Kinetic and Equilibrium Studies of the Sodium(I) Cryptates $[Na.C211]^+$ and $[Na.C21C_5]^+$, and the Sodium(I) Diaza Crown Ether Complex $[Na.C21]^+$ in Non-aqueous Solution

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Abstract

To assess the effects of ligand structure and solvent size variation on the stability constants (K) and formation (k_f) and decomplexation (k_d) rate constants of the sodium(I) cryptates, $[Na.C211]^+$ and $[Na.C21C_5]^+$, and the sodium(I) diaza crown ether complex, $[Na.C21]^+$, (all of which possess the fifteen-membered 4,7,13-trioxa-1,10-diazacyclopentadecane ring as a common structural feature) have been studied in dimethylformamide (dmf), diethylformamide (def) and dimethylacetamide (dma) using potentiometric and ^{23}Na NMR methods. For $[Na.C211]^+$, $[Na.C21C_5]^+$ and $[Na.C21]^+$ $\log K$ ($dm^3\ mol^{-1}$) at 298.2 K = 5.20, 2.87 and 2.10 in dmf; 5.10, 2.52 and 3.19 in def; and 4.74, 2.05 and 2.88 in dma respectively. For $[Na.C211]^+$ k_f ($dm^3\ mol^{-1}\ s^{-1}$) and k_d (s^{-1}) at 298.2 K = 1.92×10^6 and 12.1; 2.29×10^6 and 18.2; and 2.49×10^6 and 45.2 in dmf, def and dma respectively. For $[Na.C21C_5]^+$ in dmf $k_f = 2.14 \times 10^7\ dm^3\ mol^{-1}\ s^{-1}$ and $k_d = 2.88 \times 10^4\ s^{-1}$ at 298.2 K, but the exchange process is too rapid to come into the NMR timescale in the other two solvents, as is also the case for $[Na.C21]^+$ in all three solvents. These results demonstrate the dominant effect of the fourth oxygen donor atom in C211 in greatly increasing the stability and decreasing the lability of $[Na.C211]^+$ by comparison with those of $[Na.C21C_5]^+$ and $[Na.C21]^+$. The variation in the molecular size of dmf, def and dma, which are of similar electron donating strength, has little effect on the stability and lability of the sodium(I) complexes studied.

Introduction

The complexation of alkali metal ions by polyoxadiazabicycloalkane ligands, or cryptands [1–9], and by polyoxacycloalkanes, or crown ethers [10–14], has been the subject of numerous studies. A major objective of these studies has been the determination of the factors controlling complex stability and lability, which are reflected in the magnitudes of the stability constant, K, and formation and decomplexation rate constants, k_f and k_d, respectively in the generalised reaction

$$Na^+ + L \underset{k_d}{\overset{k_f}{\rightleftharpoons}} [Na.L]^+ \qquad (k_f/k_d = K) \qquad (1)$$

for the formation of a sodium(I) cryptate or crown ether complex where L represents a cryptand or a crown ether respectively. In this study L represents the cryptands 4,7,13,18-tetraoxa-1,10-diazabicyclo-[8.5.5.]eicosane (C211) and 4,7,13-trioxa-1,10-diazabicyclo[8.5.5]eicosane ($C21C_5$), and also the diaza crown ether 4,7,13-trioxa-1,10-diazacyclopentadecane (C21) shown in Fig. 1, all of which possess the same fifteen-membered ring containing three ether oxygen and two amine nitrogen atoms. However, in the case of C211 and $C21C_5$ the two nitrogens are linked by $-CH_2CH_2OCH_2CH_2-$ and $-(CH_2)_5-$ respectively to form a second ring, while monocyclic C21 has no such linkage. These differences facilitate an assessment of the effect of a systematic variation of ligand structure on sodium(I) complex stability and lability. The study has been carried out in three solvents of similar type: dimethylformamide (dmf), diethylformamide (def) and dimethylacetamide (dma), which have similar electron donating abilities as expressed through their Gutmann donor numbers (D_N) [15] of 26.6, 30.9 and 27.8, respectively, but which have significantly different molecular shapes and sizes. It has previously been shown that these differences produce marked variations in the solvent lability and stoichiometries of solvated cobalt(II) and nickel(II) [16]. It is therefore of interest to examine the

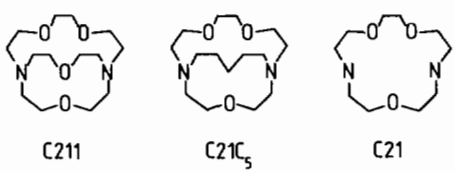

Fig. 1. Structures of the ligands C211, $C21C_5$ and C21.

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effect of the variation of these solvent characteristics on the complexation of sodium(I) by C211, $C21C_5$ and C21.

