

**Iranian Chemical Isotope Exchange Research:  
Boron, Lithium and Uranium**

**Mark Gorwitz  
April 2020**

## **Part I: Boron Isotope Exchange Related Research**

### **Thesis:**

#### **Separation of Boron Isotopes by Distillation of (CH<sub>3</sub>)<sub>2</sub>O-BF<sub>3</sub> Complex**

, M.Sc. Thesis Sharif University of Technology, Abdollahi, Mojtaba (Author) ; Outokesh, Mohammad (Supervisor) ; Ahmadi, Javad (Supervisor)

### **Abstract**

Natural boron includes two stable isotopes <sup>10</sup>B and <sup>11</sup>B with 19.3 and 80.7 weight percent respectively. <sup>10</sup>B isotope has a high thermal neutron absorption cross section. So isotope <sup>10</sup>B material is suitable for making atomic reactor control rods. Other and even more important applications of <sup>10</sup>B are in disclosing neutrons in order to measure neutron reactors fluxes and also are in nuclear physics laboratories and medical radiation. This isotope also is used in the pharmaceutical and the military industries. There are several methods for separating boron isotopes. Among the distillation methods, thermal diffusion of BF<sub>3</sub>, distillation of BF<sub>3</sub>, distillation of methyl borate, boric acid distillation by steam, distillation with isotope exchange between liquid complex (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O-BF<sub>3</sub> with BF<sub>3</sub> gas and distillation together with isotope exchange between complex liquid (CH<sub>3</sub>)<sub>2</sub>O-BF<sub>3</sub> with BF<sub>3</sub>, can be mentioned. Among the stated methods, distillation method with isotope exchange is used in the industrial scale.

#### **Experimental Study and Optimization of Nuclear Grade Boric Acid Production Process**

, M.Sc. Thesis Sharif University of Technology, Ahmadian Koudakan, Payam (Author) ; Outokesh, Mohammad (Supervisor) ; Aflaki Pashaki, Fereydoon (Supervisor)

### **Abstract**

Boric acid (H<sub>3</sub>BO<sub>3</sub>) is a weak monobasic acid that exist as a white powder in the standard conditions. In industry, it is used in manufacturing of fiberglass filaments, precious metals soldering and production of flat panel LCD displays. In all of these applications, normal grade boric acid is used, but nuclear industry demands an ultrapure boric acid (UPA) for controlling of the reactivity and power levels in pressurized water reactors. Annual consumption of UPA in Bushehr Power Plant (BPP) is around 60 metric tons. Currently, this amount is imported from Russia, but atomic energy organization of Iran plans to displace it by the acid made inside the country. Domestic production of UPA in addition to covering the need of the BPP, can generate a surplus for the national pharmaceutical industries. The present study can be considered as the first phase of the atomic energy's mother project, and it was aimed at preparation of UPA from the commercially available boric acid. Our method of purification was a combination of cation exchange (CX), anion exchange (AX) and recrystallization (RC). Solubility of boric acid increases with temperature dramatically, and it precipitates from a saturated solution at lower temperatures. Thus, it was necessary to carry out both of the CX and AX operations at medium to high temperatures (50 < T < 80 oC) and in the stirred vessels, instead of the fixed bed columns. We designed and tested 28 purification processes, whose difference was number of the employed CX, AX and RC stages, as well as the order of their appearing in the process. The obtained UPA in each process was analyzed for measuring of

concentration of the major impurities. Out of the 28 examined processes, 4 could meet the standard limits of the impurities for all of the checked ions. The next step of the project was finding optimum purification process between the aforementioned five options. Our criterion for such optimization was the overall economical balance. Three factors affecting economic balance were number of stages and yield of the process. The final selected process had the following abbreviated scheme: CX→AX →CX→AX→RC.

### **Preparation of High Purity BF<sub>3</sub> Gas and Feasibility Study on Separation of Boron Isotopes by its Injection into a Gas Centrifuge**

, M.Sc. Thesis Sharif University of Technology, Hashemi Baragoori, Keyvan (Author) ; Outokeh, Mohammad (Supervisor) ; Karimi-Sabet, Javad (Supervisor)

#### **Abstract**

Natural Boron consists of two stable isotopes, <sup>10</sup>B (19.3%) and <sup>11</sup>B (80.7%). <sup>10</sup>B isotope has a large thermal neutron absorption and therefore, use widely in such aspects as modern industry, atomic energy industry (as control rods, chemical shim and etc.), Medical science and applications in disclosing neutrons to measure neutron reactors fluxes. Boron trifluoride is most importantly used as a reagent in organic synthesis, typically as a Lewis acid. In this study, we designed and built the related setup for preparation of high purity BF<sub>3</sub> gas. And then we tried to optimize the efficiency with process design tools such as response surface methodology (RSM). At the end of this study, we were able to achieve over 80% purity and efficiency of the process.

#### **Journal Articles:**

**Application of ideal temperature gradient technology to optimize the chemical exchange and distillation process of boron isotopes separation by (CH<sub>3</sub>)<sub>2</sub>O-BF<sub>3</sub> complex,** Chemical Engineering and Processing 76 · January 2013

Mojtaba Abdollahi, Sharif University of Technology  
Seyed Javad Ahmadi, Atomic Energy Organization of Iran

#### **Abstract**

To exert the optimum effect, the chemical exchange process to boron isotope separation was investigated. In this enrichment method the distillation of dimethyl ether-boron trifluoride complex, which was one of the most efficient industrial methods for purification of isotope boron-10, was optimized. In chemical exchange process of boron isotopes separation two chemical reactions occur. The first one is the decomposition reaction that is an endothermic reaction. The second one is the exchange reaction that is a pyrogenic reaction. With increasing temperature, the decomposition reaction is speeded while the exchange reaction is slowed down. Affecting on both decomposition and exchange reactions, the temperature gradient of column is very important. The separation column is covered by 18 tubular electrical heaters with 350 watt power. Each electrical heater is controlled by a separated monitor controller. The monitor controlling system can apply accurate, continuous and various vertical temperature gradients of distillation column. The highest separation factor for each theoretical stage was determined 1.026 at T<sub>bp</sub> = 92 °C and  $\partial T / \partial Z = 7.56 \text{ } ^\circ\text{C/m}$ . T<sub>bp</sub> of complex in industrial plant of boron enrichment

is 97 °C and the maximum separation factor for a theoretical stage was recorded 1.016 in uncontrolled temperature gradient of distillation column.

**Application of ideal temperature gradient technology to optimize the chemical exchange and distillation process of boron isotopes separation by  $(CH_3)_2O-BF_3$  complex,** Chemical Engineering and Processing: Process Intensification, Volume 76, February 2014, Pages 26–32

- Mojtaba Abdollahi<sup>a</sup>,
- Seyed Javad Ahmadi<sup>b</sup>
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## Highlights

- Modification the method of boron isotopes separation by chemical exchange and distillation.
- Application continuous, accurate and customizable temperature gradient technology.
- Increasing the separation factor of 1.016–1.026 for each theoretical stage of column.
- Reducing the total cost of boron isotope separation process to 66.67%.

