A Thermodynamic Study of Complex Formation Between Dicyclohexyl-18-Crown-6 (DCH18C6) and La\(^{3+}\), UO\(_2^{2+}\), Ag\(^{+}\), and NH\(_4^{+}\) Cations in Acetonitrile–Tetrahydrofuran Binary Media Using Conductometric Method\(^{1}\)

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Abstract—The complex formation between La\(^{3+}\), UO\(_2^{2+}\), Ag\(^{+}\), and NH\(_4^{+}\) cations and macrocyclic ligand, dicyclohexyl-18-crown-6 (DCH18C6), was studied in acetonitrile–tetrahydrofuran (AN–THF) binary mixtures at different temperatures using the conductometric method. The results show that with the exception of complexation of the NH\(_4^{+}\) cation with DCH18C6 in pure acetonitrile, the stoichiometry of all the complexes is being 1 : 1 (M : L). The stability constants of the complexes were determined using a GENPLOT computer program. The nonlinear behavior which was observed for changes of log\(K_f\) of the complexes versus the composition of the mixed solvent was discussed in terms of solvent–solvent interaction in their binary solution, which results in changing the chemical and physical properties of the constituent solvents when they mix with one another and, therefore, changing the solvation capacities of the metal cations, crown ether molecules, and even the resulting complexes with changing the mixed solvent composition. The results show that the selectivity of DCH18C6 for the studied cations changes with the composition of the AN–THF binary system. The sequence of stabilities of complexes in an AN–THF binary solution (mol. % AN = 75.0) at 25°C is [(DCH18C6)La\(^{3+}\)]\(^{+}\) > [(DCH18C6)UO\(_2^{2+}\)]\(^{2+}\) > [(DCH18C6)Ag\(^{+}\)]\(^{+}\) ~ [(DCH18C6)NH\(_4^{+}\)]\(^{+}\), but in the case of other binary systems of AN/THF (mol. % AN = 25.0 and 50.0) is [(DCH18C6)La\(^{3+}\)]\(^{+}\) > [(DCH18C6)Ag\(^{+}\)]\(^{+}\) ~ [(DCH18C6)UO\(_2^{2+}\)]\(^{2+}\) > [(DCH18C6)Ag\(^{+}\)]\(^{+}\).

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The values of enthalpy changes (\(\Delta H^\circ\)) for complexation reactions were obtained from the slope of the van’t Hoff plots and the changes in standard entropy (\(\Delta S^\circ\)) were calculated from the relationship

\[
\Delta G_{c, \text{298.15}}^\circ = \Delta H^\circ - 298.15\Delta S^\circ.
\]

The obtained results show that the thermodynamics of complexation reactions is affected by nature and composition of the mixed solvent and in all cases, positive values of \(\Delta S^\circ\) characterize the formation of the complexes. A non-monotonic behavior was observed for changes in \(\Delta S^\circ\) and the composition of an AN–THF binary solvent.

INTRODUCTION

A group of chemical compounds called crown ethers has been studied in recent years because of their characteristics, which are of importance in preparative chemistry and biology. New fields of application in research and potential uses in industry have been found for these macrocyclic compounds [1–3]. The crown ethers are the neutral synthetic compounds which were found to be able to form stable complexes with metal cations [4–7] and nonmetallic cations such as NH\(_4^{+}\) cation [7–9] as well as, with small organic molecules or their fragments [10, 11]. The ether oxygen atoms, which are placed regularly around the inside wall of the cavity, can act as electron donor ligand atoms and, consequently, metal cations are incorporated into the cavity [12]. The process of complex formation depends on the cavity size of crown ether, cation size, and the solvation capability of solvent system [13–16]. In order to achieve appropriate solvent properties, we often use mixtures of two or more solvents (mixed solvents). Although mixtures of water and organic solvents are most frequently used, mixtures of two organic solvents are also used in many applications, such as electrochemistry, separations, and organic synthesis. The effect of mixed solvent properties on the formation of crown ether-metal cation complexes is of interest due to

\(^{1}\) The text was submitted by the authors in English.
the fact among other things that the solvation capacities of crown ether molecules and cations and even the resulting complexes change with changing the mixed solvent composition [17, 18].

A variety of physicochemical techniques, such as calorimetry [19, 20], polarography [21], potentiometry [22, 23], NMR spectrometry [24, 25], and conductometry [26, 27], have been used to study the complex formation between crown ethers and various metal ions in solutions. In the present paper, we report the results which are obtained in conductometric study of complexation of La$^{3+}$, Ag$^{+}$, and cations by dicyclohexyl-18crown-6 (DCH$_{18}$C$_6$) in acetonitrile–tetrahydrofuran binary systems at different temperatures.

EXPERIMENTAL

DCH$_{18}$C$_6$ (Merck), lanthanum nitrate (Merck), uranyl nitrate, silver nitrate, and ammonium nitrate (all from Riedel) were used without further purification. The solvents acetonitrile (Merck) and tetrahydrofuran (Merck) were used with the highest purity.

The experimental procedure to obtain the formation constants of the complexes is as follows: a solution of metal salt ($1 \times 10^{-4}$ M) was placed in a titration cell, thermostated at a given temperature, and the conductance of the solution was measured. The crown ether solution ($2 \times 10^{-3}$ M) prepared in the same solvent was added to the titration cell step by step using a microburette, and the conductance of the solution in the cell was measured after each transfer at the desired temperature. The conductance measurements were performed using a digital AMEL conductivity apparatus, model 60, in a water-bath thermostated at a constant temperature, which was maintained within $\pm 0.03^\circ$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 0.73 cm$^{-1}$ was used throughout the studies.

RESULTS AND DISCUSSION

The dependences of molar conductivity ($\Lambda_m$) on the ligand to the cation molar ratio ([L]: [M]) for complexation of DCH$_{18}$C$_6$ with La$^{3+}$, UO$_2^{2+}$, Ag$^+$, and NH$_4^+$ cations in AN–THF binary systems were measured at different temperatures. For example, the changes of $\Lambda_m$ versus [L]: [M] for the formation of the [(DCH$_{18}$C$_6$)La]$^{3+}$ and [(DCH$_{18}$C$_6$)NH$_4$]$^+$ complexes at different temperatures in pure AN are shown in Fig. 1. The stability constants of [(DCH$_{18}$C$_6$)La]$^{3+}$, [(DCH$_{18}$C$_6$)UO$_2^{2+}$], [(DCH$_{18}$C$_6$)Ag]$^+$, and [(DCH$_{18}$C$_6$)NH$_4$]$^+$ complexes at each temperature were calculated from changes in the molar conductance as a function of [L]: [M] molar ratios using a GENPLOT computer program [28]. The values of stability constants ($\log K_f$) for the DCH$_{18}$C$_6$M$^{n+}$ (M$^{n+}$ = La$^{3+}$, UO$_2^{2+}$, Ag$^+$, and NH$_4^+$) complexes in various solvent systems

![Fig. 1. Molar conductance–mole ratio plots for the [(DCH$_{18}$C$_6$)La]$^{3+}$ (a) and [(DCH$_{18}$C$_6$)NH$_4$]$^+$ (b) complexes in pure acetonitrile at different temperatures: 15 (1), 25 (2), 35 (3), 45 (4), 55°C (5).]