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 (CH3)2O-BF3 Complex

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

Abstract

Natural boron includes two stable isotopes 10B and 11B with 19.3 and 80.7 weight percent respectively. 10B isotope has a high thermal neutron absorption cross section. So isotope 10B material is suitable for making atomic reactor control rods. Other and even more important applications of 10B 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 BF3, distillation of BF3, distillation of methyl borate, boric acid distillation by steam, distillation with isotope exchange between liquid complex (C2H5)2O-BF3 with BF3 gas and distillation together with isotope exchange between complex liquid (CH3)2O-BF3 with BF3, 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 (H3BO3) 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 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 BF3 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) ; Outokesh, Mohammad (Supervisor) ; Karimi-Sabet, Javad (Supervisor)

Abstract
Natural Boron consists of two stable isotopes, 10B (19.3%) and 11B (80.7%). 10B 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 BF3 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 (CH3)2O-BF3 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 Tbp = 92 °C and ∂T/∂Z = 7.56 °C/m. Tbp 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$_3$)$_2$O-BF$_3$ complex**, Chemical Engineering and Processing: Process Intensification, Volume 76, February 2014, Pages 26–32

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  - $^b$ Nuclear Fuel Cycle School, Nuclear Science and Technology Research Institute, End of North Karegar Avenue, P.O. Box 1439951113, Tehran, Iran

**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%.

**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 6Li at 7.5% and 7Li 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. 6Li has considerable neutron cross section capturing in thermal neutron range about 945 barns while this feature for 7Li is insignificant about 0.037 barns. This difference makes them to play different roles in nuclear uses. 7LiOH is applied for pH adjustment of coolant in light water reactors. 6Li 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 7Li in twenty stages up to 5% and more than 1% for 6Li in 5 stages, demonstrating a substantial separation factor between 1.04 to 1.06 for LiOH and 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
Lithium has two stable isotopes, 6Li and 7Li. Abundance of these isotopes are 7.53% and 92.43% respectively. Each isotope has an important role in nuclear industry. For example, 6Li 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. 7LiOH 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 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/cm²”. 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, 1st 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, 1st National Conference on Application of Stable Isotopes, Ferdowsi University, Science Department, Mashhad, Iran, 2013


M.R. Kosari, S.J. Ahmadi, M. Outokesh and J. Rafee, Lithium Isotopes Enrichment in order to Production of $^6$Li as Elementary Material in Fusion, 3rd National Conference on New Technology of Chemistry and Chemical Engineering, Islamic Azad University, Ghoohan, Iran, 2014
Journal Articles:

Habibollah Khajesharifi & Mojtaba Shamsipur
Department of Chemistry, Razi University, Kermanshah, Iran

Abstract
Complexation of Li⁺ and 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 Kᵢ and the mole fraction of DMF in the solvent mixtures. The ΔH°-TΔS° 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.

Ebrahim Karkhaneei, Abbas Afkhami & Mojtaba Shamsipur

Abstract
Lithium-7 NMR measurements were used to determine the stoichiometry and stability of 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 ⁷Li chemical shift with the crown/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 Kᵢ of the complexes and the mol fraction of acetonitrile in the solvent mixtures.
LITHIUM-7 AND SODIUM-23 NMR STUDIES OF COMPLEXATION OF Li⁺ AND Na⁺ 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⁺ and Na⁺ 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⁺ forms more stable complexes than Na⁺ and, for each cation, the stability order of the resulting complexes is 1,10-phenanthroline > 2,2'-bipyridine > 8-hydroxyquinoline.

Ebrahim Karkhaneei, Javad Zolgharnein, Abbas Afkhami & Mojtaba Shamsipur

Abstract:
⁷Li, ²³Na and ¹³C NMR measurements were used to study the stoichiometry and stability of Li⁺ and Na⁺ 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⁺ and Na⁺ 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.

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 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.