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## Abstract

To exert the optimum effect, the chemical exchange process to boron isotope separation was investigated. In this enrichment method the distillation of dimethyl ether-boron trifluoride complex, which was one of the most efficient industrial methods for purification of isotope boron-10, was optimized. In chemical exchange process of boron isotopes separation two chemical reactions occur. The first one is the decomposition reaction that is an endothermic reaction. The second one is the exchange reaction that is a pyrogenic reaction. With increasing temperature, the decomposition reaction is speeded while the exchange reaction is slowed down. Affecting on both decomposition and exchange reactions, the temperature gradient of column is very important. The separation column is covered by 18 tubular electrical heaters with 350 W power. Each electrical heater is controlled by a separated monitor controller. The monitor controlling system can apply accurate, continuous and various vertical temperature gradients of distillation column. The highest separation factor for each theoretical stage was determined 1.026 at  $T_{bp} = 92$  °C and  $\partial T/\partial Z = 7.56$  °C/m.  $T_{bp}$  of complex in industrial plant of boron enrichment is 97 °C and the maximum separation factor for a theoretical stage was recorded 1.016 in uncontrolled temperature gradient of distillation column.

## **Part II: Lithium chemical isotope exchange related research**

### **Thesis:**

**The separation of lithium isotopes: physical and chemical methods, Abouzar Kiyani, undated**

### **Lithium Isotopes Separation by Amalgam Electrolysis Method**

**Aryanpur, Vahid / 2010**

1. Type of Document: M.Sc. Thesis
2. Language: Farsi
3. Document No: 40554 (46)
4. University: Sharif University of Technology
5. Department: Energy Engineering
6. Advisor(s): Outokesh, Mohammad; Ahmadi, Javad
7. Abstract:
8. Lithium has two stable isotopes naturally including  $^{6}\text{Li}$  at 7.5% and  $^{7}\text{Li}$  at 92.5% relative abundance. In spite of the similarities of lithium isotopes in common chemical reactions, they have some completely distinctive behaviors in nuclear reactions.  $^{6}\text{Li}$  has considerable neutron cross section capturing in thermal neutron range about 945 barns while this feature for  $^{7}\text{Li}$  is insignificant about 0.037 barns. This difference makes them to play different roles in nuclear uses.  $^{7}\text{LiOH}$  is applied for pH adjustment of coolant in light water reactors.  $^{6}\text{Li}$  is not only used as a shielding material against thermal neutrons, but also is known as a source of tritium in the blanket of fusion reactors which in turn increase the importance of lithium isotopes separation. Electrolysis is one of the most known lithium isotopes separation methods, involving mercury cathode and a neutral anode like titanium or graphite. In this project mass transfer has been determined as the slowest step which controls the rate of amalgam formation reaction theoretically and practically and the effects of an extensive range of parameters, including types of lithium compounds, temperature of the solution, type of the anode and of course electrolysis of mixture salts as a new idea to reach higher current efficiency and higher separation factor. An acceptable separation has attained for  $^{7}\text{Li}$  in twenty stages up to 5% and more than 1% for  $^{6}\text{Li}$  in 5 stages, demonstrating a substantial separation factor between 1.04 to 1.06 for  $\text{LiOH}$  and  $\text{LiCl}$  respectively.

### **Lithium Isotopes Separation by Electrolysis Amalgam by a Continuous Method**

**Kowsari, Mohammad Reza / 2013**

1. Type of Document: M.Sc. Thesis
2. Language: Farsi
3. Document No: 44570 (46)
4. University: Sharif University of Technology
5. Department: Energy Engineering

6. Advisor(s): Otukesh, Mohammad; Ahmadi, Javad
7. Abstract:
8. Lithium has 9 isotopes which two isotopes are stable and remaining isotopes are unstable and have half-life. Lithium stable isotopes include  $^{6}\text{Li}$  and  $^{7}\text{Li}$  that their abundance is 7.53% and 92.47% respectively. Importance of lighter lithium isotope appears for its small cross section against thermal neutron and producing fusion reactors fuel in nuclear industries. Thermal neutron absorption cross section for  $^{6}\text{Li}$  and  $^{7}\text{Li}$  are 950 barn and 37 mbarn respectively. Interesting of these isotopes in nuclear industry is due to the large difference in the absorption cross section. $^{6}\text{Li}$  compounds implied for tritium producing in coat of nuclear fusion reactor with DT fuel. Following tritium is used in diagnosis of diseases such as thalassemia.  $^{6}\text{LiD}$  compound applied as fuel in fusion nuclear reactors which worked by laser inertial encapsulation method.  $^{7}\text{Li}$  in form of  $^{7}\text{LiOH}$  applied in adjusting cooled fluid pH in light water reactor and as anti-corrosion compound in fission reactor.  $^{7}\text{Li}$  is used in generating reactor (Breeding Reactor). The main use of  $^{6}\text{Li}$ , however, is as the source of tritium producing and used in nuclear fusion reactor. In 1388s, first experiment on lithium isotope separation by electrolysis carried on laboratory scale and batch method in IRAN. In this project imply same separation method but distinction is the scale is pilot and continuous method is chosen and important parameters have been studied. In this method, is used from mercury cathode and lithium hydroxide as feed which flow counter current into electrolysis cell. Implied anodes materials are stainless steel and coated titanium with ruthenium oxide. Parameters in this experiment are feed and mercury flow rate, lithium hydroxide concentration, current, anode type and amount of implied anode surface. Effect of each parameter studies on separation factor, efficiency, amount of lithium lost in feed and amount of lithium gained in product. In this project, separation is done by separation factors in range of 1.02 to 1.122 in single stage and in each step enrichment level was 0.2% and even was reached to 0.5%

(See also: Mohammadreza Kosari, **Lithium Isotope Separation in a Castner-Kellner Cell by Electrolysis Amalgam System by a Continuous Method**, MSc)

#### **Study on Momentary and Overall Separation Factors in Lithium Isotopes Separation by Batch Electrolysis**

##### **Azad, Mohsen / 2015**

1. Type of Document: M.Sc. Thesis
2. Language: Farsi
3. Document No: 47883 (46)
4. University: Sharif University of Technology
5. Department: Energy Engineering
6. Advisor(s): Otukesh, Mohammad; Ahmadi, Javad; Kowsari, Mohammad Reza
7. Abstract:
8. Lithium has two stable isotopes,  $^{6}\text{Li}$  and  $^{7}\text{Li}$ . Abundance of these isotopes are 7.53% and 92.43% respectively. Each isotope has an important role in nuclear industry. For example,  $^{6}\text{Li}$  compounds is used in production of tritium in nuclear fusion reactors coated with DT fuel and as fuel in nuclear fusion reactors that operate with laser inertial

confinement method applied.  $7\text{LiOH}$  is used to adjust the pH of the fluid coolant in light water reactors and also in Breeding Reactors. Lithium isotope separation in different ways so far been brought into operation. The other aspect to this work, it can be both continuous and batch for action. Lithium isotopes for the first time by electrolysis using the amalgam and mercury as cathode and titanium as an anode and a lithium salt dissolved done. Modelling of separation factor of lithium isotopes in a batch electrolysis cell with mercury cathode was subject of the current study. Modelling of this system can help design of the employed system to use in the separation units. The study investigated effects of different operational parameters including current density, and  $\text{LiOH}$  concentration and then modelling of them to predict the both momentary and overall separation factors. Between the both examined parameters, effect of current density was found to be the more significant than the other. The maximum single stage separation factor achieved in the present work was 1.136, which was obtained by using the current density of “0.184 Amp/cm<sup>2</sup>”. Theoretical elucidation of the observed phenomena was accomplished using migration-diffusion theory, and the Bell-Gurneys’ mechanism with special attention onto role of the chemical exchange. Accepting this postulate that “when a rate determining step prevails over the kinetics, its corresponding separation factor will determine separation factor of the system” would greatly simplify the theoretical interpretation.

