INTRODUCTION

The first synthesis of crown ethers, which are macrocyclic polyether having usually the ethyleneoxy units as the basic repeating structure, was reported by Pedersen in 1967. The ability of these ligands to form strong complexes with metal ions have become a very popular field of research. The complexes are held by electrostatic forces involving ion-dipole interaction between the positively charge cation and the negatively polar oxygen or nitrogen atoms. The stability of metal-ion-crown complexes depends on several factors such as: the relative size of the cation (metal ion) and the macrocyclic cavity, the number, kind and arrangement of donor atoms, the ligand substituents, the solvent nature and the counter anion.

Several methods have been used to determine the stability constants of macrocyclic formed. Most of these methods are based on calorimetric titration, ion-selective electrode (potentiometric titration), spectrophotometric methods and conductometric methods which will be used in this study. Thermodynamic data, enthalpy and entropy, provide much information about the nature of cation interaction with crown ethers.

The coordination chemistry of azacrown ethers (ligand incorporate both oxygen and nitrogen donor atoms) have received intense efforts. Complexes of macrocyclic azacrown ethers with different ring sizes and number of nitrogen atoms have been reported. The degree of coordination in the complexes formed from the interaction of the transition metal ions with the azacrown ethers depend on the nature of the macrocycle, especially the ability of its backbone to aid or restrict the attainment of particular coordination geometries.

The stability constants for the 1:1 complexes of the alkali and alkaline earth metal ions with 1,10-diaza-18-crown-6 (D18C6) have extensively been determined in various pure solvents. It was of high interest to study the effect of the cation radius, cation nature on the interaction of metal ions with two crown ethers in pure solvent.

In this work, we report a conductance study of the thermodynamics of Mn²⁺, Co²⁺, Ni²⁺ and Cu²⁺ ion complexes with 1,7-dioxa-4,10-diazacyclododecane (1,7-diaza-12-crown-4) (L1) and 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (1,10-diaza-18-crown-6) (L2) in acetonitrile solution. The chemical structures of the crown ethers used are shown in Fig. 1.

Keywords: Conductometric titration, 1,7-Diaza-12-crown-4, 1,10-Diaza-18-crown-6, Formation constant, Acetonitrile.
EXPERIMENTAL

The crown ethers, 1,7-dioxa-4,10-diazacyclododecane (1,7-diaza-12-crown-4) (L1) and 1,4,10,13-tetraoxa-7,16-diazacycloclooctadecane (1,10-diaza-18-crown-6) (L2), (Fluka) were of high purity (>96%) and were used as received. The metal salts used were all of reagent grade, Cu(ClO4)2·6H2O, Ni(ClO4)2·6H2O, Mn(ClO4)2·6H2O, Co(ClO4)2·6H2O (BDH) with 98, 97, 95 and 99%, purity, respectively (Fluka). HPLC-grade acetonitrile with 99.6% purity was purchased from (Gainleind Chemical Company) and was used as a solvent without further purification. The conductivity of the solvent was less than 1 × 10⁻⁷ S cm⁻¹ at 25 °C.

The conductance measurements were carried out with a Metrohm-E 518 conductivity meter. The cell constant at the different temperature used was determined by measuring the conductivity of 0.010 mol L⁻¹ solution of analytical grade KCl in triply distilled de-ionized water. The specific conductances of this solution at various temperatures have been reported in the literature Gmbh U.Co., Type F3 thermostat.

In a typical experiment, 25 mL of the desired metal was placed in the titration cell thermostated to the desired temperature and the conductance of the solution was measured. Then, a known amount of a concentrated crown ether was added in a stepwise manner using a calibrated micropipette.

After stirring the solution magnetically for about 1 min and thermostating it for about 5 min, the conductance was measured after each addition. The same procedure was repeated until the desired ratio of ligand to metal salt was attained.

The formation constants and the limiting molar conductances on 1:1 ratio at various temperatures were evaluated by fitting the observed molar conductance as a function of the free and complexed ions. The formation constants were calculated by using a nonlinear least squares program "simplex" reported elsewhere²⁸.

