

measurements on these compounds as a function of temperature.

Since the present work has been restricted to compounds having just six carbons, we do not observe those effects peculiar to longer chains such as segmental motion and kinks in the alkane chain.¹² As we extend this work to include molecules of higher molecular weight, we expect those effects to enter the regression analysis.

It is interesting to note that diastereotropic methyl groups have different values for T_1 , and hence different values for τ_{eff} and $\tau(1,2)$. In 4-methyl-2-pentanol the difference in $\tau(1,2)$ is not great, 10.4 vs. 10.5 ps, but in 2-methyl-3-pentanol one methyl has a $\tau(1,2)$ of 7.89 ps and the other a $\tau(1,2)$ of 9.49 ps. From our shift reagent work² we know the assignments for these two methyls and the average conformation of the molecule. Methyl-50, with the shorter $\tau(1,2)$, is the more crowded and hence may be subject to a threefold barrier to rotation and thus have a reduced barrier to rotation compared to methyl-49.

Conclusion

Careful measurement of the spin-lattice relaxation values for most of the carbons in these 18 isomeric alcohols followed by regression analysis of the results has given new insight into the relationships between T_1 , molecular structure, and molecular dynamics. No general applicability can be claimed for the regression coefficients determined in this work since they are a function of such things as solvent, concentration, temperature,

the functional groups present, and the solution viscosity; however, the trends observed should have general applicability. We expect to be able to extend these correlations to include some of these other factors as we measure the relaxation times of higher homologues. Variable-temperature measurements will clarify the energetics of methyl group rotation. Ultimately theoretical calculations, which can be compared with the experimental results of the present work, will clarify the interactions responsible for the observed values of the carbon spin-lattice relaxation times in these molecules.

Acknowledgment. This work was supported by grants from the National Institute of Arthritis and Metabolic Diseases (AM-21381) to K. L. Williamson and from the National Science Foundation (CHE-8103004) to T. R. Stengle. We acknowledge the contribution of C. P. Beeman at an early point in the study.

Registry No. 1-Hexanol, 111-27-3; 2-hexanol, 626-93-7; 3-hexanol, 623-37-0; 2-methyl-1-pentanol, 105-30-6; 3-methyl-1-pentanol, 589-35-5; 4-methyl-1-pentanol, 626-89-1; 2-methyl-2-pentanol, 590-36-3; 4-methyl-2-pentanol, 108-11-2; 2-methyl-3-pentanol, 565-67-3; 3-methyl-3-pentanol, 77-74-7; 2,2-dimethyl-1-butanol, 1185-33-7; 3,3-dimethyl-2-butanol, 464-07-3; 2,3-dimethyl-2-butanol, 594-60-5; 3,3-dimethyl-1-butanol, 624-95-3; 2-ethyl-1-butanol, 97-95-0; *erythro*-3-methyl-2-pentanol, 1502-93-8; *threo*-3-methyl-2-pentanol, 1502-94-9; 2,3-dimethyl-1-butanol, 19550-30-2.

Sodium Cation Complexation by Large Crown Ethers: ²³Na NMR Chemical Shifts and Longitudinal and Transverse Relaxation Rate Studies of Sodium Tetraphenylborate-Dibenzo-24-crown-8 Complexes in Nitromethane

Harald D. H. Stöver, Alfred Delville,[†] and Christian Detellier*

Contribution from the Ottawa-Carleton Chemistry Institute, Ottawa University Campus, Ottawa, Ontario K1N 9B4, Canada. Received November 21, 1984

Abstract: The complexation of sodium tetraphenylborate by dibenzo-24-crown-8 has been studied in nitromethane solutions by Na-23 nuclear magnetic resonance spectroscopy at three different fields. Chemical shifts show the presence in solution of two major cationic species: solvated sodium and the 1:1 sodium/crown complex. Longitudinal relaxation rates are field-independent and indicate the formation of higher aggregates whose stoichiometry is plausibly $(n + 1)/n$ sodium/crown. An aggregation model based on this stoichiometry is proposed, and equilibrium constants for the aggregation have been calculated. The average number of crowns in the species varies from 1 to 3.8 which confirms that Na-23 relaxation times belong to the extreme-narrowing limit. Only 2% of the total sodium concentration is distributed among the aggregated species with a maximum contribution for $n = 1$. Transverse relaxation rates are field-dependent. The temperature variation of $\ln T_1^{-1}$ and $\ln T_2^{-1}$ shows that the T_2 's are affected by two relaxation mechanisms which can be separated: quadrupolar and chemical exchange.

