

The Association Constant of Macrocyclic Ether–Cation Interactions in 1,4-Dioxane/Water mixtures. III [1]

Effect of Temperature on the Binding

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Abstract. The association constant, K_a of Na^+ with [12]crown-4, [15]crown-5 and [18]crown-6 crown ethers were determined in a binary mixture, 1,4-dioxane/water (50/50) using a Na^+ ion selective electrode at different temperatures. K_a values were determined with the relationship, $1/K_a [\text{L}_o]^{n+m-1} = (1-nP)^n (1-mP)^m/P'$, for various stoichio-

metries, (n:m), where P' is the mole fraction of the complexed cation. The exothermic association constants and the thermodynamic data for cation–macrocycle complexes explained in terms of Eigen-Winkler binding mechanism are given. The binding power found for Na^+ , however, was the highest with [18] crown-6.

The cation association of the macrocycles influenced by the mother solvent have been widely investigated [2–5]. Our study deals with Na^+ association constants of [12]crown-4, [15]crown-5, and [18]crown-6 in dioxane/water mixtures at different temperatures using potentiometry. The binary mother solvent mixture was chosen to enhance the macrocycle–cation interaction power [1, 6]. We recently developed a formalism for the calculation of association constants K_a , see Eqs. 1–4. In this expressions, $[\text{L}]$ is the free macrocycle ligand, and $[\text{A}^+]$ is the free ion concentration with the complexed cation concentration, $[\text{A}_n^+ \text{L}_m]$ of m:n ligand/cation ratio of a complex. However, the identical initial cation and ligand concentrations, $[\text{L}_o] = [\text{A}^+_o]$ are used in the solution, then Eqs. 1–4 are established. The mole fraction of a complexed ligand, $P = [\text{A}_n^+ \text{L}_m] / \{[\text{L}] + [\text{A}_n^+ \text{L}_m]\}$ and $P' = P / [1 + (m-1)P]$ would be used in mole balance relationships in Eqs. 1,2 to obtain the simple expressions, Eqs. 3,4 [5–8].



$$K = [\text{A}_n^+ \text{L}_m] / [\text{A}^+]^n [\text{L}]^m \quad (2)$$

$$1 / \{K_a [\text{L}_o]^{n+m-1}\} = (1-nP)^n (1-mP)^m / P' \quad (3)$$

$$1 / \{K_a [\text{L}_o]\} = (1-P')^2 / P' \quad (\text{if } n=1, m=1 \text{ and } P=P') \quad (4)$$

The inverse of initial cation concentration plotted versus $(1-nP)^n (1-mP)^m / P'$ give the association constant, K_a , from the inverse of the slope. The calculations by using the least squares method give the association constants quite precisely, Figs. 1, 2 [5–8].

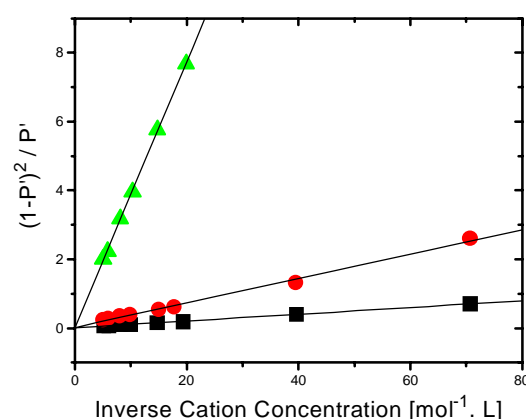


Fig. 1 Plots of $(1-P')^2/P'$ versus inverse initial Na^+ concentration for the 1:1 association constants of [12]crown-4 (\blacktriangle), [15]crown-5 (\bullet) and [18]crown-6 (\blacksquare) at 10 °C, Eq 4, Table 2.

