



King Saud University
Arabian Journal of Chemistry

www.ksu.edu.sa
www.sciencedirect.com



ORIGINAL ARTICLE

Study of complex formation between $C_{18}H_{36}N_2O_6$ and UO_2^{2+} cation in some binary mixed non-aqueous solutions

G.H. Rounaghi *, Z. Eshaghi, L. Zare

Department of Chemistry, Faculty of Sciences, Payame Noure University of Mashhad, Mashhad, Iran

Received 25 June 2012; accepted 23 October 2012

KEYWORDS

$C_{18}H_{36}N_2O_6$ (kryptofix 222);
 UO_2^{2+} cation;
Binary mixed organic sol-
vents;
Conductometry

Abstract The complexation reaction between UO_2^{2+} cation and the macrobicyclic ligand $C_{18}H_{36}N_2O_6$ was studied in acetonitrile–dimethylformamide (AN–DMF), acetonitrile–tetrahydrofuran (AN–THF), acetonitrile–dichloromethane (AN–DCM) binary solvent solutions at different temperatures using the conductometric method. In most cases, $C_{18}H_{36}N_2O_6$ forms a 1:1 [M:L] complex with the UO_2^{2+} cation. But in some of the studied solvent systems, in addition to formation of a 1:1 complex, a 1:2 [M:L₂] complex is formed in solution. A non-linear behavior was observed for changes of $\log K_f$ of the $(C_{18}H_{36}N_2O_6 \cdot UO_2)^{2+}$ complex versus the composition of the binary mixed solvents. The sequence of the stability of the $(C_{18}H_{36}N_2O_6 \cdot UO_2)^{2+}$ complex in pure solvent systems at 25 °C decreases in the order: AN > THF > DMF. In the case of binary solvent solutions, the stability constant of the complex at 25 °C was found to be: AN–DCM > AN–THF > AN–DMF. The values of thermodynamic quantities (ΔS_c° , ΔH_c°), for the formation of the complex were obtained from temperature dependence of the stability constant of the complex using the van't Hoff plots. The results show that in all cases, the complex is both entropy and enthalpy stabilized and both of these parameters are affected by the nature and composition of the mixed solvent systems.

© 2012 King Saud University. Production and hosting by Elsevier B.V. All rights reserved.

1. Introduction

Uranium is a radioactive metal that exists ubiquitously in the environment (Gongalsky Konstantin, 2003). Since uranium is one of the main sources in nuclear energy generation and enriched uranium is a major component in nuclear weapons, human beings have a high chance of being exposed to

uranium, which can cause severe effects on human health (Craft et al., 2004; Zhou and Gu, 2005). A large amount of uranium in drinking water may lead to harmful biological effects in humans. Chemical toxicity caused by natural uranium poses a major risk to the kidneys. Also it is important to monitor the concentration of uranium at various stages of preparation of uranium dioxide fuel pellets (Murty et al., 1997) and also in the environment safety assessment related to the nuclear industry (Miller et al., 1994). For these reasons, detection of uranium is very important. In nature, hexavalent uranium is commonly associated with oxygen as the uranyl ion, UO_2^{2+} .

Thermodynamic studies on the complexation of $C_{18}H_{36}N_2O_6$ with the UO_2^{2+} cation have been performed in order to elucidate the nature of the cation-binding behavior from the thermodynamic point of view and also to gain insights into

* Corresponding author.

E-mail address: ghrounaghi@yahoo.com (G.H. Rounaghi).

☆ Peer review under responsibility of King Saud University.



Production and hosting by Elsevier

the factors governing cation–ligand complexation phenomena (Davidson et al., 1984; Matthes et al., 1987; Arnold et al., 1987; Adamic et al., 1985, 1986). The ability of the solvent molecules to compete with the donor atoms of the ligand toward the cation, is one of the critical factors that can thermodynamically influence the complexation process (Solov'ev et al., 1996).

In order to achieve appropriate solvent properties, mixtures of two solvents are often used. The physiochemical properties of mixed solvents are interesting both from theoretical and practical points of view, because many chemical and electrochemical reactions might be carried out advantageously in these media. Usually mixed solvents do not behave as expected from statistical considerations; the solvating ability of solvents in their mixtures can be different from those of neat media. The deviations from ideal behavior are indicative of the extent of preferential solvation and the existence of specific solvent–solute and solvent–solvent interactions (Kinisinger et al., 1973; Burger, 1983).

Ion–solvent interactions play a very important role in the studies of stoichiometry, structure, and the stability of metal cation complexes with crown ethers. Knowledge of the ionophore solvation properties enables one to choose a suitable solvent for complexation studies and to obtain detailed information on the solvent effect. To control the chemical reactions in non-aqueous and mixed solvents, it is necessary to select an appropriate solvent (Marcus, 1985). This is a complicated problem because of an exceptionally great variety and specificity of chemical reactions in solutions. Recently, we have investigated the complexation processes of crown ethers with various metal cations in pure and some binary mixed organic solvent solutions (Rounaghi and Mohammad Zadeh Kakhki, 2009; Rounaghi et al., 2008, 2001, 2011; Razghandi et al., 2011; Shamsipur and Khayatian, 2001).

