

Solvation Effects on Cesium Complexation with Crown Ethers from Liquid to Supercritical Fluids

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Objectives of this research

To study solvation effects on cesium
crown ether complexation using

NMR techniques

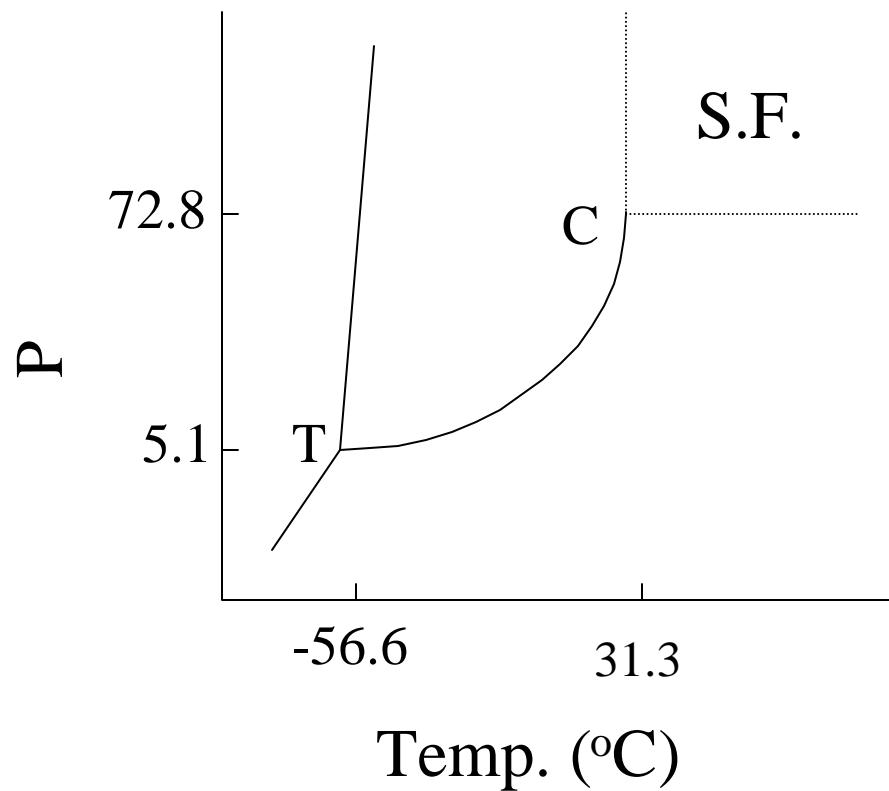
Supercritical CO₂ as a model system

NMR Studies of Cesium Crown Ether Complexes

Cesium NMR	Isotope Abundance	Nuclear Spin
^{133}Cs	100%	7/2
Proton NMR		
^1H	99.98%	1/2
^{13}C NMR		
^{13}C	1.1%	1/2

Carbon Dioxide:

$$T_c = 31.1 \text{ } ^\circ\text{C}, P_c = 72.8 \text{ atm}, \rho_c = 0.47 \text{ g/cm}^3$$



