Complexation Study
of 4,13-Didecyl-1,7,10,16-tetraoxa-4,13-diazacyclooctadecane (Kryptofix 22DD) with the Co^{2+}, Cr^{3+}, Tl^+, and UO_2^{2+} Cations in Acetonitrile, Methanol, and Their Binary Mixtures[1]

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Abstract—Complexation between 4,13-didecyl-1,7,10,16-tetraoxa-4,13-diazacyclooctadecane (kryptofix 22DD) and the Co^{2+}, Cr^{3+}, Tl^+, and UO_2^{2+} cations in acetonitrile, methanol, and their binary mixtures was studied by conductometry at different temperatures. The experimental results showed the formation of 1 : 1 [ML] complexes between the studied metal cations and the macrocyclic ligand in most solvent systems. The stability constants of the resulting 1 : 1 complexes were determined by computer fitting the conductance–mole ratio data. The stability of the metal–ion complexes in pure acetonitrile at 15 and 25°C was found to decrease in the order : $[Tl\ (kryptofix\ 22DD)]^+$ > $[Co(kryptofix\ 22DD)^{2+}]$ > $[UO_2(kryptofix\ 22DD)]^{2+}$. Along with 1 : 1 [ML] complexes, 2 : 1 $[M_2L]$, 2 : 2 $[M_2L_2]$, 2 : 3 $[M_2L_3]$, 1 : 2 $[ML_2]$, and 1 : 3 $[ML_3]$ complexes are likely to be formed in some of the solvent systems. The thermodynamic parameters (ΔS_c^0, ΔH_c^0) of the complex formation in the studied nonaqueous solvents, obtained from the temperature dependences of the stability constants of the complexes, showed that the process is athermic.

Keywords: kryptofix 22DD; Co^{2+}, Cr^{3+}, Tl^+, UO_2^{2+} complexes, nonaqueous solvents, conductometry

INTRODUCTION

Cryptands are an important family of synthetic multidentate ligands. They are commercially available under the tradename Kryptofix. The 3D inner cavity of cryptands provides a binding site for cations to form host–guest complexes called cryptates. Cryptands are more expensive and difficult to prepare, but they offer much better selectivity and strength of binding than other complex-forming agents such as crown ethers [1–4].

The factors responsible for the selectivity of host species in the host–guest interaction include the relative free energy of desolvation of the guest species and the ligand and the free energy of the structural rearrangement of the host molecule to adopt a conformation suitable for binding. It is known that the solvation phenomenon plays the major role in ion selectivity by influencing the stability and nature of host–guest complexes [5].

Solvation of macrocyclic polyethers in various solvent media is a result of competition of solute–solute and solvent–solvent interactions and also depends on the conformational changes of the solute structure in solution. Ion–solvent interactions play a very important role in the stoichiometry, structure, and stability of metal cation complexes in solutions. Knowledge of the solvation properties of the ionophore, metal cation, and even complex enables one to choose a suitable solvent for complexation studies and to obtain detail information on the solvent effect [6]. To control chemical reactions in nonaqueous and mixed solvents, it is necessary to select an appropriate solvent for complex formation [7]. This is a complicated problem because of an exceptionally great variety and specificity of chemical reactions in solutions [5].

For appropriate solvent properties, mixtures of two solvents are often used. The physicochemical properties of mixed solvents are interesting both from the theoretical and practical points of view. Usually mixed solvents do not behave as expected from

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[1] The text was submitted by the authors in English.

statistical considerations; the solvation ability of solvents in their mixtures can be different from that in the neat media [8]. The deviations from ideal behavior are indicative of the extent of preferential solvation and existence of specific solvent–solute and solvent–solvent interactions [6, 9, 10].

Conductometry is a high-precision and inexpensive technique with a simple experimental setting for the determination of formation constants of metal cation complexes, especially in the case of weak or medium-strength interactions at extremely low concentrations in solutions. In principle, by measuring the variation of electrical conductance with the concentration of metal salts and receptors one can determine the selectivity, stoichiometry, stability constant, and thermodynamic characteristics of complex formation and thus gain insight into the nature of interactions taking place in the solution [11–13].

Hexavalent uranium associated with oxygen as uranyl cation (UO_2^{2+}), is the most common uranium ion in aqueous media. Uranyl ion complexes extract readily into organic solvents. This is the basis of a widely used Purex Process for reprocessing spent nuclear reactor fuel reprocessing and weapons production [14].

