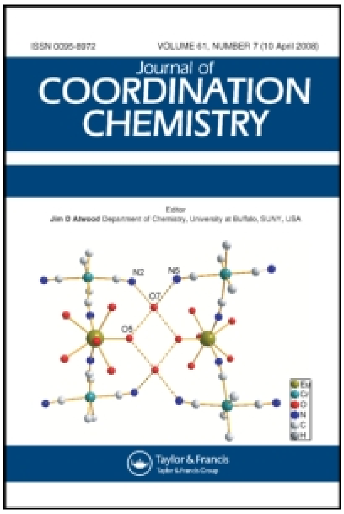

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SOLVENT EFFECTS ON CRYPTAND (222) COMPLEXATION

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The formation of Tl^+, Na^+ and K^+ cryptates with the ligand (222) in 10 nonaqueous solvents has been investigated by cyclic voltammetry at 25°C. Based on the results obtained the dependencies of stability constants of resulting 1 : 1 complexes on Gutmann donor numbers (DN) of the solvents and on standard Gibbs transfer energies of the metal ions from water to given solvent have been analyzed. It was found that DN describe the medium effect far better than the corresponding ΔG_t^o values. It can be deduced, therefore, that the stability constant changes are essentially limited by the cation desolvation free energies, but the residual solvation of the cation encapsulated in the ligand cavity is also important.

Keywords: Cryptands; stability constants; solvent effects

INTRODUCTION

Solvent effects are major factors influencing the stability of macrocyclic complexes. The relationship between standard free energies of solvation, ΔG^o_{solv}, and stability constants, K_s, is described by the following equation:

$$-RT \ln K_s = \Delta G^o_{solv}(ML^+) - \Delta G^o_{solv}(L) - \Delta G^o_{solv}(M^+) \tag{1}$$

in which ML^+, L and M^+ represent complex, ligand and metal ion, respectively. Of the three terms on the right-hand side of (1), the last one determines at least qualitatively the corresponding K_s values and for that reason several attempts have been made to correlate the stability constants with the

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parameters describing cation-solvation ability. Among them, the reciprocal of electric permittivity[1] and the Kirkwood function[2–4] were applied for binary mixtures of organic solvents with water[1–3] and for a series of pure alcohols.[4] On the other hand, some macrocyclic complexes in dipolar aprotic media were reported to show inverse relationships between $\log K_s$ and DN,[5–10] the Gutmann donor number. The existence of such dependencies is not surprising since $\Delta G^{\circ}_{\mathrm{solv}}(\mathrm{M}^+)$ values are almost linearly dependent on DN.[11]

Quite recently, however, Solov'ev *et al.*[12] have suggested the use of standard Gibbs transfer energies $\Delta G^{\circ}_{\mathrm{t}}(\mathrm{M}^+, \mathrm{W} \to \mathrm{S})$ of the metal cation from water (W) to a given solvent (S) as the parameter explaining solvent dependencies of $\log K_s$. From a theoretical point of view, such a proposition is fully justified. This follows from (2) which relates the stability constants in S and W to the free energies of transfer from S to W of the species involved in the complexation equilibrium

$$-RT\ln[K_s(\mathrm{S})/K_s(\mathrm{W})] = \Delta G^{\circ}_{\mathrm{t}}(\mathrm{ML}^+, \mathrm{W} \to \mathrm{S}) - \Delta G^{\circ}_{\mathrm{t}}(\mathrm{L}, \mathrm{W} \to \mathrm{S}) - \Delta G^{\circ}_{\mathrm{t}}(\mathrm{M}^+, \mathrm{W} \to \mathrm{S}). \quad (2)$$

When the complexed cations are shielded from direct interaction with the solvent, the first two terms on the right-hand side of (2) cancel or nearly so (see, *e.g.*, Ref. 13 and references therein), and, therefore (3) results.

$$RT\ln[K_s(\mathrm{S})/K_s(\mathrm{W})] \approx \Delta G^{\circ}_{\mathrm{t}}(\mathrm{M}^+, \mathrm{W} \to \mathrm{S}). \quad (3)$$

