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Calculation of Lithium Isotope Effects in Extraction Systems with Benzo-15-crown-5 and Its Derivatives

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Abstract—With taking into account the β-factor value of the lithium ion aqua complex found earlier, the single stage extraction coefficient of isotope separation (α) of the ^{6}Li–^{7}Li pair has been calculated for the extraction system containing the benzo-15-crown-5–Li$^+$ (H_2O)Cl$^-$ complex in the organic phase, which corresponds to a real extraction process. Similar calculations have been carried out for other anions, as well as for various benzo-15-crown-5 derivatives with varying the number and type of donor atoms and different substituents in the benzene ring. Quantum-chemical calculations of the vibrational frequencies of the isotopic forms of the crown ether complex were performed using the Firefly program with the RHF/6-311++G** basis set. It has been shown that the isotope separation factor in this case is lower than in the case of the anhydrous benzo-15-crown-5–Li$^+$Cl$^-$ complex and the model benzo-15-crown-5–Li$^+$ (H_2O) complex.

Keywords: extraction, isotope effects, structures, quantum-chemical calculations

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Industrial separation of lithium isotopes is an urgent task. Currently, there is a great need for pure lithium-7 isotope. In particular, in China, two types of reactors are being developed with a molten lithium salt as a coolant, and each of these reactors will need to operate thousands of kilograms of lithium-7. For comparison, the annual need for it of all 65 US power units with PWR reactors (similar to Russian VVERs) is ~300 kg [1]. The use of lithium enriched in ^{7}Li, rather than natural lithium, in these cases is necessary, since the ^{6}Li isotope interacts with the neutron via the (n, α) reaction to give tritium [1].

The well-known amalgam method for the separation of lithium isotopes [2], despite the high value of the separation factor, has a number of significant drawbacks, primarily related to its environmental hazard. In this regard, the urgent task is to develop alternative chemical methods for the separation of lithium isotopes [3]. Chemical methods for the separation of lithium isotopes, not associated with the use of mercury, are represented by extraction and ion-exchange separation methods. The latter are based on the exchange between a lithium salt in the aqueous phase and a solid sorbent. As a sorbent, both organic ion-exchange resins [4] and inorganic sorbents [5] are used. For the organization of the industrial separation process, ion-exchange methods are inconvenient; their other significant disadvantage is the low isotope separation factor.

Thus, extraction methods of separation are the best nowadays. They are based on the exchange between an aqueous solution of a lithium salt, in which the lithium cation is in the form of an aqua complex, and a liquid organic phase immiscible with water [6]. Given the strength of the lithium aqua complex and the affinity of lithium for the aqueous phase, the lithium cation will pass into the organic phase in appreciable amounts only if it forms a sufficiently strong complex in the organic phase. Therefore, an organic solution of substances forming complexes with the lithium cation, primarily macrocycles (crown ethers [7–9] and cryptands [10–12]), is usually used as the organic phase.

The requirements for such ligands are highly controversial. On the one hand, if the ligand forms a strong complex with a cation in the organic phase, this ensures a good extraction into the organic phase. On the other hand, the high strength of the complex means a high strength of the bonds formed by the cation (that is, high force constant values), and this, in turn, means a weak difference between the environment of the cation and its environment in the aqua complex and, therefore, a small value of the isotope separation factor. To ensure a significant isotope separation factor, it is desirable that the lithium–ligand bonds be significantly weaker than the lithium bonds with water in the aqua complex. However, weak bonds with the ligand will lead to poor extraction. Such contradictory requirements for organic ligands make the search for an optimal extraction system a challenging task. Taking into account the laboriousness of the experimental determination of the isotope separation factor in extraction systems and the high cost of organic ligands, it is advisable to use computational quantum-chemical methods to search for optimal systems [13, 14].

Our calculations of β factors and separation factors in extraction systems show good agreement with the experimental data obtained for these systems earlier, which indicates the reliability of the obtained calculation data.

Earlier [13], we carried out quantum-chemical calculations of the isotopic properties (β factors and separation factors α) of complexes of some crown ethers with lithium. It has been shown that the isotopic properties of the complexes depend primarily on the size of the crown ether ring, and benzo-15-crown-5 is the best in terms of both the isotope effect magnitude and the extraction characteristics. Thus, the size of the crown ether ring is the dominant factor. At the same time, both the computational and experimental data show that there is also a dependence of the β factor and separation factor on the anion in the lithium complex with crown ether. This dependence is much weaker than the dependence on the ring size; however, it may be of interest for selecting a suitable lithium salt in the practical separation of isotopes.

The first task of this work was to study this dependence by quantum-chemical calculations of the isotopic properties of lithium-benzo-15-crown-5 complexes with various anions. The second task was to elucidate the effect on the β value of the number and type of donor atoms in the crown ether ring, as well as the influence of substituents in the external moieties (in the benzene ring).