### **Lithium Recovery from Brine Sources of Iran by Precipitation Method**

#### **Jandaghi, Mohammad Reaz / 2014**

1. Type of Document: M.Sc. Thesis
2. Language: Farsi
3. Document No: 46456 (07)
4. University: Sharif University of Technology
5. Department: Materials Science and Engineering
6. Advisor(s): Askari, Masoud
7. Abstract:
8. Lithium is one of the most commonly used metals in industry with a wide variety of applications including batteries, lubricating grease and pharmaceutical products. Demand for lithium is expected to rise with the increasing adoption of electric vehicles. Market reports have predicted that world lithium demand will increase by 2.5 times from 2010 to 2020. Therefore, there is a pressing need to develop new sources of lithium to support this anticipated increase in demand. Lithium can be extracted from salt brine and lithium containing minerals as lithium compounds.
9. Salt brines are the most abundant lithium sources available in the world, comprising about 60% of all known lithium deposits. Producing lithium by evaporating salt brine is also less costly than directly extracting it from lithium minerals. This makes salt brines as an important sources of lithium to meet future market demand in the world. Chemical composition of brine determines sufficient method for extraction of lithium from it.
10. A major limitation of lithium extraction from salt brine is the difficulty in processing

brine with a high magnesium to lithium (Mg/Li) ratio. It is important for the extracted lithium compounds to have low magnesium content to avoid magnesium contamination in the downstream products. This makes lithium extraction from salt lakes with a high Mg/Li ratio a difficult task, as additional steps and costs are incurred to reduce the magnesium content of the brine solution to an acceptable level. The additional cost varies directly with the Mg/Li ratio.

11. This research was done on KHOR-BIYABANAK as very high Mg/Li salt brines in the world with proportion of magnesium to lithium about 300 and the main lithium source of Iran. In this regard caustic soda, ammonia, dolomite, calcium carbonate and lithium hydroxide were utilized as magnesium and boron removing agent and Sulfuric acid used for calcium exclusion from brine. Also Di sodium phosphate and di sodium carbonate were employed as precipitant for lithium phosphate and lithium carbonate production respectively. Furthermore effect of parameters like reaction time and temperature, solution rest time and amount of precipitants and how are added to brine on lithium recovery and final product purity were investigated. Results indicated that production of high purity lithium phosphate (99/9%) from KHOR-BIYABANAK's brine is achievable. But production of lithium carbonate is faces more problem compared with lithium phosphate because of higher solubility of lithium carbonate comparison to lithium phosphate and higher limit of lithium concentration in solution for lithium carbonate precipitation. So optimized condition for lithium carbonate precipitation reaction leads to production of 97% purity lithium carbonate.

#### **Conference Papers:**

M.R. Kosari, M. Outokesh, S.J. Ahmadi, J. Rafeei and A. Aminian, **Application of Lithium Isotopes and Their Separation Method**, 1<sup>st</sup> National Conference on Application of Stable Isotopes, Ferdowsi University, Science Department, Mashhad, Iran, 2013

M.R. Kosari, S.J. Ahmadi, M. Outokesh, A. Aminian and J. Rafeei, **Study on Efficiency of Electrolysis System for Lithium Isotope Separation**, 1<sup>st</sup> National Conference on Application of Stable Isotopes, Ferdowsi University, Science Department, Mashhad, Iran, 2013

M.R. Kosari, S.J. Ahmadi, M. Outokesh, E. Najjarzade and M.A. Kiani, **Lithium Isotopes Production Technology by Amalgam Electrolysis Method**, The Conference on Commercialization, National Development and Engineering Sciences, Mazandaran, Iran, 2013

M.R. Kosari, S.J. Ahmadi, M. Outokesh and J. Rafee, **Lithium Isotopes Enrichment in order to Production of <sup>6</sup>Li as Elementary Material in Fusion**, 3<sup>rd</sup> National Conference on New Technology of Chemistry and Chemical Engineering, Islamic Azad University, Ghochan, Iran, 2014

**Journal Articles:**

**SPECTROPHOTOMETRIC STUDY OF THE THERMODYNAMICS OF COMPLEXATION OF LITHIUM AND SODIUM IONS WITH DIBENZO-24-CROWN-8 IN BINARY DIMETHYLFORMAMIDE-ACETONITRILE MIXTURES USING MUREXIDE AS A METALLOCHROMIC INDICATOR ,** Journal of Coordination Chemistry, Volume 35, Issue 3-4, 1995, pages 289-297

Habibollah Khajesharifi<sup>a</sup> & Mojtaba Shamsipur<sup>a</sup>

Department of Chemistry, Razi University, Kermanshah, Iran

**Abstract**

Complexation of  $\text{Li}^+$  and  $\text{Na}^+$  with dibenzo-24-crown-8 has been studied in dimethylformamide-acetonitrile mixtures by means of a competitive spectrophotometric technique using murexide as metal ion indicator. Stabilities of the resulting 1:1 complexes were investigated at various temperatures and enthalpies and entropies of complexation were determined from the temperature dependence of the formation constants. Sodium forms a more stable complex with the crown ether than lithium. There is an inverse linear relationship between  $\log K_f$  and the mole fraction of DMF in the solvent mixtures. The  $\Delta H^\circ - T\Delta S^\circ$  plot of all thermodynamic data, obtained for both crown complexes in different solvent mixtures, shows a fairly good linear correlation, indicating the existence of an enthalpy-entropy compensation effect in complexation.

**NUCLEAR MAGNETIC RESONANCE STUDY OF LITHIUM ION COMPLEXES WITH SEVERAL CROWN ETHERS IN BINARY ACETONITRILE-NITROMETHANE MIXTURES,** Journal of Coordination Chemistry, Volume 39, Issue 1, 1996, pages 33-42  
Ebrahim Karkhaneei<sup>a</sup>, Abbas Afkhami<sup>a</sup> & Mojtaba Shamsipur<sup>b</sup>

**Abstract**

Lithium-7 NMR measurements were used to determine the stoichiometry and stability of  $\text{Li}^+$  complexes with 12-crown-4 (12C4), 15-crown-5 (15C5), benzo-15-crown-5 (B15C5), 18-crown-6 (18C6), dicyclohexyl-18-crown-6 (DC18C6) and dibenzo-18-crown-6 (DB18C6) in various acetonitrile-nitromethane mixtures at 27°C. In all cases studied, the variation in the  ${}^7\text{Li}$  chemical shift with the crown/ $\text{Li}^+$  mol ratio indicated the formation of 1:1 complexes in solution. The formation constants of the resulting complexes were evaluated from computer fitting of the mol ratio data to an equation which relates the observed chemical shifts to the formation constant. It was found that, in all solvent mixtures used, the stabilities of the resulting complexes vary in the order 15C5 > B15C5 > DC18C6 > 12C4 > 18C6 > DB18C6. There is an inverse relationships between  $\log K_f$  of the complexes and the mol fraction of acetonitrile in the solvent mixtures.

**LITHIUM-7 AND SODIUM-23 NMR STUDIES OF COMPLEXATION OF Li<sup>+</sup> AND Na<sup>+</sup> IONS WITH 1,10-PHENANTHROLINE, 2,2"-BIPYRIDINE AND 8-HYDROXYQUINOLINE IN SOME NON-AQUEOUS SOLUTIONS,**  
**POLYHEDRON** 1996, Volume 15, Number 20; Page(s) 3647 To 3652.

Author(s): MADRAKIAN T., AFKHAMI A., GHASEMI J., SHAMSIPOUR M.

