

PHYSICAL CHEMISTRY
OF SOLUTIONS

Complexation of Cd^{2+} , Ni^{2+} , and Ag^+ Metal Ions
with 4,13-Didecyl-1,7,10,16-tetraoxa-4,13-diazacyclooctadecane
in Acetonitrile–Ethylacetate Binary Mixtures¹

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Abstract—Conductometric titrations have been performed in acetonitrile–ethylacetate (AN–EtOAc) binary solutions at 288, 298, 308, and 318 K to obtain the stoichiometry, the complex stability constants and the standard thermodynamic parameters for the complexation of Cd^{2+} , Ni^{2+} , and Ag^+ cations with 4,13-didecyl-1,7,10,16-tetraoxa-4,13-diazacyclooctadecane (cryptand 22DD). The stability constants of the resulting 1 : 1 complexes formed between the metal cations and the ligand were determined by computer fitting of the conductance–mole ratio data. There is a non-linear relationship between the $\log K_f$ values of complexes and the mole fraction of ethylacetate in the mixed solvent system. In addition, the conductometric data show that the stoichiometry of the complexes formed between the Cd^{2+} , Ni^{2+} , and Ag^+ cations with the ligand changes with the nature of the solvent. The standard enthalpy and entropy values for the 1 : 1 [ML] complexation reactions were evaluated from the temperature dependence of the formation constants. Thermodynamically, the complexation processes of the metal cations with the C22DD, is mainly entropy governed and the values of thermodynamic parameters are influenced by the nature and composition of the binary mixed solvent solutions.

Keywords: cryptand 22DD, Cd^{2+} , Ni^{2+} , and Ag^+ metal ions, acetonitrile–ethylacetate, conductometry.

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INTRODUCTION

Macrocyclic polyethers (such as crown ethers and cryptands) are multidentate ligands that exhibit selectivity for specific metal ions in solutions containing other chemically similar ions. They have become model systems for understanding molecular recognition and ligand selectivity due to the enzyme-like specificity in their interactions with cations. The study of interactions involved in complexation of different cations with crown ethers in mixtures of solvents is important for a better understanding of the mechanism of biological transport, extraction of biomolecules, potentiometric sensors, molecular recognition, and other analytical applications [1–5]. Thus, the complexation properties of macrocyclic ligands in pure and mixed solvents have been studied extensively during the last three decades [6–9].

To date, our understanding of the macrocyclic ligands solution chemistry has been based on their behavior in mixtures of solvents. The role of the solvent is very important, as the cation complexation competes with its solvation by solvent molecules [10].

Recently, solvent effects on transition metal complexes are reviewed [11] and more attention has been

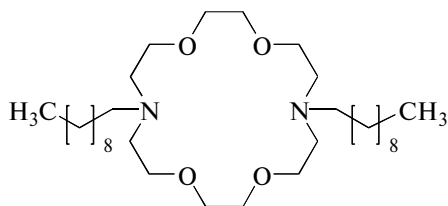
paid to binary solvent mixtures in this field [12, 13]. Solute–solvent interactions are much more complex in mixed solvent systems than in pure solvents due to the possibility of preferential solvation by any of the solvents present in the mixtures. Moreover, the solvent–solvent interactions produced in solvent mixtures can affect the solute–solvent interactions and, therefore, they can also affect preferential solvations [14].

Transition metal ions are essential micro-nutrients/minerals to humans, animal and plants, and the macrocyclic compounds, by accepting the metal ions in a more or less “lock and key” fashion, mimic in a relatively uncomplicated way the very complicated functions of biological materials such as enzymes [15]. It is this mimicry that excites the scientists. The study of complexation of various macrocyclic compounds with the metal cations in different solvents or solvent mixtures may indicate new approaches for developing pharmaceutical systems or a way to cross the blood organ barrier. In the past two decades, we have employed conductometry technique to investigate the thermodynamics of a number of metal ion–macrocyclic complexes in different non-aqueous and mixed solvents [16–19].