We now present the determination of association constants, K_a of Na^+ ion with the [12]crown-4, [15]crown-5 and [18]crown-6 in the dioxane/water (50/50) binary mixture using a sodium ISE at different temperatures. The thermodynamic data of the cation interactions with macrocyclic oxygen dipoles are discussed mainly in terms of two mechanisms, so-called associative and dissociative interactions [2, 3]. However, our results are better explained in terms of Eigen-Winkler mechanism related to the thermal data for different ratios (n:m) of cation–macrocycle complexes. The binding power of the ion–dipole interactions primarily depended on the oxy-

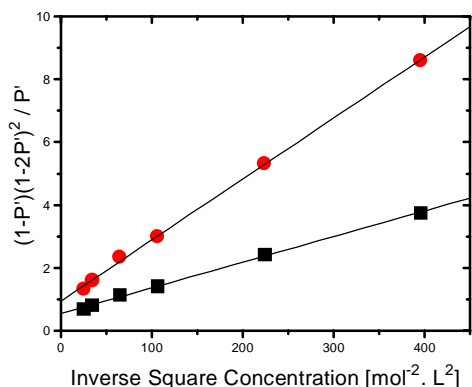


Fig. 2 Plots of $(1-P')(1-2P')^2/P'$ versus inverse square initial Na^+ concentration for the 1:2 (●) and 2:1 (■) association constants of [12]crown-4 at 10 °C, Eq. 3, Table 3.

gen number as well as the molecular conformations of a crown ether due to ligand-ion exchange but the mother solvent may influence the ligand selectivity. The coordination tendency of the alkali or alkaline earth cation and counter ion is also important to originate the different stoichiometry of complexes.

Experimental

The chemicals and macrocyclic ethers from FLUKA were used without further purification. 1,4-Dioxane was purified over metallic sodium and mixed with deionized water 50:50 (v/v). Solutions of the free cation and of equivalent amounts of the cation and the macrocycle were prepared in volumetric flasks and placed into a thermostated cell equipped with a combined Na^+ ISE from ORION (model ROSS). The mV values were measured, (± 0.05 mV) with an ORION millivolt meter (model 920 A) in a thermostated bath [6,7]. K_a values were obtained from Eqs. 1–4 with the minimum correlation coefficient, Table 1, Figs. 1, 2 [9–11].

Results and Discussion

Table 4 displays the thermodynamic results of Na^+ binding with [12]crown-4, [15]crown-5 and [18]crown-6 in dioxane/water (50/50) using Eq. 4 obtained at different temperatures, Eq. 5.

Table 1 Potentiometric 1:1 complex parameters of [18]crown-6/ Na^+ in dioxane/water (10 °C)

Conc. ^{a)}	mV ^{b)}	mV ^{c)}	Conc. ⁻¹⁾	P ^{d)}	$(1-P)^2/P$ ^{e)}	$(1-P)^2/P$ ^{f)}	Error
.193	−54.06	−86.03	5.17	.787	.0573	.0626	−.005
.167	−57.25	−89.00	6.03	.782	.0604	.0679	−.007
.126	−63.05	−92.94	7.96	.756	.0787	.0800	−.001
.100	−67.65	−95.94	9.93	.743	.0887	.0923	−.004
.068	−75.85	−100.90	14.73	.699	.1286	.1222	−.006
.050	−82.04	−104.99	19.83	.668	.1649	.1540	−.011
.012	−111.10	−125.10	80.13	.489	.5312	.5298	−.002
.005	−130.39	−139.00	202.46	.339	1.2904	1.2922	−.001

^{a)} Concentration of the [18]crown-6/ NaCl solutions (mol L^{-1}); ^{b)} mV of NaCl solutions; ^{c)} mV of complex solutions; ^{d)} Mole fraction of complexed ligand; ^{e)} Experimental values; ^{f)} Calculated values

$$\ln K_a = -\Delta H^\ddagger/RT + \Delta S^\ddagger/R \quad (5)$$

The K_a values were obtained as the slopes of the straight lines in Fig. 1 and 2; they exhibit the cation selectivity which, although, fairly depended on the type of ISE. We used 50%/50% of dioxane/water, and no higher ratios of dioxane were used to keep almost a constant junction potential for the electrodes.