Solov'ev *et al.*[12] have correlated the $\log K_s$ values of the complexes formed by some coronands and by cryptand (222) with a range of potentially usable solvent parameters and concluded that just $\Delta G^{\circ}_{\mathrm{t}}(\mathrm{M}^+, \mathrm{W} \to \mathrm{S})$ should be treated as the best one. In contrast, our studies on the complexation of 15-crown-5 and benzo-15-crown-5 and, moreover, reanalysis of the data described[12] for the 18-crown-6-K$^+$ complex led us to the conclusion that more meaningful correlations exist with DN values.[14] We assume that this is connected with the residual solvation of complexed cations, for which the validity of expression (3) may be questioned. Of course, this expression can be anticipated as a much better approximation for cryptates in which the cation size is similar to that of the ligand cavity. Therefore in the present communication we discuss solvent influence on the stability of the complexes formed by cryptand (222) with Tl$^+$, Na$^+$ and K$^+$ cations. The measurements were performed in the solvent set containing protic and aprotic liquids, namely in acetone (AC), tetramethylene sulfone (TMS), formamide (FM), acetonitrile (ACN), *N*,*N*-dimethylacetamide (DMA), *N*-methyl pyrolidinone (NMP), dimethylsulfoxide (DMSO), *N,N*-dimethylformamide (DMF), methanol (MeOH) and ethanol (EtOH). It should be pointed out that the corresponding stability constants were determined earlier in some of these solvents,[15–17] but the results reported for a given medium differ sometimes by even more than one order of magnitude. This led us to measure and/or remeasure the equilibria under well-defined conditions.

EXPERIMENTAL

Commercial cryptand (222) from Merck was used without further purification. $TlClO_4$ was prepared from Tl_2CO_3 and $HClO_4$, recrystallized twice from water and dried under vacuum. TEAP, tetraethylammonium perchlorate, from Merck was recrystallized several times from triply distilled water and dried under reduced pressure at 50°C. $NaClO_4$ and $KClO_4$ (Merck) were high purity samples. AC, ACN, DMF, DMSO, MeOH and EtOH were purchased as Fluka certified chemicals for UV spectroscopy and used without purification. All remaining solvents were dried according to procedures described in the literature[18] and then distilled twice under reduced argon pressure.

Cyclic voltammetric measurements were performed with a PAR 273A potentiostat controlled by an IBM PC AT computer by means of the software M270 from PAR. More detailed information is given in a previous paper.[14] In some cases the stability constants were independently measured *via* potentiometric titration.[19] The values of $\log K_s$ determined voltammetrically and potentiometrically were reproducible to ±0.1 log unit.

RESULTS AND DISCUSSION

In order to determine the stability constants for complexation of sodium and potassium cations with cryptand (222) we have applied a competitive complexation method in the form described by Yee *et al.*[20] At first, thallium(I) ions have been found to undergo reversible or nearly reversible reduction to the metal amalgam both in the absence and in the presence of excess (222) cryptand in all the solvents under study. Furthermore, the variation of the voltammetric "half-wave" potential upon the changes of ligand concentration was found to be in accordance with the Lingane equation for 1 : 1 complexation. Consequently, $\log K_s$ values appropriate for the (222)-Tl^+ complex (Table I) were determined in solutions containing 0.4 mM $TlClO_4$ and 0.1 M TEAP for which ~4–10 mM ligand was successively added.

TABLE I Stability constants ($\log K_s$) of (222) cryptates in various solvents at 25°C; 0.1 M $(C_2H_5)_4ClO_4$ was used as electrolyte

Cation	*Solvent*[a]									
	ACN	*TMS*[b]	*AC*	*DMF*	*DMA*	*NMP*	*DMSO*	*FM*	*MeOH*	*EtOH*[c]
Tl^+	12.3	11.7	10.3	7.8	6.7	6.5	6.2	7.0	10.0	10.7
Na^+	10.8	10.5	9.0	6.1	5.7	5.8	5.4	6.2	7.9	8.6
K^+	11.3	11.3	10.4	8.0	7.9	7.8	7.0	7.9	10.4	10.7

[a]Abbreviations for solvents as in Introduction. [b]At 30°C. [c]Owing to low solubility of $(C_2H_5)_4NClO_4$, 0.1 M tetraethylammonium iodide was used as electrolyte.