With the aim to assess the effect of the nature of the solvent system and the temperature on the complexation reactions between kryptofix 22DD and the Co^{2+}, Cr^{3+}, Tl^+, and UO_2^{2+} cations, in the present work we performed a conductometric study of the thermodynamics, stoichiometry, and stability of the complexes formed in these reactions in acetonitrile (MeCN), methanol (MeOH), and MeCN–MeOH binary solvent solutions.
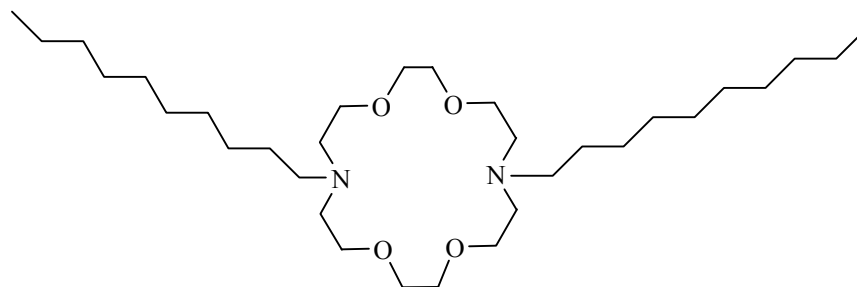
Kryptofix 22DD

EXPERIMENTAL

4,13-didecyl-1,7,10,16-tetraoxa-4,13-diazacyclooctadecane (kryptofix 22DD), $UO_2(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Cr(NO_3)_3$ and $TlNO_3$ were purchased from Merck and used without further purification. The organic solvents (Merck) were of HPLC grade.

The experimental procedure to obtain the formation constant of the 1 : 1 complexes was as follows: 20 mL of a solution of metal salt (1×10^{-4} M) was placed in a titration cell and the conductance of the solution was measured, then the crown ether concentration was increased by addition the crown ether solution in the same solvent (2×10^{-3} M) to the titration cell, using a microburette and the electrical conductance of the resulted solution was measured after each step at the desired temperature.

The conductance measurements were performed on a digital JENWAY conductometer (Model 4510) in a LAUDA water bath with its temperature maintained

within ±0.01°C. The electrolytic conductance was measured using a conductivity cell (cell constant 0.98 cm^{-1}) consisting of two platinum electrodes to which an alternating potential was applied. All experiments were performed under moderate stirring of the solutions. The stability constants of 1 : 1 [ML] complexes were obtained using a GENPLOT computer program [15].

RESULTS AND DISCUSSION

The changes in the molar conductance (Λ_m) as a function of the ligand-to-metal cation mole ratio for the complexation of kryptofix 22DD with the Co^{2+}, Cr^{3+}, Tl^+, and UO_2^{2+} cations in pure acetonitrile and methanol and their binary solvents were studied at different temperatures. The molar conductance vs. $[L]_t/[M]_t$ ratio $[L]_t$ and $[M]_t$ are the total concentration of the ligand and metal cation, respectively) for UO_2^{2+} is presented in Fig. 1. As is seen from Fig. 1, addition of kryptofix 22DD to a solution of UO_2^{2+} cation in pure
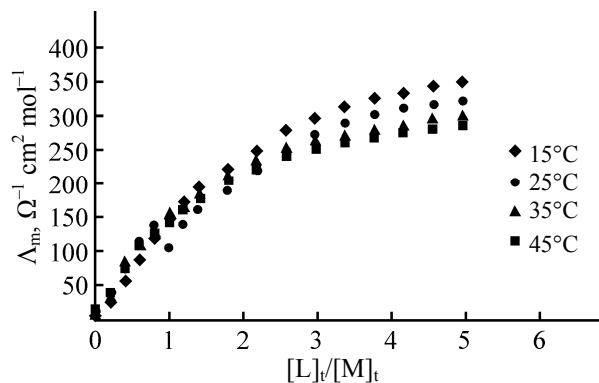
Fig. 1. Plots of molar conductance vs. ligand-to-metal ion molar ratio for the $[UO_2(kryptofix\ 22DD)]^{2+}$ complex in pure MeCN at different temperatures.