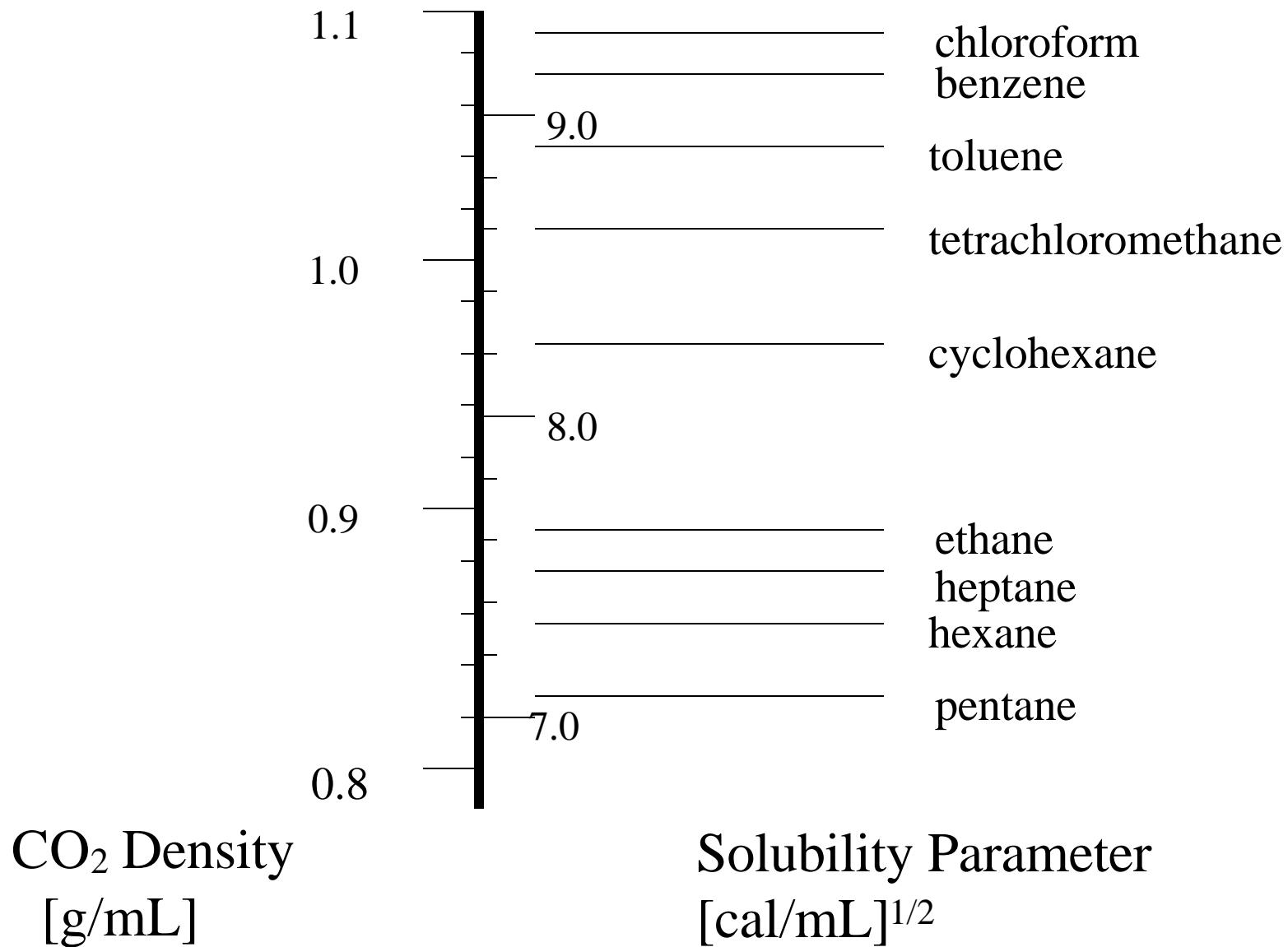
J.C. Giddings et al.
Science 1968, 162, 67

Solubility parameter of a supercritical fluid solvent

$$\mathbf{s}_1 = 1.25 (P_c)^{1/2} (\mathbf{r}_r / 2.66)$$

- The solubility parameter of supercritical carbon dioxide varies continuously with density. Therefore, its solvation strength is tunable.
- Can Supercritical carbon dioxide be used as a model system to study solvation effects on metal crown ether complexation?

Supercritical CO₂ Density and Solubility Parameter/Equivalent Common Solvents



Initial NMR Experiments

- (1) Dicyclohexano-18-crown-6 in CDCl_3 / Cs-picrate in water
- (2) Dicyclohexano-18-crown-6 in CDCl_3 / dry Cs-picrate

Observations:

^{133}Cs NMR: Large NMR shift of Cs peak between (1) and (2).

Proton NMR: A water peak found in (1) which shifts downfield with increasing crown ether concentration.

Role of water in cesium extraction from aqueous solution into a low dielectric solvent containing crown ether

