Molecular orbital estimation of reduced partition function ratios of lithium ions in ion exchanger phase of aqueous ion exchange systems

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Abstract Structures of $Li^+(H_2O)_5SO_3^-$-R with -R representing the methyl and other groups modeling the lithium ion in the ion exchanger phase of aqueous ion exchange systems were optimized based on the molecular orbital theory and the reduced partition function ratios (RPFRs) for the $^6Li/^7Li$ isotope substitutions were estimated. The structure around the lithium ion was nearly unchanged by the substitutions of the methyl group by the other groups. Correspondingly, the RPFR value did not vary substantially, either; the maximum decrease of 0.0008 was observed for -R = $-C(C_2H_5)_3$ from that of $-CH_3$. It was indicated that the equilibrium constant of the lithium isotope exchange reaction between the ion exchanger and the external solution phases could change by *ca*. 0.001 without any substantial structural change around the lithium ion in the ion exchanger phase. It was also indicated the ONIOM calculation is effective when treating isotope effects of large molecules.

Key words ion exchange • lithium • lithium isotopes • molecular orbital calculations • ONIOM calculations • reduced partition function ratio

Introduction

In relation to the large demand for isolated or enriched lithium isotopes expected in the future, ion exchange chromatography has been studied as a method of separating lithium isotopes. The lithium isotope effect that gives rise to lithium isotope fractionation in chromatographic separation processes is based on the isotope exchange reaction between the hydrated lithium ion in the solution phase and that in the ion exchanger phase:

$$(1) \qquad ^6Li^+(solution) + {}^7Li^+(ion\ exchanger) = \\ = {}^7Li^+(solution) + {}^6Li^+(ion\ exchanger),$$
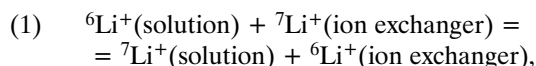
where $^6Li^+$(solution) denotes the hydrated $^6Li^+$ ion in the solution phase, and so forth. It is experimentally known that the equilibrium constant, K_{Li}, of Reaction (1) is larger than unity; the lighter isotope, ^6Li, is preferentially fractionated into the ion exchanger phase. Based on the Bigeleisen-Mayer formula [1], the K_{Li} value can theoretically be estimated by knowing all vibrational frequencies of isotopic lithium species in and out the ion exchanger phase. Unfortunately, not all frequencies are reported as to lithium ions in the solution phase; rather, it is not easy to observe even a single vibrational frequency of the hydrated lithium ion. As for the lithium ion in the ion exchanger phase, the situation is even worse. These circumstances seem to have retarded the development of the theoretical elucidation of lithium isotope effects in aqueous ion exchange systems.

A theoretical approach based on *ab initio* molecular orbital (MO) calculations seems effective to systems where

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vibrational data are hardly obtained experimentally. In a previous paper [6], we estimated the reduced partition function ratios (RPFRs) of lithium species in the solution and the ion exchanger phases based on the MO theory. In the estimation, we assumed that the lithium species in the solution phase was given as the hydrated lithium ion, $Li^+(H_2O)_n$, with the charge of +1 and n being the hydration number, and as the lithium species in the ion exchanger phase, we considered the hydrated lithium ion interacting with methyl sulfonate ion ($CH_3SO_3^-$), $Li^+(H_2O)_nCH_3SO_3^-$. Thus, we supposed the ion exchange resin to have the sulfo group as ion exchange group, and in our calculations, the methyl moiety of $CH_3SO_3^-$ served as the organic framework of the resin. Since the organic framework of a real ion exchange resin was substituted by the methyl moiety in our calculations, steric hindrance the lithium ion in the resin phase may experience in real systems was not well taken into consideration. In this paper, the methyl group was substituted by larger groups so that the organic framework of a real ion exchange resin was better modeled and consequently, the steric effect is better realized in calculations of RPFRs of the hydrated lithium ion in the resin phase. We also tried the use of ONIOM calculations [3, 5] to reduce computational times.

