Study on complex formation of dicyclohexyl-18-crown-6 with Mg$^{2+}$, Ca$^{2+}$ and Sr$^{2+}$ in acetonitrile-water binary mixtures by conductometry

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ABSTRACT
The complexation reactions between Mg$^{2+}$, Ca$^{2+}$ and Sr$^{2+}$ cations and dicyclohexyl-18-crown-6 (DCH 18C6) have been studied in acetonitrile–water binary mixtures at different temperatures by conductometry. The formation constants of the resulting 1:1 (M:L) complexes for all the three cations were determined from computer fitting of the molar conductance versus mole ratio data. The results show that the selectivity order of DCH 18C6 for the metal cations in the acetonitrile-water binary solvent at different temperatures (25, 35 and 45 ºC) was Sr$^{2+}$ > Ca$^{2+}$ > Mg$^{2+}$ based on size fit concept. A linear relationship was observed between the formation constants (log $K_f$) of these complexes and the composition of acetonitrile-water binary mixtures (70:30, 80:20, 90:10, mol%). The values of thermodynamic parameters ($\Delta H^0$ and $\Delta S^0$) for complex formation in binary systems were obtained from temperature dependence of formation constants of complexes using the van’t Hoff plots. The complex formation reactions were spontaneous and enthalpy stabilized.

Keywords: Dicyclohexyl-18-crown-6; Conductometry; Mg$^{2+}$, Ca$^{2+}$, Sr$^{2+}$ cations; Acetonitrile-water binary system; Thermodynamic parameters

INTRODUCTION
Complexation study of crown ethers with cations has been a subject of several reports [1-3], since they were first synthesized by Pedersen [4]. Among many others, these macrocyclic ligands have a remarkable property to selectively bind metal ions in solution. Further, it has been found that the selectivity of complexation depends not only on the size of cation and the crown ether cavity, but also on the solvating ability of the solvent(s) towards the cations and the complex [5,6]. Crown ethers are of practical interest for several reasons, which includes selective ion-transport [7], as solvent extraction agents [8], in the construction of ion-selective electrodes [9, 10], for selective separation from nuclear waste [11], and in liquid chromatography [12]. The stability of crown ether complexes depends on several factors. This includes relative size of cation and the macrocyclic cavity, structural flexibility, nature of the substituent, nature and number of binding sites, acid-base character of the metal ions and nature of the solvent system [13]. Numerous methods have been employed for determining formation constant like NMR [14], calorimetry [15], potentiometry [16], polarography [17], spectrophotometry [18], and conductometry [19, 20]. Apart from the other factors, solvents play a crucial role in the binding selectivity for metal ions. In solutions, the metal ion–crown complex is surrounded by solvent molecules that might play a significant role in shifting the preference for one metal ion over that for another. Thus, it is of great importance to study the effect of solvent on the complexation of metal ions to crown ethers. The combination of pure solvents to yield mixed solvents substantially increases the diversity of available reaction media. Investigation of solvent effects on thermodynamic and kinetic functions is interesting both experimentally and theoretically in chemical and biochemical analysis. Study of solvent effects on chemical and physical processes in binary mixtures is more complicated than in pure solvents, because the solute–solvent and solvent–solvent interactions can create new solvent properties leading to preferential solvation [21]. Literature reveals that alkaline earth cations have been studied with dicyclohexyl 18-crown-6 (DCH18C6) (Figure 1) in propylene carbonate-ethylene carbonate
[22] and methanol-water [23] binary solvent systems by conductometry.

![Structure of dicyclohexyl 18-crown-6](image)

In our previous work we investigated the role of methanol-water solvent system on the stability, selectivity and thermodynamic parameters for complexation of Ag⁺, Ti⁺ and Pb²⁺ with DCH18C6 [24]. In the present work, we report a thermodynamic study of complexation of Mg²⁺, Ca²⁺ and Sr²⁺ cations by DCH18C6 in acetonitrile–water binary systems at different temperatures by conductometry.

**EXPERIMENTAL**

**Materials and chemicals**

Dicyclohexyl 18-crown-6 (DCH18C6) of 99.9 % purity was obtained from Sigma Aldrich (St. Louis, MO, USA). Nitrate salts of magnesium, calcium and strontium ions were procured from Central Drug House (P) Ltd. (New Delhi, India), having purity ≥ 99.4 %. HPLC grade acetonitrile was obtained from Mallinckrodt Baker, S.A.de C.V. (Estado de Mexico, Mexico). Triple distilled water having conductivity less than 1 × 10⁻⁷ S/cm was used in the entire study. All standard solutions of DCH 18C6 and metal ions were prepared by accurately weighing known amounts of the compounds in suitable solvent systems.