Conductometry offers a simple and inexpensive experimental arrangement for such investigations. The

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advantage of conductometry is that the measurements can be carried out with high precision at very low concentration in solution systems. Conductance measurements of a solution of metal salt in the presence of a crown ether provide two valuable pieces of information: the stability of the cation-crown ether complex and transport phenomena of metal salt-crown ether complex in the solution. Also, it is one of the most reliable methods for obtaining the formation constants of cation-macrocyclic complexes [20]. So, in this article, we report the results of a conductometric study for determination of the stoichiometry, stability and thermodynamic parameters of cryptand 22DD



complexes with cadmium(II), nickel(II), and silver(I) cations in acetonitrile–ethylacetate (AN–EtOAc) binary solvent solutions.

EXPERIMENTAL

Reagents and Apparatus

Reagent grade 4,3-didecyl-1,7,10,16-tetraoxa-4,13-diazacyclooctadecane (cryptand 22DD), ethylacetate (EtOAc) and acetonitrile (AN), were purchased from Merck chemical company and used as received. The analytical grade nitrate salts of cations were of the highest purity available from Fluka and used without any further purification except for vacuum drying. All conductance titrations were performed using a digital Metrohm conductometer (model 712). The temperature of all solutions was thermostated at a constant temperature that was maintained within ± 0.01 K by circulation of thermostated water through the outer jacket of the cell. The solutions were stirred with a magnetic stirrer, and the electrolytic conductance was measured using a double-walled glass conductivity cell consisting of two platinum electrodes to which an alternating potential was applied. The calibration of conductometric cell was made with the use of an aqueous KCl (0.1 mol L^{-1}) solution and the cell constant was determined to be 0.89 cm^{-1} .

Procedure

The experimental procedure to obtain the stability constant of the complexes by conductometric procedure was as follows: a solution of metal salt ($1.0 \times 10^{-4} \text{ mol L}^{-1}$, 20 mL) was placed in a titration cell, thermostated at a given temperature, and the conductance of the solution was measured. Then the solution of the ligand ($2 \times 10^{-3} \text{ mol L}^{-1}$) was transferred step-by-step to the titration cell using a precalibrated

microburette and the conductance of the solution was measured after each transfer at the desired temperature. Addition of the ligand solution was continued until the total concentration of the ligand was approximately five times higher than that of the metal ion. The conductance of the solution was measured after each addition and the data were used for the calculation of the stability constant of the complexes.

RESULT AND DISCUSSION

Conductance Studies

In order to evaluate the influence of adding C22DD on the molar conductance of cadmium(II), nickel(II), and silver(I) ions in AN–EtOAc binary mixtures, the molar conductance at a constant salt concentration ($1.0 \times 10^{-4} \text{ mol L}^{-1}$) was monitored while increasing the ligand concentration at various temperatures. Some of the resulting molar conductances vs. C22DD/cation mole ratio plots are shown in Fig. 1. As is evident from this figure, addition of C22DD to the solution of the cations in AN–EtOAc (20% AN) binary solution at different temperatures results in an increase in molar conductivity with an increase in the ligand concentration which indicates that the $(\text{C22DD} \cdot \text{Cd})^{2+}$, $(\text{C22DD} \cdot \text{Ni})^{2+}$, and $(\text{C22DD} \cdot \text{Ag})^{+}$ complexes are more mobile than the free solvated cations. A similar behavior was observed in most of the solvent systems.

The slope of the corresponding molar conductivity versus ligand/cation mole ratio plots changes at the point where the ligand-to-cation mole ratio is about 1, which is an evidence for formation of a relatively stable 1 : 1 [ML] complex between C22DD and Cd^{2+} , Ni^{2+} , and Ag^{+} cations in solutions. The [ML] program selected gave the best statistical fit with the titration data which emphasizes the formation of a 1 : 1 complexes.

A very different behavior was observed for complexation of Ag^{+} cation with C22DD in pure AN and AN–EtOAc (80% AN) binary solvent solution and also for complexation of Ni^{2+} cation with C22DD in pure EtOAc. It is clear from Fig. 2, that addition of the ligand to Ag^{+} cation solution in pure acetonitrile (AN), causes the molar conductivity to decrease until the mole ratio reaches to about 1 and then to increase sharply. It seems that addition of the C22DD ligand to Ag^{+} ion solution in pure acetonitrile results in formation of a stable 1 : 1 [ML] complex which is less mobile than free Ag^{+} solvated cation. It seems that further addition of the ligand to the solution may results in formation of a 1 : 2 [ML_2] complex which is much less solvated than [ML] complex in solution, therefore, the molar conductivity of the solution increases sharply.