Naturally occurring cyclic antibiotic ionophores such as valinomycin, a 36-membered cyclic dodecadepsipeptide can highly discriminate between K^+ and Na^+ .¹ Valinomycin folds around the potassium cation, being stabilized by intramolecular N-H...O=C hydrogen bonds. Other cyclic antibiotic ionophores, such as enniatin, form 1:1 and 2:1 ionophore/cation complexes^{1b,c} and display lower cation selectivity than valinomycin. These cryptand-like three-dimensional complexes differ strikingly from the synthetic cryptands² or spherands³ by their higher lability; the decomplexation rate is faster in the case of the wrapped ionophore complex^{4a} than in the case of the encaging cryptand.^{4b} This is one of the reasons why synthetic models have been designed,

incorporating a crown cavity and a potentially folding side arm capable of complexing the cation.⁵ Such "lariat ethers" form three-dimensional labile cryptand-like complexes.⁶ Large 24-

(1) (a) Burgermeister, W.; Winkler-Oswatitsch, R. *Top. Curr. Chem.* **1977**, *69*, 91-196. (b) Ovchinnikov, Yu. *FEBS Lett.* **1974**, *44*, 1-21. (c) Hilgenfeld, R.; Saenger, W. *Top. Curr. Chem.* **1982**, *101*, 1-82. (d) Hamilton, J. A.; Sabesan, M. N.; Steinrauf, L. K. *J. Am. Chem. Soc.* **1981**, *103*, 5880-5885.

(2) Lehn, J. M. *Acc. Chem. Res.* **1978**, *11*, 49-57.

(3) Cram, D. J.; Lein, G. M.; Kaneda, T.; Helgeson, R. C.; Knobler, C. B.; Maverick, E.; Trueblood, K. N. *J. Am. Chem. Soc.* **1981**, *103*, 6228-6232.

(4) (a) Liesegang, G. W.; Eyring, E. M. In "Synthetic Multidentate Macrocyclic Compounds"; Izatt, R. M.; Christensen, J. J., Eds.; Academic Press: New York, 1978; p 245. (b) Cox, G. G.; Garcia-Rosas, J.; Schneider, H. *J. Am. Chem. Soc.* **1981**, *103*, 1054-1059.

(5) Dishong, D. M.; Diamond, C. J.; Cinoman, M. I.; Gokel, G. W. *J. Am. Chem. Soc.* **1983**, *105*, 586-593.

[†] Chargé de Recherche FNRS. Permanent address: Institut de Chimie Organique et de Biochimie B6, Université de Liège au Sart-Tilman, B-4000 Liège, Belgique.

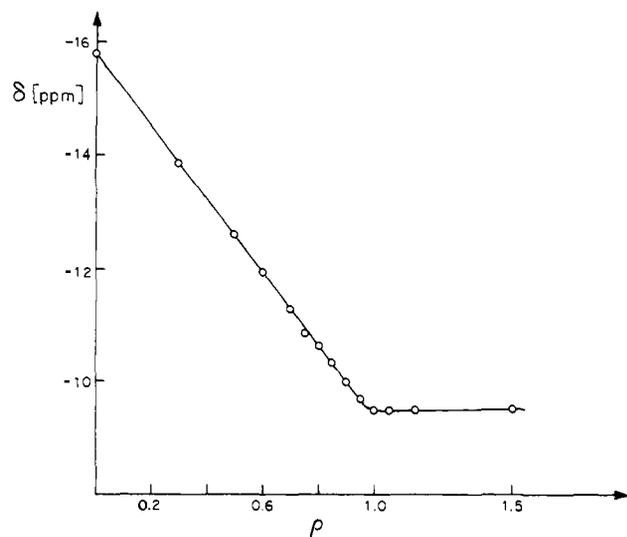


Figure 1. Na-23 chemical shifts as a function of the ratio [crown]/[sodium tetrphenylborate] (ρ) at 79.35 MHz in nitromethane [NaBPh_4] = 0.0369 M.

or 30-membered rings like dibenzo-24-crown-8 (DB24C8) or dibenzo-30-crown-10 (DB30C10)⁷ are known to form such three-dimensional complexes in nonpolar solvents. DB24C8 wraps around the sodium cation in solution, expelling from its coordination sphere solvent molecules and counteranion.^{8,9} An X-ray structure has been reported for the complex K^+ -DB30C10,¹⁰ showing a complete covering of the cation by the crown oxygen, with a similar conformation in solution or in the crystalline state.¹¹ Complexes of 2:1 cation/crown have been reported in nitromethane solution in the case of DB30C10- Na^+ ^{9,12} or in the solid state in the case of DB24C8- Na^+ ,¹³ K^+ ,¹⁴ or DB30C10-sodium isothiocyanate.¹⁵

Alkali-metal cation nuclear magnetic resonance is a powerful method for studying the complexation kinetics and thermodynamics and to detect aggregation in solution.¹⁶ Na-23, Li-7, and C-13 NMR have been used to determine the structure of the Na^+ -monensin complex in methanol solution¹⁷ and its kinetic parameters of complexation.¹⁸ Potassium-ionophore complexes have been characterized by K-39 NMR.¹⁹ Crown or cryptand-cation decomplexation kinetic parameters have been measured in a few cases, using Na-23 or K-39 NMR: Na^+ -DB18C6 in *N,N*-dimethylformamide²⁰ or in a number of solvents,²¹ K^+ -