Experimental

Materials

The ligands C211 and C21 were distilled and dried commercial products (Merck), and $C21C_5$ was prepared as previously described [6]. The solvents dmf, def and dma (Fluka) were distilled and dried over Linde 4A molecular sieves under dry nitrogen. Their water content was <100 ppm. Sodium perchlorate (Fluka) was dried at 353–363 K under vacuum for 48 h and was stored over P_2O_5 under vacuum. Tetraethylammonium chloride (BDH) was converted to tetraethylammonium perchlorate through ion exchange of chloride on Amberlite IRA-400 resin in the hydroxide form followed by precipitation of the perchlorate with perchloric acid. This was followed by two recrystallisations from water, and vacuum drying at 335 K for 24 h to produce anhydrous tetraethylammonium perchlorate which was stored over P_2O_5 under vacuum.

Stability Constant Determinations

Stability constants were determined potentiometrically in duplicate using a Radiometer G502 specific sodium ion electrode and an Orion Research 701A digital analyser. Titrations of 25 cm^3 10^{-3} mol dm^{-3} $NaClO_4$ solutions with 10^{-2} mol dm^{-3} ligand solutions, both of which were 0.05 mol dm^{-3} in tetraethylammonium perchlorate, were carried out in a water-jacketed Princeton Applied Research vessel at 298.2 ± 0.02 K under a dry nitrogen stream which both stirred the titration solutions and prevented the ingress of moisture. The reproducibility of the stability constant determinations was ±5%.

NMR Kinetic Measurements

All ^{23}Na NMR spectra were run on a Bruker CXP-300 spectrometer at 79.39 MHz except those of the $[Na.C211]^+$ system which were run on a Bruker HX-90E spectrometer at 23.81 MHz. Solutions of $NaClO_4$ and ligand were sealed under vacuum in 7 mm NMR tubes which were coaxially mounted in 10 mm NMR tubes containing acetone-d_6 which acted as the lock solvent. For each solution an average of 6000 transients was collected in a 2048 point data base at temperature intervals of ~5 K. Sample temperature was controlled to within ±0.3 K by a Bruker B-VT1000 variable temperature unit. The Fourier transformed spectra were subjected to complete lineshape analysis [17] on a Nicolet BNC12 minicomputer. The ^{23}Na linewidths and chemical shifts and their temperature dependencies employed in the lineshape analyses were obtained through a combination of extrapolation from low temperature where no exchange modification occurred, and the determination of ^{23}Na linewidths and chemical shifts in solutions containing either solvated Na^+ or $[Na.C211]^+$ alone in the coalescence temperature range observed for solutions containing both species.

Results and Discussion

The Na^+ ion is too large (r = 1.02 Å [18]) to fit into the approximately spherical cavities ($r \sim 0.8$ Å [2]) of either C211 or $C21C_5$, and X-ray crystallographic studies show [Na(C211)(NCS)] and [Na($C21C_5$)(NCS)] to be exclusive cryptates in which Na^+ resides on the face of the fifteen-membered ring containing three ether oxygen and two amine nitrogen atoms, which are bound to sodium(I) [7]. The sixth sodium(I) coordination site is occupied by thiocyanate in each case. There is no published X-ray crystallographic study of [Na(C21)-NCS], but it has been shown for the potassium(I) analogue that potassium(I) is sited centrally above C21 (to which it is bound through three ether oxygens and two amine nitrogens) which exhibits a puckered planar conformation [14]. Potassium(I) is also coordinated to a thiocyanate nitrogen and an oxygen of a second C21 ligand. In the case of dilute solutions of the perchlorate salts of the sodium(I) complexes discussed herein a substantial degree of perchlorate coordination is unlikely, but coordination of solvent probably produces cations of stoichiometry: $[Na.C211(solvent)_n]^+$, $[Na.C21C_5\text{-}(solvent)_n]^+$ and $[Na.C21(solvent)_n]^+$ (where $n \leqslant 2$) in which the interaction between sodium(I) and the cryptands and diaza crown ether is similar to that observed in the solid state structures discussed above. As the precise stoichiometry of these cations and the solvated sodium(I) cation is not known with respect to solvent, however, solvent is omitted from their formulae in subsequent discussion.

