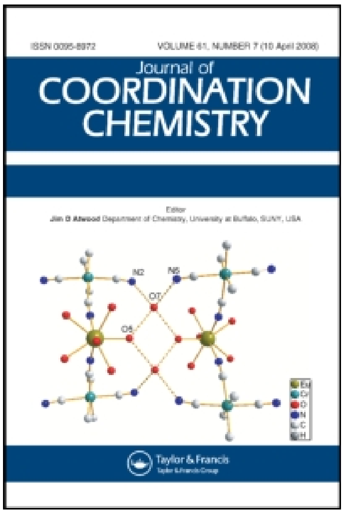

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COMPLEX FORMATION BETWEEN ALKALI AND ALKALINE EARTH CATIONS AND CROWN ETHERS AND CRYPTANDS IN AQUEOUS SOLUTION

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The complexation of alkali and alkaline earth cations in aqueous solution by crown ethers, diaza crown ethers and cryptands has been studied using pH-metric, calorimetric and competitive calorimetric titrations. Use of different experimental techniques makes it possible for the first time to obtain a large number of stability constants and thermodynamic parameters for complexation between these cations and ligands.

Keywords: Cryptands; crown ethers; complexes; stability consants; thermodynamic properties

INTRODUCTION

Stability constants for the complexation of alkali and alkaline earth cations with cryptands were reported for the first time more than 20 years ago.[1] The authors of this article demonstrated that it is possible to form complexes with these cations and the stability constants of the complexes formed may differ by several order of magnitude. In the meantime a large number of articles have been published reporting the complexation of cryptands with a varity of cations in different solvent.[2–3]

However, for a number of cations only upper limits of the stability constants with cryptands in aqueous solution have been reported. In some cases the published values do not agree very well. Therefore we decided to remeasure the stability constants and to estimate reaction enthalpies for complex formation.

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EXPERIMENTAL

The crown ether 18-crown-6 (18C6), the diaza crown ethers (21) and (22) and the cryptands (211), (221) and (222) (all Merck) were used without further purification.The salts $LiNO_3$, $NaClO_4$, $KClO_4$, $RbClO_4$, $CsNO_3$, $Ca(ClO_4)_2$, $Sr(ClO_4)_2$, $Ba(ClO_4)_2$, $(CH_3)_4NClO_4$ and $(CH_3)_4NOH$ were of the highest purity commercially available.

Most stability constants, as indicated in Table I, were measured by pH-metric titrations. A solution of one ligand (1×10^{-2} mol dm^{-3}), one salt (1×10^{-2} mol dm^{-3}) and hydrochloric acid (2.5×10^{-2} mol dm^{-3}) was titrated with a solution of tetramethylammonium hydroxide (3×10^{-2} mol dm^{-3}). The ionic strength was kept constant with tetramethylammonium perchlorate (5×10^{-2} mol dm^{-3}). The pH values were measured using a glass electrode (Metrohm 6.0203.100) with internal reference. Typical titration curves for the cryptand (222) are shown in Figure 1.

TABLE I Stability constants (K in dm^3/mol) and thermodynamic values ΔH and T Δ S (in kJ/mol^{-1}) for the reaction of alkali and earth cations with macrocyclic and macrobicyclic ligands in aqueous solution at 25°C (ionic radii[9], cavity radii[10])