Theory and procedure of calculations

Isotope exchange equilibria and reduced partition function ratios (RPFRs)

Isotope effects based on molecular translational, rotational and vibrational motions can be theoretically estimated by calculating RPFRs of the chemical species participating in the isotope exchange reaction in concern [1]. That reaction may be expressed, without losing any generality, as

(2)   AX + BX' = AX' + BX,
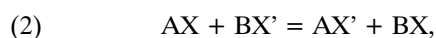
where X and X' are the heavier and lighter isotopes of the element in concern and A and B are polyatomic groups. The equilibrium constant, K, of Reaction (2) (strictly speaking, the equilibrium constant estimated quantum mechanically divided by that estimated classically) can be given as

(3) $\ln K = \ln(s/s')f_{BX} - \ln(s/s')f_{AX}$,

where $(s/s')f_{AX}$ and $\ln(s/s')f_{BX}$ are the RPFRs of the chemical species AX and BX, respectively. The general formula of the RPFR of a species is given, under the Born-Oppenheimer and harmonic oscillator approximations, as

(4) $$(s/s')f = \prod_i^f \frac{u_i \exp(-u_i/2)/\{1-\exp(-u_i)\}}{u_i' \exp(-u_i'/2)/\{1-\exp(-u_i')\}}$$

where

(5) $u_i = hc\omega_i/(kT)$,

and

(5') $u_i' = hc\omega_i'/(kT)$.

Here, f is the degree of freedom of the vibrational motion, h the Planck's constant, c the velocity of light, ω_i and ω_i' are the wavenumbers of the ith molecular vibration of the heavier and lighter isotopic species, respectively, k is the Boltzmann's constant and T the temperature.

Modeling of lithium ions in ion exchanger phase and *ab initio* molecular orbital calculations

In the ion exchanger phase, we consider the penta-aquolithium ion (i.e., n=5) interacting with $R-SO_3^-$ where R represents a variety of groups (mostly hydrocarbon groups) as listed in the 2nd column of Table 1. The structure of $Li^+(H_2O)_5CH_3SO_3^-$ optimized with HF/6-31G(d) in the previous paper [6] is depicted in Fig. 1 (**1**). The three water molecules (**W1**, **W2** and **W3** of **1** in Fig. 1) out of the five are directly bonded to the lithium ion and $CH_3-SO_3^-$ is also directly bonded to the lithium ion through one of its oxygen atoms, thus located in the primary solvation sphere. Therefore, the solvation number in the primary solvation sphere is four. The remaining two waters (**W4** and **W5**) move off to the secondary solvation sphere.

All the *ab initio* calculations were made with personal computers using the Gaussian 98W program package. To maintain the consistency with the previous calculations [6], the MO theory and the basis set used were restricted to HF/6-31G(d), except for ONIOM calculations. In the ONIOM calculations, each species considered was divided into two layers, high and low, and the former and the latter were treated with HF/6-31G(d) and HF/STO-3G in the geometry optimization, respectively. The value of the scale factor was 0.95829 [6], and the isotopes of hydrogen, carbon, oxygen and sulfur were ^{1}H, ^{12}C, [16]O and [32]S, respectively, in all the calculations.

Results and discussion

The optimized structures are drawn in a simplified way in Fig. 1. Bonds between the lithium ion and the oxygen atoms directly bonded to it in the primary solvation sphere are not shown for **2–15**. No negative frequency was calculated for each of the structures. Thus, they are all at the global or local minima of the potential energy surfaces. A rough look at these drawings reveals that the structure around the lithium ion is not substantially altered by the substitutions of the methyl group by the other groups; the relative positions and orientations of five water molecules and $-SO_3^-$ group around the lithium ion are nearly unchanged.

