



Conductometric measurements of complexation study between 4-Isopropylcalix[4]arene and Cr^{3+} cation in THF–DMSO binary solvents



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ABSTRACT

In the present work, the conductometric measurements for complexation process between Cr^{3+} cation and the macrocyclic ionophore, 4-Isopropylcalix[4]arene (IPC4) were studied in tetrahydrofuran–dimethylsulfoxide (THF–DMSO) binary non-aqueous medium at different temperatures. The results reveal that the stoichiometry of the IPC4– Cr^{3+} complex in all binary mixed solvents is 1:1. A non-linear behavior was observed for changes of $\log K_f$ of this complex versus the composition of the binary mixed solvents, which was explained on the basis of changes occurring in the structure of the mixed solvents and also the preferential solvation of the cation, ionophore and the resulting complex in the solution. The thermodynamic parameters (ΔH°_c and ΔS°_c) for the formation of IPC4– Cr^{3+} complexes were obtained from the temperature dependence of the stability constant using the van't Hoff plots. The results obtained in this study, show that the formed complex is enthalpy destabilized, but entropy stabilized and the values of the mentioned parameters are affected strongly by the nature and composition of the binary mixed solvents. The experimental data was tested by using artificial neural network (ANN) program and was in a good agreement with the estimated data.

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1. Introduction

Calixarenes as a new generation of macrocyclic compounds with pre-organized and semi-rigid molecular structure as well as three dimensional nature of the complexation cavity, exhibit high selectivity with enhanced complexation properties toward target ions. Therefore, they can be used as ideal ionophores with high selectivity

in the fabrication of novel ISEs with superior low detection limit and wide dynamic range [1–6]. The selectivity of ionophore can be explained in terms of the thermodynamic stability, which is a complicated combination of enthalpy and entropy of forming complex. The higher stability of complexes implies more selective interactions that occur between macrocyclic compounds and metal ions [7–14].

The conductometric measurements have been commonly used for complexes reactions studies between the macrocyclic ligands and various species of ions in different solvents due to such advantages of inexpensive cost, instrumental easy used, accurate and sensitive measurements and a simple experimental arrangement [15–18].

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Other physicochemical techniques like potentiometry [19–24], NMR spectrometry [25], spectrophotometry [26–28], calorimetry [29] and polarography [30] have been reported besides the conductometry method for the investigation of complexation process. Such studies can initiate a new horizon to investigate the effect of solvents and their mixtures in the development of pharmaceutical systems or a way to cross the blood organ barrier [31,32].

The selectivity of macrocyclic ligands toward the target cations and the stability of formed complexes is followed by several factors such as the density of charges and polarizability of metal cations, the number of donor atoms and the nature of substituents in the macrocyclic compounds, the properties of co-anion with the cations and the cavity size of macrocyclic ligand [33–35]. Moreover, the type of solvent which is used in complexation reactions influences the stability and even in some cases, the stoichiometry of the formed complexes [36].

Numerous studies on complexation reaction between the macrocyclic ligands and metal cations in different non-aqueous solvents have been reported until now, but the characteristic studies of complex formation based on non-aqueous mediums were far fewer [37–39]. In fact, non-aqueous mediums have enormous applications in a wide range of pure and applied chemistry [40–44]. Hence, this study makes a great effort to investigate the influence of solvent properties on the thermodynamic parameters of complex formation between 4-Isopropylcalix[4]arene with chromium (III) ion in tetrahydrofuran–dimethylsulfoxide (THF–DMSO) binary mixtures based on the conductometric method at different temperatures. To our certain knowledge, heretofore, there have been no reports of the thermodynamic study between IPC4 with any metal cations.

2. Experimental

2.1. Materials

The novel ionophore namely 4-Isopropylcalix[4]arene from Aldrich and chromium (III) nitrate from Merck were purchased and used as received and dried in a vacuum desiccator over P₂O₅. Tetrahydrofuran (THF) and dimethylsulfoxide (DMSO) (all from the Merck) were used as received with the highest purity.

