

COMPLEXATION OF CRYPTAND-222 AND 18-CROWN-6 WITH SOME ALKALI METAL IONS IN SEVERAL DIOXANE–WATER SOLVENT MIXTURES *

REED M. IZATT ** and GENG WU

Department of Chemistry, Brigham Young University, Provo, UT 84602 (U.S.A.)

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ABSTRACT

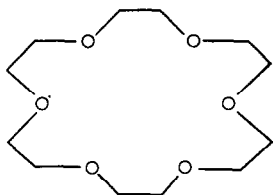
The complexation of cryptand-222 and 18-crown-6 with some alkali metal ions in several dioxane–water solvent mixtures was investigated by a competitive calorimetric titration method. The stabilities of the resulting metal ion complexes in the solvent mixtures are discussed in terms of ligand structural features and preferential solvation properties. The results showed that the macrobicyclic diaza polyether with a three-dimensional cavity has a larger capability than 18-crown-6 to encapsulate ionic species and to screen the interactions between encapsulated cations and solvent molecules. Formation of cryptates was both enthalpy and entropy stabilized, whereas the complexes of 18-crown-6 were only enthalpy stabilized.

INTRODUCTION

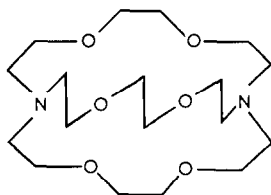
Macrocyclic and macrobicyclic ligands, which either partially or completely encapsulate cations on complexation, offer the possibility to study ionic solvation and the effectiveness of ligands in shielding metal cations from solvents [1–5]. NMR experiments involving cryptates showed an insignificant dependence of the metal resonance frequencies on the solvent involved [6,7], indicating that the metal ion in cryptands was well screened from the solvent. Abraham and Ling [8] studied the free energy and entropy of transfer of M^+-222 and M^+-18C6 from water to methanol. They concluded that the effect of 18C6 (Scheme 1) on modifying the properties of the M^+ cations in the solutions is much nearer to that of cryptand-222 (Scheme 1), than would be expected from the crystal structures of the respective metal complexes. It seems reasonable that, for a complexation reaction taking place in a series of mixed solvent systems, it would be

* Dedicated to Professor James J. Christensen in memory of his contribution to innovation in calorimetry.

** Author to whom correspondence should be addressed.



18-Crown-6 (18C6)



Cryptand-222

Scheme 1

possible to trace the amplified differences of solvation between various ionic species because of preferential solvation. In general, cations will interact preferentially with one of the solvent components in mixed solvents. In most complexed cases, however, preferential solvation of the central cation is less evident unless the ligand involved cannot completely encapsulate the cation.

This study investigated the relative effectiveness of cryptand-222 and 18C6 on shielding metal cations from the solvents in various dioxane–water solvent mixtures. Log K , ΔH and $T\Delta S$ values for the complexation of these macrocycles with K^+ and Na^+ are reported for a series of dioxane–water compositions. The results show that preferential solvation occurs only in the M^+ –18C6 system, supporting the view [6,7] that the shielding ability of cryptand-222 from the solvent is much larger than that of 18C6.

EXPERIMENTAL

Materials

$NaNO_3$ (A.C.S. reagent), KNO_3 (A.C.S. reagent) and dioxane (spectrophotometric grade) were obtained from the Aldrich Chemical Corporation. Cryptand-222 was obtained from Fluka and 18C6 from Parish Chemical Company. Cryptand-222 solutions prepared for the complexation reactions were standardized by calorimetric titration of cryptand-222 with $AgNO_3$.

