Ab initio Molecular Orbital Calculations of Reduced Partition Function Ratios of Hydrated Lithium Ions in Ion Exchange Systems

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Molecular orbital (MO) calculations at the HF/6-31G(d) level were carried out for the aquolithium ions, $Li^+(H_2O)_n$ ($n = 3$, 4, 5, 6, 8, 10 and 12) and the aquolithium ions interacting with the methyl sulfonate ion (MeS^-), $Li^+MeS^-(H_2O)_n$ ($n = 0$, 3, 4, 5, 6, 7, 8 and 10) which were, respectively, intended to be substitutes for lithium species in the solution and resin phases of ion exchange systems for lithium isotope separation. For each of the species considered, at least one optimized structure with no negative frequency was obtained, and the ^7Li-to-^6Li isotopic reduced partition function ratio (RPFR) was estimated for the optimized structure. The solvation number in the primary solvation sphere was four, both in the solution and resin phases; three waters and MeS^- formed the primary solvation sphere in the resin phase. Additional water molecules moved off to the secondary solvation sphere. It was found that consideration on the primary solvation sphere alone was insufficient for estimations of reduced partition function ratios of aquolithium ions. Although the agreement between the experimentally obtained lithium isotope fractionation and the calculated results is not satisfactory, it is pointed out that the HF/6-31G(d) level of the theory is usable for elucidation of lithium isotope effects in aqueous ion exchange systems.

Key words: Ab initio Molecular Orbital Calculations; Reduced Partition Function Ratios: Hydrated Lithium Ion; Lithium Isotope Effects; Ion Exchange.

1. Introduction

Enriched ^6Li will be required for the tritium breeder blanket of deuterium-tritum fusion reactors: $^6Li + n \rightarrow T + {}^4He$. Various methods for lithium isotope separation have been developed, and their applicability to large-scale enriched lithium isotope production has been assessed [1]. Ion exchange chromatography is among the promising methods. The use of ion exchanges for lithium isotope separation was first proposed by Taylor and Urey [2]. Since then, several papers dealing with chromatographic lithium isotope separation have been published [3]. In the majority of such studies, strongly acidic cation exchange resins having the sulfo group ($-SO_3H$) as the exchange group have been used as column packing materials, and lithium isotope effects on the order of 10^{-3} have been obtained. Such effects are based on the isotope exchange reaction between the hydrated lithium ions in the solution and those in the resin:

$$\begin{aligned} &{}^6Li^+(\text{solution}) + {}^7Li^+(\text{resin}) \\ &\quad = {}^7Li^+(\text{solution}) + {}^7Li^+(\text{resin}). \end{aligned} \tag{1}$$

It is experimentally known that ^6Li is preferentially fractionated into the resin phase.

An early attempt at theoretical elucidation of lithium isotope effects in aqueous ion exchange systems was published by Lee and Begun [4]. They tried to explain their experimental results by a simple concept of partial dehydration of lithium ions in the resin phase. Glueckauf [5] attributed the lithium isotope effects to the difference in the Pauling radii of the two isotopes. In [3], we attempted to decompose the experimentally observed lithium isotope fractionation into a few fundamental isotope effects based on the theory of isotope distribution between two phases by Kakihana and Aida [6]. These attempts are lacking ample experimental support.

Based on Bigeleisen-Mayer's theory of isotope effects [7], the equilibrium constant K_{Li} of (1) is given as the ratio of the reduced partition function ratios (RPFRs) of the lithium species in the solution and the resin. If the lithium concentration is not very high, the former can be regarded as the hydrated lithium ion. The latter may be regarded as the hydrated lithium ion interacting with the ion exchange group of the resin.

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The RPFR of a chemical species can be calculated if all the vibrational frequencies of the isotopic species are known. Except for very simple chemical species, these frequencies are not obtained experimentally with sufficient accuracy. Therefore the analysis of the vibrational modes of the hydrated lithium ion in aqueous solution is practically impossible. As for the lithium ion in the resin 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 vibrational data are hardly obtained experimentally. In previous papers [8, 9], using MO calculations, we estimated ^{11}B-to-^{10}B RPFRs of polyboric acids and polyborates anions, for which few vibrational frequencies are experimentally observed, and demonstrated the importance and effectiveness of such calculations in the study of isotope effects. Encouraged by the satisfactory results in those papers [8, 9], we carried out MO calculations on aquolithium ions, hoping that the lithium isotope effects observed in ion exchange chromatographic systems may be reproduced and elucidated by such calculations.