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 Shamsipur1, Ebrahim Karkhaneei2 and AbbasAfkhami2

1 Department of Chemistry, Razi University, Kermanshah, Iran

2 Department of Chemistry, Bouali Sina University, Hamadan, Iran

**Abstract**

The exchange kinetics of $\text{Li}^+\text{C221}$ 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°), 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: $E_a=22\pm2$ kJ mol$^{-1}$; $\Delta H^\ddagger=20\pm2$ kJ mol$^{-1}$; $\Delta S^\ddagger=-144\pm8$ J mol$^{-1}$ K$^{-1}$. While for the bimolecular mechanism they are: $E_a=9.9\pm0.4$ kJ mol$^{-1}$; $\Delta H^\ddagger=8.0\pm0.4$ kJ mol$^{-1}$; $\Delta S^\ddagger=-146\pm2$ J mol$^{-1}$ K$^{-1}$. 
Mojtaba Shamsipur  & Tayyebeh Madrakian

Abstract
Lithium NMR measurements were used to determine the stoichiometry and stability of Li⁺ complexes with 12-crown-4, 15-crown-5 and benzo-15-crown-5 in acetonitrile solution. A competitive ⁷Li NMR technique was also employed to probe the complexation of Mg²⁺, Ca²⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺ and Cd²⁺ 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. Ca²⁺ and Cd²⁺ 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⁺ 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 Mg²⁺, Ca²⁺, Ba²⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺ and Cd²⁺ 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 Ba²⁺ > Ca²⁺ > Cd²⁺ > Mg²⁺ approximate to Cu²⁺ > Ni²⁺ > Co²⁺ > Zn²⁺.

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+ 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+ > B15C5. Li+ > DB15C5. Li+ > 12C4. Li+ > B12C4. Li+. The optimized structures of the free ligands and their 1:1 and 2:1 complexes with Li+ 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+ > B12C4. Li+. The optimized structures of the free ligands and their 1:1 and 2:1 complexes with Li+ ion were predicted by ab initio theoretical calculations using the Gaussian 98 software, and the results are discussed.
A comparison of complexation of Li$^+$ 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
Department of Chemistry, University of Guilan, Namjoo Street, Rasht 41335-1914, Iran

Abstract

Lithium-7 NMR measurements were used to investigate the stoichiometry and stability of Li$^+$ 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$^+$ 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 AN in the solvent mixtures. The stability order of the 1:1 complexes was found to be 15C5·Li$^+$ > B15C5·Li$^+$ > DB15C5·Li$^+$ > 12C4·Li$^+$. The optimized structures of the free ligands and their 1:1 and 2:1 complexes with Li$^+$ ion were predicted by ab initio theoretical calculations using the Gaussian 98 software, and the results are discussed.

A Comparison of Complexation of Li$^+$ 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$^+$ 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$^+$ 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$^+$ > B15C5·Li$^+$ > DB15C5·Li$^+$ > 12C4·Li$^+$. The optimized structures of the free ligands and their 1:1 complexes with the Li$^+$ ion were predicted by ab initio theoretical calculations using the Gaussian 98 software.
**Enrichment of $^6$Li using dispersive liquid–liquid microextraction as a highly efficient technique,** Annals of Nuclear Energy

Volume 62, December 2013, Pages 499-503

Mehrdad Davoudi and Mohammad Hassan Mallah

Nuclear Fuel Cycle Research School, Nuclear Science & Technology Research Institute, Atomic Energy Organization of Iran, End of North Karegar Ave., Tehran, Iran

**Highlights**

- Isotopic separation of lithium by system $\text{H}_2\text{O}/C_2\text{Cl}_4/C_3\text{H}_6\text{O}$ is investigated using benzo-15-crown-5.

- The maximum isotope enrichment factor $\varepsilon_{\text{max}}$ 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 $\text{H}_2\text{O}/C_2\text{Cl}_4/C_3\text{H}_6\text{O}$ 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 $\varepsilon_{\text{max}}$ 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.)