2.2. Apparatus and procedure

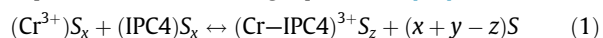
Conductance measurements were carried out with a digital Cyberscan conductivity/TDS/°C/°F meter (model 510 CON). The conductivity/TDS electrode with a cell constant of 1.0 cm⁻¹ made of stainless steel rings was used throughout the studies. In all measurements, a thermostated water-bath was applied for thermostating the cell at the desired temperatures within ± 0.01 °C.

The experimental procedure was prepared according to previous literatures [15]. The formation constant of the complexes will be obtained by using the procedure designated as follows. A solution of metal ion with the concentration of 5.0 × 10⁻⁴ M was prepared and fixed in a titration cell. After that, the ligand with concentration of 2.5 × 10⁻² M was added to the titration cell using a

micropipette. During the reaction, the desired temperature was fixed and a magnetic stirrer has been used to form a homogenized condition in a titration cell. The conductivity values were measured before and after each titration of the ligand's solution. The procedure was repeated for all formed complexes between the IPC4 and Cr(III) cations in THF–DMSO binary system (mol% THF; 0.00%, 9.99%, 22.66%, 39.73%, 63.72% and 100.00%) at different temperature (15, 25, 35 and 45 °C).

2.3. Complex Formation Constant (K_f)

The formation constant of resulted 1:1 complex between IPC4 compound and Cr(III) metal cation can be expressed in the following equilibrium [45]:



where S is the solvent molecule, and x, y and z are the solvation numbers of the Cr(III) cation, the IPC4 ligand, and the resulting complex, respectively. According to the equilibrium 1, the complex formation process affected by various factors such as the nature of metal cation, macrocyclic compound and solvent molecules. Solvation of the metal cation (Cr³⁺) and ligand (IPC4) by the solvent molecules can be resulted to enhance or reduce the resulted 1:1 complex formation constant. The complex reaction of IPC4 ligand with Cr³⁺ cations lead to reduce the number of free metal cations in the solution. Due to the different mobility of free cations and their complexes, the conductivity of the solution will be changed [46]. Then, the conductometric method can be applied for the investigation of complex reaction of IPC4 ligand with Cr³⁺ cation in this study. The equilibrium 2 can be expressed for the 1:1 complexation of Cr³⁺ cation with IPC4 ligand [47]:



The corresponding equilibrium constant, K_f, is expressed as:

$$K_f = \frac{[\text{Cr-IPC4}^{3+}] \cdot f_{(\text{Cr-IPC4})^{3+}}}{[\text{Cr}^{3+}] [\text{IPC4}] \cdot f_{(\text{Cr}^{3+})} \cdot f_{(\text{IPC4})}} \quad (3)$$

In this equation, [Cr–IPC4³⁺], [Cr³⁺] and [IPC4] represent the molar concentration of the resulted 1:1 complex, free Cr(III) cation and free IPC4 macrocyclic ligand, respectively. *f* denotes the activity coefficients of the species in the electrolyte solution. Since the highly dilute condition was used in this work, the activity coefficient of macrocyclic compound, *f*_(IPC4), the free metal ions, *f*_(Cr³⁺) and complex, *f*(Cr–IPC³⁺), reasonably assumed to be unity. Dilute condition is where the ionic strength is less than 0.001 M. According to the Debye–Hückel limiting law of electrolytes leads to the conclusion that *f*_(Cr–IPC³⁺) ≈ *f*_(Cr³⁺) [48]. Thus, the above equation can be simplified as illustrated below:

$$K_f = \frac{[\text{Cr-IPC4}^{3+}]}{[\text{Cr}^{3+}] [\text{IPC4}]} \quad (4)$$

The specific conductivity (*k*) of each ionic species in the titration reaction can be expressed by the following equation which is presented by K_(Cr³⁺) and K_(Cr–IPC³⁺) the conductivity of cationic salt and 1:1 resulted complex, respectively:

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