The higher stoichiometries of the ligand and the cation interactions involved larger free energies, ΔG , although, similar enthalpy–entropy compensations are involved [9–12]. This is also observed in our ^{13}C -NMR dipole-dipole relaxation rate studies for the determination of stability of macrocycle-cation complexes, [5] showing that the results originated from the mechanism of cation–macrocycle interactions depend on the cation radii, solvent and the structures [2, 3, 9].

On the other hand, the results emphasized the role of solvent dioxane/water, and K_a were higher compared to results obtained in pure water [7]. However, the temperature effect particularly the existing preferred complexed, like solvent separated, ion pairs due to exothermic equilibrium of the thermodynamically distinct species [13, 15]. The results displayed also the performance of ISE.

Accordingly, the results particularly showed that the selectivity and the mechanisms of cation–macrocycle interactions are primarily solvent dependent as discussed by Izatt *et al.* [2]. This is strongly supported by our studies on ^{13}C NMR dipole–dipole relaxation time [5], conductometry [1] and fluorescence spectroscopy [8].

The 1:1 complexing selectivity of Na^+ with the three macrocycles was found in the order of [18]crown-6 > [15]crown-5 > [12]crown-4. However, the Eigen-Winkler mechanism [2, 3] supported by NMR results is the best to explain the observations regarding a dissociative reaction among the distinct species, Table 4 [13, 15]. The associative exchange processes, although, are likely to proceed simultaneously, as given in Eq. 6, which is also related to a conformational route of a macrocycle [1]. In most cases the equilibrium rate constant k_{-1} is larger than k_1 but the ratio of the association rates, k_a/k_{-1} , which are depended on the solvent, ligand conformation and counter ion caused a complicated equilibrium, Eq. 6.

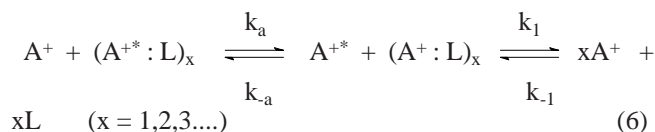


Table 2 Na⁺ association constants, K_a (1:1) of macrocycles in dioxane/water at different temperatures

Crown Ether	temp. (°C)	$\ln K_a$	$\log K_a$	ΔG^θ (kJ·mol ⁻¹)	corr. coef.	y-intercept
[12]crown-4	10	1.43	0.62	-3.35	0.998	-0.039
[15]crown-5	10	4.05	1.76	-9.49	0.999	0.029
[18]crown-6	10	5.08	2.21	-11.90	0.999	0.030
[12]crown-4	20	1.17	0.51	-2.84	0.992	0.029
[15]crown-5	20	3.69	1.60	-8.95	0.999	0.013
[18]crown-6	20	4.62	2.00	-11.20	0.999	0.007
[12]crown-4	40	0.96	0.42	-2.49	0.999	0.032
[15]crown-5	40	3.45	1.49	-8.94	0.999	0.064
[18]crown-6	40	4.34	1.88	-11.24	0.999	0.042

Table 3 Association constants of Na⁺/[12]crown-4 for different stoichiometries (n:m)

temp. (°C)	ratio	$\ln K_a$	$\log K_a$	$-\Delta G^\theta$ (kJ mol ⁻¹)	corr. coeff	y-intercept
10	1:2	2.11	0.91	4.94	0.997	0.595
10	2:1	1.75	0.76	4.09	0.996	1.126
10	2:2	3.15	1.37	7.38	0.980	1.486
20	1:2	1.97	0.86	4.78	0.997	0.677
20	2:1	1.63	0.71	3.95	0.996	1.357
20	2:2	2.99	1.30	7.25	0.988	1.839
40	1:2	1.87	0.81	4.84	0.990	0.012
40	2:1	1.53	0.66	3.96	0.988	2.521
40	2:2	2.89	1.26	7.49	0.956	3.070

