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Thermodynamic Study of the Complexation of Cd^{2+} Cation with 1,4,10-Trioxa-7,13-diazacyclopentadecane (Kryptofix 21) in Acetonitrile and Its Binary Mixtures with Methanol and Ethyl Aacetate[1]

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Abstract—The complexation processes between Cd^{2+} cation and a macrocyclic ligand, 1,4,10-trioxa-7,13-diazacyclopentadecane (Kryptofix 21) were studied by the conductometric method in pure acetonitrile and acetonitrile–methanol and acetonitrile-ethyl acetate binary mixtures at different temperatures. In some cases, the stoichiometry of the complex formed between Kryptofix 21 with Cd^{2+} cation is 1 : 1 [ML], whereas in some solvent systems 1 : 2 [ML_2] and 1 : 3 [ML_3] complexes are formed in addition to [ML]. The thermodynamic parameters (ΔS_c^0, ΔH_c^0) for the formation of the Kryptofix 21–Cd^{2+} complex were obtained from the temperature dependence of the stability constant of the [ML] complex. The complexation reaction between Cd^{2+} and Kryptofix 21 is athermic or exothermic, depending on the solvent system.

Keywords: Kryptofix 21, Cd^{2+} cation, nonaqueous solvents, conductometry

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Crown ethers are macrocyclic compounds containing oxygen, sulfur, and/or nitrogen as donor atoms. The first crown ether, dibenzo-18-crown-6, was synthesized in 1967 by Pedersen, and it has gained attention for its ability to form stable complexes with metal cations within its central cavity [1]. With the discovery of crown ethers, the focus on complexation through covalent interactions shifted to that of non-covalent interactions. By accepting metal cations in a more or less "lock and key" fashion, macrocyclic compounds mimic in a relatively uncomplicated way the very complicated functions of biological materials such as enzymes. It is this mimicry that excites the scientists for study of the complexation of crown ethers with various cations in solution; therefore, these compounds can be used as models for ion transport through membranes in biological systems [2]. Study of various macrocyclic compounds in different solvents or solvent mixtures may indicate new approaches for developing pharmaceutical systems or a way to cross the blood organ barrier. Various physicochemical techniques such as spectrophotometry [3], polarography [4], NMR spectrometry [5], calorimetry [6], potentiometry [7], and conductometry [8–14] have been used to study complex formation between macrocyclic polyethers (crown ethers) and various metal cations in solution. Among these methods, the conductometric technique is a sensitive and inexpensive method with a simple experimental arrangement.

The widespread use of nonaqueous solvents began in 1950s in various fields of pure and applied chemistry and has contributed greatly to later advances in chemical science and technology [15]. Numerous data have been published on equilibrium constants and thermodynamic functions of complex formation of crown ethers with metal cations and small organic molecules in pure organic solvents [16, 17]. The very small number of data concerning the complex formation in mixed nonaqueous solvents [18, 19] was the reason for undertaking this kind of studies in our laboratory. The nature and composition of the solvent system has been found to strongly influence the stoichiometry, selectivity, thermodynamic stability, and exchange kinetics of metal ion–crown ether complexes [20].

Although the complexation processes between large macrocyclic crown ethers and metal cations in solution

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

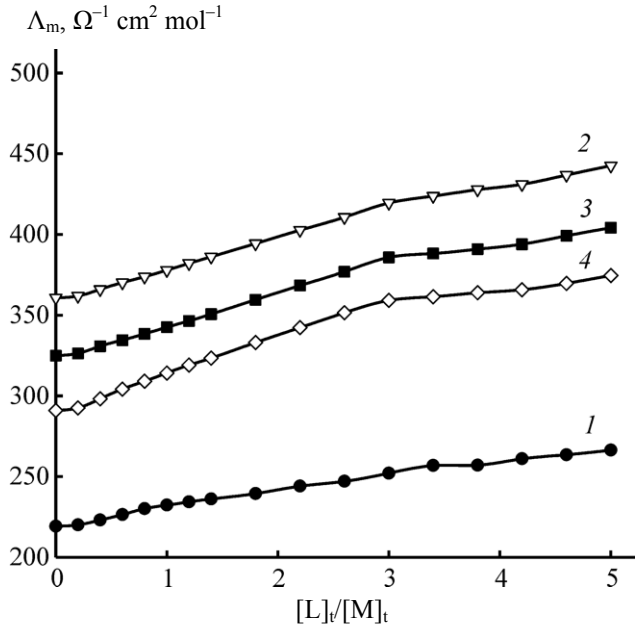


Fig. 1. Molar conductance vs. molar ratio plots for the complex formation of Cd^{2+} with Kryptofix 21 in MeCN–MeOH (75 : 25 mol %) at (*1*) 15, (*2*) 25, (*3*) 35, and (*4*) 45°C.