Procedure and calculations

The procedure used to determine log K , ΔH and ΔS values from calorimetric titration data has been described in refs. 9–11. Limitations inherent in this procedure require that log K lies approximately between the limits of 1.5 and 5 and that sufficient heat be generated in the reaction. The principal reactions for which log K values were determined are given in Table 1 as reactions (1), (4) and (5). Attempts to determine log K and ΔH

TABLE 1

Thermodynamic values for the indicated reactions at 25 °C

Reactions	Dioxane wt. %	Log K^a	ΔH^a (kJ mol ⁻¹)	$T\Delta S$ (kJ mol ⁻¹)
(1) $\text{Na}^+ + 18\text{C6} = \text{Na}^+ - 18\text{C6}$	0	0.80 ^b	-9.4 ^b	-4.8 ^b
	20	1.19	-10.4	-3.6
	35	1.48	-11.2	-2.7
	50	1.78	-11.9	-1.7
	70	2.16	-17.2	-4.8
	100	4.54 ^c	-	-
(2) $\text{Na}^+ - 18\text{C6} + 222$ $= \text{Na}^+ - 222 + 18\text{C6}$	50	4.63	-23.1	-1.8
	70	4.77	-19.4	-7.8
(3) $\text{Na}^+ - 222 + \text{K}^+$ $= \text{Na}^+ + \text{K}^+ - 222$	20	1.90	-17.3	-6.5
	35	2.07	-17.2	-5.4
	50	1.99	-18.2	-5.3
	70	2.41	-18.1	-4.3
(4) $\text{Na}^+ + 222 = \text{Na}^+ - 222$	0	3.90 ^d	-31.0 ^d	-8.7 ^d
	20	4.81	-32.6	-5.1
	35	5.51	-33.8	-2.3
	50	6.41	-35.0	0.1
	70	6.93	-36.6	2.9
(5) $\text{K}^+ + 222 = \text{K}^+ - 222$	0	5.40 ^d	-47.7 ^d	-16.9 ^d
	20	6.71	-49.9	-11.6
	35	7.58	-51.0	-7.7
	50	8.40	-53.2	-5.2
	70	9.34	-54.7	-1.4

^a Each value, except those from the references indicated, is the average of at least three determinations. The uncertainties of log K and ΔH are always less than 0.05 log K unit and 0.4 kJ mol⁻¹, respectively.

^b Values taken from ref. 10.

^c Value taken from ref. 12.

^d Values taken from ref. 13.

values by direct calorimetric titration of the salt into the cryptand failed in the cases of (4) and (5) because the log K values for the reactions were too large. This difficulty was circumvented by using a procedure involving competitive reactions to arrive at the appropriate log K values of the overall reactions, (2) and (3). Log K , ΔH and $T\Delta S$ values for reactions (4) and (5) were then calculated by combination of thermodynamic quantities for appropriate reactions. A computer program (REACTION) was used to handle the calculations of log K and ΔH from the competitive complexation reactions. The heat capacities of the dioxane-water solvent mixtures over the weight percentage range of 0-70% at 25 °C were measured calorimetrically and have the form $C_p = 1.0008 - 0.3995 R - 0.1905 R^2$, where R is the weight percentage of dioxane in pure water and C_p is in cal ml⁻¹ °C⁻¹.

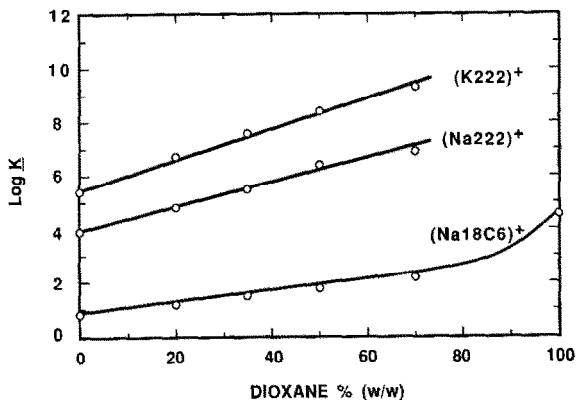


Fig. 1. Plot of $\log K$ versus the wt.% of dioxane in water.

RESULTS AND DISCUSSION

$\log K$, ΔH , and $T\Delta S$ values are listed in Table 1 for the various reactions studied. This table includes values determined by direct calorimetric measurement, those calculated by combining values from other reactions (see previous section) and those from previous references. Direct calorimetric measurements in solvents containing 80% or more dioxane were not possible because of the insufficient solubilities of the metal salts.