Uranium is at the heart of commercial nuclear power and is vital to the entire nuclear enterprise. Its presence and use worldwide has resulted in a vast literature, not only on uranium complexation and separation reactions, but also on all aspects of the uranium fuel cycle, mining and, milling, isotope enrichment, reactor fuel manufacturing and spent reactor fuel. The uranyl ion UO_2^{2+} is the most common uranium ion in aqueous media. Uranyl ion complexes extract readily into organic solvents. This is the basis of the widely used purex process for reprocessing spent nuclear reactor fuel reprocessing and weapons production.

In the present work, we studied the complexation process between $\text{C}_{18}\text{H}_{36}\text{N}_2\text{O}_6$ (Fig. 1) and the UO_2^{2+} cation in pure acetonitrile, tetrahydrofuran, dichloromethane and dimethylformamide and also in acetonitrile–tetrahydrofuran (AN–THF), acetonitrile–dichloromethane (AN–DCM) binary mixtures at different temperatures using the conductometric method.

2. Experimental

$\text{C}_{18}\text{H}_{36}\text{N}_2\text{O}_6$ (Merck) and $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Riedel company) were used without further purification. The solvents: acetonitrile, dimethylformamide, dichloromethane, tetrahydrofuran, all from (Merck), were used with the highest purity.

The experimental procedure to obtain the formation constant of the complex was as follows: a solution of metal salt (1×10^{-4} M) was placed in a titration cell and the conductance

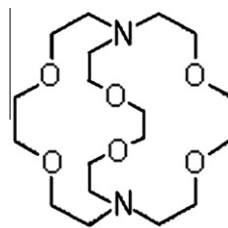


Figure 1 Structure of kryptofix 222.

of the solution was measured, then a step-by-step increase in the $\text{C}_{18}\text{H}_{36}\text{N}_2\text{O}_6$ concentration was performed by a rapid transfer of $\text{C}_{18}\text{H}_{36}\text{N}_2\text{O}_6$ solution in the same solvent (2×10^{-3} M) to the titration cell, using a microburette and the conductance of the resulting solution was measured after each step at the desired temperature. The conductance measurements were performed on a conductivity meter LF (model 538) in a water bath (Julabo model F12) thermostated at a constant temperature maintained within ± 0.01 °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 0.84 cm^{-1} was used throughout the studies.

3. Data analysis program

The 1:1 complexation of a metal cation, M^{n+} , with a macrobicyclic ligand [L] is represented by the following equilibrium:



The corresponding equilibrium constant, K_f , is given by:

$$K_f = [\text{ML}^{n+}] f_{\text{ML}^{n+}} / [\text{M}^{n+}] f_{\text{M}^{n+}} \cdot [\text{L}] f_L \quad (2)$$

where $[\text{ML}^{n+}]$, $[\text{M}^{n+}]$ and $[\text{L}]$ represent the equilibrium molar concentration of the complex, free cation, and free ligand, respectively and f represents the activity coefficient of the species indicated. Under the highly dilute conditions used in this investigation, the activity coefficient of the uncharged ligand, f_L can be reasonably assumed as unity (Takeda, 1983). Thus the complex formation constant in terms of molar conductance can be expressed as:

$$K_f = [\text{ML}^{n+}] / [\text{M}^{n+}][\text{L}] = \Lambda_M - \Lambda_{\text{obs}} / \Lambda_{\text{obs}} - \Lambda_{\text{ML}} \quad (3)$$

where

$$C_L = C_M (\Lambda_M - \Lambda_{\text{obs}}) / (\Lambda_M - \Lambda_{\text{ML}}) \quad (4)$$

Here Λ_M is the molar conductance of the metal ion before addition of the ligand, Λ_{ML} is the molar conductance of the complexed ion, Λ_{obs} is the molar conductance of the solution during titration, C_L is the analytical concentration of the L added, and C_M is the analytical concentration of the metal ion. The complex formation constant, K_f , and the molar conductance of the complex, Λ_{ML} , were obtained by computer fitting of Eqs. (3) and (4) to molar conductance as a function of the ligand/metal cation mole ratio data, using a non-linear least-squares program GENPLOT (Genplot, 1989). All calculated stability constants are summarized in Table 1. The details of the calculation of the stability constants of the metal ion complexes by the conductometric method have been described elsewhere (Rounaghi et al., 1997).

Download English Version:

<https://daneshyari.com/en/article/5142157>

Download Persian Version:

<https://daneshyari.com/article/5142157>

[Daneshyari.com](https://daneshyari.com)