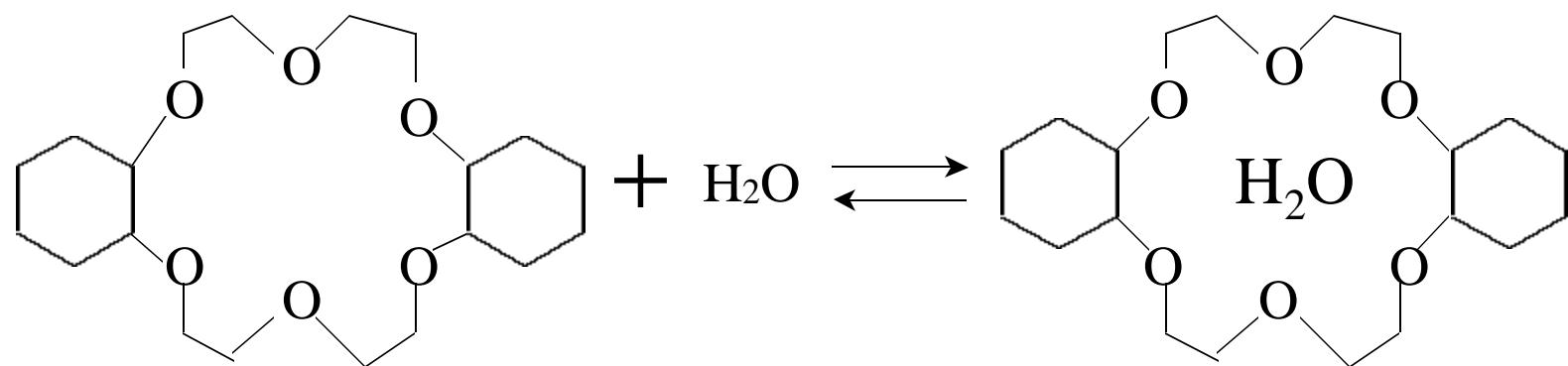
Chloroform

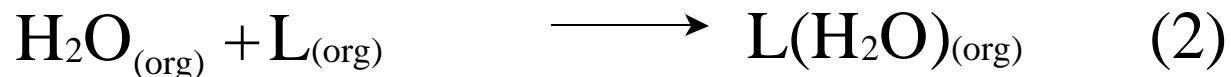
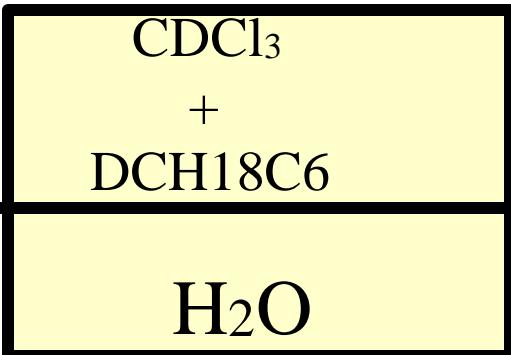
Dielectric constant ~ 4.8 at 20 °C

Solubility of water in CHCl_3

~ 0.05 mol/L at room temperature

Equilibrium between free water and bound water in DCH₁₈C₆/CDCl₃ system





$$K = [\text{L} \bullet \text{H}_2\text{O}_{(\text{org})}] / [\text{L}_{(\text{org})}][\text{H}_2\text{O}_{(\text{org})}] \quad (3)$$

Fraction of L bound
with water

$$k = \frac{[\text{L} \bullet \text{H}_2\text{O}_{(\text{org})}]}{[\text{L} \bullet \text{H}_2\text{O}_{(\text{org})}] + [\text{L}_{(\text{org})}]} \quad (4)$$

Total H₂O in the organic phase $[\text{H}_2\text{O}_{(\text{org})}]^o$

$$[\text{H}_2\text{O}_{(\text{org})}]^o = [\text{H}_2\text{O}_{(\text{org})}] + [\text{L} \bullet \text{H}_2\text{O}_{(\text{org})}] \quad (5)$$

free water bound water

Total ligand in the organic phase

$$[\text{L}_{(\text{org})}]^o = [\text{L}_{(\text{org})}] + [\text{L} \bullet \text{H}_2\text{O}_{(\text{org})}] \quad (6)$$

$$[\text{H}_2\text{O}_{(\text{org})}]^o = k[\text{L}_{(\text{org})}]^o + [\text{H}_2\text{O}_{(\text{org})}] \quad (7)$$

$$k = \frac{K[\text{H}_2\text{O}_{(\text{org})}]}{1 + K[\text{H}_2\text{O}_{(\text{org})}]} \quad (8)$$

From NMR measurement

$$\frac{\delta - \delta_0}{\delta_1 - \delta_0} = \frac{[L \bullet H_2O_{(org)}]}{[H_2O_{(org)}]^o} \quad (9)$$

$$\delta = \delta_0 + k(\delta_1 - \delta_0) \quad \frac{[L_{(org)}]^o}{[H_2O_{(org)}]^o} \quad (10)$$