**Conductometric procedure**

The conductance measurements were carried out using Metrohm 856 conductivity module. A dip-type conductivity cell having a cell constant of 0.88/cm was used. The cell constant of the conductivity cell was determined by measuring the conductivity of aqueous potassium chloride solutions of different concentrations [25]. A thermostated water-bath was used to maintain a constant solution temperature at the desired value having an accuracy of ±0.1 °C. In order to determine the complex formation constants, 25 mL (5 × 10⁻⁴ M) solution of the desired metal salt solution in appropriate solvent was placed in specially designed water jacketed cell equipped with a magnetic stirrer. To maintain a constant temperature it was connected to a thermostated circulator water bath and the conductance of the solution was measured. Then a known amount of DCH 18C6 solution (5 × 10⁻³ M) was added in a stepwise manner and the conductivity of the mixture was measured after stirring (1.0 min) and temperature equilibration. This procedure was repeated in the same manner for each addition until the DCH 18C6 to metal ion ratio was about 3:1. The same procedure was followed at 25, 35 and 45°C, and the conductivity data was used for the calculation of the formation constant of the complexes at the desired temperatures. The conductivity data was analyzed using a non linear least squares curve fitting procedure for 1:1 complex formation model as reported previously [13].

**RESULTS AND DISCUSSION**

To study the complexation of DCH 18C6 with the nitrate salts of Mg²⁺, Ca²⁺ and Sr²⁺ ions, the molar conductance (Λm) of the solution was monitored as a function of mole ratio of DCH 18C6/Mn⁺ ions in different acetonitrile-water binary mixtures (mol %) at three different temperatures. The resulting molar conductance-mole ratio plots are presented in Figure 2A-C. As can be seen, there is a gradual decrease in Λm with increase in DCH 18C6/Mn⁺ mole ratio for all three cations. This indicates that the mobility of Mg²⁺-DCH18C6, Ca²⁺-DCH18C6, and Sr²⁺-DCH18C6 complexes in acetonitrile-water binary mixtures is greater than the free solvated Mg²⁺, Ca²⁺ and Sr²⁺ cations. The slope of the corresponding mole ratio plots of DCH18C6/Mn⁺ changes where the DCH 18C6 to cation ratio is close to unity. This suggests formation of 1:1 complex for all the three cations at different temperatures. Subsequent addition of DCH 18C6 resulted in no significant change in molar conductance. The general reaction for 1:1 complexation with DCH 18C6 can be represented by the following equilibrium expression:

$$\text{M}^{n+} + \text{L} \leftrightarrow \text{ML}^{n+}$$

The equilibrium constant for this reaction can be expressed as,

$$K_e = \frac{[\text{ML}^{n+}]f(\text{ML}^{n+})}{[\text{M}^{n+}]f(\text{M}^{n+})f(L)}$$

where [MLⁿ⁺], [Mⁿ⁺], [L] and \(f\) represent the equilibrium molar concentrations of the complex, the free cation, the free ligand and the activity coefficients of the species indicated, respectively. Under the dilute conditions used, where the ionic strength is less than 0.001 M, the activity coefficient of the uncharged ligand, \(f(L)\) can be reasonably assumed to be unity. Based on Debye–Huckel limiting law of electrolytes the activity coefficient of \(f(\text{ML}^{n+})\) \(\approx f(\text{M}^{n+})\), thus the above equation reduces to

$$K_e = \frac{[\text{ML}^{n+}]}{[\text{M}^{n+}][\text{L}]}$$

The formation constant (log \(K_e\)) values for all three cations were evaluated using a nonlinear least-squares curve fitting program from the corresponding molar conductance vs. mole ratio plots at three different temperatures (Table 1). In all the solvent mixtures of acetonitrile-water, the stability of complexes of Mg²⁺, Ca²⁺ and Sr²⁺ cations with DCH18C6 follows the order Sr²⁺ > Ca²⁺ > Mg²⁺. A similar selectivity order was observed for these complexes in methanol-water solvent system in a previous study [23]. However, the complex formation constants were somewhat lower compared to the present study, possibly due to higher solvation strength of methanol (DN = 19.0) compared to acetonitrile (DN = 14.1).
Table 1 Formation constants and thermodynamic parameters for dicyclohexyl 18-crown-6 (DCH 18C6) complexes in acetonitrile (ACN)-water binary mixtures