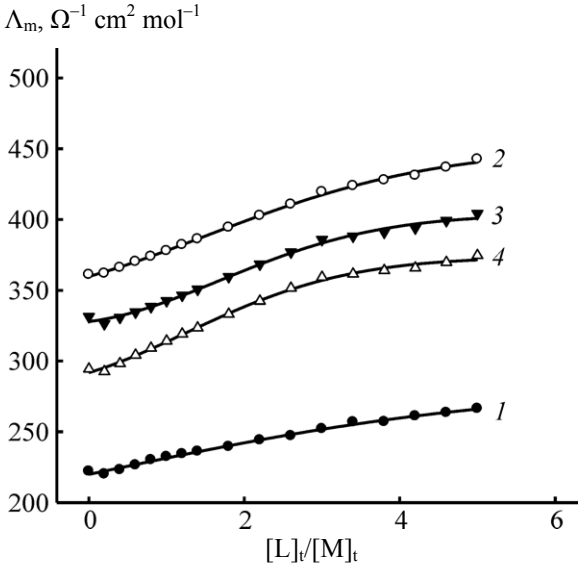
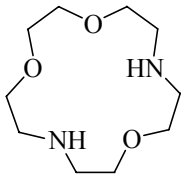


Fig. 2. Molar conductance vs. molar ratio fitting curves for the complex formation of Cd^{2+} with Kryptofix 21 in MeCN–MeOH (75 : 25 mol %) at (*1*) 15, (*2*) 25, (*3*) 35, and (*4*) 45°C.

have been extensively studied, the complexation of metal cations by small crown ethers such as Kryptofix 21 has been studied to a very limited extent especially in nonaqueous solvents and binary solvent mixtures. With the aim of studying the influence of solvent properties on the interaction of metal ions with crown ethers, in this article we report the results of a thermodynamic study of the complexation reaction between Kryptofix 21 and Cd^{2+} cation in pure acetonitrile and acetonitrile–methanol (MeCN–MeOH) and acetonitrile–ethyl acetate (MeCN–EtOAc) binary mixtures at different temperatures using the conductometric method.



1,4,10-Trioxa-7,13-diazacyclopentadecane (Kryptofix 21).

The changes of the molar conductance (Λ_m) versus the ligand-to-metal cation molar ratio, $[L]_t/[M]_t$ for the complexation of Kryptofix 21 with Cd^{2+} in MeCN–MeOH and MeCN–EtOAc binary systems were studied at different temperatures. Here, $[L]_t$ is the total concentration of the ligand, and $[M]_t$ is the total concentration of the metal cation. Three typical series of molar conductance values as a function of $[L]_t/[M]_t$ in MeCN–MeOH, pure MeOH, and MeCN–EtOAc are shown in Figs. 1, 3, and 4, respectively.

The stability constants ($\log K_f$) of the Kryptofix 21–Cd^{2+} complex at each temperature (Table 1) were obtained from the variation of the molar conductance as a function of $[L]_t/[M]_t$ using Genplot computer program [21]. The calculation details were given in [22]. The changes in the standard enthalpy (ΔH_c^0) for the 1 : 1 [ML] complexation were determined in the usual manner from the slope of the van't Hoff plots assuming that ΔC_p is equal to zero over the examined temperature range. The changes in the standard entropy (ΔS_c^0) were calculated from the relationship $\Delta G_{c,298.15}^0 = \Delta H_c^0 - 298.15\ \Delta S_c^0$.