2. Theory and Procedure of Calculations

2.1. Isotope Exchange Equilibria and Reduced Partition Function Ratios

Isotope effects based on molecular translational, rotational and vibrational motions can be estimated by calculating the RPFRs of the chemical species participating in the isotope exchange reaction in concern [7]. That reaction may be expressed, without losing any generality, as

$$\mathrm{AX} + \mathrm{BX'} = \mathrm{AX'} + \mathrm{BX}, \tag{2}$$

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

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

where $(s/s')f_{\mathrm{AX}}$ and $\ln (s/s')f_{\mathrm{BX}}$ 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

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

where

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

and

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

Here f is the degree of freedom of the vibrational motion, h the Planck 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 Boltzmanns constant and T the temperature.

2.2. Modeling of Lithium Ions in the Solution and Resin and ab initio Molecular Orbital Calculations

We assume that the lithium species in the solution phase is given as the hydrated lithium ion, $\mathrm{Li^+(H_2O)}_n$, with the charge of +1, n being the hydration number. Calculations are made for n = 3, 4, 5, 6, 8, 10, and 12. In the resin phase, we consider the hydrated lithium ion interacting with the methyl sulfonate ion ($\mathrm{CH_3SO_3^-}$), $\mathrm{Li^+MeS^-(H_2O)}_n$, with $\mathrm{MeS^-} = \mathrm{CH_3SO_3^-}$ and n = 0, 3, 4, 5, 6, 7, 8, and 10. Thus we suppose the ion exchange resin to have the sulfo group as ion exchange group, the methyl moiety of MeS$^-$ serving as the framework of the resin.

All the *ab initio* calculations were made with a Fujitsu personal computer using the Gaussian 98W program package. The Plux program is used for the graphics. Based on the fact that the Hartree-Fock self-consistent field method theory with the 6-31G(d) basis set (HF/6-31G(d)) gives satisfactory results on boron isotope effects [8], the *ab initio* MO theory and the basis set used were restricted to HF/6-31G(d).

Due to the nature of the present work, we have let up to as many water molecules as possible hydrate the lithium ion at the center. In general, this kind of structure seems the most stable among optimized structures [11, 12]. For each species the geometry was first optimized and then the vibrational frequencies of the isotopic species were calculated. The calculated frequencies were corrected by the scale factor (corrected fre-

Table 1. Total energies, Li–O bond distances and RPFRs of optimized structures of $Li^+(H_2O)_n$ and $Li^+MeS^-(H_2O)_n$ at 25 °C at the HF/6-31G(d) level.

Species	Phase[a]	Symbol	Total energy/ hartree[b]	$Li–OH_2$ distance/Å[c,d]	RPFR	RPFR of the species
$Li^+(H_2O)_3$	sol	F3	–235.430	1.919	1.08342	1.08342
$Li^+(H_2O)_4$		F4	–311.472	1.971	1.08772	1.08772
$Li^+(H_2O)_5$		F5	–387.508	1.967	1.09011	1.09011
$Li^+(H_2O)_6$		F6	–463.539	1.974	1.08916	1.09040
		F6-2	–463.542	1.968	1.09052	
		F6-3	–463.527	2.154	1.05644	
$Li^+(H_2O)_8$		F8	–615.594	1.962	1.09384	1.09671
		F8-2	–615.599	1.968	1.09671	
$Li^+(H_2O)_{10}$		F10	–767.663	1.991	1.09018	1.09180
		F10-2	–767.665	1.982	1.09211	
$Li^+(H_2O)_{12}$		F12	–919.732	1.989	1.08889	1.08890
		F12-2	–919.732	1.992	1.08896	
		F12-3	–919.727	1.983	1.09228	
Li^+MeS^-	resin	R0	–669.188	1.873	1.06945	1.06945
$Li^+MeS^-(H_2O)_3$		R3	–897.319	1.980 (1.974)	1.09396	1.09396
$Li^+MeS^-(H_2O)_4$		R4A	–973.348	1.979	1.09202	1.09082
		R4B	–973.352	1.979 (1.982)	1.09082	
$Li^+MeS^-(H_2O)_5$		R5A	–1049.379	1.986	1.08968	1.08749
		R5B	–1049.384	1.989 (1.989)	1.08749	
$Li^+MeS^-(H_2O)_6$		R6A	–1125.409	1.980	1.09105	1.08809
		R6B	–1125.409	1.986 (1.986)	1.08809	
$Li^+MeS^-(H_2O)_7$		R7B	–1201.437	(1.985)	1.08856	1.08820
		R7B-2	–1201.439	(1.986)	1.08820	
$Li^+MeS^-(H_2O)_8$		R8B	–1277.475	1.982 (1.982)	1.08949	1.08949
$Li^+MeS^-(H_2O)_{10}$		R10B	–1429.526	1.981 (1.981)	1.08856	1.08856

[a] sol = solution phase, resin = resin phase.