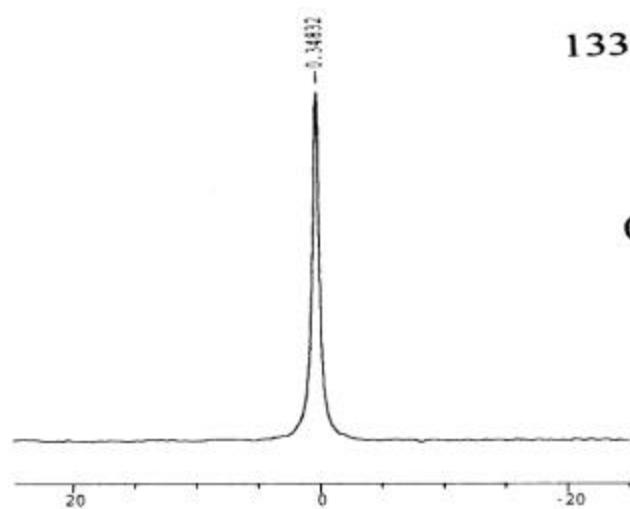
δ_0 = shift of free water in $CDCl_3$

δ_1 = shift of bound water in $CDCl_3$

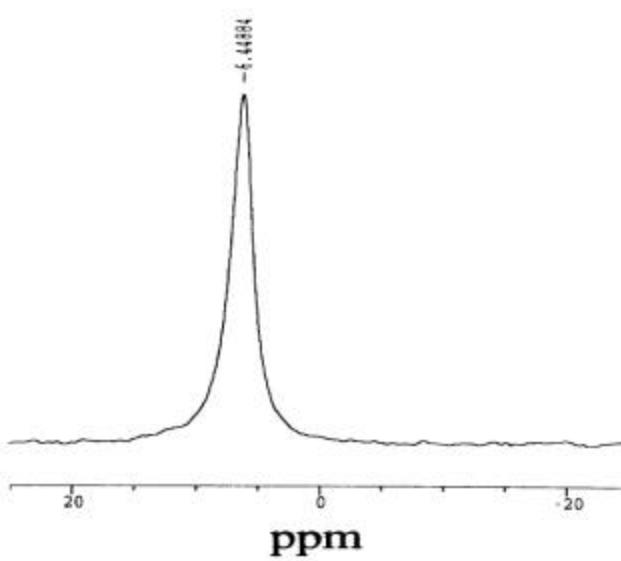
δ = observed shift due to rapid exchange
between free and bound water