ligand		*18C6*	*21*	*22*	*211*	*221*	*222*
		(r = 1.4Å)	*(r = 0.9Å)*	*(r = 1.4Å)*	*(r = 0.8Å)*	*(r = 1.1Å)*	*(r = 1.4Å)*
cation	*value*						
Li^+	log K	$>1^{a}$	b	b	6.6^{c}	3.4^{c}	b
(r=0.73 Å)					$>5^{a}$		1.9^{a}
							1.5^{d}
	− ΔH				20.2	e	6.4
	T Δ S				17.3		4.4
Na^+	log K	$>1^{a}$	b	b	3.8^{c}	5.4^{c}	4.6^{c}
(r=1.02Å)					3.4^{a}		4.1^{a}
	− ΔH				22.5	27.9	36.1
	T Δ S				−0.9	2.8	−10.0
K^+	log K	2.27^{a}	b	b	2.7^{c}	3.8^{c}	6.0^{c}
(r=1.38Å)					2.5^{a}	4.1^{a}	
	− ΔH	15.4			0.9	36.3	52.3
	T Δ S	−2.5			14.4	−14.7	−18.2
Rb^+	log K	1.79^{a}	b	b	b	3.2^{c}	5.7^{c}
(r=1.49Å)					$<2^{a}$		
	− ΔH	12.3				29.9	51.0
	T Δ S	−2.1				−11.7	−18.6
Cs^+	log K	$>1^{a}$	b	b	b	b	3.3^{c}
(r=1.70Å)					a		3.4^{a}
	− ΔH						2.4
	T Δ S						−16.4
Ca^{2+}	log K	$>1^{a}$	b	b	3.7^{c}	7.7^{c}	5.9^{c}
(r=1.00Å)					3.3^{a}	$>5^{a}$	$>5^{a}$
	− ΔH				6.91	5.3	2.3
	T Δ S				14.1	28.5	31.2

TABLE I *(Continued)*

ligand		*18C6*	*21*	*22*	*211*	*221*	*222*
		(r = 1.4Å)	*(r = 0.9Å)*	*(r = 1.4Å)*	*(r = 0.8Å)*	*(r = 1.lÅ)*	*(r=1.4Å)*
cation	*value*						
Sr^{2+}	log k	2.81^a	[b]	[b]	3.1^c	7.2^c	7.3^c
(r=1.6 Å)					2.6^a	$>5^a$	$>5^a$
	– ΔH	11.9			10.4	28.5	43.4
	T ΔS	4.1			7.2	12.4	–1.9
Ba^{2+}	log K	3.50^a	[b]	[b]	2.6^c	5.8^c	9.5^c
(r=1.36 Å)					2.6^a	$>5^a$	$>5^a$
	– ΔH	–30.7			11.6	31.0	62.8
	T Δ S	–10.8			3.2	2.0	–8.8

[a] Stability constants calculated from calorimetric titrations.
[b] No complex formation observable from pH-metric titrations.
[c] Stability constants calculated from pH-metric titrations.
[d] Stability constant calculated from a competitive calorimetric titration with Na^+
[e] Not possible to calculate from the thermogram.

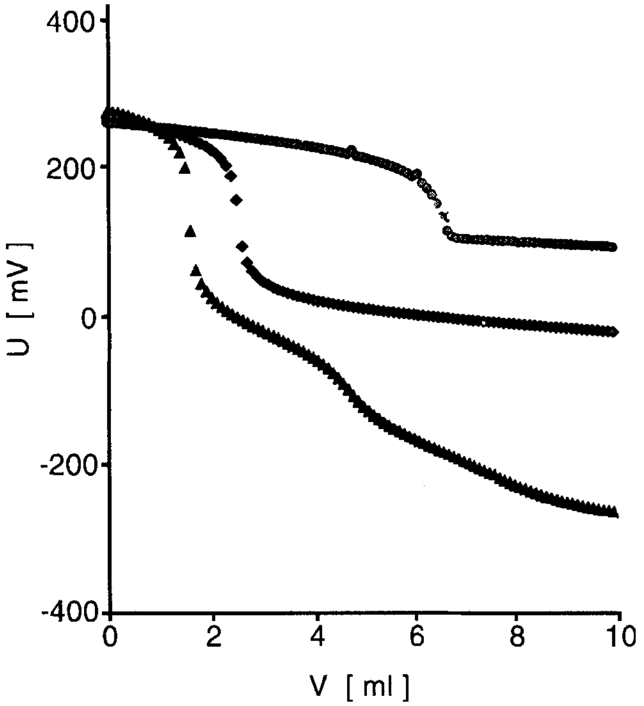

FIGURE 1 Experimental titration curves of aqueous solutions containing a (▲) the cryptand (222) (1×10^{-2} mol dm^{-3}) and hydrochloric acid (2.5×10^{-2} mol dm^{-3}); b) (◆) the cryptand (222) (1×10^{-2} mol dm^{-3}), hydrochloric acid (2.5×10^{-2} mol dm^{-3}) and $Ca(ClO_4)_2$ (1×10^{-2} mol dm^{-3}); c) (●) the cryptand (222) (1×10^{-2} mol dm^{-3}), hydrochloric acid (2.5×10^{-2} mol dm^{-3}) and $Ba(ClO_4)_2$ ($1 \times$ mol dm^{-3}) with solutions of tetrametylammonium hydroxide (3×10^{-2} mol dm^{-3}) at 25ºC.