[b] 1 hartree = 2623.75 kJ/mol.

[c] Average of Li–O distances between the Li^+ ion and oxygens of water molecules in the primary solvation sphere.

[d] Numbers in the parentheses denote the average of Li–O distances between the Li^+ ion and oxygens of water molecules and $-SO_3^-$ in the primary solvation sphere.

quencies) and, using the corrected frequencies, the RPFR of the species was computed.

In most of the frequency calculations, the isotopes of hydrogen, carbon, oxygen and sulfur were ^1H, ^{12}C, ^{16}O and ^{32}S, respectively. In some calculations, however, atoms in the methyl moiety of MeS^- were given much larger weights to better reflect the actual situation in which the sulfonato group ($-SO_3^-$) is fixed to the organic framework of the ion exchange resin. The framework hardly moves due to the vibrational motion of the lithium ion.

No symmetry consideration was made in the geometry optimization calculations: For each of the structures considered, the bond lengths, angles and dihedral angles, were varied independently to achieve the geometry optimization.

3. Results and Discussion

3.1. Optimized Structures

Optimized structures of $Li^+(H_2O)_n$ ($n = 3, 4, 5, 6, 8, 10$ and 12) and $Li^+MeS^-(H_2O)_n$ ($n = 0, 3, 4, 5, 6, 7, 8$ and 10), modeling lithium ions in solution and the resin phases are depicted, except $Li^+MeS^-(H_2O)_0$, in Figs. 1 and 2, respectively. No negative frequency was calculated for these structures. Thus, they are all at the global or local minima of the potential energy surfaces. Their total energies and bond distances between the Li^+ ion and the oxygen atoms of the water molecules in the primary solvation sphere are summarized in the fourth and fifth columns of Table 1, respectively.