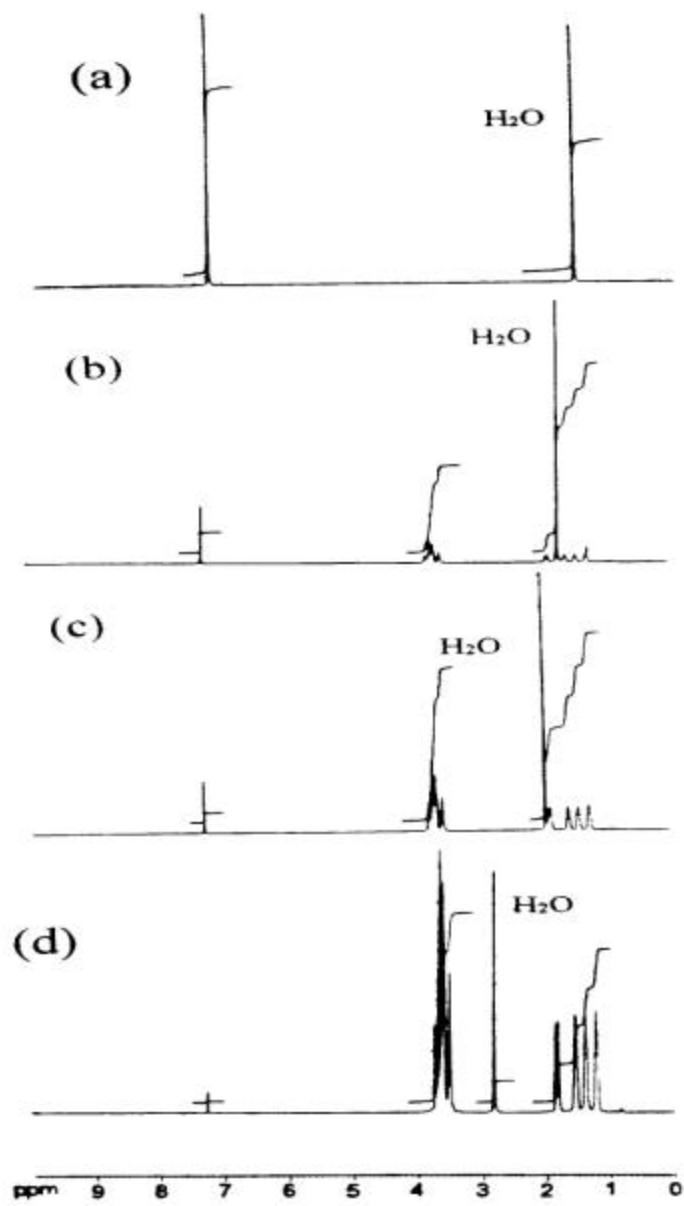
^{133}Cs NMR Spectra

(a) $\text{CDCl}_3\text{-DCH}18\text{C}6$
 $/\text{Cs-picrate-H}_2\text{O}$



(b) $\text{CDCl}_3\text{-DCH}18\text{C}6$
 $/\text{Cs-picrate(solid)}$





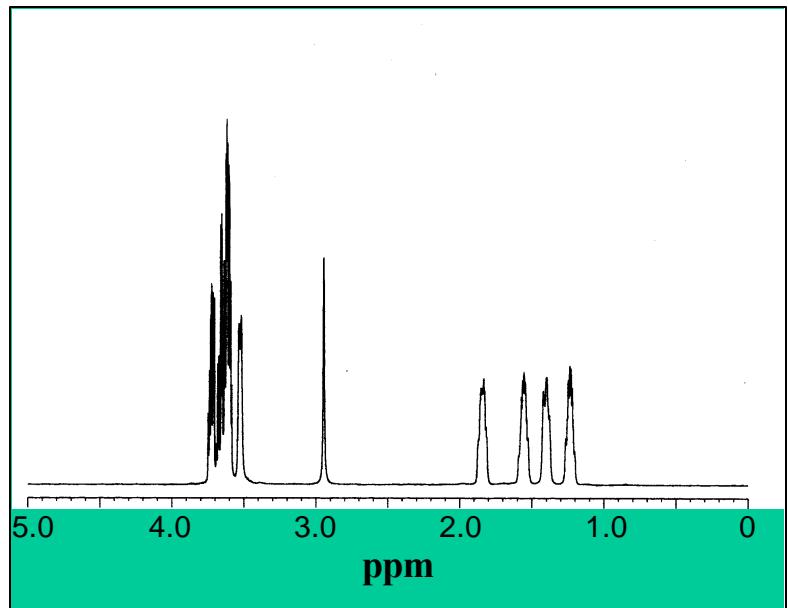
Proton NMR spectra of the DCH18C6/ CDCl_3 phase after shaking with water. The shift of water peak suggests a rapid exchange between free water and crown bound water.

(a) free water in CDCl_3
(No DCH18C6)

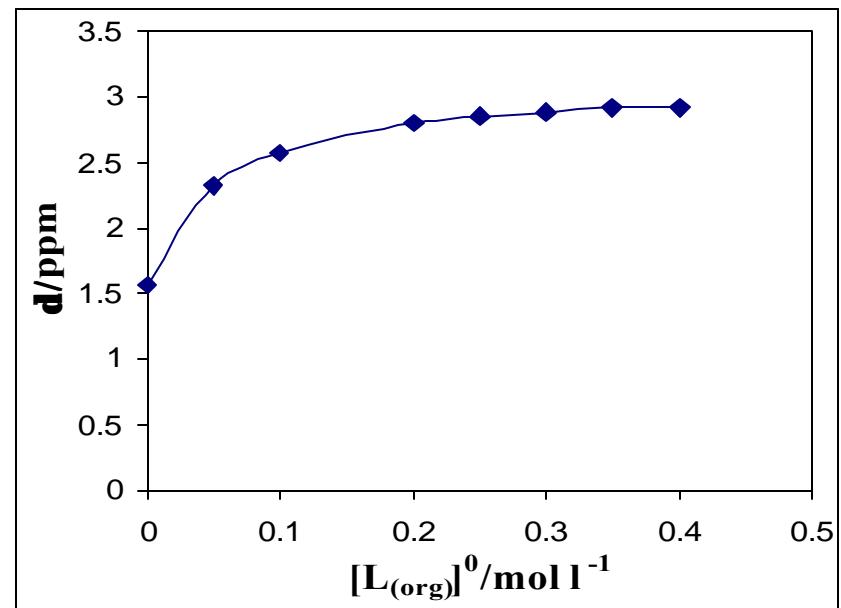
(b) 0.005 M DCH18C6
in CDCl_3

(c) 0.02 M DCH18C6

(d) 0.2 M DCH18C6

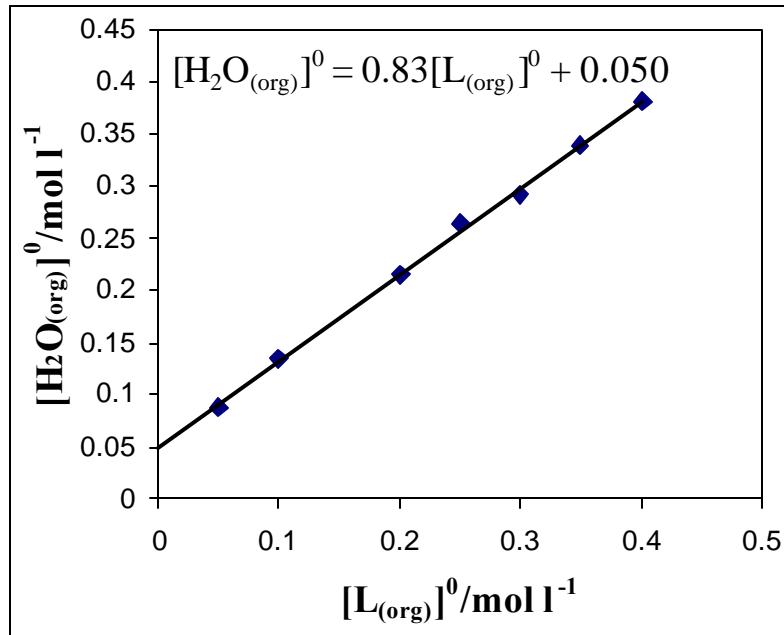


(a)