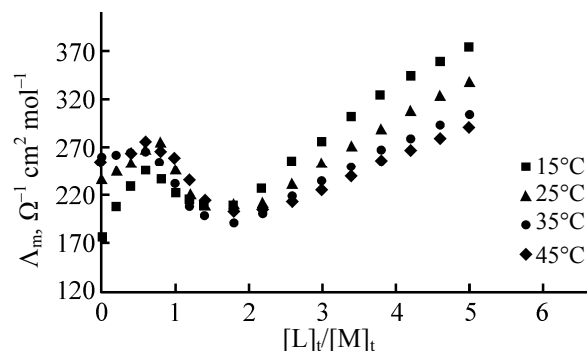**Fig. 2.** Fitting and experimental curves for the $[UO_2(kryptofix\ 22DD)]^{2+}$ complex in pure MeCN at different temperatures.

Fig. 3. Plots of molar conductance vs. ligand-to-metal ion molar ratio for the $([Tl(kryptofix\ 22DD)]^+$ complex in the 50% MeCN–50% MeOH binary solvent at different temperatures.

Fig. 4. Plots of molar conductance vs. ligand-to-metal ion molar ratio for the $([Tl(kryptofix\ 22DD)]^+$ complex in the 75% MeCN–25% MeOH binary solvent at different temperatures.

MeCN results in an increase in molar conductance, which indicates that the $[UO_2(kryptofix\ 22DD]^{2+}$ complex is more mobile than free solvated UO_2^{2+} cation. The slope of the curves in Fig. 1 changes sharply at the point where the ligand-to-metal cation molar ratio is about 1, implying formation of a fairly stable 1 : 1 complex in pure MeCN.

The validity of the 1 : 1 [ML] complexation model was confirmed by fitting and experimental curves using Sigma Plot computer program. The fitting and the experimental curves for $[UO_2(kryptofix\ 22DD)]^{2+}$ complex in MeCN are shown in Fig. 2. As evident from this figure, there is a very good agreement between the fitting and experimental data. Hence, our assumption of a 1 : 1 stoichiometry of the complexation process seems reasonable. Similar behavior was observed for the complexation of Co^{2+}
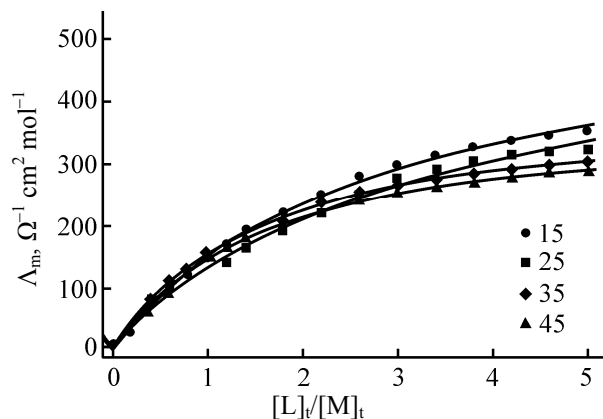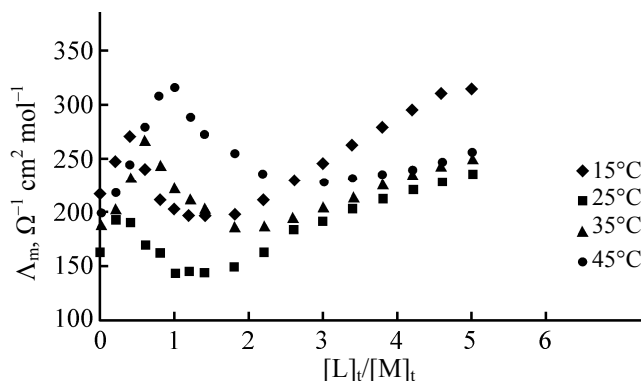
and Tl^+ in pure MeCN and also for the complexation of Cr^{3+} in the MeCN–MeOH binary solvent.

The calculated stability constants ($\log K_f$) for the 1 : 1 complexes of kryptofix 22DD with Co^{2+}, Cr^{3+}, Tl^+, and UO_2^{2+} at each temperature in various solvent systems are listed in Table 1.