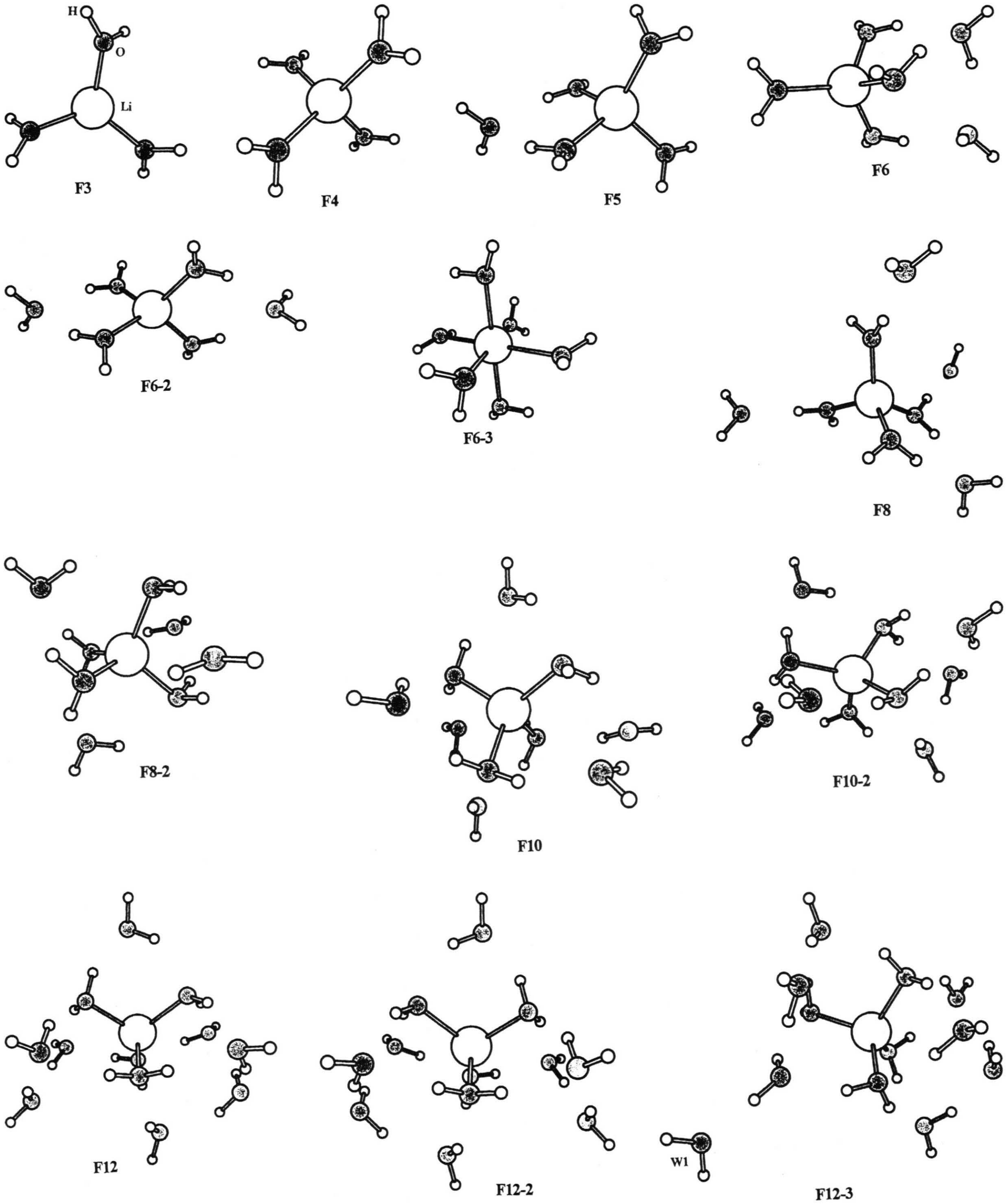

Fig. 1. Optimized structures of $Li^+(H_2O)_n$ ($n = 3, 4, 5, 6, 8, 10,$ and 12). The relative sizes of the spheres have nothing to do with atomic or ionic radii.