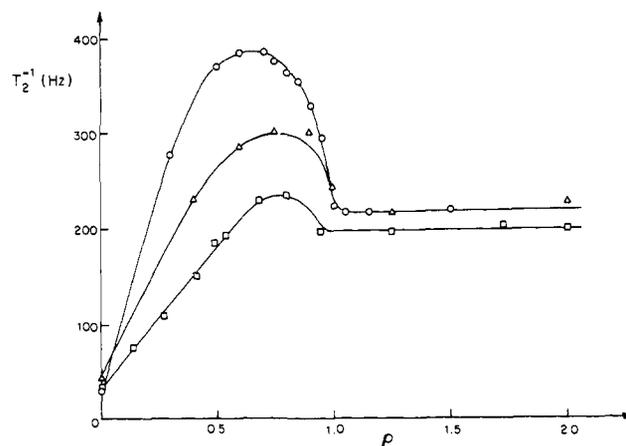


Figure 2. Na-23 transverse relaxation rates as a function of the ratio [crown]/[NaBPh_4] (ρ) at 79.35 MHz (O), 52.92 MHz (Δ) and 21.04 MHz (\square) in nitromethane. [NaBPh_4] = 0.0369 M. Temperatures of measurement are 294 K (79.35 MHz and 52.92 MHz) and 297 K (21.04 MHz). All line shapes are Lorentzian.

DB18C6 in methanol,²² Na^+ -2,2,2-cryptand in ethylenediamine²³ or in water, tetrahydrofuran, and pyridine.²⁴ So far, NMR has only been used a few times to study the kinetics of side-chain-bearing crown ethers.²⁵ Chock has determined the thermodynamic and kinetic constants for complexation and decomplexation of the alkali-metal cations by DB30C10 by using temperature-jump relaxation.²⁶ Stopped-flow techniques²⁷⁻²⁹ and ultrasonic absorption³⁰ have also been applied to this problem.

We have decided to study in more detail the system formed by sodium tetrphenylborate and DB24C8 in nitromethane.⁸ The relaxation of the quadrupolar sodium-23 nucleus can be the result of two mechanisms: quadrupolar relaxation and exchange kinetics. Formation of Na^+ /DB24C8 complexes having a stoichiometry of $(n+1)/n$ is not unexpected in a poorly solvating medium such as nitromethane (Gutman Donicity Number, DN = 2.7),³¹ leading to an asymmetrical electrostatic environment for sodium engaged in such complexes and to a high value of the reorientational correlation time.

In the present paper, we separate the effects of chemical exchange and aggregation upon the relaxation times of Na-23 by measuring Na-23 transverse and longitudinal relaxation times. We propose a model of aggregation where $(n+1)/n$ sodium crown complexes are formed ($n < 5$), when the sodium cation is in slight excess with respect to the crown. The next paper³² in this issue focuses on the kinetic NMR study.

Results

Na-23 chemical shifts are shown in Figure 1 for sodium tetrphenylborate dissolved in nitromethane in the presence of

(6) Kaifer, A.; Durst, H. D.; Echegoyen, L.; Dishong, D. M.; Schultz, R. A.; Gokel, G. W. *J. Org. Chem.* **1982**, *47*, 3195-3197.

(7) Pedersen, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 7017-7036.

(8) Bisnaire, M.; Detellier, C.; Nadon, D. *Can. J. Chem.* **1982**, *60*, 3071-3076.

(9) Shamsipur, M.; Popov, A. I. *J. Am. Chem. Soc.* **1979**, *101*, 4051-4055.

(10) (a) Bush, M. A.; Truter, M. R. *J. Chem. Soc., Perkin Trans.* **1972**, *2*, 345-350. (b) Hasek, J.; Hlayata, D.; Huml, K. *Acta Cryst.* **1980**, *B36*, 1782-1785.

(11) Live, D.; Chan, S. I. *J. Am. Chem. Soc.* **1976**, *98*, 3769-3778.

(12) Stöver, H. D. H.; Maurice, L. J.; Delville, A.; Detellier, C. *Polyhedron*, in press.

(13) Hughes, D. L. *J. Chem. Soc., Dalton Trans.* **1975**, 2374-2378.

(14) Mercer, M.; Truter, M. R. *J. Chem. Soc., Dalton Trans.* **1973**, 2469-2473.

(15) Owen, J. P.; Truter, M. R. *J. Chem. Soc., Dalton Trans.* **1979**, 1831-1835.

(16) (a) Detellier, C. In "NMR of Newly Accessible Nuclei"; Laszlo, P., Ed.; Academic Press: New York, 1983; Chapter 5, pp 105-151. (b) Laszlo, P. In "NMR Spectroscopy: New Methods and Applications"; Levy, G. C., Ed.; Wiley: New York, 1982; ACS Symp. Ser. No. 191, pp 63-96. (c) Dechter, J. *J. Progr. Inorg. Chem.* **1982**, *29*, 285-385. (d) Forsen, S.; Lindman, B. *Methods Biochem. Anal.* **1981**, *27*, 289-486.

(17) Gertenbach, P. G.; Popov, A. I. *J. Am. Chem. Soc.* **1975**, *97*, 4738-4744.

(18) Degani, H. *Biophys. Chem.* **1977**, *6*, 345-349.

(19) Neurohr, K. J.; Drakenberg, T.; Forsen, S.; Lilja, H. *J. Magn. Reson.* **1983**, *57*, 460-469.

(20) Shchori, E.; Jagur-Grodzinski, J.; Luz, Z.; Shporer, M. *J. Am. Chem. Soc.* **1971**, *93*, 7133-7138.