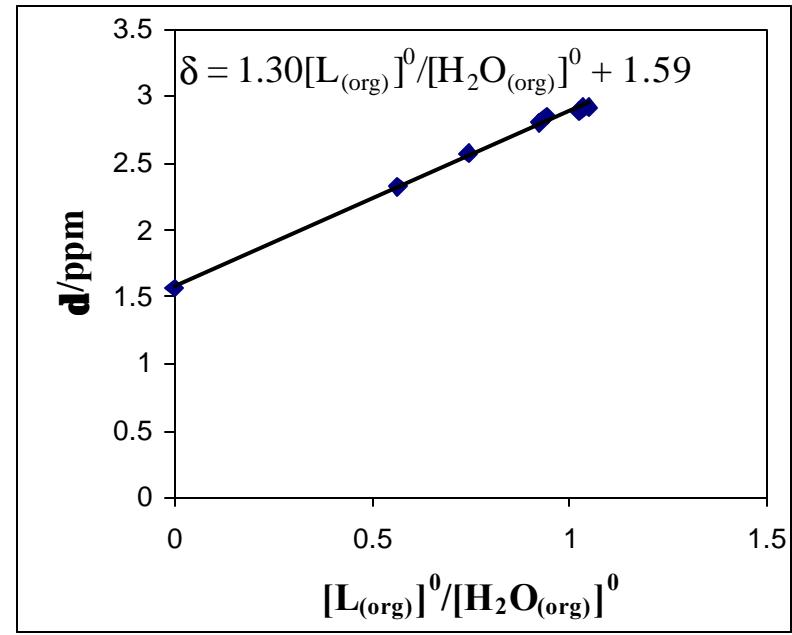


(b)

Figure 1. (a) A typical PNMR spectrum of DCH24C8 in the CDCl_3 phase after equilibration with water (water peak at 2.92 ppm). (b) Change of the observed PNMR chemical shift of water with respect to the concentration of DCH24C8 in CDCl_3 phase ($\delta_0 = 1.53$ ppm for pure water in CDCl_3).



(a)



(b)

Figure 2. Linear relationship between: (a) total water and DCH24C8 concentration in chloroform; (b) observed chemical shift of water and the ratio $[L_{(org)}]^0/[H_2O_{(org)}]^0$ in chloroform.

Table. 1 Equilibrium and chemical shift parameters for extraction of water into chloroform by various crown ethers^a

Crown	k	K/mol ⁻¹	[H ₂ O] _(org) /mol l ⁻¹	δ ₀ /ppm	δ ₁ /ppm
12C4	0.22	5.3	0.055	1.58	2.64
15C5	0.48	15.8	0.058	1.52	3.08
18C6	1.01 ^b		0.058	1.55	3.11
DCH18C6	0.85	93	0.060	1.61	3.23
DCH24C8	0.83	97	0.050	1.59	3.16

^a The error in these numbers is about ±5%.

^b This number should be regarded as essentially 1.0. It is not evidence for a water/ligand ratio >1.