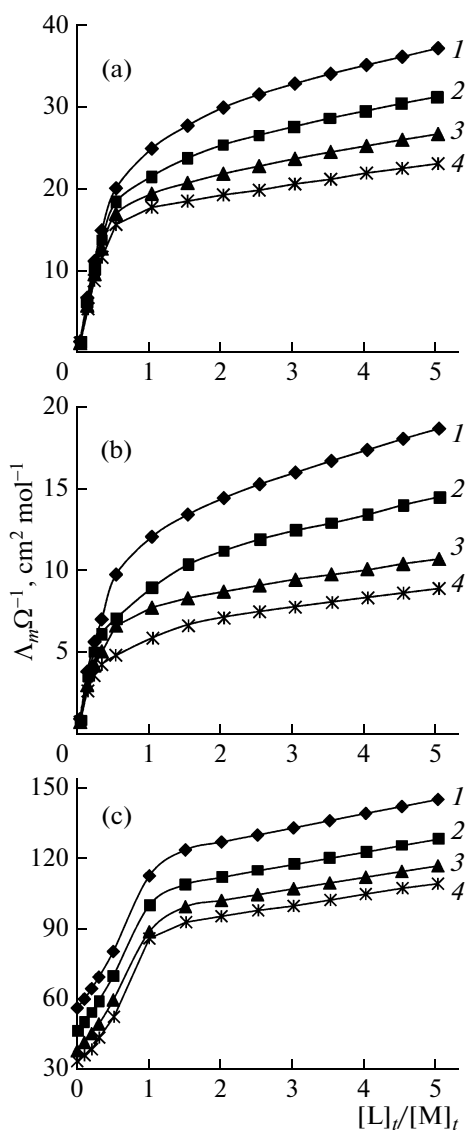
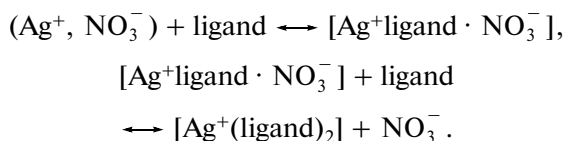


Fig. 1. Molar conductance–mole ratio plots for the (C22DD · M)ⁿ⁺ complexes in AN–EtOAc ([AN] = 20%) binary solution at different temperatures: (1) 288, (2) 298, (3) 308, (4) 318 K. The Mⁿ⁺ cations are (a) Cd²⁺, (b) Ni²⁺, and (c) Ag⁺.

Such behavior may be described according to the following equilibria:



The results obtained in this study reveals that the mechanism of the complexation processes between the macrocyclic ligands and the metal cations may be changed by the nature and composition of the solvent system.

Calculation of complex formation constant was determined as in [21]. The calculations were obtained from approximately 14 experimental points in each

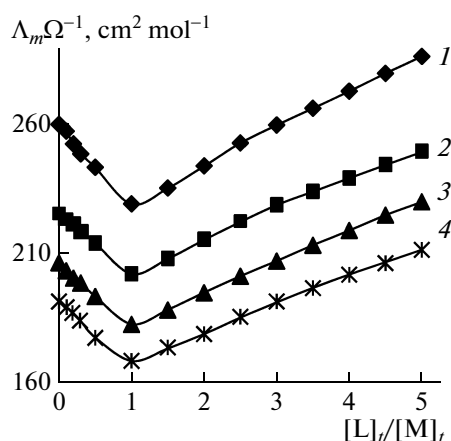


Fig. 2. Molar conductance–mole ratio plots for the (C22DD · Ag)⁺ complex in pure AN at different temperatures; (1–4) see Fig. 1.

titration using the computer program GENPLOT [22]. Since the concentration of C22DD was kept low (2.0×10^{-3} mol L⁻¹) during the experiments, corrections for the viscosity changes were also neglected. The stability constants ($\log K_f$) of (C22DD · Cd)²⁺, (C22DD · Ni)²⁺, and (C22DD · Ag)⁺ complexes are listed in Table 1.