Table 4 Thermodynamic data for the 1:1 (n:m) associations of Na⁺ with macrocycles at 25 °C

Crown Ether	$-\Delta H^\ddagger$ (kJ mol ⁻¹)	ΔS^\ddagger	$T\Delta S^\ddagger$	$-\Delta G^\ddagger$ (kJ mol ⁻¹)	corr. coeff
[12]crown-4	11.11	-27.59	-8.22	2.89	0.976
[15]crown-5	14.04	-16.55	-4.93	9.11	0.962
[18]crown-6	17.24	-19.53	-5.82	11.42	0.955

Table 5 Sodium binding data (trans) earlier reports

Macrocycles	solvent	$-\Delta H^\ddagger$ (kJ mol ⁻¹)	$T\Delta S^\ddagger$	$-\Delta G^\ddagger$ (kJ mol ⁻¹)
[12]crown-4 ^{a)}	methanol	3.00	-1.00	2.00
[15]crown-5 ^{b)}	methanol	5.50	-1.23	4.27
[15]crown-5 ^{c)}	methanol	7.41	-2.21	5.26
[18]crown-6 ^{b)}	methanol	7.50	-1.55	5.98
[18]crown-6 ^{c)}	methanol	8.13	-3.28	5.89

^{a)} Ref [2], pages 12, 18; ^{b)} Ref [17]; ^{c)} Ref [18].

The association constants in dioxane/water are larger compared to those observed in water as expected since the hydration of the host molecules in water is partially broken by 1,4-dioxane molecules in all steps of Eq. 6. However, the dissociation process of consecutive exchanges of the macrocycle-metal interactions along with solvent-metal association are ruling out thermal effects [2, 3, 9].

The smaller size of macrocycles possess lower $\log K_a$ values, and are more likely to exist as stable 2:1 or even higher ratio of ligand/cation complexes in the equilibrium of 1:1 ratio of binding as observed with [12]crown-4 where there is no complete encapsulation [7, 8]. The internal motion of oxyethylene units involved in a complex would effect the binding of a large macrocycle [5]. Therefore, the cation is not completely encapsulated by the macrocycle but may be stabilized by the solvent molecules. It is interesting also to note that K_a mostly found for 1:1 ratio is smaller than the K_a for

1:2 ratio which is even smaller than K_a for 2:2 ratio of complexes as shown from [12]crown-4 data, Fig 2. Mostly the thermodynamics of enthalpy-stabilized complexes exhibit $\Delta H < 0$ and $\Delta S > 0$ or $\Delta H < 0$ and $\Delta S < 0$ values as found in our work, as shown in Table 4, whilst the entropy stabilized binding exhibits $\Delta H > 0$ and $\Delta S > 0$ of a thermal behavior [2]. The overall K_a of the four equilibrium constants in Eq. 6 is mostly governed by rate constants ratio, k_a/k_{-a} exhibiting the effect of the dissociation rate of a complexed macrocycle. We think that the mechanism is best explained with Eq. 6, since we just measure experimentally the total $[A^+]$ in the total equilibrium, Eq. 6 [1-12].

However, our results were comparable with those reported by Buschmann [4] and Reisee *et al.* in methanol [16], which were summarized in Table 5. On the other hand, the largest size of macrocycles like dibenzo[30]crown-10 could arrange the macrocyclic-backbone for encapsulation of the cation like

K⁺, involving the conformational site exchange of the oxyethylene units, which is a rate determining step for the binding kinetics. The cation could be embedded into the macrocycle as a whole being stabilised with oxygen coordination favoring a 1:1 ratio of the complex [5, 7, 14]. This could explain also the results of favoured Na⁺ ion binding with [18]crown-6 in this work.

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