Reversible or nearly reversible cyclic voltammetric curves were also observed after progressive addition of 10–40 mM of $NaClO_4$ and $KClO_4$, respectively, to the abovementioned solutions. Thus, applying the formalism discussed in detail,[20] we have calculated the stability constants of (222)-Na^+ and (222)-K^+ complexes which are also collected in Table I. Note that in the calculations we have ignored ion association effects, although in acetone, for example, incomplete dissociation of alkali metal perchlorates is expected.[21] This follows from Buschmann, who argued that if the values of the stability and the ion-pair formation constant differ by at least one order of magnitude the existence of ion pairs does not influence calculated K_s values.[17]

As mentioned above, many results for metal cryptates are available in the literature for comparison.[15,16] It is noteworthy, therefore, that the data presented in Table I for (222)-Na^+ and (222)-K^+ systems in DMF, DMSO, ACN, MeOH and EtOH are generally in excellent agreement with those reported[22] except for (222)-Na^+ in ACN, for which the authors[22] obtained the value of $\log K_s = 9.63$ compared with the present value of $\log K_s = 10.8$. The latter, however, agrees satisfactorily with the values of 10.68[23,24] and 10.9[25] determined in other laboratories.

The results of Table I show the stability constants for the cryptates to be strongly sensitive to solvent variation. To rationalize this observation we have first correlated $\log K_s$ with the corresponding $\Delta G_t^o(M^+, W \rightarrow S)$ values, as proposed.[12] We have extracted necessary Gibbs' energies from the Marcus monograph[26] and the resulting quantities are given in Table II. It is noticeable that the values of $\log K_s$ for (222)-Tl^+, (222)-Na^+ and (222)-K^+ in water (6.4, 4.0 and 5.5, respectively) being also object of interest, are averages of literature data.[15,16,27]

It is concluded that the $\log K_s$ and $\Delta G_t^o(M^+, W \rightarrow S)$ quantities are poorly correlated in the solvents investigated. Moreover, inclusion of water additionally decreases the resulting r and F values. On the other hand, the

TABLE II Parameters of the correlation equation $\log K_s = \alpha \Delta G_t^o(M^+, W \rightarrow S) + \beta$

Cryptate	n^a	α^b	β^b	r^c	F^d
(222)-Tl^+	6^e	0.203 ± 0.087	11.53 ± 1.39	0.886	29.1
	7^f	0.170 ± 0.136	9.26 ± 1.59	0.820	10.3
(222)-Na^+	9^g	0.137 ± 0.098	7.81 ± 1.14	0.781	11.0
	10^f	0.130 ± 0.125	7.41 ± 1.37	0.648	5.8
(222)-K^+	10	0.130 ± 0.078	9.48 ± 0.78	0.807	14.9
	11^f	0.117 ± 0.117	9.06 ± 1.12	0.601	5.1

[a] Number of solvents. [b] Ninety-five percent confidence intervals are given. [c] Correlation coefficient of linear regression. [d] Fisher's statistical test. [e] $\Delta G_t^o(Tl^+, W \rightarrow S)$ values for S = TMS, AC, FM and DMA are not available in Ref. 26. [f] Water is added to the solvent set. [g] $\Delta G_t^o(Na^+, W \rightarrow S)$ value for S = AC is not available in Ref. 26.

correlations are considerably improved when $\Delta G_t^o(M^+, ACN \rightarrow S)$, Gibbs transfer energies, based on the *bis*(biphenyl)chromium assumption[28] are used instead of $\Delta G_t^o(M^+, W \rightarrow S)$. For the (222)$Tl^+$ complex in all 10 solvents tabulated in Table I the following regression:

$$\log K_s = (0.203 \pm 0.087)\Delta G_t^o(Tl^+, ACN \rightarrow S) + (11.53 \pm 1.39) \quad (4)$$

holds with $r = 0.886$ and $F = 29.1$. For comparison, for 6 solvents shown in the first line of Table II the corresponding r and F values are equal to 0.984 and 121.7, respectively. Next, for the (222)-Na^+ and (222)-K^+ cryptates in 9 solvents, except FM for which the appropriate $\Delta G_t^o(M^+, ACN \rightarrow FM)$ quantities are not known,[28] the following correlation equations can be written,

$$\log K_s = (0.126 \pm 0.065)\Delta G_t^o(Na^+, ACN \rightarrow S) + (9.34 \pm 1.21) \quad (5)$$

($r = 0.864$, $F = 20.7$) and

$$\log K_s = (0.170 \pm 0.066)\Delta G_t^o(K^+, ACN \rightarrow S) + (10.59 \pm 0.74) \quad (6)$$

($r = 0.916$, $F = 36.5$), respectively. Unfortunately, *bis*(biphenyl)chromium(0) is practically insoluble in water so that the values of $\Delta G_t^o(M^+, ACN \rightarrow W)$ were never measured. It is obvious, therefore, that the stability constants determined in this solvent cannot be treated in the frame of regressions (4)–(6).