Effect of Solvent Composition

The change in stability constants ($\log K_f$) of (C22DD · Cd)²⁺ and (C22DD · Ni)²⁺ complexes versus the composition of AN–EtOAc binary solution shows a nonlinear profile at all temperatures. This profile for (C22DD · Cd)²⁺ and (C22DD · Ni)²⁺ complexes are plotted in Fig. 3. This behavior can be explained on the basis of the solvent–solvent intractions between the two constituent solvent molecules which result in changing the structure of the solvent systems with their composition and, therefore, changing the solvation numbers of the cations, C22DD and even the resulting complexes in solutions. In addition, it may be due to the formation of mixed solvates in the binary mixed solvent solutions. In addition, this nonmonotonic behavior, probably reflects a balance between the solvation properties, donicity, dielectric constant, hydrogen bonding ability, etc. of the solvent systems.

Thermodynamic Calculations

To have a better understanding of the thermodynamics of the complexation reaction, the enthalpic and entropic contributions of the reaction were evaluated from the slope and intercept of the van't Hoff equation, respectively [23].

$$2.303R \log K_f = -\Delta H/T + \Delta S.$$

The van't Hoff plots of $\log K_f$ versus $1/T$ in all cases were linear, a typical example of these plots is shown in

Table 1. Stability constant ($\log K_f \pm \text{SD}$) values for $(\text{C22DD} \cdot \text{Cd})^{2+}$, $(\text{C22DD} \cdot \text{Ni})^{2+}$, and $(\text{C22DD} \cdot \text{Ag})^+$ complexes in AN–EtOAc binary solutions at different temperatures

AN, mol %	288 K	298 K	308 K	318 K
$(\text{C22DD} \cdot \text{Cd})^{2+}$				
0	b	b	b	b
20	4.57 ± 0.02	4.67 ± 0.26	4.82 ± 0.34	5.00 ± 0.46
40	4.50 ± 0.08	4.57 ± 0.09	4.64 ± 0.09	4.70 ± 0.08
60	4.32 ± 0.08	4.35 ± 0.08	4.39 ± 0.08	4.43 ± 0.08
80	4.40 ± 0.1	4.48 ± 0.1	4.44 ± 0.10	4.44 ± 0.09
100	4.66 ± 0.12	4.66 ± 0.12	4.65 ± 0.12	4.64 ± 0.12
$(\text{C22DD} \cdot \text{Ni})^{2+}$				
0	b	b	b	b
20	4.41 ± 0.18	4.24 ± 0.19	4.07 ± 0.3	3.92 ± 0.23
40	4.21 ± 0.05	4.25 ± 0.03	4.267 ± 0.07	4.208 ± 0.09
60	4.23 ± 0.05	4.08 ± 0.05	3.97 ± 0.05	3.88 ± 0.03
80	4.34 ± 0.08	4.30 ± 0.08	4.27 ± 0.06	4.24 ± 0.07
100	4.75 ± 0.15	4.20 ± 0.09	4.45 ± 0.07	4.74 ± 0.13
$(\text{C22DD} \cdot \text{Ag})^+$				
0	c	c	c	c
20	4.72 ± 0.06	4.79 ± 0.06	4.85 ± 0.07	4.90 ± 0.04
40	4.49 ± 0.1	4.54 ± 0.11	4.59 ± 0.11	4.63 ± 0.15
60	2.57 ± 0.2	2.67 ± 0.09	2.76 ± 0.07	2.85 ± 0.11
80	b	b	b	b
100	b	b	b	b

Note: SD is standard deviations. b, The data can not be fitted in equations. c, The salt is not dissolved.

Fig. 4. The values of the corresponding standard thermodynamic quantities are given in Table 2.

It is immediately obvious from these data, that in most of cases, the standard enthalpy values for formation of the complexes are positive with positive entropic changes. This means that the complexation processes between the cadmium(II), nickel(II), and silver(I) cations with C22DD are chiefly entropy

driven. As seen from Table 2, the changes of the thermodynamic parameters for the complexation processes are affected by the nature and composition of the solvents, but they do not vary monotonically with the solvent composition. The interaction between unlike solvent molecules plays an important supplementary role. This leads to large deviations from the ideal behavior expected from Raoult's law of vapour