<table>
<thead>
<tr>
<th>DCH 18C6-metal ion complex</th>
<th>Log $K_f$</th>
<th>$\Delta G$ (kJ/mol)</th>
<th>$\Delta H$ (kJ/mol)</th>
<th>$\Delta S$ (J/mol/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25 °C</td>
<td>35 °C</td>
<td>45 °C</td>
<td>ACN-H$_2$O (70:30, mol%)</td>
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<tr>
<td></td>
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<td></td>
<td>ACN-H$_2$O (80:20, mol%)</td>
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<td>ACN-H$_2$O (90:10, mol%)</td>
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<tr>
<td>DCH18C6-Mg$^{2+}$</td>
<td></td>
<td></td>
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<td>ACN-H$_2$O (70:30, mol%)</td>
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<td>ACN-H$_2$O (90:10, mol%)</td>
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<tr>
<td>DCH18C6-Ca$^{2+}$</td>
<td></td>
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<td></td>
<td>ACN-H$_2$O (70:30, mol%)</td>
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<td>ACN-H$_2$O (80:20, mol%)</td>
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<td>ACN-H$_2$O (90:10, mol%)</td>
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</tbody>
</table>

Figure 2 Molar conductance versus mole ratio plots for DCH18C6-Mg$^{2+}$, DCH18C6-Ca$^{2+}$ and DCH18C6-Sr$^{2+}$ complexes in acetonitrile-water at 25 °C, 35 °C and 45 °C. The variation of log $K_f$ for the formation of DCH18C6-Mg$^{2+}$, DCH18C6-Ca$^{2+}$ and DCH18C6-Sr$^{2+}$ complexes and the ionic radii of the cations in acetonitrile-water binary mixtures is shown in Figure 3A-C.
It is clearly seen that the Sr$^{2+}$ cation forms a more stable complex with DCH18C6 compared to other cations based on size-fit concept. This seems reasonable as the ionic size of the cation Sr$^{2+}$ (1.18Å) is more close to the size of the DCH18C6 cavity (1.34Å - 1.55Å) than the other cations. Ca$^{2+}$ having an ionic radius of 1.00Å show greater stability than Mg$^{2+}$. Since the ionic size of Mg$^{2+}$ (0.72 Å) is much smaller than the size of DCH 18C6 cavity, it does not have a good fit condition and thus forms a less stable complex compared to Sr$^{2+}$ and Ca$^{2+}$ cations.

Additionally, the complexation reactions between Ca$^{2+}$, Mg$^{2+}$ and Sr$^{2+}$ cations with DCH18C6 were sensitive to the solvent composition such that the stability of all the complexes increased with increase in acetonitrile-water binary mixtures (Table 1). This observation can be attributed lower solvation capacity of acetonitrile compared to water. In a strong solvating solvent such as water with a relatively high Gutmann donor number (DN = 33), the solvation of the metal cation is high compared to acetonitrile (DN =14.1), thus the formation of the complex is weakened as the concentration of water increases in acetonitrile-water binary mixtures. However, the solvent-solvent interaction between acetonitrile and water does not have any significant impact and there was a linear relationship between the log $K_f$ of the complexes and the composition of acetonitrile-water binary mixtures.

For understanding the thermodynamics of DCH 18C6 complexes with the cations, it is important to evaluate the enthalpy and entropy of these reactions. The influence of temperature on the formation constants of these metal complexes shows that the stability decreases as the temperature is increased (Table 1). This indicates that the process of complex formation is exothermic. The data in table shows that the values of thermodynamic parameters for complexation reactions vary with the nature and composition of the mixed solvents. The negative values for free energy ($\Delta G^o$) indicate that the complexation process is spontaneous. The plots of log $K_f$ vs. 1000/T were linear for all the three cations (Figure 4A-C). The values for thermodynamic quantities $\Delta H^o$ and $\Delta S^o$ were computed from the slopes and intercepts of these plots by applying a linear least square analysis according to the van’t Hoff equation,

$$2.303 \log K_f = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R}$$

The values of enthalpy and entropy for complexation reactions varied monotonically with the solvent composition. The experimental values of $\Delta H^o$ and $\Delta S^o$ illustrate that all complexes were enthalpy as well as entropy stabilized except for DCH18C6-Ca$^{2+}$ in 90:10, mol% and DCH18C6-Sr$^{2+}$ in 90:10 and 80:20, mol%, which were entropy destabilized. Nonetheless, the unfavorable contribution of entropy was adequately compensated by the magnitude of $T\Delta S^o$ values, which favored the process of complexation. Since there are many factors which contribute to changes in complexation enthalpies and entropies, therefore it is not expected to find a regularity between these parameters for binary solvent mixtures.

CONCLUSION

In the present work, the results obtained for the complexation between DCH 18C6 and Ca$^{2+}$, Mg$^{2+}$ and Sr$^{2+}$ cations can be explained in terms of the size-fit concept, where the crown ether forms a most stable complex with a cation having a size which fits best with its cavity size. The results also show that the formation...
constants depend on the composition and concentration of the mixed solvent systems. The thermodynamic parameters for complexation of DCH 18C6 with Ca$^{2+}$, Mg$^{2+}$ and Sr$^{2+}$ demonstrate that all the complexation reactions were spontaneous and enthalpy stabilized.

REFERENCES


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