The calculated results are summarized in Table 1. The average distance ($r_{Li-O(W)}$) between the lithium ion and the oxygen atoms of the waters in the primary solvation sphere and the distance ($r_{Li-O(S)}$) between the lithium ion and the oxygen atom of $-SO_3^-$ directly bonded to it are tabulated in the 3rd and 4th columns, respectively. As for $r_{Li-O(W)}$, the only substantial deviation from that of **1** is observed for **15**. In **15**, the second $-SO_3^-$ is located relatively close to the **W1** and **W5** waters, which is probably responsible for the enlargement of $r_{Li-O(W)}$. Compared to the fluctuation in $r_{Li-O(W)}$ from species to species, that of $r_{Li-O(S)}$ is large. This is understandable because substitutions at the methyl site is
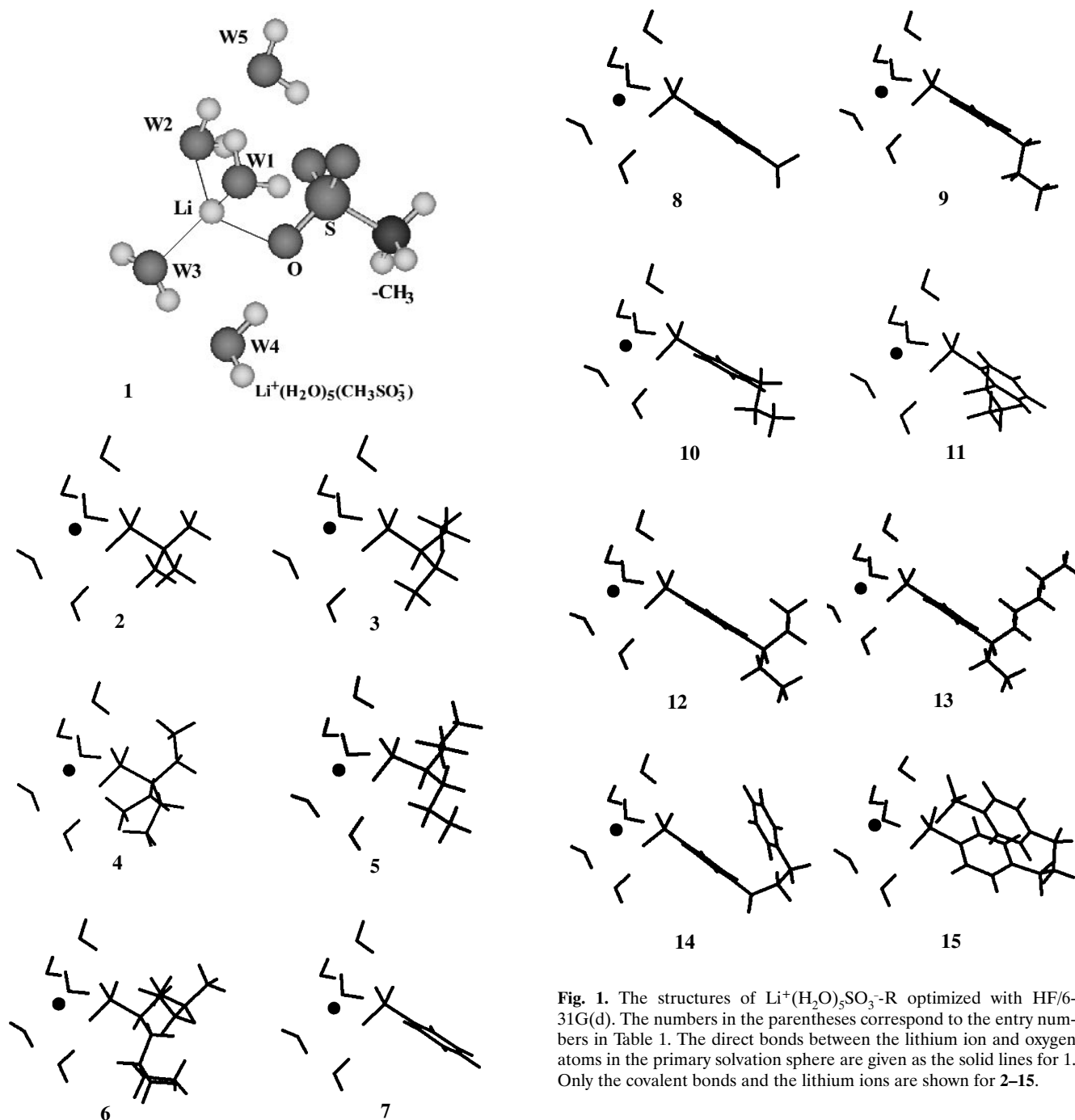
Fig. 1. The structures of $Li^+(H_2O)_5SO_3^-$-R optimized with HF/6-31G(d). The numbers in the parentheses correspond to the entry numbers in Table 1. The direct bonds between the lithium ion and oxygen atoms in the primary solvation sphere are given as the solid lines for 1. Only the covalent bonds and the lithium ions are shown for **2–15**.

expected to influence $r_{Li\text{-}O(S)}$ more strongly than $r_{Li\text{-}O(W)}$. It is also observed that $r_{Li\text{-}O(S)}$s of the species having aryl groups (**7–15**) are, in general, shorter than those of the species lacking ones (**1–6**).