**Abstract:**

NMR spectra of lithium-7 and sodium-23 were used to study the interactions of Li<sup>+</sup> and Na<sup>+</sup> ions with 1,10-phenanthroline, 2,2"-bipyridine and 8-hydroxyquinoline in nitromethane, nitrobenzene, acetonitrile and acetone solutions. The stoichiometry and stability of the resulting complexes were evaluated from non-linear least-squares fitting of the chemical shift-mole ratio data to appropriate equations. There is an inverse relationship between the stability of the complexes and the solvating ability of the solvents, as expressed by Gutmann donor numbers. In all solvents studied, Li<sup>+</sup> forms more stable complexes than Na<sup>+</sup> and, for each cation, the stability order of the resulting complexes is 1,10-phenanthroline > 2,2"-bipyridine > 8-hydroxyquinoline.

**LITHIUM-7 AND SODIUM-23 NMR STUDIES OF THE COMPLEXATION OF Li<sup>+</sup> AND Na<sup>+</sup> IONS WITH 1,13-DIBENZO-24-CROWN-8 IN BINARY NITROMETHANE-ACETONITRILE MIXTURES,** Journal of Coordination Chemistry, Volume 46, Issue 1, 1998, pages 1-11

Ebrahim Karkhaneei<sup>a</sup>, Javad Zolgharnein<sup>b</sup>, Abbas Afkhami<sup>a</sup> & Mojtaba Shamsipur<sup>b</sup>

**Abstract:**

<sup>7</sup>Li, <sup>23</sup>Na and <sup>13</sup>C NMR measurements were used to study the stoichiometry and stability of Li<sup>+</sup> and Na<sup>+</sup> complexes with dibenzo2-4-crown-8 in binary nitromethane-acetonitrile mixtures. The resulting chemical shift-mol ratio data clearly reveal the formation of both 1:1 and 2:1 (metal/ligand) complexes in solution. Formation of the two adducts in nitromethane and acetonitrile solutions was further supported by monitoring the molar conductance of Li<sup>+</sup> and Na<sup>+</sup> solutions as a function of macrocycle/metal ion mol ratio. Stepwise formation constants of the 1:1 and 2:1 complexes were evaluated from computer fitting of the NMR mol ratio data to equations which relate observed metal ion chemical shifts to formation constants. In all solvent systems, sodium forms more stable complexes with the crown ether than lithium. There is an inverse linear relationship between the logarithms of the stability constants and the mol fraction of acetonitrile in the solvent mixtures.

**NMR STUDY OF EXCHANGE KINETICS OF THE LITHIUM ION WITH CRYPTAND C222 IN BINARY ACETONITRILE-NITROMETHANE MIXTURES,** Journal of Coordination Chemistry, Volume 44, Issue 1-2, 1998, pages 23-32  
Mojtaba Shamsipur<sup>a</sup>, Ebrahim Karkhaneei<sup>b</sup> & Abbas Afkhami<sup>b</sup>

**Abstract**

The exchange kinetics of the lithium ion with cryptand C222 were studied in acetonitrile-nitromethane mixtures by lithium-7 NMR line-shape analysis. In all solvent mixtures used, and over the entire temperature range studied, the chemical exchange of the Li<sup>+</sup> ion between the solvated and complexed sites was found to occur via a bimolecular mechanism. The activation

parameters  $E_a$ ,  $\delta H^\ddagger$ ,  $\delta S^\ddagger$  and  $\delta G^\ddagger$  for the exchange have been determined. The free energy barrier for the exchange process appears to be nearly independent of the binary mixture composition. The results confirm the preferential solvation of the lithium ion with acetonitrile in the binary mixed solvent systems used.

**NMR STUDY OF EXCHANGE KINETICS OF THE LITHIUM ION WITH CRYPTAND C222 IN BINARY ACETONITRILE-NITROMETHANE MIXTURES,** Journal of Coordination Chemistry, Volume 44, 1998 - Issue 1-2, p23-32  
Mojtaba Shamsipur , Ebrahim Karkhaneei & Abbas Afkhami

### Abstract

The exchange kinetics of the lithium ion with cryptand C222 were studied in acetonitrile-nitromethane mixtures by lithium-7 NMR line-shape analysis. In all solvent mixtures used, and over the entire temperature range studied, the chemical exchange of the  $\text{Li}^+$  ion between the solvated and complexed sites was found to occur *via* a bimolecular mechanism. The activation parameters  $E_a$ ,  $\delta H^\ddagger$ ,  $\delta S^\ddagger$  and  $\delta G^\ddagger$  for the exchange have been determined. The free energy barrier for the exchange process appears to be nearly independent of the binary mixture composition. The results confirm the preferential solvation of the lithium ion with acetonitrile in the binary mixed solvent systems used.

**Lithium-7 NMR study of the exchange kinetics of the lithium ion with cryptand C221 in methanol solution. Temperature dependence of the exchange mechanism,** Polyhedron, Volume 17, Issue 21, 14 October 1998, Pages 3809-3815

Mojtaba Shamsipur<sup>1</sup>, Ebrahim Karkhaneei<sup>2</sup> and Abbas Afkhami<sup>2</sup>

1

Department of Chemistry, Razi University, Kermanshah, Iran

2

Department of Chemistry, Bouali Sina University, Hamadan, Iran

### Abstract

The exchange kinetics of  $\text{Li}^+$ C221 cryptate in methanol solution was studied by lithium-7 NMR line-shape analysis at a wide range of temperature. Depending on the temperature, two different exchange mechanisms were found to coexist to different extents. A dissociative pathway dominates at high temperatures (from 5 to 25°C), while a bimolecular mechanism prevails at lower temperatures (from -30 to -60°C). At the temperature range of -30 to 5°C, both the dissociative and bimolecular mechanisms contribute to the metal exchange. For the dissociative pathway, the activation parameters were calculated as:  $E_a=22\pm2 \text{ kJ mol}^{-1}$ ;  $\Delta H^\ddagger=20\pm2 \text{ kJ mol}^{-1}$ ;  $\Delta S^\ddagger=-144\pm8 \text{ J mol}^{-1} \text{ K}^{-1}$ . While for the bimolecular mechanism they are:  $E_a=9.9\pm0.4 \text{ kJ mol}^{-1}$ ;  $\Delta H^\ddagger=8.0\pm0.4 \text{ kJ mol}^{-1}$ ;  $\Delta S^\ddagger=-146\pm2 \text{ J mol}^{-1} \text{ K}^{-1}$ .

**COMPETITIVE NMR STUDY OF THE nCOMPLEXATION OF SOME ALKALINE EARTH AND TRANSITION METAL IONS WITH 12-CROWN-4, 15-CROWN-5 AND BENZO-15-CROWN-5 IN ACETONITRILE SOLUTION USING THE LITHIUM-7 NUCLEUS AS A PROBE**, Journal of Coordination Chemistry, Volume 52, Issue 2, 2000, pages 139-149

Mojtaba Shamsipur<sup>a</sup> & Tayyebeh Madrakian<sup>a</sup>

**Abstract**

<sup>7</sup>Lithium NMR measurements were used to determine the stoichiometry and stability of Li<sup>+</sup> complexes with 12-crown-4, 15-crown-5 and benzo-15-crown-5 in acetonitrile solution. A competitive <sup>7</sup>Li NMR technique was also employed to probe the complexation of Mg<sup>2+</sup>, Ca<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup> and Cd<sup>2+</sup> ions with the same crown ethers. In all cases, the stability of the resulting 1:1 complexes was found to decrease in the order 15-crown-5 > benzo-15-crown-5 > 12-crown-4. Ca<sup>2+</sup> and Cd<sup>2+</sup> ions formed the most stable complexes in the series.