As seen from Fig. 1, addition of Kryptofix 21 to a solution of Cd^{2+} in MeCN–MeOH (75 mol % of MeCN) at different temperatures shows an increase in the molar conductivity with increase in the ligand concentration. This behavior indicates that the complex formed by the ligand with Cd^{2+} cation is more mobile than free solvated Cd^{2+} cation. The change in the slope of the molar conductivity curves at all temperatures is low, which may be due to formation of a weak [ML] complex. In order to make the 1 : 1 [ML] complexation model clearer, the fitting and experimental curves for the Kryptofix 21–Cd^{2+} complex in MeCN–MeOH

Table 1. Stability constants ($\log K_f$) of the Kryptofix 21–Cd^{2+} complex in acetonitrile and its binary mixtures with methanol and ethyl acetate at different temperatures

Solvent	log K_f			
	15°C	25°C	35°C	45°C
Pure MeCN	3.6±0.1	3.7±0.1	3.8±0.1	3.6±0.1
MeCN–MeOH (75 : 25 mol %)	3.0±0.1	3.0±0.1	3.0±0.2	3.4±0.1
MeCN–EtOAc (75 : 25 mol %)	2.9±0.1	3.1±0.1	3.1±0.1	3.2±0.0

Table 2. Stability constants ($\log K_f$) and thermodynamic parameters for the formation of the Kryptofix 21–Cd^{2+} complex in acetonitrile and its binary mixtures with methanol and ethyl acetate

Solvent	log K_f (25°C)	$-\Delta G_c^0$, kJ/mol	ΔH_c^0, kJ/mol	ΔS_c^0, J mol^{-1} K^{-1}
Pure AN	3.7±0.1	21.4±0.7	~0	91.9±27.3
MeCN–MeOH (75 : 25 mol %)	3.0±0.1	16.9±0.7	– 22.4±11.3	132.1±35.9
MeCN–EtOAc (75 : 25 mol %)	3.1±0.1	17.5±0.4	–13.4±2.1	103.5±5.6

are shown in Fig. 2. A very good agreement between the fitting and the experimental data is observed.

The complexation of Cd^{2+} with Kryptofix 21 in pure methanol showed a different behavior. As follows from Fig. 3, the molar conductivity remains virtually constant upon addition of Kryptofix 21 to a solution of Cd^{2+} in pure methanol at 15 and 25°C up to a [L]/[M] value of 2 and then increases. At higher temperatures, the molar conductivity initially decreases until the [L]/[M] molar ratio reaches a value of about unity and then increases.

It seems that the solvation of Cd^{2+} and its complex with Kryptofix 21 by methanol molecules changes with temperature in such a way that the mobilities of the solvated cation and solvated complex are almost similar at 15 and 25°C, but the mobility of the complex at higher temperatures is lower than the mobility of the solvated metal cation. Therefore, the molar conductivity decreases up to [L]/[M] ≈ 1. Such behavior may be explained according to following equilibrium:

$$Cd^{2+} + \text{Kryptofix 21} \leftrightarrow (\text{Kryptofix 21}\cdot Cd)^{2+}.$$

It seems that addition of the ligand to cadmium cation solution, results in the formation of a 1 : 1 complex which is present as an ion pair. Addition of the second ligand molecule to the ion pair complex gives a stable 1 : 2 complex with a sandwich structure $[(\text{Kryptofix 21})_2\cdot Cd]^{2+}$, which reduces the space for diffusion and interaction between NO_3^- anion and Cd^{2+} cation. This leads to dissociation of the ion pair and hence the conductivity increases.