As a subsequent step of analysis we tried to correlate the $\log K_s$ values (Table I) with DN; thus calculated parameters of regressions are shown in Table III. First, the correlations of $\log K_s$ against DN are considerably more meaningful in comparison with those obtained with $\Delta G_t^o(M^+, W \rightarrow S)$ and $\Delta G_t^o(M^+, ACN \rightarrow S)$ as indicative parameters. Secondly, the correlations

TABLE III Parameters of the correlation equation $\log K_s = \alpha \mathrm{DN} + \beta$

Cryptate	*n*	α	β	*r*	*F*
(222)-Tl^+	7[a]	-0.350 ± 0.112	17.04 ± 2.82	0.963	63.7
	10[b]	-0.388 ± 0.087	17.47 ± 1.97	0.964	106.0
	11[c]	-0.346 ± 0.086	16.65 ± 2.06	0.949	81.5
(222)-Na^+	10[b]	-0.345 ± 0.065	15.20 ± 1.47	0.974	150.1
	11[c]	-0.341 ± 0.051	15.11 ± 1.22	0.980	222.0
(222)-K^+	10[b]	-0.282 ± 0.061	15.48 ± 1.38	0.967	114.0
	11[c]	-0.299 ± 0.052	15.80 ± 1.25	0.974	165.6

[a]The same solvent set as in the second line of Table II. [b]All the solvents studied in this work. [c]Water is included in the solvent set.

are statistically significant after inclusion of water. We assume, however, that one important question should be clarified; this concerns the DN of protic liquids. Although the solvents have DN values defined for their isolated molecules in 1,2-dichloroethane, the corresponding $\mathrm{DN_{bulk}}$ (bulk donicities) are also explored. It is well known that particularly glaring discrepancies exist between DN and $\mathrm{DN_{bulk}}$ for highly structured protic solvents, such as water, alcohols and formamide; in these cases arbitrary choice of appropriate values decides whether or not the correlation will be successful. It should be stressed, therefore that the values of 33, 19, 20 and 24 for water, MeOH, EtOH and FM,[11] respectively, served to establish straight lines presented in Table III; other possible values of donicities[29] do not yield linear relationships.

It can be safely concluded that in the solvent set examined the solvent DN describes better the medium effect on the complexation equilibria of the cryptand (222) than does the Gibbs energy of transfer of a metal cation. Since this finding is in contradiction to an essential earlier conclusion,[12] we would like to reconsider some results reported in that paper. Recall that Solv'ev *et al.*[12] have correlated the stability constants of (222) complexes with Li^+, Na^+, K^+ and Ag^+ cations with $\Delta G_t^o(M^+, W \rightarrow S)$. Using tabulated $\log K_s$ values[22] they have found the regressions characterized by correlation coefficients and Fisher's statistical test given in the first three lines of Table IV. The results of our computations, in which the corresponding DN values served as the explaining parameters, are presented for comparison. Also, taking into account the $\log K_s$ values for the complexes (222)-Rb^+ and (222)-Cs^+[22] we have correlated them both with $\Delta G_t^o(M^+, W \rightarrow S)$ and DN. Note that the abovementioned systems were not considered by Solov'ev *et al.*[12]

As can readily be seen from Table IV, more meaningful correlations exist with DN for all the complexes under consideration, except for the lithium cryptate for which the solvent set is small. It is also quite evident that after

TABLE IV Statistical characteristics of linear regressions $\log K_s = \alpha P + \beta$