**COMPETITIVE LITHIUM-7 NMR STUDY OF THE COMPLEXATION OF SOME ALKALINE EARTH AND TRANSITION METAL IONS WITH 18-CROWN-6 IN ACETONITRILE AND ITS 50 : 50 MIXTURES WITH NITROBENZENE AND NITROETHANE**, POLYHEDRON, JULY 2000 , Volume 19 , Number 14; Page(s) 1681 To 1685.

Author(s): SHAMSIPOUR M.\*, MADRAKIAN T.

\* Dept Chem, Kermanshah, Iran.

**Abstract:**

Lithium-7 NMR spectroscopy was used to investigate the stoichiometry and stability of a Li<sup>+</sup> complex with 18-crown-6 (18C6) in pure acetonitrile and its 50:50 (w/w) mixtures with nitrobenzene and nitromethane. A competitive Li-7 NMR method was also employed to probe the complexation of Mg<sup>2+</sup>, Ca<sup>2+</sup>, Ba<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup> and Cd<sup>2+</sup> ions with 18C6 in the same solvent systems. In all solvents, the stability of the resulting 1:1 complexes was found to vary in the order Ba<sup>2+</sup> > Ca<sup>2+</sup> > Cd<sup>2+</sup> > Mg<sup>2+</sup> approximate to Cu<sup>2+</sup> > Ni<sup>2+</sup> > Co<sup>2+</sup> > Zn<sup>2+</sup>.

**Lithium-7 NMR and ab initio calculation studies of complexation of Li<sup>+</sup> ions with 12-Crown-4, Benzo-12-Crown-4, 15-Crown-5, Benzo-15-Crown-5 and Dibenzo-15-Crown-5 in binary nitromethane-acetonitrile**, Polish Journal of Chemistry, 2007, Vol. 81, p1743-174, Shamsipur, M., Alizadeh, N., Rofouei, M.K. and Alizadeh, K.

#### Abstract

Complexes of 12-crown-4 (12C4), benzo-12-crown-4 (B12C4), 15-crown-5 (15C5), benzo-15-crown-5 (B15C5) and dibenzo-15-crown-5 (DB15C5) with Li<sup>+</sup> ion were investigated by lithium-7 NMR in a number of nitromethane (NM)-acetonitrile (AN) binary mixtures. In all cases, the exchange between the free and complexed lithium ion was fast on the NMR time scale and a single population average resonance was observed. Both 1:1 and 2:1 (sandwich) complexes were observed between lithium ion and 12C4 and B12C4 in pure nitromethane solution. Stepwise formation constants of the 1:1 and 1:2 (metal/ligand) complexes were evaluated from computer fitting of the NMR mole ratio data to equations which relate the observed metal ion chemical shifts to formation constants. There is an inverse linear relationship between the logarithms of the stability constants and the mole fraction of acetonitrile in the solvent mixtures. The stability of the complexes varies inversely with the Gutmann donor number of the solvent. The stability order of the complexes was found to be 15C5.Li<sup>+</sup> > B15C5.Li<sup>+</sup> > DB15C5.Li<sup>+</sup> > 12C4.Li<sup>+</sup> > B12C4.Li<sup>+</sup>. The optimized structures of the free ligands and their 1:1 and 2:1 complexes with Li<sup>+</sup> ion were predicted by ab initio theoretical calculations using the Gaussian 98 software, and the results are discussed.

**Nuclear magnetic resonance study of the stoichiometry and stability of lithium ion complexes with two small size crown ethers in binary nitromethane-acetonitrile mixtures**, Journal of Inclusion Phenomena and Macrocyclic Chemistry (2010) 68(3-4) 431-436, Alizadeh N and Shamsipur M

#### Abstract

Lithium-7 NMR spectrometry was used to study the complexation reaction between lithium ions and different small size crown ethers 12-crown-4 (12C4), benzo-12-crown-4 (B12C4) in a number of binary nitromethane (NM)-acetonitrile (AN) mixtures. The exchange between the free and complexed lithium ion was fast on the NMR time scale and a single population average resonance was observed. Both 1:1 and 2:1 (sandwich) complexes were observed between lithium ion and 12C4 and B12C4 in pure nitromethane solution. Stepwise formation constants of the 1:1 and 2:1 (ligand/metal) complexes were evaluated from computer fitting of the NMR-mole ratio data to equations which relate the observed metal ion chemical shifts to formation constants. There is an inverse linear relationship between the logarithms of the stability constants and the mole fraction of acetonitrile in the solvent mixtures. The stability order of the 1:1 and 2:1 complexes was found to be 12C4. Li<sup>+</sup> > B12C4. Li<sup>+</sup>. The optimized structures of the free ligands and their 1:1 and 2:1 complexes with Li<sup>+</sup> ion were predicted by ab initio theoretical calculations using the Gausian 98 software, and the results are discussed.

**A comparison of complexation of Li<sup>+</sup> ion with macrocyclic ligands 15-crown-5 and 12-crown-4 in binary nitromethane–acetonitrile mixtures by using lithium-7 NMR technique and *ab initio* calculation,** Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, Volume 78, Issue 1, January 2011, Pages 488-493

Nina Alizadeh

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### Abstract

Lithium-7 NMR measurements were used to investigate the stoichiometry and stability of Li<sup>+</sup> complexes with 15-crown-5 (15C5), benzo-15-crown-5 (B15C5), dibenzo-15-crown-5 (DB15C5) and 12-crown-4 (12C4) in a number of nitromethane (NM)-acetonitrile (AN) binary mixtures. In all cases, the exchange between the free and complexed lithium ion was fast on the NMR time scale and a single population average resonance was observed. While all crown ethers form 1:1 complexes with Li<sup>+</sup> ion in the binary mixtures used, both 1:1 and 2:1 (sandwich) complexes were observed between lithium ion and 12C4 in pure nitromethane solution. Stepwise formation constants of the 1:1 and 2:1 (ligand/metal) complexes were evaluated from computer fitting of the NMR-mole ratio data to equations which relate the observed metal ion chemical shifts to formation constants. There is an inverse linear relationship between the logarithms of the stability constants and the mole fraction of acetonitrile in the solvent mixtures. The stability order of the 1:1 complexes was found to be 15C5·Li<sup>+</sup> > B15C5·Li<sup>+</sup> > DB15C5·Li<sup>+</sup> > 12C4·Li<sup>+</sup>. The optimized structures of the free ligands and their 1:1 and 2:1 complexes with Li<sup>+</sup> ion were predicted by *ab initio* theoretical calculations using the Gaussian 98 software, and the results are discussed.

**A Comparison of Complexation of Li<sup>+</sup> Ion with Macroyclic Ligands 15-Crown-5 and Benzo-derivatives in Binary Nitromethane-Acetonitrile Mixtures by Using Lithium-7 NMR Technique and Ab Initio Calculation,** Applied Magnetic Resonance (2011) 40(3) 303-310,  
Alizadeh N

### Abstract

Lithium-7 nuclear magnetic resonance (NMR) measurements were used to investigate the stoichiometry and stability of Li<sup>+</sup> complexes with 15-crown-5 (15C5), benzo-15-crown-5 (B15C5) and dibenzo-15-crown-5 (DB15C5) in a number of nitromethane (NM)-acetonitrile (AN) binary mixtures. In all cases, the exchange between the free and complexed lithium ion was fast on the NMR time scale and a single population average resonance was observed. While all crown ethers form 1:1 complexes with Li<sup>+</sup> ion in the binary mixtures used, stepwise formation constants of the 1:1 (ligand/metal) complexes were evaluated from computer fitting of the NMR-mole ratio data to equations which relate the observed metal ion chemical shifts to formation constants. There is an inverse linear relationship between the logarithms of the stability constants and the mole fraction of AN in the solvent mixtures. The stability order of the 1:1 complexes was observed to be 15C5·Li<sup>+</sup> > B15C5·Li<sup>+</sup> > DB15C5·Li<sup>+</sup>. The optimized structures of the free ligands and their 1:1 complexes with the Li<sup>+</sup> ion were predicted by ab initio theoretical calculations using the Gaussian 98 software.