(21) Shchori, E.; Jagur-Grodzinski, J.; Shporer, M. *J. Am. Chem. Soc.* **1973**, *95*, 3842-3846.

(22) Shporer, R.; Luz, Z. *J. Am. Chem. Soc.* **1975**, *97*, 665-666.

(23) Ceraso, J. M.; Dye, J. L. *J. Am. Chem. Soc.* **1973**, *95*, 4432-4434.

(24) Ceraso, J. M.; Smith, P. B.; Landers, J. S.; Dye, J. L. *J. Phys. Chem.* **1977**, *81*, 760-766.

(25) Bouquand, J.; Delville, A.; Grandjean, J.; Laszlo, P. *J. Am. Chem. Soc.* **1982**, *104*, 686-691.

(26) Chock, P. B. *Proc. Natl. Acad. Sci. U.S.A.* **1972**, *69*, 1939-1942.

(27) Liesegang, G. W. *J. Am. Chem. Soc.* **1981**, *103*, 953-955.

(28) Balko, B.; Bowen, P.; Berger, R. L.; Anderson, K. *J. Biochem. Biophys. Methods* **1981**, *4*, 1-28.

(29) (a) Cox, B. G.; Firman, P.; Schneider, H. *Inorg. Chim. Acta* **1982**, *64*, L263-L265. (b) Cox, B. G.; Van Truong, N.; Garcia-Rosas, J.; Schneider, H. *J. Phys. Chem.* **1984**, *88*, 996-1001.

(30) (a) Liesegang, G. W.; Farrow, M. M.; Purdie, N.; Eyring, E. M. *J. Am. Chem. Soc.* **1976**, *98*, 6905-6908. (b) Liesegang, G. W.; Farrow, M. M.; Vazquez, F. A.; Purdie, N.; Eyring, E. M. *J. Am. Chem. Soc.* **1977**, *99*, 3240-3243. (c) Rodriguez, L. J.; Liesegang, G. W.; Farrow, M. M.; Purdie, N.; Eyring, E. M. *J. Phys. Chem.* **1978**, *82*, 647-650.

(31) Gutmann, V. "Coordination Chemistry in Non-Aqueous Solvents"; Springer-Verlag: Vienna, 1968.

(32) Delville, A.; Stöver, H. D. H.; Detellier, C. *J. Am. Chem. Soc.*; following paper in this issue.

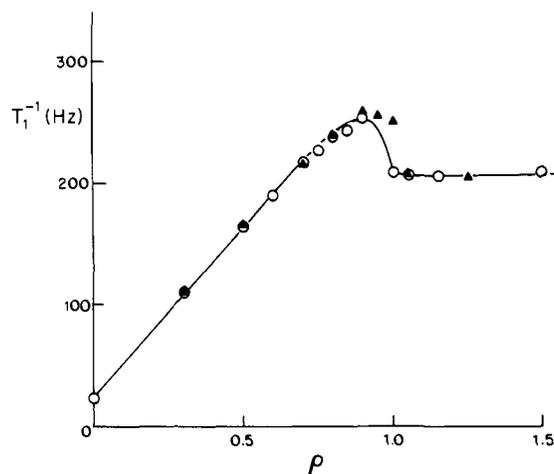


Figure 3. Na-23 longitudinal relaxation rates as a function of ρ at 79.35 MHz (O) and 52.92 MHz (Δ), under the same experimental conditions as Figures 1 and 2. The points are experimental, and the curve is fitted by using the model described by eq 1-8.

DB24C8. The chemical shift behavior is characteristic of strong complexation of the sodium cation by the crown to form a 1:1 complex ($K_f \geq 10^5$).¹¹ The 1:1 complex displays a chemical shift very close to the one observed in other solvents or with other counteranions^{8,9} and is diagnostic of solvent and anion exclusion from the first coordination sphere of the cation. The value of the chemical shift of the complex is in the range of Na-23 chemical shifts in ether solvents.³³ The linearity of the curve in the range [crown]/[Na⁺] (ρ) = 0.0–1.0 suggests the coexistence of only two species: solvated and 1:1 complexed sodium (Figure 1).

On the basis of the chemical shift behavior, one would expect a similar curve for the transverse relaxation rate as a function of the crown/sodium ratio, the observed relaxation rate being the average mean of the characteristic relaxation rates of the solvated and complexed species. However, one observes an increase of the transverse relaxation rate, displaying a maximum at a ratio 0.65 at 79.35 MHz. This maximum could be attributed to a 2:1 sodium/crown species as it was observed in the case of DB30C10.^{9,12} But the maximum is shifted to higher ρ values at lower frequencies, and the observed relaxation rate decreases with decreasing frequencies (Figure 2). The relaxation rates of both solvated and 1:1 complexed sodium do not show any frequency dependence, outside of the homogeneity limits. The frequency-dependent increase of the relaxation rate observed for ρ values between 0 and 1 could be attributed to two relaxation mechanisms: quadrupolar relaxation in nonextreme narrowing conditions for some sodium cations belonging to large chemical species, or chemical-exchange broadening. To test those two possibilities, we have measured the longitudinal relaxation rates as a function of the crown/sodium ratio at 79.35 and 52.92 MHz (Figure 3).