In def and dma solution the exchange of sodium(I) between the cryptate and solvated state is sufficiently slow for the observation of separate ^{23}Na resonances arising from sodium(I) in these two states (Fig. 2). As the rate of exchange of sodium(I) between these environments increases the ^{23}Na resonances broaden and coalesce, and the lifetimes of sodium(I) in the cryptate (τ_c) and solvated (τ_s) environments may be determined through complete lineshape analyses [17] (Fig. 2). The relationship between the sodium(I) exchange rate and these lifetimes is given by

$$k_d = \text{exchange rate}/[Na.L^+] = 1/\tau_c = X_s/\tau_s X_c$$
$$= (k_B T/h) \exp(-\Delta H_d^{\ddagger}/RT + \Delta S_d^{\ddagger}/R) \quad (2)$$

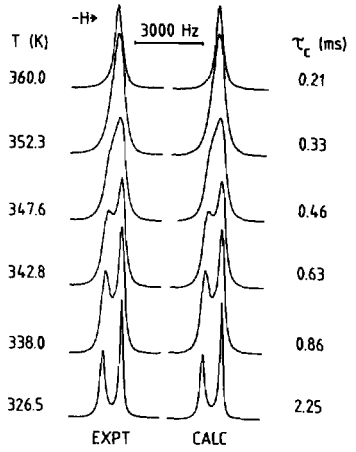

Fig. 2. Typical exchange modified 79.39 MHz ^{23}Na NMR spectra of a dimethylacetamide solution of $NaClO_4$ (0.111 mol dm^{-3}) and C211 (0.052 mol dm^{-3}). Experimental temperatures and spectra appear at the left of the figure, and best fit calculated lineshapes and corresponding τ_c values appear to the right. The resonance of $[Na.C211]^+$ appears downfield from that of solvated Na^+.

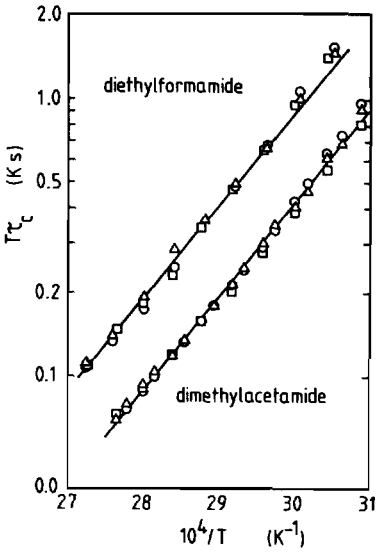

Fig. 3. The temperature variation of $T\tau_c$ for Na^+ exchange on $[Na.C211]^+$. The upper data set is derived from diethylformamide solutions (i)–(iii) whose data points are represented by triangles, squares and circles respectively. The lower data set is derived from dimethylacetamide solutions (iv)–(vi) whose data points are represented by triangles, squares and circles respectively. The solid curves represent the simultaneous best fit of the data derived from each set of three solutions to eqn. (2).

where X_c and X_s are the mole fractions of sodium(I) in the cryptate and solvated environments respectively, and all other symbols have their usual meaning. The semilogarithmic plots of $T\tau_c$ against $1/T$ (derived from complete lineshape analyses similar to those shown in Fig. 2) which appear in Fig. 3 show that in def and dma τ_c is independent of concentration in the ranges shown in Table I. This is consistent with the predominant decomplexation mechanism involving a unimolecular reaction of $[Na.C211]^+$ in the rate determining step, as is also the case in a range of other solvents including dmf. The kinetic parameters derived for the six solutions studied are given in Table I as are the kinetic parameters derived from the τ_c data of the three solutions in the two solvents fitted simultaneously to eqn. (2). At similar concentrations the $[Na.C21]^+$ system is in the fast exchange limit of the ^{23}Na NMR timescale in dmf, def and dma, as is also the case for $[Na.C21C_5]^+$ in the two latter solvents. In dmf the $[Na.C21C_5]^+$ sodium(I) exchange process falls within the NMR timescale (Table II), and is seen to be substantially faster than that of $[Na.C211]^+$.

The stability constants characterising $[Na.C211]^+$ are greater than those characterising $[Na.C21C_5]^+$ and $[Na.C21]^+$ by two orders of magnitude or more (Table II). Clearly the greater stability of $[Na.C211]^+$

TABLE I. Kinetic Parameters[a] for $[Na.C211]^+$ Decomplexation in Diethylformamide and Dimethylacetamide

Solution	$[Na_{solvated}^+]$ (mol dm^{-3})	$[Na.C211^+]$ (mol dm^{-3})	k_d (350.0 K) (s^{-1})	$\Delta H_d^{\ddagger}$ (kJ mol^{-1})	$\Delta S_d^{\ddagger}$ (J K^{-1} mol^{-1})
Diethylformamide					
i	0.068	0.037	1150 ± 40	65.0 ± 2.8	−1.8 ± 7.9
ii	0.051	0.040	1220 ± 40	69.8 ± 2.8	12.3 ± 7.8
iii	0.024	0.069	1190 ± 40	66.7 ± 3.1	3.1 ± 8.5
(i–iii)			1180 ± 30	67.1 ± 1.9	4.4 ± 5.0
Dimethylacetamide					
iv	0.067	0.039	2510 ± 70	64.2 ± 2.0	2.2 ± 5.9
v	0.059	0.052	2580 ± 70	67.2 ± 1.9	11.1 ± 5.4
vi	0.033	0.068	2590 ± 90	62.1 ± 2.6	−3.5 ± 7.2
(iv–vi)			2550 ± 55	64.8 ± 1.5	4.3 ± 4.4

[a]The quoted errors represent two standard deviations for the linear regression fit of each data set to eqn. (2).