**Enrichment of  ${}^6\text{Li}$  using dispersive liquid–liquid microextraction as a highly efficient technique, Annals of Nuclear Energy**

Volume 62, December 2013, Pages 499-503

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**Highlights**

- Isotopic separation of lithium by system  $\text{H}_2\text{O}/\text{C}_2\text{Cl}_4/\text{C}_3\text{H}_6\text{O}$  is investigated using benzo-15-crown-5.
- The maximum isotope enrichment factor  $\varepsilon_{\max}$  for  ${}^6\text{Li}/{}^7\text{Li}$  obtained in the present study was  $0.081 \pm 0.0021$ .
- ${}^6\text{Li}$  was concentrated in the receiving phase, whereas in most of cases,  ${}^7\text{Li}$  was enriched in the source phase.

**Abstract**

Isotope separation of lithium by the dispersive liquid–liquid microextraction system  $\text{H}_2\text{O}/\text{C}_2\text{Cl}_4/\text{C}_3\text{H}_6\text{O}$  is investigated using benzo-15-crown-5 for finding an efficient way for the enrichment of  ${}^6\text{Li}$ . Samples collected in the best and worst conditions were used for the isotopic analysis by inductively coupled plasma–mass spectrometry. The maximum isotope enrichment factor  $\varepsilon_{\max}$  for  ${}^6\text{Li}/{}^7\text{Li}$  obtained in the present study was  $0.082 \pm 0.0021$ . As a result, the lighter isotope,  ${}^6\text{Li}$ , was concentrated in the receiving phase, whereas in most of cases the heavier isotope,  ${}^7\text{Li}$ , was enriched in the source phase.

(Mehrdad Davoudi received his PhD in May 1994 from Carleton University, Canada and then returned to the Department of Chemistry, Imam Hossein University where he continued to perform research lithium ion chemistry.)

**Comparison of the selectivity of  $[\text{M}(12\text{-Crown-4})]^{++}$  ( $\text{M} = \text{Li}^{++}, \text{Na}^{++}, \text{K}^{++}$ ) complexes for halide anions and some neutral molecules; a computational study, J. Theor. Comput. Chem. **14**, 1550057 (2015) [16 pages] DOI**  
Faranak Dastineh<sup>1</sup>  
Sadegh Salehzadeh<sup>1</sup>  
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A theoretical study on the selectivity of a series of  $[\text{M}(12\text{C4})]^{++}$  ( $\text{M} = \text{Li}^{++}, \text{Na}^{++}, \text{K}^{++}$ ,  $12\text{C4} = 12\text{-crown-4}$ ) complexes for  $\text{F}^-$ ,  $\text{Cl}^-$  and  $\text{Br}^-$  anions and a number of neutral molecules ( $\text{CH}_3\text{CN}$ ,  $\text{CH}_3\text{OH}$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ , py, and  $12\text{C4}$ ) is reported. At first, it was shown that in the gas phase among all studied halide anions and neutral molecules, halides have much

more bonding interaction with all  $[M(12C4)]^{+ +}$  cations. Calculated interaction energies of above anions and  $[M(12C4)]^{+ +}$  cations decrease from  $F^-$  to  $Br^-$ . Also the interaction energy of halide anions with  $[M(12C4)]^{+ +}$  complexes, decreases from  $[Li(12C4)]^{+ +}$  to  $[K(12C4)]^{+ +}$ . The electron decomposition analysis showed that the bond between  $[M(12C4)]^{+ +}$  complexes and both the neutral and anion guests is mainly electrostatic in nature. Then the selectivity of  $[M(12C4)]^{+ +}$  complexes for studied anions and neutral molecules are compared in methanol, acetone, acetonitrile, and nitromethane solutions. It was shown that both the desolvation process of reactants and the strength of host-guest interactions have significant effect on the selectivities. Thus the selectivity of  $[Li(12C4)]^{+ +}$  cation for  $NH_3$  and  $H_2O$  neutral molecules in solution, in contrast to the gas phase, is higher than that for bromide anion. The results of calculations showed that all  $[M(12C4)]^{+ +}$  complexes, specially  $[Li(12C4)]^{+ +}$ , have high selectivity for  $F^-$  over other halide anions and neutral molecules.

#### **Conference papers:**

A. R. Fakhari and M. Shamsipur, **An NMR Study of the Stoichiometry and Stability of Lithium Ion Complexes with 12-crown-4,15-Crown-5 and 18-Crown-6 in Binary Acetonitrile-Nitrobenzene Mixtures**, Proceeding of 9th Iranian of Analytical Chemistry, University of Tabriz, June 8-10, 1999, p. 15.

E. Karkhaneei, M. H. Zebarjadian and M. Shamsipur, **Lithium-7 NMR Study of Several Li<sub>+</sub>-Crown Ether Complexes in Binary Acetone-Nitrobenzene Mixtures**, ibid, p. 108.

N. Alizadeh, M. Shamsipur, M. K. Rofouei and K. Alizadeh, **Lithium-7 NMR and an initio Calculation Studies of Complexation of Li<sub>+</sub> Ion with 12-crown-4, Benzo-12-crown-4, 15-crown-5 in Binary Nitromethane-Acetonitrile Mixtures**, ibid, p. 124.

#### **Tritium Isotope Production Related Research**

#### **Journal Articles:**

A.R. Abbasian, M.R. Rahimipour and Z. Hammabard, Initial Sintering Kinetics of Lithium Meta Titanate at Constant Rates of Heating, *Iranian Journal of Materials Science and Engineering*, 2013, Volume 10(3), pp44-53

### Part III: Uranium chemical isotope exchange related research

#### Journal Articles:

**Electrochemical behavior of U(VI) nitrate in chloroform at a mercury electrode: the dependence on supporting electrolyte**, Journal Sci. I.R., 1997, Vol. 8(3), p156-160

M.H. Pournaghi-Azar and R. Zargharian

Electroanalytical Chemistry Laboratory, Faculty of Chemistry, University of Tabriz

#### Abstract

The mechanistic aspects of the electrochemical reduction of U(VI) nitrate at a mercury electrode in chloroform, using three different supporting electrolytes, are described. In the presence of tetrabutylammonium perchlorate (TBAP) as a neutral electrolyte,  $\text{UO}_2(\text{NO}_3)_2$  reduced in two irreversible electrochemical steps to form a U(VI)-U(V) binuclear complex and U(IV), respectively. In the presence of 0.75 M piperidinium perchlorate (PP) + 0.25 M piperidine (P) as supporting electrolyte, the reduction of  $\text{UO}_2(\text{NO}_3)_2$  occurred according to a one-electron irreversible process to U(V). The same behaviour was observed in the presence of 0.5 M tributylammonium perchlorate + 0.3 M tributylamine. The diffusion coefficients of U(VI) and U(VI)-U(V) binuclear complex determined by chronoamperometric measurement are  $8.8 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$  and  $5.37 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$  respectively.