Faranak Dastineh$^1$
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A theoretical study on the selectivity of a series of [M(12C4)]$^+$ (M = Li$^+$, Na$^+$, K$^+$, 12C4 = 12-crown-4) complexes for F$^-$, Cl$^-$ and Br$^-$ anions and a number of neutral molecules (CH$_3$CN, CH$_3$OH, NH$_3$, H$_2$O, py, and 12C4) 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 \[\mathrm{M(12C4)}\] + + cations. Calculated interaction energies of above anions and \[\mathrm{M(12C4)}\] + + cations decrease from \(\mathrm{F}\) to \(\mathrm{Br}\). Also the interaction energy of halide anions with \[\mathrm{M(12C4)}\] + + complexes, decreases from \[\mathrm{[Li(12C4)] + + to [K(12C4)] + +}\. The electron decomposition analysis showed that the bond between \[\mathrm{M(12C4)}\] + + complexes and both the neutral and anion guests is mainly electrostatic in nature. Then the selectivity of \[\mathrm{M(12C4)}\] + + 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 \[\mathrm{[Li(12C4)] + + cation for NH}_3\ and \mathrm{H}_2\mathrm{O}\ neutral molecules in solution, in contrast to the gas phase, is higher than that for bromide anion. The results of calculations showed that all \[\mathrm{M(12C4)}\] + + complexes, specially \[\mathrm{[Li(12C4)] + +}\, have high selectivity for \(\mathrm{F}\) over other halide anions and neutral molecules.

Conference papers:


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


Tritium Isotope Production Related Research

Journal Articles:

Part III: Uranium chemical isotope exchange related research

Journal Articles:

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, UO₂(NO₃)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 piperidine perchlorate (PP) + 0.25 M piperidine (P) as supporting electrolyte, the reduction of UO₂(NO₃)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(IV) binuclear complex determined by chronoamperometric measurement are 8.8 x 10⁻⁷ cm² s⁻¹ and 6.37 x 10⁻⁷ cm² 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 ravesh-e 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}(3{sup 4}) 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}(2{sup 7}) 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 of Iran, Jaber Ibn Hayan Research Laboratories, Tehran (Iran, Islamic Republic of)

Abstract:

The formation and autoxidation of U(III) in HCl, HClO4 and H2SO4 solution of uranyl ion (UO ) 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 O) ] was determined by titration method and spectrophotometric method at 726 nm. Uranium (III) is thermodynamically capable 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 UO2 2+ cation in different non-aqueous binary solutions,** Journal of Inclusion Phenomena and Macrocyclic Chemistry volume 63, Article number: 117 (2009)
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Department of Chemistry, Faculty of Sciences, University of Mashad

Abstract

In the present work the complexation process between UO2 2+ 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 . UO2)2+ complex in all binary mixed solvents is 1:1. A non-linear behavior was observed for changes of log Kf of this complex versus the composition of the binary mixed solvents. The stability constant of (DB18C6 . UO2)2+ 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 (∆H°, ∆S°) 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 UO2 2+ 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 (UO2 2+) in some binary mixed aqueous and non-aqueous solvents,** Asian Journal of Chemistry, 2008, in press
M. Ansari Fard, G.H. Rounaghi, M. Chamaz and K. Taheri

**Complexing ability of a macrocyclic ligand, dibenzo-24-crown-8, with UO2 2+ 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
F. Razghandi$^1$ (Department of Chemistry, Faculty of Sciences, Ferdowsi University of Mashad)
G. H. Rounaghi$^1$ & Z. Eshaghi$^2$ (Department of Chemistry, Piam Noor University of Mashad)

Abstract

In the present work, the complexation process between 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 UO$_2^{2+}$ cation is 1:1 [M:L], but in some solvent systems also a 1:2 [M:L$_2$] complex is formed in solutions. The values of stability constant of (DCH18C6·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·UO$_2$)$^{2+}$ complex versus the composition of the binary mixed solvents. The values of thermodynamic quantities $\Delta H^\circ$ and $\Delta S^\circ$ for formation of (DCH18C6·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.

Gholam Hossein Rounaghi$^1$, Bahareh Nouri$^1$ & Somayeh Tarahomi$^1$

Abstract

The complexation reaction of N-phenylaza-15-crown-5 (PhA15C5) with 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 UO$_2^{2+}$ cation in most cases is 1:1 [M:L], but in some solvent systems a 1:2 [M:L$_2$] complex is formed in solutions. The results revealed that, the stability constant of (PhA15C5·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 logKf of (PhA15C5·UO2)2+ complex versus the composition of the binary mixed solvents. The corresponding standard thermodynamic parameters (ΔH°, ΔS°) 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.