In the 5th column of Table 1 listed is the shortest non-bonding distance ($r_{H\text{-}R}$) between a hydrogen atom of the waters and the atom in -R closest to it (the kind of atom is shown in the parenthesis). This value should be compared with the sum of the van der Waals radii: 2.65–3.15 Å for H-C, 2.40–2.90 Å for H-H and 2.70–2.90 Å for H-O [2]. Except for **15**, $r_{H\text{-}R}$ is larger than or equivalent to the sum of the van der Waals radii, which shows that a hydrophobic group does not come close to a water molecule beyond the van der Waals radius limit. Contrary to this, $-SO_3H$, a hydrophilic group, interacts with water molecules at shorter distances (**15**).

The RPFR values at 25°C are listed in the 6th column of Table 1. As a whole, substitutions of the methyl group with other groups yield only slight changes in RPFR. This is probably because in the present calculations, -Rs are not located so close to the $Li^+(H_2O)_5SO_3^-$ moiety as they can cause substantial structural changes around the lithium ions, as is understood from the $r_{H\text{-}R}$ values. Except $-C_6H_4\text{-}C_3H_6\text{-}C_6H_5$ (**14**), the other substituents of the methyl group reduce or little affect RPFR values, and the largest reduction in RPFR is observed for $-C(C_2H_5)_3$ (**4**). When -Rs are alkyl groups (**1–6**), a moderately good correlation between the RPFR value and $r_{H\text{-}R}$ is observed; the shorter the distance is, the smaller the RPFR value is. The decrease in RPFR value is especially clear when $r_{H\text{-}R}$ is within the range of the sum of the van der Waals radii (**2**, **4** and **6**). This observation could indicate that the existence of a hydrophobic group at around the distance of van der Waals interaction from waters slightly disturbs coordina-
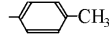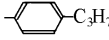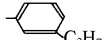
Table 1. Some interatomic distances of the optimized structures and RPRF values.
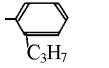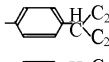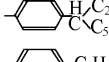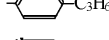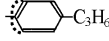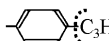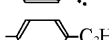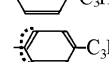
Entry	-R	$r_{Li-O(W)}$[a]	$r_{Li-O(S)}$[a]	r_{H-R}[a]	RPFR[b]	δK_{Li}[a]
1	-CH$_3$	1.985	2.012	3.341 (H)	1.0875	–
2	-C(CH$_3$)$_3$	1.985	2.013	2.485 (H)	1.0872	0.0003
3	-CH(C$_2$H$_5$)$_2$	1.958	2.010	2.997 (H)	1.0874	0.0001
4	-C(C$_2$H$_5$)$_3$	1.984	2.029	2.414 (H)	1.0867	0.0008
5	-CH(C$_3$H$_7$)$_2$	1.985	2.010	3.003 (H)	1.0874	0.0001
6	-CH(C$_5$H$_{11}$)$_2$	1.987	2.012	2.544 (H)	1.0869	0.0006
7	(phenyl)	1.986	2.005	3.624 (C)	1.0874	0.0001
8	(phenyl)-CH$_3$	1.987	2.003	3.625 (C)	1.0875	0.0000
9	(phenyl)-C$_3$H$_7$	1.987	2.003	3.624 (C)	1.0875	0.0000
10	(phenyl)-C$_3$H$_7$	1.987	2.004	3.621 (C)	1.0875	0.0000
11	(phenyl) C$_3$H$_7$	1.987	2.007	3.523 (H)	1.0871	0.0004
12	(phenyl)-CH(C$_2$H$_5$)(C$_2$H$_5$)	1.987	2.003	3.624 (C)	1.0875	0.0000
13	(phenyl)-CH(C$_2$H$_5$)(C$_5$H$_{11}$)	1.987	2.003	3.623 (C)	1.0875	0.0000
14	(phenyl)-C$_3$H$_6$-(phenyl)	1.987	2.000	3.619 (C)	1.0876	-0.0001
14a[c]	(phenyl)-C$_3$H$_6$-(phenyl)		2.009		1.0872	0.0003
14b[c]	(phenyl)-C$_3$H$_6$-(phenyl)		2.002		1.0875	0.0000
15	(phenyl)-C$_3$H$_6$-(phenyl)-SO$_3$H	1.992	1.992	2.161 (O)	1.0871	0.0004
15a[c]	(phenyl)-C$_3$H$_6$-(phenyl)-SO$_3$H		2.012		1.0870	0.0005