In order to have a deep insight of thermodynamics of the complexation of metal ions with the studied crown ether (L1 and L2), it is worthy to investigate the enthalpic and entropic contributions in these reactions. The quantities ΔH° and ΔS° of the complexation reactions were calculated from the corresponding ln Kc and temperature, T, data by applying a linear least square analysis according to the van’t Hoff equation:

\[ \ln K_c = -\frac{\Delta H^°}{RT} + \frac{\Delta S^°}{R} \]

RESULTS AND DISCUSSION

Transition metals interaction with L1: The molar conductance (Λ), of the hydrated metal perchlorates; Cu(ClO4)2·6H2O, Ni(ClO4)2·6H2O, Mn(ClO4)2·6H2O and Co(ClO4)2·6H2O in acetonitrile at constant salt concentration was monitored as a function of the ligand to metal ion mole ratio at various temperatures. The corresponding plot of the observed molar conductance vs. mole ratio at the temperatures 283, 293, 303 and 313 K is presented in Fig. 2 (initial total metal concentration, [M²⁺] = 5.06 × 10⁻⁵ mol L⁻¹; [L1] = 1.28 × 10⁻³ mol L⁻¹).

In all cases, there is a gradual decrease in the molar conductance with the addition of the crown ether and tends to level off at a mole ratio of ligand to metal of about one, which indicates the formation of a relatively stable (1:1) stoichiometry complexes.

The formation constants of (1:1) complexes of crown ethers (L1) with Cu²⁺, Ni²⁺, Mn²⁺ and Co²⁺ metal ions at various temperatures, obtained by computer fitting of the molar conductance-mole ratio data are summerized in Table-1. The plots of ln Kc vs. 1/T for different M²⁺-L1 macrocycle complexes were linear (Fig. 4). The thermodynamic parameters ΔH° and ΔS° of complexation were determined from the slopes and intercepts of the plots, respectively and presented in Table-1.

The diameter of the metal cations as shown in Table-2 predicts a best match between Ni²⁺ and the ligand (L1) (diameter: 1.20-1.50 Å)²⁸. But from the values of ln K in Table-1, the order of stability decrease in the order: Co²⁺ > Mn²⁺ > Cu²⁺ > Ni²⁺. It is clear that, the "ion-in-the hole" model has limited usefulness in predicting the stability of the metal ion complexes. However the solvation terms and the crown ether conformational change play a role in determining the stability of the complexes.

The thermodynamic parameters given in Table-1 also shows that Co²⁺ has the most stable interaction due to the
TABLE-1
FORMATION CONSTANTS AND THERMODYNAMIC PARAMETERS (ΔH° AND ΔS°) FOR 1:1 COMPLEXES OF L1 WITH Cu²⁺, Ni²⁺, Mn²⁺ and Co²⁺ IONS IN AN SOLUTION AT DIFFERENT TEMPERATURES

<table>
<thead>
<tr>
<th>Crown ether</th>
<th>Metal ion</th>
<th>ln Kf</th>
<th>-ΔH° (kJ/mol)</th>
<th>ΔS° (J/mol K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1</td>
<td>Cu²⁺</td>
<td>11.52 ± 0.01</td>
<td>11.77 ± 2.43</td>
<td>53.91 ± 8.18</td>
</tr>
<tr>
<td></td>
<td>Ni²⁺</td>
<td>8.95 ± 0.01</td>
<td>8.39 ± 1.34</td>
<td>44.55 ± 4.49</td>
</tr>
<tr>
<td></td>
<td>Mn²⁺</td>
<td>12.48 ± 0.02</td>
<td>21.02 ± 3.60</td>
<td>29.53 ± 12.1</td>
</tr>
<tr>
<td></td>
<td>Co²⁺</td>
<td>13.75 ± 0.01</td>
<td>13.22 ± 2.75</td>
<td>68.05 ± 9.25</td>
</tr>
</tbody>
</table>

Fig. 4. van’t Hoff plots for the 1:1 complexation of L1-M(II)

The formation constants of (1:1) complexes of crown ethers (L2) with Cu²⁺, Ni²⁺, Mn²⁺ and Co²⁺ ions at various temperatures, obtained by computer fitting of the molar conductance-mole ratio data are summarized in Table-5.