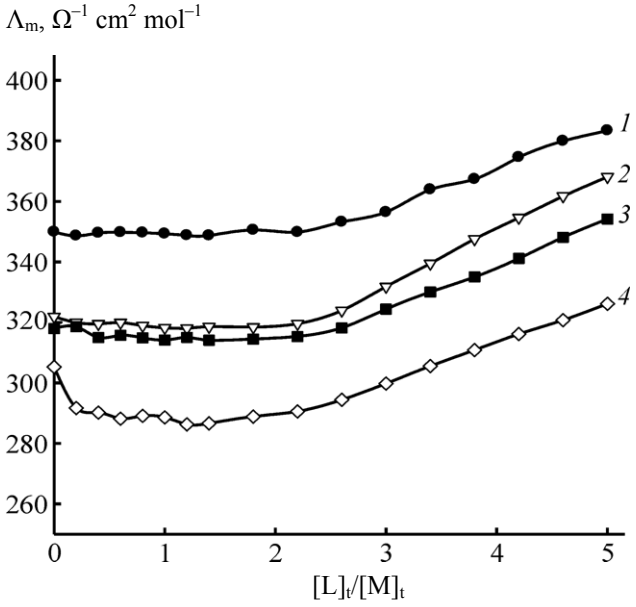


Fig. 3. Molar conductance vs. molar ratio plots for the complex formation of Cd^{2+} with Kryptofix 21 in pure methanol at (*1*) 15, (*2*) 25, (*3*) 35, and (*4*) 45°C.

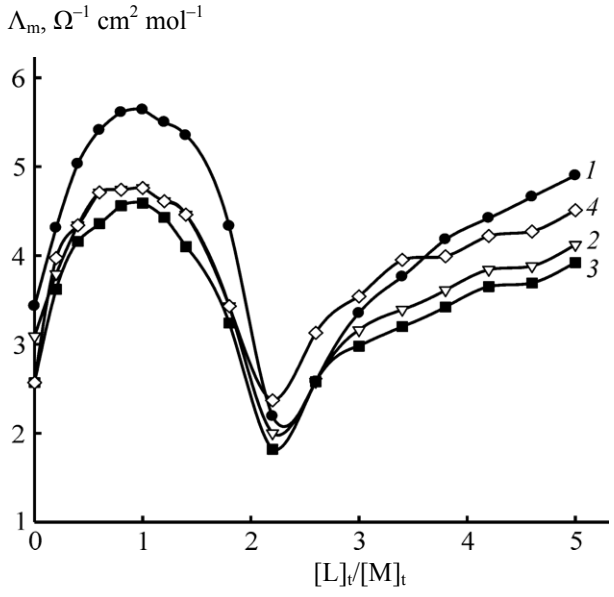


Fig. 4. Molar conductance vs. molar ratio plots for the complex formation of Cd^{2+} with Kryptofix 21 in MeCN–EtOAc (25 : 75 mol %) at (*1*) 15, (*2*) 25, (*3*) 35, and (*4*) 45°C.

An interesting behavior was observed in the complexation of Cd^{2+} with Kryptofix 21 in MeCN–EtOAc (25 mol % of MeCN). As shown in Fig. 4, addition of Kryptofix 21 to a solution of cadmium nitrate in MeCN–EtOAc at different temperatures increases the molar conductivity until the molar ratio [L]/[M] reaches 1 : 1. The Λ_m value then decreases until [L]/[M] ≈ 2 : 1 and increases again. This pattern can be rationalized by the following chemical equations:

$$(\text{Kryptofix 21}\cdot \text{Cd})^{2+} + \text{Kryptofix 21} \leftrightarrow [(\text{Kryptofix 21})_2\cdot\text{Cd}]^{2+},$$

$$[(\text{Kryptofix 21})_2\cdot\text{Cd}]^{2+} + \text{Kryptofix 21} \leftrightarrow [(\text{Kryptofix 21})_3\cdot\text{Cd}]^{2+}.$$

Somewhat similar behavior was observed for the complexation of Cd^{2+} with the macrocyclic ligand in a MeCN–EtOAc binary mixture containing 50 mol % of each component. Presumably, addition of the ligand to a solution of Cd^{2+} results in the formation of a relatively stable 1 : 1 [ML] complex whose mobility is higher than that of free solvated Cd^{2+} ion; addition of the second ligand molecule to the 1 : 1 complex gives 1 : 2 [ML_2] complex with lower mobility than the mobility of the 1 : 1 complex, and further addition of the ligand to the 1 : 2 [ML_2] complex leads to the formation of the 1 : 3 [ML_3] complex. The lower molar conductivity of [ML_2] compared to [ML] and [ML_3] may be due to stronger solvation of the former in MeCN–EtOAc (25 : 75 mol %). In fact, the solvation of the complexes depends on their chemical structure and conformation in solution. Presumably, the structure of the 1 : 2 complex is more favorable for the solvation by MeCN–EtOAc binary solvent, and hence the molar conductivity of this complex is lower than those of the other two complexes. In addition, the conformation of the solvated macrocyclic ligand in MeCN–EtOAc (25 and 50 mol % of MeCN) at all studied temperatures may be suitable for the formation of 1 : 2 and 1 : 3.