To solve these problems, a quantum-chemical calculation of the molecules of extractable complexes based on benzo-15-crown-5 was carried out. The type of counterion, the number of oxygen donor atoms, heteroatoms, and the number and type of substituents in the benzene ring were varied [13].

THEORY

As is known from thermodynamics of chemical isotope exchange [15], in the isotope exchange reaction for element X

$$AX^* + BX = AX + BX^*, \qquad (1)$$

the isotope separation factor $\alpha_{X^*/X}$ (X^* is a heavy isotope of element X), which is by definition

$$\alpha_{X^*/X} = \frac{\{[X^*]/[X]\}_A}{\{[X^*]/[X]\}_B}, \qquad (2)$$

can be calculated as

$$\alpha_{X^*/X} = \frac{\beta(A)}{\beta(B)}, \qquad (3)$$

where [X] and [X*] are the concentrations of isotopes in the compound, β(A) and β(B) are the so-called “isotopic reduced partition function ratios” [15] or β factors, which are the ratio of quantum statistical sums for the isotopic forms of a given compound divided by the same ratio for classical statistical sums. The quantity β is often referred to as the RPFR or $(s/s')f$. In the harmonic approximation, the β factor is determined only by vibrational frequencies of the isotopic forms of the molecule and is calculated by the equation [16–18]:

$$\ln\beta = \frac{1}{N_{\text{at}}}\sum_{j=1}^{N_{\text{freq}}} \ln\left\{\frac{\sinh[u_j/2]}{\sinh[u_j^*/2]}\left[\frac{u_j^*}{u_j}\right]\right\}, \qquad (4)$$

where N_{at} is the number of equivalent atoms in the molecule substituted by the isotope atoms, N_{freq} is the number of vibrational frequencies, $u_j = hc\nu_j/kT$ are dimensionless reduced frequencies, ν_j are vibrational frequencies in cm^{-1}, h is the Planck constant, k is the Boltzmann constant, c is the speed of light, and T is the absolute temperature.

It is evident that to calculate the isotope separation factor α for extraction, it is necessary to calculate the β factor of the lithium ion aqua complex (aqueous phase) [19] and the lithium complex with crown ether (organic phase).

RESULTS AND DISCUSSION

Previously, we have demonstrated by X-ray crystallography and IR spectroscopy that the lithium complexes with benzo-15-crown-5 and its derivatives extracted from aqueous solutions of lithium salts contain the water molecule that displaces the anion into the outer coordination sphere [20, 21]. An exception is the complex formed by lithium fluoroborate, which is of no practical interest for the isotope separation for technological reasons. In this complex, the Li^+ ion is bound to one of the fluorine atoms in the BF_4^- ion. The complex with lithium thiocyanate also has an anhydrous form in which the lithium cation is bound to the nitrogen atom; however, we also have shown the existence of an aqueous complex [22].

We have performed ab initio calculation of isotopic properties (lnβ) of the above complexes. The calculated structures of the Li^+ complexes with macrocycles are identical to those determined by single crystal X-ray diffraction. Calculations of the lithium cation with crown ethers were performed using the RHF/6-311++G** basis set [23, 24]. The calculation procedure has been described in detail elsewhere [13]. For comparison, we also calculated the model complex benzo-15-crown-5–$Li^+(H_2O)$without the conterion in the outer sphere. The calculation results are presented in Table 1.

According to Table 1, the presence of the chloride ion in the second coordination sphere leads to some increase in the theoretical $\ln\beta$ value as compared with the model complex and, accordingly, to a decrease in the separation factor. This is clearly seen from comparison of the β values for the model complex benzo-15-crown-5–$Li^+(H_2O)$ with analogous values for the complexes containing chloride or perchlorate anion. It is evident that the presence of a negative ion in the second coordination sphere leads to an increase in the effective negative charge on the oxygen atom in the water molecule. This leads to the shortening of the lithium–water oxygen bond and to the increase in its force constant. In particular, the length of this bond in the benzo-15-crown-5–$Li^+(H_2O)$ complex is 1.99 Å, whereas in the benzo-15-crown-5–$Li^+(H_2O)ClO_4^-$ and benzo-15-crown-5–$Li^+(H_2O)Cl^-$, this distance is 1.922 and 1.905 Å, respectively. At the same time, the insignificant difference between the β factors of complexes with different counterions makes it possible, when selecting a suitable counterion, to focus on technological characteristics, first of all, on extraction characteristics and stability of the system.