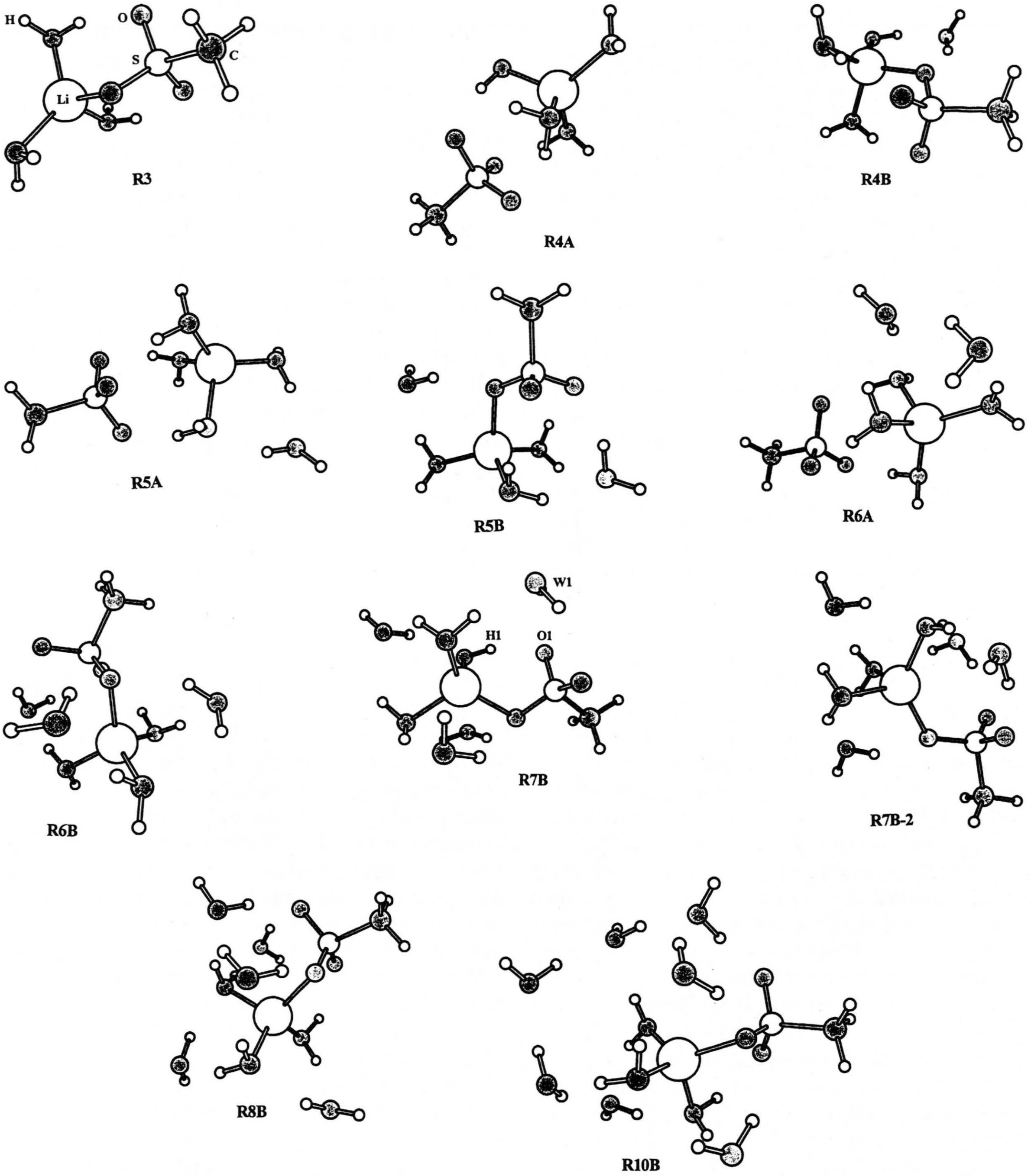

Fig. 2. Optimized structures of $Li^+MeS^-(H_2O)_n$ ($n = 3, 4, 5, 6, 7, 8$ and 10). The relative sizes of the spheres have nothing to do with atomic or ionic radii.

3.1.1. Lithium ion in the solution phase

The number of optimized structures of $Li^+(H_2O)_n$ considered in the present study is three for $n = 6$ and 12, two for $n = 8$ and 10, and one for $n = 3$, 4 and 5. For $n = 3$, our **F3** structure is equivalent to **IIIa** of Feller et al. [10] and **3**(D_3) of Glendening and Feller [11]. According to the results of the latter authors, **F3** is most likely at the global minimum of the potential energy surface. In **F4** ($n = 4$), four water molecules are directly hydrated to the lithium ion. In **F5** ($n = 5$), only four out of five water molecules are directly bonded to the lithium ion, forming the primary hydration sphere, and the fifth water moves off to the secondary sphere, hydrating to two of the waters in the primary hydration sphere. For $n = 6$ or larger, the numbers of potential configurations are expected to be large [12], and for $n = 6$, we consider three structures. In two of the three, four waters directly hydrate to the lithium ion and the remaining two waters are located in the secondary hydration sphere (**F6** and **F6-2**), while in **F6-3**, all six waters are directly bonded to the lithium ion. The distances between the lithium ion and oxygen atoms of waters in the primary hydration sphere in **F6-3** are long compared to those of **F6** and **F6-2**, and **F6-3** is a much higher-energy conformer of $Li^+(H_2O)_6$ than **F6** and **F6-2** (Table 1). The largest structural difference between **F6** and **F6-2** is that, while the two waters in the secondary hydration sphere are *trans* to each other in **F6-2**, they are *cis* in **F6**. The stability is in the decreasing order of **F6-2** > **F6** > **F6-3**. In both **F8** and **F8-2** ($n = 8$), four water molecules are bonded to the lithium ion, and the other four form the secondary hydration sphere, each being hydrogen-bonded to waters in the primary hydration sphere. We tried in vain to obtain a structure where six waters are directly bonded to the lithium ion and the remaining two move off to the secondary hydration sphere. The largest structural difference between **F8** and **F8-2** is in the orientation of waters in the secondary hydration sphere. **F8-2** seems to relax towards the structure with D_{2d} symmetry, which is equivalent to the structure of the octaaquolithium ion by Pye et al. [13]. **F8-2** is more stable than **F8** by *ca.* 12 kJ/mol. For $n = 10$, two conformers (**F10** and **F10-2**) are considered. They, with four water molecules in the primary hydration sphere, are basically different from each other in the location and orientation of waters in the secondary hydration sphere. For $n = 12$, one of the optimized structures is **F12** in which the numbers of waters in the primary and secondary hydration sphere are four and eight, respectively. This is probably equivalent to the dodecaaquolithium ion by Pye et al. [13]. The second one (**F12-2**) is structurally different from **F12** mainly in the orientation of the waters in the secondary hydration sphere. The third structure is **F12-3**, where one water molecule (**W1** of **F12-3** in Fig. 1) is located in the third hydration sphere.