Supercritical Fluid Extraction

SFE Apparatus

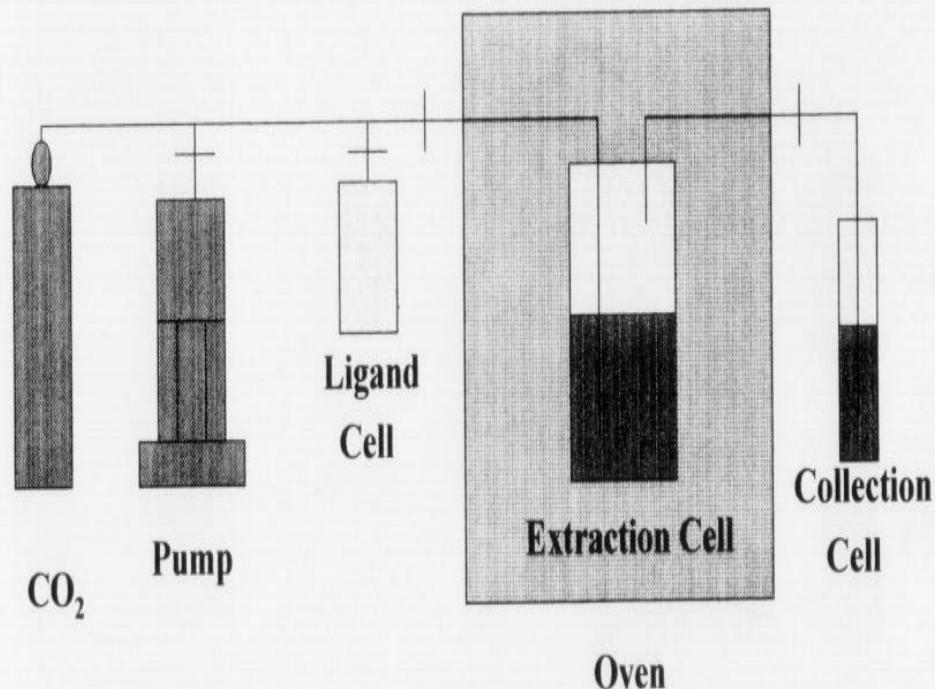


Table 1. Extraction of Sr²⁺, Ca²⁺, and Mg²⁺ from water by supercritical fluid CO₂ containing DC18C6 and perfluorinated counteranion PFOA⁻ or PFOSA⁻ at 60 °C and 100 atm

Mole Ratio			% Extraction		
Sr ²⁺ : DC18C6 : PFOA-H	Sr ²⁺	Ca ²⁺	Mg ²⁺		
1 10 0	1	0	0		
1 0 10	4±1	1±1	1±1		
1 5 10	36±2	1±1	1±1		
1 10 10	52±2	2±1	1±1		
1 10 50	98±2	7±2	2±1		
Sr ²⁺ : DC18C6 : PFOSA-N(C ₂ H ₅) ₄					
1 0 10	12±2	6±2	2±1		
1 5 10	98±2	45±4	2±1		
1 10 10	99±1	66±5	2±1		
Sr ²⁺ : DC18C6 : PFOSA-K					
1 10 10	97±2	8±2	2±1		

The aqueous solution contained a mixture of Sr²⁺, Ca²⁺, and Mg²⁺ with a concentration of 5.6x10⁻⁵ M each; pH of water under

equilibrium with SF CO₂ = 2.9; 20 min static followed by 20 min dynamic flushing at a flow rate of 2 mL/min.

PFOA-H = CF₃(CF₂)₆COOH; PFOSA-N(C₂H₅)₄ = CF₃(CF₂)₆CF₂SO₃[N(C₂H₅)₄]; PFOSA-K = CF₃(CF₂)₆CF₂SO₃K.

Table 2. Extraction of Sr^{2+} , Ca^{2+} , and Mg^{2+} from 1.3 M HNO_3 by supercritical fluid CO_2 containing DC18C6 and PFOAH or PFOSA salt at 35 °C and 200 atm.

Mole Ratio			% Extraction		
Sr^{2+}	DC18C6	PFOA-H	Sr^{2+}	Ca^{2+}	Mg^{2+}
1	10	0	1	0	0
1	10	50	18±2	2±1	1±1
Sr^{2+} : DC18C6 : PFOSA-K					
1	10	50	60±3	8±2	2±1
1	20	50	76±3	8±2	1±1
Sr^{2+} : DC18C6 : PFOSA-N(C_2H_5) ₄					
1	10	50	61±3	7±2	2±1

The acid solution contained a mixture of Sr^{2+} , Ca^{2+} , and Mg^{2+} with a concentration of 5.6×10^{-5} M each; 20 min static followed by 20 min dynamic flushing at a flow rate of 2 mL/min. PFOA-H = $\text{CF}_3(\text{CF}_2)_6\text{COOH}$; PFOSA-N(C_2H_5)₄ = $\text{CF}_3(\text{CF}_2)_6\text{CF}_2\text{SO}_3[\text{N}(\text{C}_2\text{H}_5)_4]$; PFOSA-K = $\text{CF}_3(\text{CF}_2)_6\text{CF}_2\text{SO}_3\text{K}$.