A very different behavior was observed for the complexation of kryptofix 22DD with Tl^+ cation in the MeCN–MeOH binary solvent (50 : 50 mol %). It is clearly seen from Fig. 3, on addition of the ligand to the Tl^+ solution the molar conductance increase until the molar ratio reaches about 1, then decreases sharply up to the mole ratio 2, and then again starts to increase. Such behavior may be explained according to the following equilibria:

$$Tl^+ + kryptofix\ 22DD \leftrightarrow [Tl\ kryptofix\ 22DD]^+, \qquad (1)$$

Table 1. Formation constants (log K_f) of the kryptofix 22DD metal complexes in MeCN, MeOH, and MeCN–MeOH binary solvents at different temperatures

Solvent	log $K_f \pm$ SD[a]			
	15°C	25°C	35°C	45°C
[Cr(kryptofix 22DD)]$^{3+}$				
10.0% MeCN−90.0% MeOH		b	b	b
50.0% MeCN−50.0% MeOH		b	4.51 ±0.11	4.39 ±0.12
75.0% MeCN−25.0% MeOH		4.31 ±0.15	4.39 ±0.11	4.09 ±0.16
90.0% MeCN−10.0% MeOH		4.49 ±0.09	4.53 ±0.09	4.38 ±0.09
[Co(kryptofix 22DD)]$^{2+}$				
MeCN	4.06 ±0.09	4.11 ±0.04	3.98 ±0.08	4.08 ±0.08
75.0% MeCN−25.0% MeOH	b	b	b	b
50.0% MeCN−50.0% MeOH	b	b	b	b
25.0% MeCN−75% MeOH	b	b	b	b
MeOH	b	b	b	b
[UO$_2$(kryptofix 22DD)]$^{2+}$				
MeCN	3.83 ±0.04	3.62 ±0.11	4.09 ±0.03	4.07 ±0.02
75.0% MeCN−25.0% MeOH	b	b	b	b
50.0% MeCN−50.0% MeOH	b	b	b	b
25.0% MeCN−75% MeOH	b	b	b	b
MeOH	b	b	b	b
[Tl(kryptofix 22DD)]$^{+}$				
MeCN	4.45 ±0.14	4.14 ±0.13	4.42 ±0.18	4.40 ±0.14
75.0% MeCN−25.0% MeOH	b	b	b	b
50.0% MeCN−50.0% MeOH	b	b	b	b
25.0% MeCN−75% MeOH	b	b	b	b
MeOH	b	b	b	b

[a] (SD) Standard deviation. [b] The data could not be fitted by the equation.

$$[\text{Tl kryptofix 22DD}]^+ + \text{kryptofix 22DD}$$
$$\leftrightarrow [\text{Tl (kryptofix 22DD)}_2]^+, \quad (2)$$

$$[\text{Tl (kryptofix 22DD)}_2]^+ + \text{kryptofix 22DD}$$
$$\leftrightarrow [\text{Tl (kryptofix 22DD)}_3]^+. \quad (3)$$
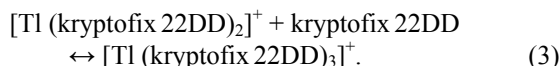
The temperature behavior of the plot of molar conductance vs. ligand-to-metal ion molar ratio for complexation of kryptofix 22DD with Tl$^+$ cation in MeCN–MeOH strongly changes when the composition of the binary solvent changes from 50 : 50 to 75 : 25 mol % (Fig. 4). As seen from the figure, on addition of kryptofix 22DD to the Tl$^+$ solution at 15, 25, and 35°C the molar conductance increases to the mol ratio about 0.5, then decreases until the molar ratio reaches about 1, and then again increases. Such behavior can be explained by the formation of 2 : 1 [M$_2$L], 2 : 2 [M$_2$L$_2$], and 2 : 3 [M$_2$L$_3$] complexes at these temperatures in this solvent system. However, for the complexation of Tl$^+$ cation with kryptofix 22DD in this binary solvent at 45°C, addition of the

ligand to the Tl$^+$ solution increases the Λm until the ligand-to-metal ion molar ratio is of about one; further addition of the ligand to the solution decrease the Λm until the molar ratio reaches about 2 and then increases. These finding suggest formation of 1 : 1 [ML], 1 : 2 [ML$_2$], and 1 : 3 [ML$_3$] complexes at 45°C.