As is evident from Table 1, the stability constant ($\log K_f$) of the Kryptofix 21–Cd^{2+} complex in pure acetonitrile at all studied temperatures is higher than in MeCN–MeOH and MeCN–EtOAc binary mixtures. It has been shown that the solvating ability of solvent, as expressed by the Gutmann donor number [23], plays a fundamental role in complexation reactions [24]. Since acetonitrile has a lower donor ability (DN = 14.1) than methanol (DN = 20) and ethyl acetate (DN = 17.1), the stability constant ($\log K_f$) of the Kryptofix 21–Cd^{2+} complex in pure acetonitrile is higher than in its binary mixtures with methanol and ethyl acetate. Although the donor ability of EtOAc is lower than that of MeOH, it is obvious from the data in Table 2 that the stability constants of the Kryptofix 21–Cd^{2+} complex in MeCN–MeOH (75 : 25 mol %) and MeCN–EtOAc (75 : 25 mol %) are almost similar at all temperatures. Since the dielectric constant of EtOAc (ε = 6.2) is lower than that of MeOH (ε = 32.6), some amount of $Cd(NO_3)_2$ in MeCN–EtOAc may be present as ion pairs.

As expected, the values of ΔH_c^0 and ΔS_c^0 strongly depend on the solvent nature. The value and sign of the standard entropy changes are expected to depend on various factors such as flexibility of the macrocyclic ligand during the complexation process and cation–solvent, ligand–solvent, complex–solvent interactions. As is evident from Table 1, the stability constant ($\log K_f$) of the Kryptofix 21–Cd^{2+} complex in pure acetonitrile does not change with temperature within the experimental error; therefore, the standard enthalpy for the complexation of Cd^{2+} with the macrocyclic ligand in pure acetonitrile is almost zero ($H_c^0 \approx 0$). The H_c^0 values in MeCN–MeOH (75 : 25 mol %) and MeCN–EtOAc (75 : 25 mol %) are negative, indicating that the complexation process in these binary solvents is favorable from the enthalpy viewpoint. The data in Table 2 also show that the 1 : 1 complex [ML] is entropy-stabilized in both pure acetonitrile and its binary mixtures with methanol and ethyl acetate.

In summary, our experimental results obtained for the complexation between Cd^{2+} cation and Kryptofix 21 in pure acetonitrile and acetonitrile–methanol (75 : 25 mol %) and acetonitrile–ethyl acetate (75 : 25 mol %) binary mixtures show that the stoichiometry and the stability of the complex formed change with the nature and composition of the nonaqueous solvent system. The standard thermodynamic parameters for the formation of the Kryptofix 21–Cd^{2+} complex (obtained from the temperature dependence of the stability constant) indicate that the complexation process is enthalpy-stabilized in the binary solvent mixtures. The 1 : 1 [ML] complexation is favorable from the entropy viewpoint in both pure acetonitrile and its binary mixtures with methanol and ethyl acetate.

EXPERIMENTAL

Commercial Kryptofix 21 (Merck) and cadmium nitrate (Merck) were used without further purification. The solvents (acetonitrile, methanol, and ethyl acetate)

of highest purity grade (Merck) were used. The experimental procedure for the determination of the stability constants was as follows: a solution of cadmium nitrate ($c = 10^{-4}$ M) was placed in a titration cell, and the conductance of the solution was measured. A solution of Kryptofix 21 in the same solvent ($c = 2 \times 10^{-3}$ M) was then added in portions using a microburette, and the conductance of the resulting solution was measured after each step at a required temperature. The conductance measurements were performed on a digital Metrohm conductivity apparatus (model 712) in a water bath maintained at a constant temperature within ± 0.01°C. The electrolytic conductance was measured using a cell consisting of two platinum electrodes to which an alternating potential was applied. A conductometric cell with a cell constant of 0.86 cm^{-1} was used throughout the studies.

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