- Abstract

The complexation reaction between UO₂⁺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 UO₂⁺² cation. But in some of the studied solvent systems, 1: 2 [M: L₂] and also 1: 3 [M: L₃] 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 (ΔS°, ΔH°) for the formation of (Kryptofix 21–UO₂)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 is most solvent systems, the 1: 1 complexation reaction between UO₂⁺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 Lithoi: 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:**

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:


Japan:


Isao Okada and Nobufusa Saito, Enrichment of Li-6 by Countercurrent Electromigration with Molten LiNO3-NH4NO3 System, Journal of Nuclear Science and Technology, 1974, Vol. 11, pp314-316

Romonia:

Ilie Hodor, Lithium isotope separation by 6Li/7Li 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
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 μm, 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 $D_{\bar{v}}=209.7 \, \mu m$ and the spread $\sigma_v=39.1 \, \mu m$.

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

US:


Harold Urey, Separation of Isotopes, Reports on Progress in Physics, 1939, Vol. 6, pp48-77

Herrick L. Johnston and Clyde A. Hutchison, Efficiency of the Electrolytic Separation of Lithium Isotopes, Journal of Chemical Physics, 1940, Vol. 8, pp869-877

J.S. Drury, Application of Liquid-Liquid Systems to the Separation of Lithium Isotopes, Y-785, June 1951, declassified March 1957
R.E. Blanco, A.H. Kibbey and J.T. Roberts, Determination of the Efficiency of an Ion Exchange System in Separating the Lithium Isotopes (preliminary Study), CF-54-7-12, July 1955, declassified February 1959


Y.A. Allred and Ivan B. Cutler, Chemical Methods for the Separation of Lithium Isotopes, ORNL-1592, July 1953, declassified July 1979


Los Alamos looked at the separation of lithium isotopes by using electrolysis in lithium amalgam systems and reported on this research in a declassified September 1950 report.

J.W. Kennedy, Lithium Isotope Separation by Electrolysis, LA-1156, September 1950, declassified October 1986

Union Carbide Nuclear Company, Separation of Lithium-6 and Lithium-7, March 1957

Few engineering details of the Colex process have been described in the open literature:


USSR:


A.M. Rozen and A.I. Mikhailichenko, Some Laws of Isotope Separation by Chemical Exchange (With Special Respect to the Extractive Separation of Lithium Isotopes), Isotoppenpraxis, 1969, Vol. 5, pp105-112


**Uranium-235 Chemical Isotope Exchange Research**


**Proliferants Chemical Isotope Exchange Research**

North Korea:

Pak Ki-ch’o’l and Mun Ch’o’l-tu, Studies on the Formation Character of Boron Trifluoride-Phenol Complex in Packed Column, *Kim Il-so’ng Taehak Hakpo: Chayo’n Kwahak*, 2005, pp83-85, KPP20060115019007

Pak Yo’ng-mi, Ko Pyo’ng-ch’un, and Kim Su’ng-ch’o’l, Theoretical research on the Effect of C6H5OH Injection Rate and Reaction Temperature on the Axis-Direction Distribution of Concentration of BF3-C5H6OH in Recombination Unit of the Boron Isotope Separation Column, Ko Pyo’ng-ch’un, June 2008, pp82-85

Pak Yo’ng-mi, Ch’oe Chu-yo’ng and Ko Pyo’ng-ch’un, Theoretical Research to Determine Separation Step Height of Boron Isotope Separation Column by Chemical Exchange Method, *Kim Il-so’ng Taehak Hakpo: Chayo’n Kwahak*, 2008, pp95-98, KPP20090429106022

Kim Yong-hun, Investigation on the Manufacture and Characteristics of BF3 Gas Collecting Unit for Boron Isotope Enrichment, *Kim Il-so’ng Taehak Hakpo: Chayo’n Kwahak*, March 2015, KPR2016092354485990