As shown in Figs. 5 and 6, the evidence for the formation of 1:1 complexes of the metal ions with L2 comes from the change in the slope of the corresponding molar conductance ratio plots. According to the values of ln Kf in Table-5, the

values of ΔH° and ΔS° [the most negative ΔG° values (ΔG° = ΔH°-TΔS°)].

Transition metals interaction with (L2): The corresponding plots of the observed molar conductance vs. mole ratio at various temperatures (283, 293, 303 and 313 K) are represented in Fig. (5). (initial total metal concentration, [M²⁺] = 5.06 × 10⁻⁵ mol L⁻¹, [L2] = 1.28 × 10⁻³ mol L⁻¹).

A sample of the resulting plots for all metal ions in acetonitrile at 293 K is shown in Fig. 6.

The plots of ln Kf vs. 1/T for different M²⁺-macrocycle complexes were linear as shown in Fig. 7.

The thermodynamic parameters ΔH° and ΔS° of complexation were determined from the slopes and intercepts of the plots of ln Kf vs. 1/T, respectively and presented in Table-5.

The plots of ln Kf vs. 1/T for different M²⁺-macrocycle complexes were linear as shown in Fig. 7.
The formation constant of the complexes decrease in the following order: Co²⁺ > Ni²⁺ > Cu²⁺ > Mn²⁺ with L2 (diameter 2.68-2.86 Å).

From the diameter of the metals (Table-3) predicts the best match between Mn²⁺ and L2. So that the idea "ion-in-the-hole" model can not be the base for the prediction of the stability of interactions between the cations and the ligands always. The ΔH° values in Table-3 show that Ni²⁺ complexes have a more negative than the other complexes, suggesting a stronger binding between the nitrogen donor atoms of L2 and Ni²⁺.

The formation constants obtained in this study at 20°C are in satisfactory arrangement with the previously reported values for L1 and L2 presented in Table-4. However, the difference in formation constant values are probably attributed to nature of solvent, temperature, nature and concentration of ionic strength salt.

The low values of ΔH° for some metals, as a result of interaction with L1 and L2, may due to the weak interaction with these ligands, the solvation of the ligands with the solvent acetonitrile and the coordination of ether oxygen to the metal might be considered to be an endothermic process. The Ni²⁺ interaction with L2 is entropy unfavored but the others are favored and there is enthalpy-entropy compensation effect. This can be explained as due to the conformational entropy change and to structural difference between Cu²⁺ and Ni²⁺ complexes. Previous X-ray studies on solid complexes indicated that the copper forms five-coordinate complexes while the nickel forms pseudo-octahedral complexes²⁴,²⁶.

With respect to the Mn²⁺ interaction with L2 is entropy unfavored. The conformational entropy change of the ligand L2 might have an additional effect. However, the stability of Mn²⁺ complexes is enthalpy governed.

The entropy change of the metal ion-diazacrown systems upon complexation is related to some factors such as the change in the conformational entropy of the ligand and the diameter of crown ether, the extent of crown solvent interaction and the different in the solvation of the free and complexed cation.

In the case of complexation of crown ether ligands, the following factors can significantly influence the stability of their metal ion complexes: (i) the cation size, (ii) the ionic solvation of the charged species involved and (iii) conformations of the free and complexed crown ethers. As shown in Tables 2 and 3, the observed increase (or decrease, depending on the nature of the metal ion and ligand) in ΔH value will be compensated by an increase (or decrease) in the corresponding ΔS value. The existence of such a compensating effect between ΔH and ΔS values has been reported for several ligand-metal systems²⁸. This effect causes the overall change in the AG value of the complex to be smaller than might be expected from the change in either ΔH or ΔS independently.

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REFERENCES