The stability constant, K, for complex formation with cations is calculated using the following equation with protonation constants K_1 and K_2 and the total concentrations of the salt, C_M and of the ligand, C_L,

$$K = \frac{1}{\frac{b \cdot C_M}{b \cdot C_L - a \cdot C}} \cdot \frac{b}{c}$$

with

$$a = 1 + K_1[H^+] + K_1K_2[H^+]^2$$
$$b = K_1[H^+] + 2K_1K_2[H^+]^2$$

and

$$c = c_{H+} - c_{OH+} - [H^+] + [OH^-]$$

where C_{H+} is the total concentratin of the acid and the C_{OH-} that of the base. The actual concentration of free protons, [H+], is calculated from the potential measured by means of Nernst's equation and the actual concentration of hydroxy ions $[OH^-]$ is obtained using the ionic product of water under the given experimental conditions. Values of protonation constants used have been published recently.[4]

If the value of the stability constant of the complex formed in solution is smaller than $10^{2.5}$ dm^3 mol^{-1} the expiremental curves for the deprotonation of the ligand in the presence and the absence of a cation are nearly identical. Under these circumstances no stability constants can be calculated from pH-metric titrations. In these cases calometric titrations were performed to measure stability constants.A solution of the ligand (8×10^{-2} mol dm^{-3}) was added continously to a solution of the salt (5×10^{-3} mol dm^{-3}). As solvent a 0.1 mol dm^{-3} solution of tetramethylammonium hydroxide was used to prevent any protonation of the ligands. The heat, Q, produced during the titration depends on the number of moles, Δ n, of the complex formed and the reaction enthalpy, Δ H, after correction for all non-chemical effects, as follows.

$$Q = \Delta n \cdot \Delta H.$$

The number of moles, Δ n, of the complex formed depends on the stability of this complex, so it is possible to calculate both the stability constant and the reaction enthalpy from one thermogram.[5–7] If the stability constant is higher than 10^5 dm^{-3} mol^{-1} only the value of the reaction enthalpy can be caclculated from the thermogram.

During titration of solutions containing $LiClO_4$ with solutions of cryptand (222) only small changes in temperature were observed. As a result the stability constant and the reaction enthalpy calculated from the thermogram may not be very accurate. Thus a competitive calorimetric titratuion was performed, as follows.

$$Na^{+} + (222Li^{+}) \rightleftharpoons (222Na^{+}) + Li^{+}.$$

The calculated stability constant and reaction enthalpy for this cation exchange are log K = 2.62 and $- \Delta H = 38.4$ kJ mol^{-1}. It has been shown previously that potentiometric, calometric and the corresponding competitive titrations give the same results within experimentall error.[8]

RESULTS AND DISCUSSION

All experimental results for the complexation of alkali and alkaline earth cations with 18-crown-6, diaza crown ethers and cryptands in aqueous solution are summarized in Table I. From the cations examined, only K^{+}, Rb^{+}, Sr^{2+} and Ba^{2+} form complexes with the crown ether 18C6. The replacement of two oxygen donor atoms of the crown ether by nitrogen donor atoms results in a complete loss of complexing properties of this ligand towards alkali and alkaline earth cations. Differences between the ring sizes of the diaza crown ethers (21) and (22) show no influence upon the ability of these ligands to form complexes with the examined cations. The ability to complex hard cations such as alkali and alkaline earth cations is influenced by the donor atoms of the ligands. Ether donor atoms are known to be hard and nitrogen donor atoms to be soft.

In contrast the macrobicyclic cryptands are able to complex most alkali and alkaline earth cations in aqueous solution. Agreement between ionic radii and cavity radii of the ligands plays an important role for the stability of complexes formed. If the dimensions of the cations and cryptands are comparable the most stable complexes are formed, even if the cavity of the ligand is larger than the cation raduis. However, complexes also are formed when a mis-match in size is evident.

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