Three main features have to be noted: (a) T_1 is different from T_2 , except for the limiting values (solvated and 1:1 complexed sodium cation). (b) T_1 is frequency-independent. (c) T_1^{-1} displays a maximum at a ratio $\rho = 0.95$ and a plateau for $\rho \geq 1.0$. A catastrophic T_1^{-1} increase is observed when a slight excess of sodium over crown is present.

These results (Figures 2 and 3) can rule out any interpretation based only on nonextreme narrowing conditions for two reasons: (a) The curves observed at one particular frequency for T_2^{-1} and T_1^{-1} are not in phase, which would be the case if the enhancement of the relaxation rates was the result of the presence of some slowly reorienting sodium-containing species.¹⁶ (b) T_1 is independent of the frequency.¹⁶

In order to test for the exchange-broadening contribution, we made a temperature study. The variation of $\ln T_1^{-1}$ and $\ln T_2^{-1}$ as a function of T^{-1} , the inverse of the temperature, is shown in

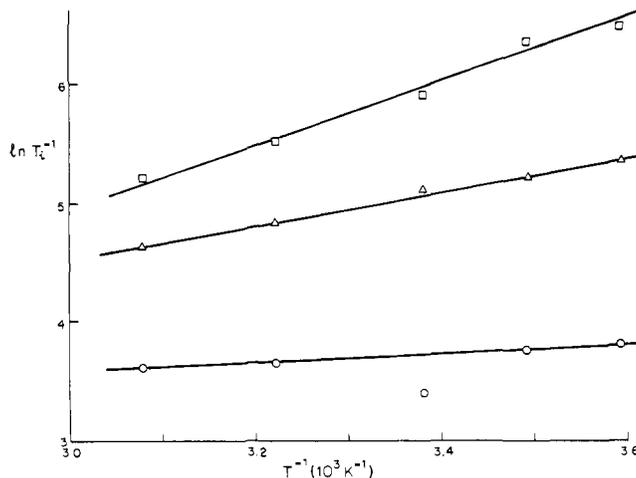


Figure 4. Na-23 transverse (O, \square) and longitudinal (Δ) relaxation rate logarithms as a function of the inverse of the temperature, for [crown]/[sodium] ratios of 0.0 (O) and 0.50 (Δ , \square).

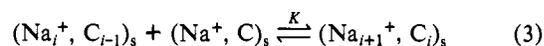
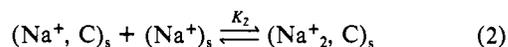
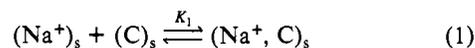
Figure 4 for a particular case ($\rho = 0.50$). The behavior is similar for $\rho = 0.30$ and 0.80.

A linear relationship is observed between $\ln T_1^{-1}$ or $\ln T_2^{-1}$ and T^{-1} . However, the slope of the observed straight line is larger in the case of T_2^{-1} than in the case of T_1^{-1} : a characteristic behavior of moderately rapid exchange.³⁴ We are clearly in the presence of two relaxation mechanisms affecting the transverse relaxation time T_2 : quadrupolar effect and exchange broadening. Because T_1 is unaffected by chemical exchange in the conditions of moderately rapid exchange,³⁵ we can separate the two contributions.³²

For $\rho \geq 1.0$ and $\rho = 0.0$, in the limits of the homogeneity, $T_1 = T_2$. For $0.0 < \rho < 1.0$, the observed T_1 is the average mean of the different contributions from the different species in solution. Figure 3 shows the presence in solution of sodium-containing species other than the solvated and the 1:1 complexed sodium. These species are detected mainly for a slight excess of sodium over crown and plausibly have a $(n + 1)/n$ sodium/crown stoichiometry. Sodium/DB30C10 complexes (2:1 and 3:2) have been shown to exist in nitromethane solution.^{9,12}

Aggregation Model

We use the following model in order to interpret the T_1 data



where the subscript s stands for solvated. $(\text{Na}_2^+, \text{C})_s$ is a nucleating species for further aggregation.

From eq 1-3 and using the power series,³⁶ we obtain

$$[\text{Na}^+]_T = [\text{Na}_s^+] + \frac{X}{K} + \frac{K_2}{K} [\text{Na}_s^+] \left(\frac{1}{(1-X)^2} - 1 \right) \quad (4)$$

$$[\text{C}]_T = [\text{C}_s] + \frac{X}{K} + \frac{K_2}{K} [\text{Na}_s^+] \left(\frac{X}{(1-X)^2} \right) \quad (5)$$

where $X = K_1 K [\text{Na}_s^+] [\text{C}_s]$, and $[\text{Na}^+]_T$ and $[\text{C}]_T$ are the total concentrations, in sodium and crown respectively. A simultaneous

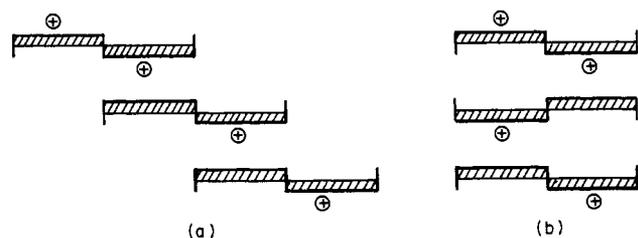
(33) Erlich, R. H.; Roach, E.; Popov, A. I. *J. Am. Chem. Soc.* **1970**, *92*, 4989-4990.