**Orthogonal array design for the optimization of reduction of U(V I) to U(IV); Behineh-e sazi-ye sharayet-e ehya-ye U(VI) be U(IV) az tarigh-e tarrahi-ye azmayesh be raveshe arayesh-e mote-amed**, Scientific Bulletin of the Atomic Energy Organization of Iran; 1999, Issue: 19, p1-9

Rezvanianzadeh, M R; Firooz Zareh, M; Khanchi, A R; Ghannadi Maragheh, M; Yamini, Y  
Atomic Energy Organization of Iran, Jaber Ibn Hayan Lab., Tehran, (Iran, Islamic Republic of)

#### Abstract:

The reduction of U(V I) to U(IV) is of great importance in nuclear and radioanalytical process. Presence of nitrate ions interfere in the reduction process and oxidizes U(IV) to U(V I). In this work it has been tried to minimize the inhibiting effect of nitrate ions by using orthogonal array design to optimize the parameters that affect the reduction of U(V I) to U(IV). The effects of temperature, acid concentration, amount of zinc and reaction time were studied first by three-level orthogonal array design with an OA<sub>9</sub>(3<sup>4</sup>) matrix without considering the interaction between the parameters. Exact levels of the parameters were then chosen and experiments were carried out by designing a two level orthogonal array with an OA<sub>8</sub>(2<sup>7</sup>) matrix and the interaction effects were taken into consideration. Finally, the optimum conditions for the reduction of U(V I) to U(IV) were proposed.

**Production and stability of Uranium (III)**, Bulletin of the Atomic Energy Organization of Iran, 2000, No. 21, p34-41

Alamdar Milani, S.; Ahmadi, S.J.; Mianji, B.; Zanjanipour, M.; Khanchi, A.R.; Channadi Maragheh, M.

Atomic Energy Organization o f Iran, Jaber Ibn Hayan Research Laboratories, Tehran (Iran, Islamic Republic of)

**Abstract:**

The formation and autoxidation of U(III) in HCl, HClO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub> solution of uranyl ion (UO<sub>2</sub><sup>2+</sup>) has been studied. The procedure was to reduce uranyl salt with zinc amalgam using a batch and a continuous equilibration technique. The concentration of [U(H<sub>2</sub>O)] was determined by titration method and spectrophotometric method at 726 nm. Uranium (III) is thermodynamically capable of reducing of reducing hydrogen ion or water with formation of hydrogen in aqueous solution. The autoxidation of Uranium (III) is also discussed.

**Thermodynamic study of complex formation between dibenzo-18-crown-6 and UO<sub>2</sub><sup>2+</sup> cation in different non-aqueous binary solutions**, Journal of Inclusion Phenomena and Macroyclic Chemistry volume 63, Article number: 117 (2009)

Gholamhossein Rounaghi<sup>1</sup> &  
Roya Mohammad Zade Kakhki<sup>1</sup>

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**Abstract**

In the present work the complexation process between UO<sub>2</sub><sup>2+</sup> cation and the macrocyclic ligand, dibenzo-18-crown-6 (DB18C6) was studied in ethylacetate–dimethylformamide (EtOAc/DMF), ethylacetate–acetonitrile (EtOAc/AN), and ethylacetate–tetrahydrofuran (EtOAc/THF) and ethylacetate–propylencarbonate (EtOAc/PC) binary solutions at different temperatures using the conductometric method. The results show that the stoichiometry of the (DB18C6 . UO<sub>2</sub>)<sup>2+</sup> complex in all binary mixed solvents is 1:1. A non-linear behavior was observed for changes of log K<sub>f</sub> of this complex versus the composition of the binary mixed solvents. The stability constant of (DB18C6 . UO<sub>2</sub>)<sup>2+</sup> complex in various neat solvents at 25 °C decreases in order: THF > EtOAc > PC > AN > DMF, and in the binary solvents at 25 °C is: THF–EtOAc > PC–EtOAc > DMF–EtOAc ≈ AN–EtOAc. The values of thermodynamic quantities ( $\Delta H^\circ_c$ ,  $\Delta S^\circ_c$ ) for formation of this complex in the different binary solutions were obtained from temperature dependence of its stability constant and the results show that the thermodynamics of complexation reaction between UO<sub>2</sub><sup>2+</sup> cation and DB18C6 is affected strongly by the nature and composition of the mixed solvents.

**Study of complex formation between diaza-15-crown-5 with uranyl cation (UO<sub>2</sub><sup>2+</sup>) in some binary mixed aqueous and non-aqueous solvents**, Asian Journal of Chemistry, 2008, in pressM. Ansari Fard, G.H. Rounaghi, M. Chamaz and K. Taheri

**Complexing ability of a macrocyclic ligand, dibenzo-24-crown-8, with UO<sub>2</sub><sup>2+</sup> in some binary mixed non-aqueous solvents**, Journal of Coordination Chemistry , Volume 63, 2010 - Issue 13, Pages 2349-2359

Gholam Hossein Rounaghi , Elahe Nazari , Arezoo Ghaemi & Massumeh Mohajeri

**Study of complex formation between dicyclohexyl-18-crown-6 and  $\text{UO}_2^{2+}$  cation in some binary mixed non-aqueous solvents using conductometric method**, Journal of Inclusion Phenomena and Macroyclic Chemistry, volume 73, pages87–92(2012)

F. Razghandi<sup>1</sup> (Department of Chemsitry, Faculty of Sciences, Ferdowsi University of Mashad)  
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## Abstract

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In the present work, the complexation process between  $\text{UO}_2^{2+}$  cation and the macrocyclic ligand, dicyclohexyl-18-crown-6 (DCH18C6) was studied in ethyl acetate/1,2-dichloroethane (EtOAc/DCE), acetonitrile/1,2-dichloroethane (AN/DCE), methanol/1,2-dichloroethane (MeOH/DCE) and ethanol/1,2-dichloroethane (EtOH/DCE) binary solutions at different temperatures using the conductometric method. The conductance data show that in most cases, the stoichiometry of the complex formed between DCH18C6 and  $\text{UO}_2^{2+}$  cation is 1:1 [M:L], but in some solvent systems also a 1:2 [M:L<sub>2</sub>] complex is formed in solutions. The values of stability constant of (DCH18C6· $\text{UO}_2^{2+}$ ) complex which were obtained from conductometric data, show that the stability of the complex is affected by the nature and also the composition of the solvent system and in all cases, a non-linear behavior is observed for the variation of ( $\log K_f$ ) of the (DCH18C6· $\text{UO}_2^{2+}$ ) complex versus the composition of the binary mixed solvents. The values of thermodynamic quantities  $\Delta H^\circ c$   $\Delta H_{\text{c}}^\circ$  and  $\Delta S^\circ c$   $\Delta S_{\text{c}}^\circ$  for formation of (DCH18C6· $\text{UO}_2^{2+}$ ) complex were obtained from temperature dependence of the stability constant using the van't Hoff plots. The experimental results show that depending on the nature and composition of the solvent systems, the complex is enthalpy stabilized or destabilized, but in most cases, it is stabilized from entropy view point and both thermodynamic parameters are affected by the nature and composition of the binary mixed solutions.