Cryptand	*n*	$P = \Delta G_t^o(M^+, W \to S)$		$P = DN$	
$(222)\text{-}Li^+$	4^a	$r = 0.999^d$	$F = 793.5^d$	$r = 0.954$	$F = 20.2$
$(222)\text{-}Na^+$	7^b	$r = 0.937^d$	$F = 35.7^d$	$r = 0.984$	$F = 153.0$
$(222)\text{-}K^+$	7^b	$r = 0.914^d$	$F = 25.3^d$	$r = 0.951$	$F = 47.0$
$(222)\text{-}Rb^+$	7^b	$r = 0.802$	$F = 9.0$	$r = 0.902$	$F = 21.8$
$(222)\text{-}Cs^+$	7^b	$r = 0.672$	$F = 4.1$	$r = 0.934$	$F = 34.1$
$(222)\text{-}Li^+$	5^c	$r = 0.996$	$F = 407.5$	$r = 0.944$	$F = 24.4$
$(222)\text{-}Na^+$	8^c	$r = 0.876$	$F = 19.9$	$r = 0.988$	$F = 246.0$
$(222)\text{-}K^+$	8^c	$r = 0.767$	$F = 2.6$	$r = 0.953$	$F = 59.8$
$(222)\text{-}Rb^+$	8^c	$r = 0.620$	$F = 3.8$	$r = 0.916$	$F = 31.1$
$(222)\text{-}Cs^+$	8^c	$r = 0.577$	$F = 3.0$	$r = 0.952$	$F = 57.6$

[a] Solvent set: MeOH, PC, ACN, nitromethane (NM). [b] Solvent set: MeOH, EtOH, PC, ACN, DMF, DMSO, NM. [c] Water is added to the solvent set. [d] Statistical characteristics given in Ref. 12.

the addition of water these correlations remain valid, which is in full accordance with the results reported in the present paper. In this context the (222)-Ag^+ cryptate needs additional comment. According to a report,[12] its $\log K_s$ values[22] fulfil a linear relationship with $\Delta G_t^o(Ag^+, W \to S)$ which holds with $r = 0.941$ and $F = 35.6$ in 7 solvents, namely in ACN, PC, DMF, DMSO, NM, MeOH and EtOH. Respective correlation with DN is considerably poorer; we have found that it is characterized by $r = 0.794$ and $F = 3.3$ and the most serious deviation is with acetonitrile. It is well known, however, that ACN forms stable complexes with silver(I) cations,[30] but one should not expect a strict reflection of this fact by the DN scale. Consequently, if this deviating value is excluded, the correlation is improved,

$$\log K_s = (-0.385 \pm 0.187)\text{DN} + (19.78 \pm 3.90) \tag{7}$$

with $r = 0.943$ and $F = 32.4$. For the same set of 6 solvents an analogous relationship with $\Delta G_t^o(Ag^+, W \to S)$ can be written as

$$\log K_s = (0.162 \pm 0.087)\Delta G_t^o(Ag^+, W \to S) + (12.64 \pm 1.79) \tag{8}$$

for which $r = 0.932$ and $F = 26.6$. Furthermore, recalculation of regressions (7) and (8) when the solvent set was extended to include water[22] led us to the following equations:

$$\log K_s = (-0.336 \pm 0.134)\text{DN} + (19.22 \pm 3.69) \tag{9}$$

$r = 0.923$, $F = 28.8$, and

$$\log K_s = (0.162 \pm 0.097)\Delta G_t^o(Ag^+, W \to S) + (12.20 \pm 1.83) \tag{10}$$

$r = 0.886$ and $F = 18.3$. Thus, an application of DN seems to be more successful in the description of solvent influence on the complexation of the silver(I) cations by the cryptand (222) as well.

We assume that the collinearity between the values of $\log K_s$ and ΔG_t^o of a given metal cation from the reference solvent to another one should be treated in terms of the energetics of free, *i.e.*, uncomplexed cation desolvation only. On the other hand, the linearity of $\log K_s$ as a function of donicity would be ascribed to the solvent variation of the Gibbs energies of solvation of both the free cation and the cation in complexed form. Hence, from the considerations presented above it can be deduced, in spite of limited evidence, that the solvent effect on the stability constants of the (222) cryptates is not restricted to the solvation of uncomplexed cations, but the residual solvation of the cation encapsulated in the ligand cavity may also be important. Interestingly, the last suggestion is consistent with several thermodynamic measurements which show that the encapsulated ion is not completely shielded from the solvent.[31,32] Proton and ^{13}C NMR studies on (221) Na^+ and K^+ cryptates also demonstrate conformational changes of the ligand as a result of the complexed ion interaction with a solvent.[33] Furthermore, in line with MD modelling it was concluded that in the (222) alkali metal cryptates the cation remains still in contact with water, MeOH[34] and ACN,[35] *i.e.*, with solvents characterized by very different donicities. Thereby the correlations presented in this work seem to gain some physical meaning. However, of the four protic solvents examined, only one (water) was characterized by the bulk donicity. This, of course, is not an enthalpic quantity but includes entropic or structural effects and their approach is still impossible.

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