(34) (a) Zdunek, L. Z.; Gold, V. *J. Chem. Soc., Faraday Trans. 2* **1982**, *78*, 1825-1833. (b) Feeney, J.; Batchelor, J. G.; Albrand, J. P.; Roberts, G. C. K. *J. Magn. Reson.* **1979**, *33*, 519-529.

(35) Woessner, D. E.; *J. Chem. Phys.*, (1961), *35*, 41-48.

(36) Poland, D. "Cooperative Equilibria in Physical Biochemistry"; Clarendon Press: Oxford, 1978; pp 35-55.

Scheme I



Newton-Gauss procedure has been used to solve 4 and 5. Under fast-exchange conditions, T_1^{-1} is given by

$$(T_1)^{-1} = \frac{P_F}{T_{1,F}} + \frac{P_C}{T_{1,C}} + \frac{\sum_{i=1}^{\infty} [(Na_{i+1}^+, C_i)_s] (T_{1,i})^{-1}}{[Na^+]_T} \quad (6)$$

where $P_F = [Na_s^+]/[Na^+]_T$; $P_C = [(Na^+, C)_s]/[Na^+]_T$. $T_{1,F}$ and $T_{1,C}$, the longitudinal relaxation rates for solvated and 1:1 complexed sodium, are experimentally determined. $T_{1,i}$ is the contribution from the $(i + 1)$ sodium cations in the $(Na_{i+1}^+, C_i)_s$ species (see below, eq 7). In this aggregate species, we assume

$$\frac{1}{T_{1,i}} = \left[2 \frac{1}{T_{1,OUT}} + (i - 1) \frac{1}{T_{1,IN}} \right] i \quad (7)$$

the coexistence of two types of sodium cations: "outside" and "inside" (Scheme I). Two "outside" sodium cations are coordinated by the crown ether and by solvent molecules and are in a similar environment than sodium belonging to the 2:1 sodium-crown complex. The remaining $(i - 1)$ "inside" sodium cations are sandwiched between two crowns, are not exposed to solvent molecules, and have an ethereal coordination sphere similar to the wrapped 1:1 complex (Scheme I). This model furnishes eq 7 where $1/T_{1,OUT}$ and $1/T_{1,IN}$ are the characteristic relaxation rates of outside and inside sodium for a fictitious complex containing only one crown molecule. The number of crown molecules in the aggregate is i and is assumed in eq 7 to be equal to the ratio of the correlation times of the sodium in the aggregate and in the 1:1 complex, respectively, in order to take into account the effect of the size of the aggregate upon the correlation time. Then, eq 6 reduces to

$$T_1^{-1} = \frac{P_F}{T_{1,F}} + \frac{P_C}{T_{1,C}} + 2 P_F \frac{K_2}{K} \frac{X}{(1-X)^2} \left[\frac{1}{T_{1,OUT}} - \frac{1}{T_{1,IN}} + \frac{1}{T_{1,IN}} \frac{1}{(1-X)} \right] \quad (8)$$

We are dealing with five unknowns: K_1 , K_2 , K , $T_{1,OUT}$, and $T_{1,IN}$. K_1 is taken as equal to 10^6 . For $T_{1,OUT}$ we use the measured value in the case of the 2:1 sodium/DB30C10 complex¹² and for $T_{1,IN}$ the measured value of the 1:1 complex ($T_{1,IN} = T_{1,C}$) (see discussion for the justification of these choices).

The mean size of the aggregate is simply given by

$$\langle SI \rangle = \frac{\sum_i i [Na_{i+1}^+, C_i]}{\sum_i [Na_{i+1}^+, C_i]} = \frac{1}{1-X} \quad (9)$$

The parameter $\langle SI \rangle$ gives the information on the average number of crowns in the aggregate phase.

The fitting of eq 8 on the data set (Figure 3) is executed by a Simplex procedure³⁷ and further checked by a generalized Newton-Gauss procedure.³⁸ Results are summarized in Tables I and II.

Figure 3 shows the experimental points (79.35 and 52.92 MHz) and the fitted curve. $\langle SI \rangle$ varies from 1 to 3.8, showing that the

Table I. Results of the T_1^{-1} Fitting Based on the Model Described by Eq 1-8

$T_{1,F}^{-1},^a$ Hz	$T_{1,C}^{-1},^a$ Hz	$T_{1,OUT}^{-1},^b$ Hz	$T_{1,IN}^{-1},^c$ Hz	K_1^d	K_2^e	K^e
22 ± 1	205 ± 5	1600	205	10^6	0.66 ± 0.06	20.3 ± 0.5

^a Observed values. ^b Taken as a lower estimate of the Na-23 characteristic relaxation rate of the 2:1 sodium/DB30C10 complex.¹² (A variation of 10% on this parameter does not modify the equilibrium constant K , but results in a 10% variation of the K_2 value.) ^c Assumed to be equal to $T_{1,C}^{-1}$ (see Discussion section). ^d K_1 is $\geq 10^5$. Any value higher than that limit gives similar results in the fitting procedure. ^e Values obtained by a Newton-Gauss fitting procedure of the 79.35-MHz results (rms = 5.5 Hz for 13 experimental points).