In order to search for promising systems for the separation of lithium isotopes, we calculated complexes with a reduced number of oxygen donor atoms (a benzo-15-crown-4 complex containing four oxygen atoms). A comparison with the benzo-15-crown-5–Li^+Cl^- complex (Table 2) shows that a decrease in the number of donor atoms does not lead to positive results: the β factor increases, which leads to a decrease in the expected isotope separation factor. The reason for this is that a decrease in the number of donor atoms leads to a shift of the lithium ion in the crown ether ring to the remaining donor atoms and a decrease in the lithium–oxygen bond lengths.

In particular, the lengths of three of the four Li–O bonds in the complex with benzo-15-crown-4 are 1.98, 2.17, and 2.33 Å, whereas in the complex with benzo-15-crown-5, the distances are 2.20, 2.28, 2.28, 2.42, and 2.42 Å. In addition, the Li–Cl bond length in the complex with benzo-15-crown-4 decreases (2.17 against 2.25 Å). This leads to an increase in force constants in the complex with 15-crown-4 and, accordingly, to an increase in the frequency of vibrations contributing to the β factor. In the benzo-15-crown-5–Li^+Cl^- complex, a pair of frequencies 460/430 cm^{-1} contributes more than 50% to the $\ln\beta$ value and in the benzo-15-crown-4–Li^+Cl^- complex, all corresponding frequencies above 500 cm^{-1} (535/521, 558/547, 546/536 cm^{-1}).

Another possibility to influence α is to replace part of the oxygen atoms in the crown ether ring with heteroatoms. Aza crown ethers are well known [25, 26]; however, the replacement of oxygen atoms with nitrogen leads to a loss in the technological effectiveness of the extraction system. We calculated the benzo-15-crown-3-thio-2–$Li^+(H_2O)Cl^-$ complex in which two oxygen atoms of the ring are replaced by sulfur atoms. A comparison with the benzo-15-crown-5–$Li^+(H_2O)Cl^-$ complex (Table 2) shows that, in this case, contrary to expectations, the value of the β factor increases sharply, and hence, a low lithium isotope separation factor can be expected. The reason for this is the same as in the benzo-15-crown-4–Li^+Cl^- complex mentioned above. It is in the case of replacing part of the donor oxygen atoms with heteroatoms that the lithium cation shifts towards the remaining oxygen atoms in the ring to form shorter and, therefore, stronger bonds, slightly different from the lithium–oxygen bonds in the aqua complex.

It has been noted in [13] that the introduction of substituents into the benzene ring in benzo-15-crown-5 has little effect on the isotopic properties. Indeed, a

Table 1. Influence of the salt anion on the isotopic properties of lithium complexes with benzo-15-crown-5 (the $^7Li/^6Li$ separation factor, $T = 300$ K), RHF/6-311++G** basis set

Complex	$\ln\beta$	$\ln\alpha$
Benzo-15-crown-5–$Li^+(H_2O)$	0.0412	0.0394
Benzo-15-crown-5–$Li^+(H_2O)Cl^-$	0.0513	0.0293
Benzo-15-crown-5–$Li^+(H_2O)ClO_4^-$	0.0497	0.0321
Benzo-15-crown-5–Li^+OH^-	0.0660	0.0145
Benzo-15-crown-5–$Li^+BF_4^-$	0.0495	0.0310
Benzo-15-crown-5–Li^+NCS^-	0.0489	0.0316
Benzo-15-crown-5–Li^+Cl^-	0.0398	0.0407
Benzo-15-crown-5–Li^+	0.0327	0.0478

The $\ln\alpha$ values were calculated using the $\ln\beta$ value (0.0806) reported in [13] for the lithium aqua complex.

Table 2. Influence of the introduction of substituents into the benzene ring and of heteroatoms into the crown ether ring on the isotopic properties of lithium complexes

Complex	$\ln\beta$	$\ln\alpha$
Benzo-15-crown-5–$Li^+(H_2O)Cl^-$	0.0514	0.0293
Benzo-15-crown-5–Li^+Cl^-	0.0390	0.0408
Benzo-15-crown-5–$Li^+(H_2O)$	0.0412	0.0394
Benzo-15-crown-4–Li^+Cl^-	0.0599	0.0208
Nitrobenzo-15-crown-5–$Li^+(H_2O)$	0.0444	0.0362
p-Dichloro-benzo-15-crown-5–Li^+Cl^-	0.0412	0.0394
Benzo-15-thio-2-crown-3–$Li^+(H_2O)Cl^-$	0.0650	0.0157

comparison of the benzo-15-crown-5–$Li^+(H_2O)$ and nitrobenzo-15-crown-5–$Li^+(H_2O)$ complexes shows a slight difference between the values of their β factors.

CONCLUSIONS

In addition to our previous article [13], it has been shown that the search for optimal extraction systems for the separation of lithium isotopes should focus on studying the effect of the anion on the separation factor in systems containing the lithium salt complex with benzo-15-crown-5, with consideration of the influence of the organic phase, i.e., the solvent. Work in this direction is underway.

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