**Solvent influence upon complexation of *N*-phenylaza-15-crown-5 with  $\text{UO}_2^{2+}$  cation in binary mixed non-aqueous solvents, Journal of Inclusion Phenomena and Macroyclic Chemistry volume 72, pages331–338(2012)**

Gholam Hossein Rounaghi<sup>1</sup>, Bahareh Nouri<sup>1</sup> & Somayeh Tarahomi<sup>1</sup>

## Abstract

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The complexation reaction of *N*-phenylaza-15-crown-5 (PhA15C5) with  $\text{UO}_2^{2+}$  cation was studied in acetonitrile–methanol (AN–MeOH), acetonitrile–butanol (AN–BuOH), acetonitrile–dimethylformamide (AN–DMF) and methanol–propylencarbonate (MeOH–PC) binary solutions, at different temperatures by conductometry method. The conductance data show that the stoichiometry of the complex formed between PhA15C5 with  $\text{UO}_2^{2+}$  cation in most cases is 1:1 [M:L], but in some solvent systems a 1:2 [M:L<sub>2</sub>] complex is formed in solutions. The results revealed that, the stability constant of (PhA15C5· $\text{UO}_2^{2+}$ ) complex in the binary mixed solvents varies in the order: AN–BuOH>AN–MeOH>AN–DMF. In the case of the pure organic solvents, the sequence of the stability of the complex changes as: AN>PC>BuOH>DMF. A non-linear

relationship was observed for changes of  $\log K_f$  of  $(\text{PhA15C5}\cdot\text{UO}_2)^{2+}$  complex versus the composition of the binary mixed solvents. The corresponding standard thermodynamic parameters ( $\Delta H_c^\circ$ ,  $\Delta S_c^\circ$ ) were obtained from temperature dependence of the stability constant. The results show that the values and also the sign of these parameters are influenced by the nature and composition of the mixed solvents.

**Study of complex formation between Kryptofix 21 and  $\text{UO}_2^{2+}$  cation in some binary mixed non-aqueous solutions**, Russian Journal of Electrochemistry volume 51, pages 758–763(2015)  
Maryam Nasiri<sup>1</sup> & Gholam Hossein Rounaghi<sup>1</sup>

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**Abstract**

The complexation reaction between  $\text{UO}_2^{2+}$  cation and the macrocyclic ligand, Kryptofix 21, was studied in acetonitrile-methanol (AN-MeOH) and acetonitrile-ethylacetate (AN-EtOAc) binary solvent solutions at different temperatures using the conductometric method. In most cases, Kryptofix 21 forms a 1: 1 [M: L] complex with the  $\text{UO}_2^{2+}$  cation. But in some of the studied solvent systems, 1: 2 [M: L<sub>2</sub>] and also 1: 3 [M: L<sub>3</sub>] complexes are formed in solutions. The results obtained in this study show that the mechanism of the complexation process between the uranyl cation and Kryptofix 21 changes with the nature and composition of the solvent system. In the case of the binary solvent solutions (mol % AN = 50 and 60), the order of stability constant of the complex at all studying temperatures was found to be: AN-EtOAc > AN-MeOH. The values of thermodynamic quantities ( $\Delta S_c^\circ$ ,  $\Delta H_c^\circ$ ) for the formation of (Kryptofix 21- $\text{UO}_2^{2+}$ ) complex were obtained from temperature dependence of the stability constant of the complex using the van't Hoff plots. The results show that the values of these parameters are influenced by the nature and composition of the mixed solvents and in most solvent systems, the 1: 1 complexation reaction between  $\text{UO}_2^{2+}$  and the macrocyclic ligand is athermic.

**Part IV: Relationship to foreign Li6 isotope exchange research**

**Brazil:**

Sandra Helena Goulart de Macedo, Separacao Isotopica De Lithio: Estudos Preliminares, Universidade Federal do Rio de Janeiro, 1998

**Canada:**

E. Yatabe and D.F. Stedman, Investigation of Various Methods of Separating Lithium Isotopes, C-69-48S, National Research Laboratories (Canada), December 1950

**China:**

Gu Zhiguo, Li Zaijun and Yamg Jie, Lithium Isotope Separation, *Progress in Chemistry*, 2011, Vol. 23, pp1822-1905

**France:**

L. Perret, L. Rozand and E. Saito, Study of the Coefficient of Separation of Several Processes for Lithium Isotopes, A/CONF.15/P/1267, Commissariat a l'Energie Atomique (Paris), December 1959

L. Perret, L. Rovland and E. Saito, Study of the coefficient of separation of some processes which are applied to lithium isotopes, CEA No. 1029, 1958

E. Saito and G. Dirian, Process for Isotopic Enrichment of Lithium by Chemical Exchange, CEA, Patent CA641016, May 08, 1962

E. Saito, Improvements to or Relating to the Separation of the Isotopes of Lithium, CEA, Patent GB872343

**India:**

D. Nandan and A.R. Gupta, Lithium Isotopes Effects in Ion-Exchange Equilibria in Mixed Solvents, *Indian Journal of Chemistry*, 1978, Vol. 16A, pp256-

A.R. Gupta, Isotope Effects in Ion-Exchange Equilibria in Aqueous and Mixed Solvent Systems, *Separation Science and Technology*, 1979, Vol. 14, pp843-857

**Japan:**

K. Okuyama, I. Okada and N. Saito, The isotope effects in the isotope exchange equilibria of lithium in the amalgam-solution system, *Journal of Inorganic and Nuclear Chemistry*, 1973, Bol. 35, pp2883-2895

Makoto Fujie, Yasuhiko Fujii, Masao Nomura and Makoto Okamoto, Isotope Effects in Electrolytic Formation of Lithium Amalgam, *Journal of Nuclear Science and Technology*, 1986, Vol. 24, pp330-337

Isao Okada and Nobufusa Saito, Enrichment of Li-6 by Countercurrent Electromigration with Molten LiNO<sub>3</sub>-NH<sub>4</sub>NO<sub>3</sub> System, *Journal of Nuclear Science and Technology*, 1974, Vol. 11, pp314-316

**Romonia:**

Ilie Hodor, Lithium isotope separation by <sup>6</sup>Li/<sup>7</sup>Li countercurrent exchange between lithium-amalgam and aqueous LiOH in a spray column, International Symposium on Isotope Separation and Chemical exchange Uranium Enrichment, Tokyo, October 29 – November 1, 1990

I.

Ilie Hodor, Lithium isotope separation, Conference on Isotopic and Molecular Processes, Romania, September 23-25, 1999

In this paper, the research made at INCDTIM concerning lithium isotope separation is summarised.

D. Radu, A. Chezan and I. Hodor, Drop size distribution of lithium amalgam produced by mercury jet cathode, Chemical Engineering Communications, 2000, Vol. 177, pp231-243

### **Abstract**

The drop size distribution of the lithium amalgam produced by mercury jet cathodes was studied experimentally. Electrolysis was done in aqueous solution, 3 mole LiOH per liter, at ambient temperature. Jets were obtained by passing mercury through small orifices made in a Plexiglas plate. The orifice diameter was varied from 28 to 70  $\mu\text{m}$ , the hydrostatic mercury pressure from 200 to 800mmHg, and the electrolysis voltage from 0 to 6 V. An optical method for drop size determination was carried out.

Within the limits of experimental errors, a unique distribution was obtained for all cases. The volume fraction vs. drop diameter curve resembled a Gaussian distribution having the mean diameter  $D_v = 209.7 \mu\text{m}$  and the spread  $\sigma_v = 39.1 \mu\text{m}$ .

### **UK:**

P.M.C. Lacey, Cascade designs for lithium isotope separation by chemical exchange, AERE CE/M 147, August 1955

Donald McIntyre, UK Nuclear History Working Paper Number 5, Project Crystal: Lithium 6 for thermonuclear weapons

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