As shown in Figs. 1 and 2, the variation of $\log K$ and ΔH with dioxane wt.% is linear for M^+-222 but not for M^+-18C6 interaction. The variation of $\log K$ with dioxane wt.% for Na^+-18C6 interaction, is understood by looking at the variations of ΔH and $T\Delta S$ for Na^+-18C6 interaction. Values of ΔH and $T\Delta S$ for Na^+-18C6 interaction depart from a linear relationship around 50–60 wt.% dioxane as shown in Fig. 2. This departure from linearity provides the evidence of preferential solvation in the case of

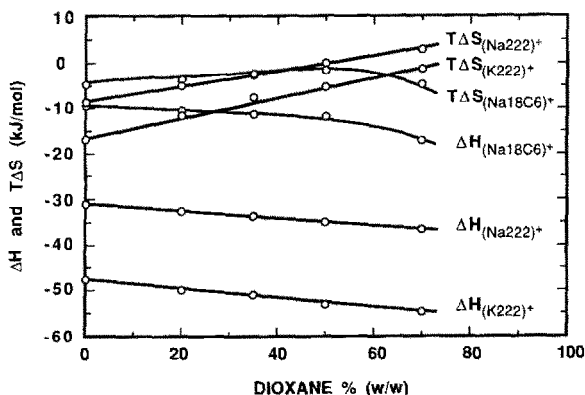


Fig. 2. Plot of ΔH and $T\Delta S$ of complexation values versus the wt.% of dioxane in water.

Na^+ -18C6. On the other hand, below 50–60 wt.% dioxane, the change of $T \Delta S$ with wt.% dioxane for Na^+ -18C6 interaction is much less than that for M^+ -222 interaction. As a result, the $T \Delta S$ term makes much less contribution to the increase of $\log K$ in the case of Na^+ -18C6. However, as dioxane wt.% increases, ΔH and $T \Delta S$ of Na^+ -18C6 become more and more separated, which results in the curving-up of the $\log K$ plot for Na^+ -18C6 above 70 wt.% dioxane. The $\log K$ value of Na^+ -18C6 in pure dioxane solvent [12] supports our argument. In fact, it is expected that the metal ion sites available for solvation in a given solvent will be greater for Na^+ -18C6 than for Na^+ -222. In the complexation of Na^+ with 18C6, the ligand 18C6 is essentially planar [14,15] leaving Na^+ coordination sites exposed above and below the least-squares plane of the ligand. During complexation at a particular dioxane wt.%, the more exposed ionic electrostatic field of Na^+ in Na^+ -18C6 makes this complex more hydrophilic than Na^+ -222. Hence, preferential solvation of Na^+ -18C6 by H_2O over dioxane should occur, as long as there are enough water molecules to compete with the dioxane molecules. As shown in Fig. 1, the $\log K$ values for Na^+ -18C6 interaction change more slowly with wt.% dioxane than those of Na^+ -222 and K^+ -222 until the last 20 or 30% of water is removed from the solvent. The greater effectiveness of water molecules in competing with dioxane molecules for the solvation sites on Na^+ -18C6 is consistent with the greater donation ability of water compared with dioxane molecules [16]. The constant difference between the $\log K$ values over the wt.% dioxane range for K^+ -222 and Na^+ -222 interactions is primarily a result of the difference in the respective ΔH values as shown in Fig. 2. This result also suggests that the constant difference in ΔH reflects the difference in the bond energies of the two complexes.

In conclusion, we believe that more information on solvation properties of ionic species could be obtained, if metal complexation studies were carried out in various solvent mixtures in which different solvent components had different donation properties. If addition of a poor solvent, i.e. dioxane in this case, has little enhancement of complexation, it is evident that preferential solvation occurs. On the other hand, if addition of a poor solvent results in a linear or nearly linear enhancement of complexation with respect to solvent composition, no preferential solvation occurs and the encapsulated ionic species is well shielded from the solvent involved.

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