Table II. Comparison of the Values of T_1^{-1} Observed and Calculated from the Model Described by Eq 1-8

ρ^c	$(T_1^{-1})_{\text{obs}},^a$ Hz	$(T_1^{-1})_{\text{calcd}},^b$ Hz	$\langle Si \rangle^d$
2.00	209 ± 5	205	
1.15	205 ± 4	205	
1.05	205 ± 5	205	
1.00	208 ± 5	211	
0.95	253 ± 5	241	3.2
0.90	253 ± 7	251	2.9
0.85	243 ± 5	250	2.6
0.80	236 ± 6	247	2.4
0.75	226 ± 3	231	2.2
0.70	217 ± 10	218	2.0
0.65	204 ± 5	204	1.9
0.60	191 ± 5	190	1.8
0.50	163 ± 4	160	1.6
0.40	135 ± 4	131	1.4
0.30	111 ± 3	103	1.3

^a Observed values. The error is taken as equal to 3σ , σ being the standard deviation given by the nonlinear regression analysis. ^b Calculated values, from the fitting procedure described in the text. ^c $\rho = [\text{crown}]/[\text{sodium}]$. ^d Average size of the aggregate $(n + 1)/n$ sodium/DB24C8 (average number of crown involved in the aggregates).

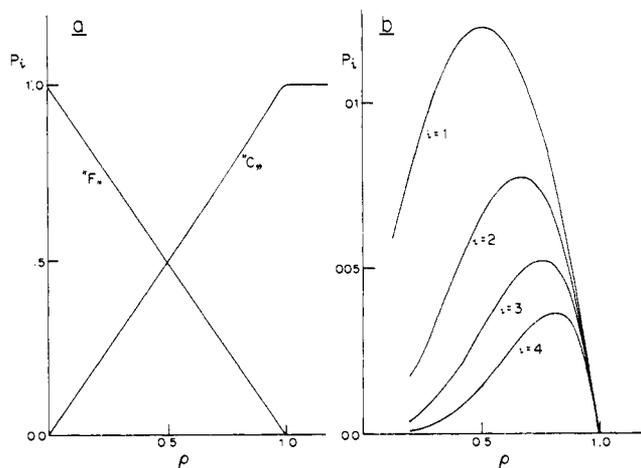


Figure 5. Populations of the different species in solution calculated by following the model described in eq 1-8 as a function of the ratio $\rho = [\text{crown}]/[\text{sodium}]$. (a) Population of free and 1:1 complexed sodium (b) Populations of the species (Na_{i+1}^+, C_i) , for $i = 1-4$.

aggregates are restrained to a size corresponding to Na-23 relaxation rates in the extreme narrowing limits. This conclusion is in agreement with the observation that T_1 is field-independent. Populations of the different species in solution are given in Figure 5. The two major species are $(Na^+)_s$ and $(Na^+, C)_s$. They account for 98% of the total sodium concentration. The remaining 2% is distributed among the aggregated species (Na_{i+1}^+, C_i) , with a maximum contribution from $i = 1$.

Discussion

DB24C8-sodium aggregates can be detected only through longitudinal relaxation rates. Their effect on transverse relaxation

(37) Deming, S. N.; Morgan, S. S. *Anal. Chem.* 1973, 45A, 278-282.

(38) We thank Dr. E. Enwall, University of Oklahoma, for the use of his generalized Newton-Gauss fitting program.

rates is masked by the chemical-exchange contribution to the broadening, and the populations of these species are too minor to produce an observable chemical shift variation.

Under extreme narrowing conditions, the spin- $3/2$ quadrupolar relaxation, responsible for the longitudinal relaxation, is given by¹⁶

$$T_q^{-1} = \frac{2\pi^2}{5} \chi^2 \tau_q \quad (10)$$

where χ is the quadrupolar coupling constant and τ_q the correlation time responsible for the quadrupolar relaxation. Even very low populations of aggregated species will be detectable if they are characterized by a high value of the $\chi^2 \tau_q$ product. The chemical shifts are much less sensitive to the presence of species in small amounts since, conceivably, their characteristic chemical shift will be in the same order of magnitude than the two limiting values (the solvated and the 1:1 complexed sodium).¹⁶ Moreover, when a crowned sodium retains solvent molecules in its first coordination shell, for example in the case of the complex DB18C6-Na⁺, the chemical shift of that complex is intermediate between the chemical shifts of the fully solvated sodium and of the solvent-excluded DB24C8-sodium complex.³⁹

The T_1^{-1} maximum observed for $\rho = 0.95$ is strongly suggestive of $(n+1)/n$ Na⁺/crown complexes and leads us to the model described by eq 1-3. This model is based on several assumptions:

(a) From all the possible stoichiometries, m/n sodium/DB24C8, we have restricted our model to $m = n + 1$. From a visual inspection of Figures 2 and 3, it is obvious that $m > n$. We exclude any species with $m > n + 1$.