Wai et al., Mendeleev Commun. 180 (1999)

SF CO₂ Extraction of Cs⁺, K⁺, and Na⁺

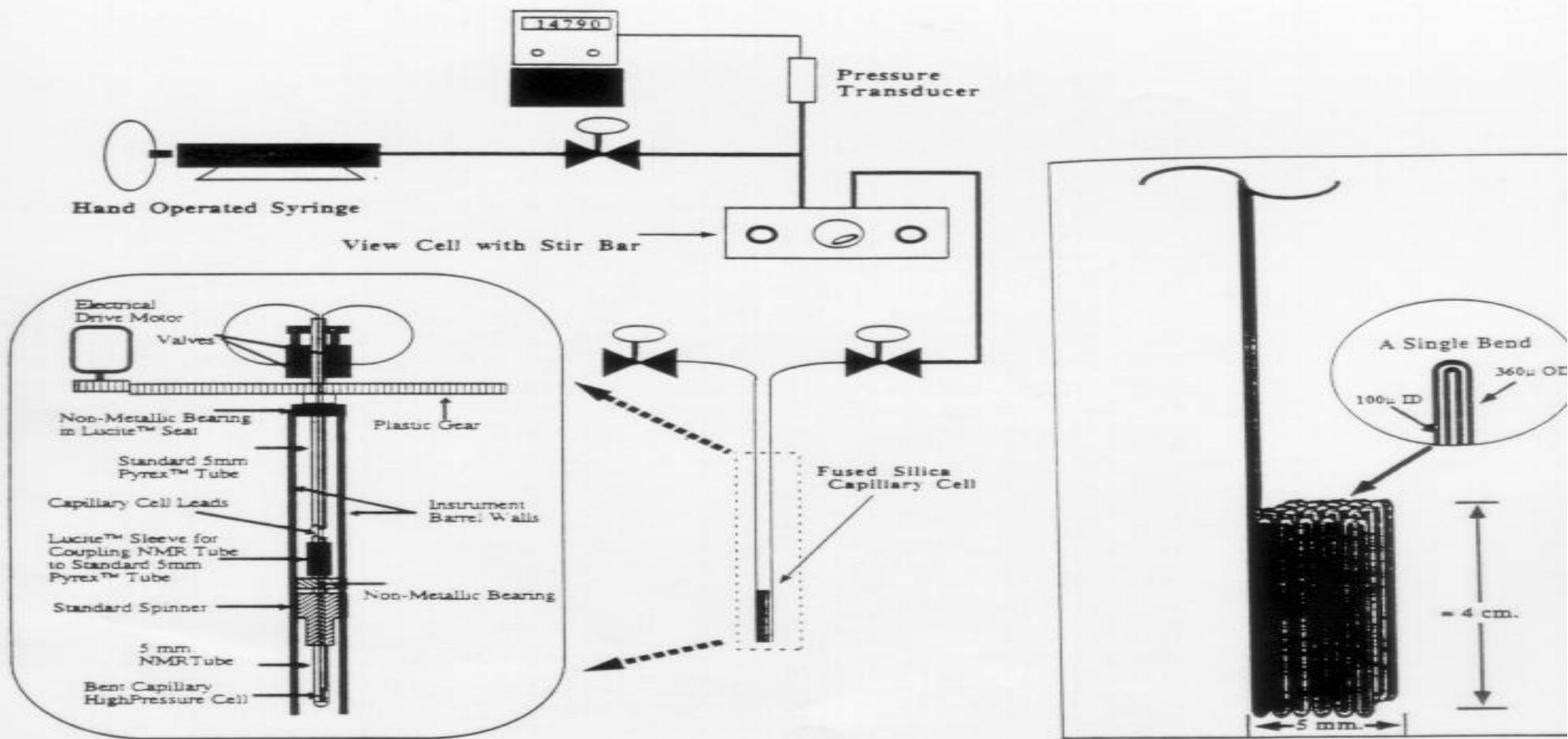
(100 atm, 20 m static, 20 m dynamic extraction)

[Cs²⁺]=[K⁺]=[Na⁺]=1.7x10⁻⁴ M

Cs:DC21C7:FPOAT=1:100:100

t, °C	% Extraction		
	Cs ⁺	K ⁺	Ca ⁺
21	67	73	1
40	63	69	1
60	55	39	1

PFOAT = CF₃(CF₂)₇SO₃[N(C₂H₅)₄]



Schematic Diagram of the High-Pressure NMR Cell
(Clem Yonker, PNNL)

Research Status:

- NMR studies of Cs-crown ether-water equilibria in organic solvents (in progress)
- NMR studies of Cs-crown ether-water equilibria in supercritical carbon dioxide (started)

Results: (Publications derived from this study)

1. “NMR investigation of water-crown ether interaction in a low dielectric solvent”, X. Ye, R. Porter, C.M. Wai, submitted to *Chemical Communications*, March 2000.
2. “Selective extraction of strontium with supercritical fluid carbon dioxide”, C.M. Wai, et al., *Chemical Communications*, 2533-2535 (1999).
3. “Supercritical carbon dioxide extraction of cesium from aqueous solutions in the presence of macrocyclic and fluorinated compounds”, C.M. Wai, et al., *Mendeleev Communications*, 180-181 (1999).