TABLE II. Kinetic and Equilibrium Data for the $[Na.C211]^+$, $[Na.C21C_5]^+$ and $[Na.C21]^+$ Systems in Dimethylformamide, Diethylformamide and Dimethylacetamide

System	k_f (298.2 K) ($dm^3\ mol^{-1}\ s^{-1}$)	k_d (298.2 K) (s^{-1})	$\Delta H_d^{\ddagger}$ ($kJ\ mol^{-1}$)	$\Delta S_d^{\ddagger}$ ($J\ K^{-1}\ mol^{-1}$)	log K ($dm^3\ mol^{-1}$) (298.2 K)
Dimethylformamide					
$[Na.C211]^{+a}$	1.92×10^6	12.1	83.5	55.8	5.20
$[Na.C21C_5]^{+b}$	2.14×10^7	2.88×10^4	40.0	−25.3	2.87
$[Na.C21]^+$	fast	fast			2.10
Diethylformamide					
$[Na.C211]^+$	2.29×10^6	18.2	67.1	4.4	5.10
$[Na.C21C_5]^+$	fast	fast			2.52
$[Na.C21]^+$	fast	fast			3.19
Dimethylacetamide					
$[Na.C211]^+$	2.49×10^6	45.2	64.8	4.3	4.74
$[Na.C21C_5]^+$	fast	fast			2.05
$[Na.C21]^+$	fast	fast			2.88

[a]Data from ref. 6. [b]Data from ref. 8.

is a consequence of the presence of the fourth ether oxygen in C211 (see Fig. 1) and its dipolar interaction with sodium(I). The similarity of the stabilities of $[Na.C21C_5]^+$ and $[Na.C21]^+$ indicates that the presence of the $-(CH_2)_5-$ moiety of $C21C_5$ has only a minor influence on the stability of the sodium(I) complex.

It has previously been observed that increase of solvent electron donating power (as indicated by increases in D_N [15]) cause k_d to increase over several orders of magnitude for both $[Na.C211]^+$ and $[Na.C21C_5]^+$, but has little effect on k_f such that the substantial variations observed in K are predominantly a consequence of the variation in k_d [8]. This clearly indicates the involvement of solvent in the rate determining step characterised by k_d. However, in the case of dmf, def and dma, which are of similar electron donating power, their differences in molecular size cause only minor variations in k_d and K for $[Na.C211]^+$. In dmf k_d characterising $[Na.C211]^+$ is ~2000 times less than k_d characterising $[Na.C21C_5]^+$. The small increase in k_d observed for $[Na.C211]^+$ in changing from dmf to def and dma solvents, if proportionately reflected in the k_d values for $[Na.C21C_5]^+$, will place this system in the fast exchange limit of the NMR timescale; and it is reasonable to conclude that the variations in K observed for $[Na.C21C_5]^+$ in def and dma are largely a consequence of variations in k_d, rather than in k_f, by analogy to the $[Na.C211]^+$ system.

The small variation in the lability of $[Na.C211]^+$ in dmf, def and dma (quantified by k_d) contrasts with the several orders of magnitude increase in the lability of the solvent exchange process observed with increase in solvent size in the $[Co(dmf)_6]^{2+}$, $[Co(def)_6]^{2+}$ and $[Co(dma)_6]^{2+}$ systems and the analogous nickel(II) systems [16]. This increase in lability is attributed to increased steric crowding in a *d* activated solvent exchange mechanism. It is also reported that increasing solvent size in the $[Mn(solvent)_6]^{2+}$ system causes a change from an *a* to a *d* activated solvent exchange mechanism [19, 20]. However, in the cases of $[Na.C211]^+$ and $[Na.C21C_5]^+$ it appears that the variations in the molecular size of dmf, def and dma, are insufficient to cause substantial variations in k_d through changes in steric interactions. Nevertheless, major variations in the stability and lability of cryptates have been observed when significant differences in D_N occur as exemplified for $[Na.C21C_5]^+$ in acetonitrile, methanol and dmf where D_N = 14.1, 19.0 and 26.6, k_d (298.2 K) = 8.48×10^1 and 1.80×10^3, and 2.88×10^4 s^{-1}, and log K ($dm^3\ mol^{-1}$) = 5.08, 3.76 and 2.87, respectively [8].

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