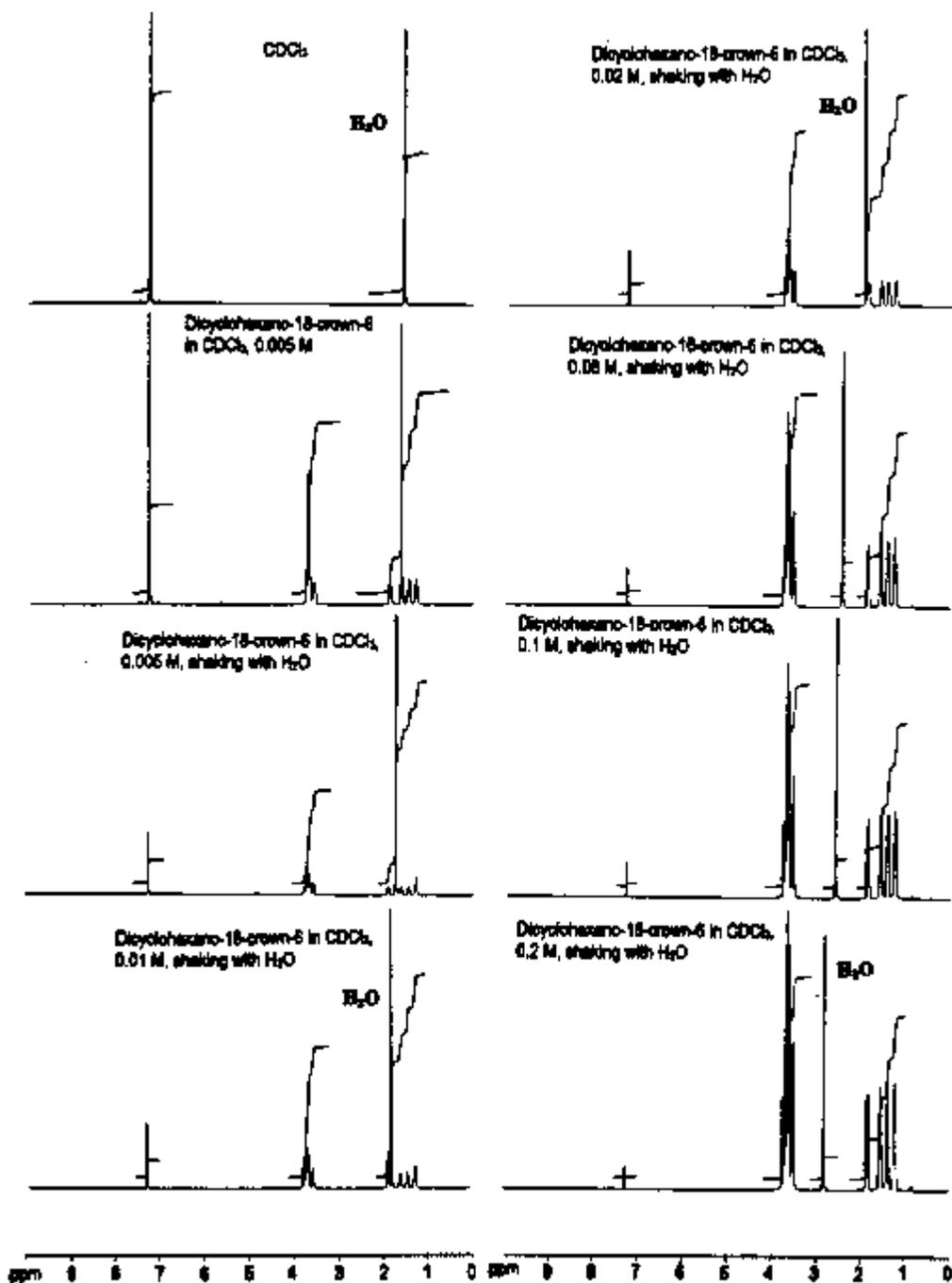


Figure 7. Proton NMR spectra of the chloroform phase after extraction of pure water into chloroform containing various concentrations of dicyclohexano-18-crown-6. The shift of water peak suggests a rapid exchange between free water and crown bound water.