[a] Definitions are given in the text.
[b] The value at 25°C.
[c] Entries for the ONIOM calculations.

tion circumstances of the lithium ion, which results in the reduction of RPFR. Substituents containing aryl groups (**7–15**) generally yield only small changes in RPFR value, compared to those of alkyl groups, simply because they are located far away from the lithium ion. Substitutions of the hydrogen of the phenyl group at the *para* position to -SO$_3^-$ by various groups practically have no influence on the RPFR value.

The changes in K_{Li} value (δK_{Li}), with $\delta K_{Li} = 0$ for -R = -CH$_3$, caused by the change in RPFR value of the ion exchanger phase is listed in the last column of Table 1. They should be compared with the experimental K_{Li} value of 1.001–1.003 obtained at 25°C [4] when ion exchangers having the sulfo group as the ion exchange group are used as column packing materials in chromatographic separation of lithium isotopes. The present results indicate that the change in K_{Li} value of up to *ca.* 0.001 could occur without any substantial structural change around lithium ions in the ion exchanger phase. Only a small perturbation in the lithium coordination circumstances caused by the existence of a hydrophobic group of an ion exchanger could change the K_{Li} value by *ca.* 0.001.

Entries **14a**, **14b** and **15a** of Table 1 are the results of ONIOM calculations. Moieties in the parentheses in the 2nd column are optimized with HF/STO-3G and the remaining parts of the systems with HF/6-31G(d). While the RPFR value of **14a** differs from that of **14** by 0.0003, which, we feel, is slightly too large when discussing the K_{Li} value of 1.001, the differences in RPFR value between **14** and **14b** and between **15** and **15a** are only 0.0001, which, we feel, are well

acceptable. Although it is difficult to compare the times required for the geometry optimization between the regular MO and ONIOM calculations, the times required for frequency calculations for **14a** and **14b** become about 1/15 and 1/5 of that of **14**, and about 1/11 of that of **15** for **15a**. Thus, as far as the lithium isotope effects on the order of 10^{-3} or larger are concerned, **14b** and **15a** can be replacements of **14** and **15**, respectively. This will be generalized and applied to other systems. The ONIOM calculation seems effective to reduce calculation times without losing confidence in calculated RPFR values when tackling isotope effects upon mono isotope substitutions in large molecules.

Conclusion

To summarize the present paper dealing with the RPFR of lithium in the ion exchanger phase of aqueous ion exchange systems, we make the following statements:

– The relative positions and orientations of five water molecules and SO$_3^-$ around the lithium ion in Li$^+$(H$_2$O)$_5$SO$_3^-$-R are nearly independent of the kind of -R within the range of the present study. Correspondingly, the RPFR value varies only slightly with changing -R. The maximum decrease of 0.0008 in RPFR value was obtained for -R = -C(C$_2$H$_5$)$_3$ from that of -R = -CH$_3$. Thus, the change in K_{Li} value of *ca.* 0.001 could occur without being accompanied by the substantial structural change around the lithium ion in the ion exchanger phase.

– The ONIOM calculation seems effective for reducing computational times especially when dealing with lithium isotope effects in systems containing many atoms. However, one should be careful in making the atom layer assignment so that the RPFR value by the ONIOM calculation agrees with the result by the regular MO calculation within the permissible limit.

In the present work, the rigidity of the organic framework of an ion exchanger is not well expressed in the calculations. This may be a point to be clarified and studied further in a future paper.

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