(b) K_1 is taken equal to 10^6 . We know from the chemical shifts that $K_1 \geq 10^5$. In the fitting procedures that we used, results were independent of the choice of K_1 , if taken higher than that limit.

(c) The formation constant of $(Na_{i+1}^+, C_i)_s$ (K) is taken equal to the formation constant of $(Na_i^+, C_{i-1})_s$, with $i \geq 2$.

(d) There are two types of sodium cations present: sandwiched (inside) and outside. In order to reduce the number of unknown parameters in the fitting procedure, we have attributed T_1^{-1} values to these species, by analogy with similar complexes. This is a major assumption. However, variations of these parameters do not significantly modify the results of the calculated equilibrium constants.

(e) The aggregated complex reorients as a whole, with a characteristic reorientational correlation time proportional to the number of crown molecules. This is a very plausible assumption based on two facts: the rigid reorientation of the DB24C8-Na⁺ complex itself⁸ and the proportionality of τ_q with the volume of the reorienting species through the Debye-Stokes-Einstein relationship⁸ (the microviscosity coefficient being assumed not to depend upon the number of crown molecules in the complex).

We can visualize the aggregates as it is shown on Scheme I (a or b).

In nitromethane, a poorly solvating medium ($DN = 2.7$), the opening of the DB24C8-sodium complex leading to small amounts of 2:1 complex ($K_2 = 0.66$) permits the further complexation by other crown molecules entering into competition with the solvent

to form sandwich complexes similar to those formed between 12C4 and Na⁺.⁴⁰ The crystallographic structure of the 1:2 DB24C8 complex with sodium *o*-nitrophenolate¹³ shows the partition of the ligand molecule in two distinct and symmetrical regions in which the sodium is hexacoordinated to the bidentate anion and the four ether oxygens. Conformations of the ligand 1,4-dioxane units are close to synclinal (C-C) or antiperiplanar (C-O). We should at this point emphasize the choice of BPh₄⁻ as a counteranion which is known to favor the formation of sandwich complexes (18-crown-6-Cs⁺ systems, for example).^{11,41} No variations of the B-11 NMR chemical shift of the tetraphenylborate counteranion has been detected, showing no formation of solvated and/or crowned ion pair. The structure depicted as b in Scheme I seems the more favorable due to stabilizing stacking interactions between aromatic rings. This aggregate is reminiscent of the polymeric structure found in some ternary "super" complexes,^{1c} or in some covalently designed channel ligands.⁴² It should be considered as a rigid (on the reorientational time scale) stacking of crown (and solvent) separated ion pairs, whose non-covalent structure is defined by conformational controls.⁴³

Experimental Section

Dibenzo-24-crown-8 (Parish Chemical Co. or synthesized following Pedersen's procedure⁷) and sodium tetraphenylborate (Aldrich, 99+%) were vacuum dried (60 °C) over P₂O₅ for at least 4 h prior to use. Nitromethane (Baker, Analyzed) was refluxed over calcium hydride, distilled, and kept under Ar over 4-Å molecular sieves. NMR tubes were tightly capped under argon. All the spectra were recorded within 24 h after preparation of the samples.

Na-23 NMR spectra were obtained at 79.35 MHz (Varian XL-300), 52.92 MHz (Varian XL-200), or 21.04 MHz (Varian FT-80), and B-11 NMR spectra were obtained at 25.52 MHz (Varian FT-80). Na-23 chemical shifts were measured with respect to a 0.1 M NaBPh₄ solution in D₂O. No lock was used on the high-field instruments. Field drift was checked frequently with the reference sample and found to be negligible with respect to the observed line widths. At 21.04 MHz, an external D₂O lock was used. The line shapes were Lorentzian at the three frequencies of observation.

T_1 measurements were done at 79.35 and 52.92 MHz, using the inversion-recovery 180°- τ -90° pulse sequence: 90° pulse widths were 22.5 μ s (79.35 MHz) and 20 μ s (52.92 MHz). At least eight points were used for each determination. T_1 was obtained from a nonlinear regression analysis. Transverse relaxation times, T_2 , were obtained directly from the line width corrected for inhomogeneity.

Acknowledgment. We gratefully acknowledge the Natural Science and Engineering Research Council of Canada (NSERCC) and Research Corp. for financial support. H.D.H.S. acknowledges NSERCC for a postgraduate scholarship and A. D. acknowledges NATO for a travel grant.

(39) Maurice, L.; Detellier, C., unpublished results.

(40) Van Remoortere, F. P.; Boer, F. P. *Inorg. Chem.* **1974**, *13*, 2071-2078.

(41) Popov, A. I. In "Stereodynamics of Molecular Systems"; Sarma, R. H., Ed.; Pergamon Press: New York, pp 197-207.

(42) Lehn, J. M. *Pure Appl. Chem.* **1980**, *52*, 2441-2459.

(43) Coxon, A. C.; Laidler, D. A.; Pettman, R. B.; Stoddart, J. F. *J. Am. Chem. Soc.* **1978**, *100*, 8261-8262.