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Unclassified
SECURITY CLASSIFICATION OF THIS PAGE

AD-A221 408

REPORT DOCUMENTATION PAGE

Approved
OMB No. 0704-0188

DTIC ELECTE MAY 08 1990 S D D

1a. REPORT SECURITY CLASSIFICATION Unclassified	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release Distribution unlimited
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report #11	5. MONITORING ORGANIZATION REPORT NUMBER(S)
6a. NAME OF PERFORMING ORGANIZATION Brigham Young University	6b. OFFICE SYMBOL (If applicable)
6c. ADDRESS (City, State, and ZIP Code) Department of Chemistry Provo, UT 84602	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research
	7b. ADDRESS (City, State, and ZIP Code) Department of the Navy Arlington, VA 22217-5000
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research	8b. OFFICE SYMBOL (If applicable) ONR
	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N000014-88-K-0115
8c. ADDRESS (City, State, and ZIP Code) 800 No. Quincy Street Arlington, VA 22217-5000	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. / PROJECT NO. / TASK NO. / WORK UNIT ACCESSION NO.

11. TITLE (Include Security Classification)
AN EVALUATION OF A DIRECT ^{1}H NMR METHOD FOR DETERMINING LOG $\underline{K}$ AND $\Delta\underline{H}$ VALUES FOR CROWN ETHER-ALKYLAMMONIUM CATION COMPLEXATION

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13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Interim	FROM _____ TO _____	April 17, 1990	

16. SUPPLEMENTARY NOTATION

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

A direct ^{1}H NMR method for determining log $\underline{K}$ values for crown ether-ammonium cation complexations using only milligram quantities of the expensive crown has been tested and evaluated for accuracy and precision by comparing the results with those obtained using the calorimetric titration method. Log $\underline{K}$ values for the interactions of a non-chiral crown ether, diketopyridino-18-crown-6 (1), with 1-(1-naphthyl)ethylammonium (NapEt) perchlorate in 50%$CDCl_3$-50%CD_3OD and 10%$CDCl_3$-90%CD_3OD at 25°C were determined by the direct ^{1}H NMR method. Log $\underline{K}$ values for the interactions of a chiral crown ether, dimethyldiketopyridino-18-crown-6 (2) with the (R) and (S) enantiomers of NapEt in pure CD_3OD at 25.0°C were also determined by the NMR method. In Table I, the results are compared with those determined by a calorimetric method. The log $\underline{K}$ values determined by the two methods are in excellent

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION	
☐ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS		
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. Harold Guard	22b. TELEPHONE (Include Area Code) (202) 696-4409	22c. OFFICE SYMBOL

DD Form 1473, JUN 86 — Previous editions are obsolete. — S/N 0102-LF-014-6603

SECURITY CLASSIFICATION OF THIS PAGE
Unclassified

agreement. This agreement suggests that reliable complexation data can be obtained in a variety of polar and non-polar solvents by the NMR method using only milligram quantities of the hard to obtain macrocyclic ligands.

^{1}H NMR Experiments: All ^{1}H NMR spectra were recorded on a Varian Gemini 200 MHz apparatus with a temperature accessor. The temperature of the NMR probe was verified with a standard thermocouple and the temperature of the sample tube and its contents was determined using a method suggested by Varian with neat ethylene glycol as the standard sample. It was found that the equilibrium temperature of the sample could be reached within 10 minutes after the sample was loaded into the probe, but the actual sample temperature was normally higher than the probe temperature by up to 2°C within the range of -50°C to +50°C. This temperature difference may be attributed to the effect of magnetic heating and sample spinning.

For each log K determination at a certain temperature, a sample containing a few milligrams of either crown ether 1 or 2 in a known amount of solvent was first loaded into the probe and a spectrum was taken. The sample was then unloaded, added to the sample tube with a small amount of the ammonium salt, reloaded into the probe, and another spectrum was taken. This process was repeated until no significant change was observed in sucessive ^{1}H NMR spectra. Usually eight to twelve spectra were taken for each log K determination. The crown ether concentrations were about 0.01-0.015 M and the ammonium salt concentrations varied from 0.0 to approximately 0.06 M for each of the experiments. In each experiment, the crown concentrations were known by dissolving accurately weighed crown ether compound in an exact volume of solvent at 25.0 °C. The balance used for the weighing was calibrated for accuracy using a standard weight from the National Institute of Standards and Technology. The salt concentrations were then calculated based on the integral ratio of a particular ammonium salt signal to a particular crown ether signal in the spectra. In order to obtain a quantitative integration, the time delay between the two pulses for each NMR acquisition was set long enough to allow sufficient relaxation of the signals of interest. The NMR parameter settings were kept the same for all of the experiments and TMS (Me_4Si) was used as the internal standard for all of the samples.

Under the conditions of fast exchange on the NMR time scale, the average chemical shift of a crown ether signal is the weighted average of the chemical shift of the free crown ether and that of the crown ether in the complex

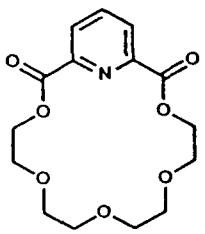
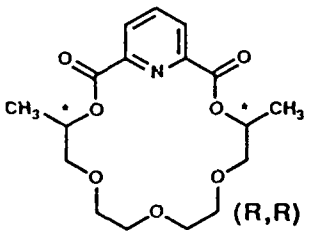
$$\delta_{ave} = X_f\delta_f + (1-X_f)\delta_c \qquad (1)$$

where δ_{ave} = average chemical shift of the crown ether, δ_f = chemical shift of the free crown ether, δ_c = chemical shift of the crown ether in the complex, and X_f = the mole fraction of free crown ether. By using a nonlinear least-squares treatment, the best fit of the experimental data points can be achieved through the minimization of the function

$$U = \Sigma[\delta_{obs,i} - X_{f,i}\delta_f - (1-X_{f,i})\delta_c]^2 \qquad (2)$$

where δ_{obs} = observed average chemical shift of the free and bound crown ether. Since X_f is a function of log K, U is therefore a function of log K also. The log K value that results in the minimum U value will be taken as the experimental result. Our log K values were calculated this way using a program on a VAX 11/780 computer.

Table I. LOG K VALUES FOR THE INTERACTION OF PYDIDINO-CROWNS WITH α-NAPETNH$_3$ClO$_4$ AT 25°C MEASURED BY NMR AND CALORIMETRY

CROWN	SALT	SOLVENT	LOG K NMR	LOG K CALORIMETRY
	NapEtClO$_4$	1:1/CDCl$_3$:CD$_3$OD	3.33±0.04	
		1:1/CHCl$_3$:CH$_3$OH		3.42±0.02
		1:9/CDCl$_3$:CD$_3$OD	2.99±0.04	
		1:9/CHCl$_3$:CH$_3$OH		2.96±0.02
 (R,R)	(S)-NapEtClO$_4$	OD$_3$OD	2.50±0.04	
		CH$_3$OH		2.47±0.01
	(R)-NapEtClO$_4$	CD$_3$OD	2.08±0.04	
		CH$_3$OH		2.06±0.01