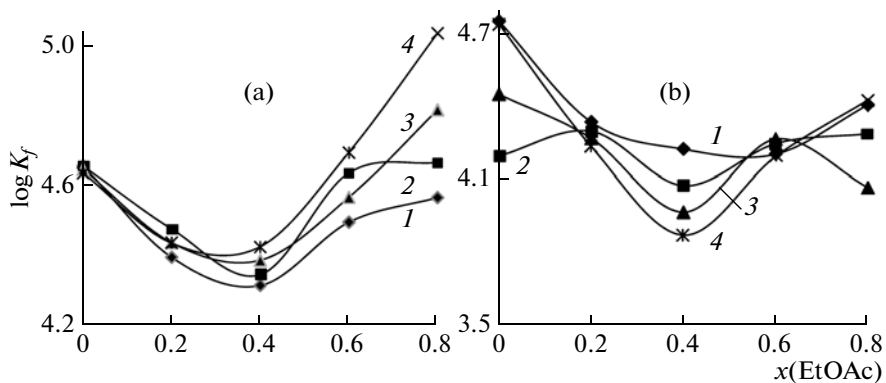


Fig. 3. Changes of the stability constant ($\log K_f$) of the $(\text{C22DD} \cdot \text{M})^{2+}$ complexes with the mole fraction of EtOAc in AN–EtOAc binary solution at different temperatures. The M^{2+} cations are (a) Cd^{2+} and (b) Ni^{2+} ; (1–4) see Fig. 1.

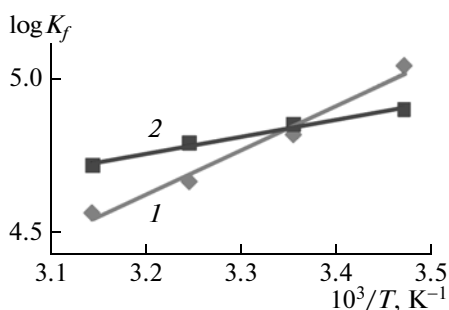


Fig. 4. van't Hoff plots for the complexation of Cd²⁺ (1) and Ag⁺ (2) with C22DD in AN–EtOAc ([AN] = 60%) binary solutions.

pressure depression of binary systems. As expected, the solute is surrounded preferably by the component of the mixture which leads to the more negative Gibbs energy of solvation, $\Delta G_{\text{solv}}^{\circ}$. Complexation enthalpy changes are mainly related to: (i) cation–crown interactions, (ii) solvation of the metal ion, the ligand, and the metal ion complex formed in solution, (iii) repulsion between neighboring donor atoms, and (iv) steric deformation of the ligand. Entropy changes are linked to: (i) change in the number of particles involved in the complexation process and (ii) conformational changes of the ligand accompanying the complexation.

Since there are many parameters which contribute to changes of enthalpy and entropy of complexation reac-

Table 2. Thermodynamic parameters (\pm SD) for (C22DD · Cd)²⁺, (C22DD · Ni)²⁺, and (C22DD · Ag)⁺ complexes in AN–EtOAc binary solutions

AN, mol %	$-\Delta G_c^{\circ}$, kJ mol ⁻¹	ΔH_c° , kJ mol ⁻¹	ΔS_c° , J mol ⁻¹ K ⁻¹
(C22DD · Cd) ²⁺			
20	26.8 ± 4.1	24.9 ± 2.9	173 ± 10
40	26.1 ± 0.2	11.6 ± 0.1	126 ± 0.4
60	24.8 ± 0.7	6.4 ± 0.5	105 ± 2
80	25.6 ± 0.6	b	90 ± 9
100	26.6 ± 0.7	b	85 ± 2
(C22DD · Ni) ²⁺			
20	24.2 ± 1.1	b	b
40	23.7 ± 0.1	b	84.2 ± 0.6
60	23.4 ± 1.5	-20.3 ± 1.1	11 ± 3.6
80	24.6 ± 0.2	-5.7 ± 0.2	63.1 ± 0.5
100	24.0 ± 0.5	b	b
(C22DD · Ag) ⁺			
20	27.3 ± 0.3	10.5 ± 0.2	127 ± 0.8
40	26.0 ± 0.2	8.1 ± 0.1	114 ± 0.4
60	15.2 ± 0.3	16.2 ± 0.2	105 ± 0.7

b, With high uncertainty.

tions in solutions, therefore, we should not expect a regularity between these thermodynamic parameters and the composition of the binary mixed solvent solutions.

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