At the same time, the behavior at 15, 25 and 35°C, can be explained by the following equilibria:

$$2\text{Tl}^+ + \text{kryptofix 22DD} \leftrightarrow [\text{Tl}_2(\text{kryptofix 22DD})]^{\uparrow 2+}, \quad (4)$$

$$[\text{Tl}_2 \text{ kryptofix 22DD}]^{2+} + \text{kryptofix 22DD}$$
$$\leftrightarrow [\text{Tl}_2(\text{kryptofix 22DD})_2]^{2+}, \quad (5)$$

$$[\text{Tl}_2(\text{kryptofix 22DD})_2]^{2+} + \text{kryptofix 22DD}$$
$$\leftrightarrow [\text{Tl}_2(\text{kryptofix 22DD})_3]^{2+}. \quad (6)$$
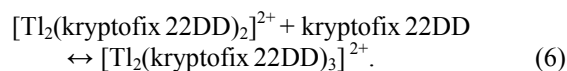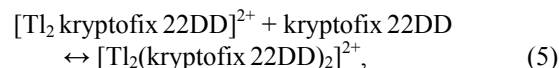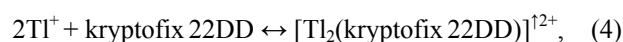
The order of stability of the metal–ion complexes in pure MeCN at 15 and 25°C was found to be: [Tl(kryptofix 22DD)]$^+$ > [Co(kryptofix 22DD)$^{2+}$] > [UO$_2$(kryptofix 22DD]$^{2+}$.

Table 2. Thermodynamic parameters for the formation of the kryptofix 22DD metal complexes in MeCN and MeCN–MeOH binary solvents

Solvent	$\log K_f \pm SD^a$ (25°C)	$-\Delta G^0_{c,298.15} \pm SD^a$, kJ/mol	$\Delta H^0_c \pm SD^a$, kJ/mol	$\Delta S^0_c \pm SD^a$, kJ/mol
[Cr(kryptofix 22DD)]$^{3+}$				
50.0% MeCN−50.0% MeOH	3.79 ±0.3	27.09±3.47	b	b
75.0% MeCN−25.0% MeOH	4.40 ±0.15	24.56± 0.87	~0	b
90.0% MeCN−10.0% MeOH	4.41 ±0.14	25.61±0.53	~0	b
[Co(kryptofix 22DD)]$^{2+}$				
MeCN	4.11 ±0.04	23.45± 0.23	~0	b
[UO$_2$(kryptofix 22DD)]$^{2+}$				
MeCN	3.62 ±0.11	20.65±0.65	b	138.08±53.12
[Tl(kryptofix 22DD)]$^+$				
MeCN	4.14 ±0.13	23.65±0.74	~0	b

[a] (SD) Standard deviation. [b] With a high uncertainity.

As expected, the standard enthalpy and entropy of the complexation reactions (ΔH^0_c and ΔS^0_c, respectively) depend strongly on the nature and composition of the mixed solvents. The value and sign of the standard entropy of the reaction depend on different parameters, such as changes in the flexibility of the macrocyclic ligand during complex formation and the extent of cation–solvent, ligand–solvent, and complex–solvent interactions [16, 17]. The Gibbs standard free energies (ΔG^0_c) for the formation of 1 : 1 complexes between kryptofix 22DD and the studied cations were obtained from the thermodynamic equilibrium constants of the complexes. The ΔH^0_c values for the complexation reactions were obtained from the slope of the van't Hoff plots (ln K_f vs. 1/T), and the ΔS^0_c values were calculated by the equation $\Delta G^0_{c,298.15} = \Delta H^0_c - 298.15\Delta S^0_c$. The resulting thermodynamic parameters are listed in Table 2. As seen from this table, the stability constants of the complexes do not change significantly with temperature and the ΔH^0_c values are negligible; therefore, we can conclude that the complexation between kryptofix 22DD and the studied cations is an athermic reaction ($\Delta H^0_c \approx 0$) in the solvent systems studied.

CONCLUSIONS

The conductometric study of the complexation of Co^{2+}, Cr^{3+}, Tl$^+$, and UO$_2^{2+}$ cations with kryptofix 22DD in acetonitrile, methanol and their binary mixtures, gave evidence for the formation of 1 : 1 complexes in solutions. Along with 1 : 1 complexes, 2 : 1, 1 : 2, 1 : 3, 2 : 2 and 2 : 3 complexes are formed in some of the solvent systems. The obtained results showed that the stoichiometry and stability of the complexes and the selectivity of the ligand for the cations change with the nature and composition of the solvent systems and even with the temperature.

ACKNOWLEDGMENTS

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