The above result that the hydration number of four around the lithium ion in the primary hydration sphere is consistent with those of previous MO calculations [10], Raman and *ab initio* work [14], while a molecular dynamics simulation yielded the hydration number of six [15]. The hydration number of the secondary hydration sphere is at least eight. Water molecules in this sphere are hydrogen-bonded to waters in the primary sphere, using their oxygen atoms. The O···H distances between oxygens of waters in the secondary hydration sphere and hydrogen of waters in the primary hydration sphere are 1.8 ~ 20 Å and slightly shorter than O···H hydrogen-bond distances calculated with HF/6-31G(D) for water clusters [16].

3.1.2. Lithium ion in the resin phase

The number of optimized structures of $Li^+MeS^-(H_2O)_n$ modeling for lithium ions in the resin phase was one for $n = 0$, 3, 8 and 10, and two for $n = 4$, 5, 6, and 7. In **R0** ($n = 0$), MeS^- interacts with the lithium ion using one of its oxygen atoms. In **R3** ($n = 3$), three water molecules are hydrogen-bonded to the lithium ion, and $-SO_3^-$ is directly bonded to the lithium ion through one of its oxygen atoms like in **R0**. In **R4B** with $n = 4$, three of four waters are hydrogen-bonded to the lithium ion and MeS^- is directly bonded to the lithium ion through one of its oxygen atoms, thus located in the primary solvation sphere (**type-B**). The Li–O distance between the lithium ion and MeS^- is nearly the same as those between the lithium ion and the three waters. The fourth water is hydrogen-bonded to one of the waters in the primary solvation sphere using its oxygen atom and is *cis* to MeS^-. In **R4A**, four waters are directly bonded to the lithium ion, and MeS^- interacts with three of the four waters between the oxygen atoms of $-SO_3^-$ and hydrogen atoms of the waters (**type-A**). **R4B** is more stable than **R4A** by *ca.* 9 kJ/mol. Similar conformers are obtained for $n = 5$ and 6 (**R5A** and **R5B**, and **R6A** and **R6B**). In **R5B** and **R6B** (**type-B**), three water molecules and MeS^- are directly bonded to the lithium ion, and the remaining waters move off to the secondary hydration sphere around the lithium ion. In **R5A** and **R6A** (**type-**

A), four waters are directly bonded to the lithium ion, and MeS^- interacts with three of the four waters between the oxygen atoms of $-SO_3^-$ and hydrogen atoms of the waters, and the remaining waters form the secondary hydration sphere of the lithium ion. **R5B** and **R6B** are more stable than **R5A** and **R6A**, respectively. For $n = 7$ or larger we consider only **type-B** structures. For $n = 7$, we consider two structures, **R7B** and **R7B-2**. The largest structural difference between the two is that, while there is a hydrogen bond between a hydrogen atom of a water in the primary hydration sphere (**H1** of **R7B** in Fig. 2) and an oxygen atom of $-SO_3^-$ (**O1**) in **R7B**, there is no such bond in **R7B-2**. Another large difference is that one water (**W1** of **R7B** in Fig. 2) is hydrogen-bonded to $-SO_3^-$ instead of to the lithium ion in **R7B**. The optimized structures for $n = 8$ and 10 (**R8B** and **R10B**) are similar to **R4B**, **R5B**, **R6B** and **R7B** as far as the primary solvation sphere is concerned.

It may generally be stated that there are basically two solvation structures around the lithium ion in the resin phase. In one structure (**type-B**), three water molecules and MeS^- form the primary solvation sphere, with the latter being bonded to the lithium ion using one of its three oxygen atoms. MeS^- thus directly interacts with the lithium ion in this type. In the other type of structure (**type-A**), four waters form the primary hydration sphere and MeS^- interacts with three of the four waters between oxygen atoms of $-SO_3^-$ and hydrogen atoms of the waters. Thus, MeS^- is not directly bonded to the lithium ion in the **type-A** structures. For a given n, the **type-B** structure is generally more stable than the **type-A** structure.

As a summary of Sect. 3.1 it may be concluded that the solvation number of a lithium ion in the primary solvation sphere is four both in the solution and resin phases. In the solution phase, four water molecules from the primary hydration sphere, and additional waters move off to the secondary or higher order hydration sphere. The number of water molecules in the secondary hydration sphere is not clarified in this study; it must be at least eight. In the resin phase, three water molecules and MeS^- form the primary solvation sphere with the latter bonded to the lithium ion through one of the oxygen atoms of $-SO_3^-$.

3.2. Determination of the Scale Factor

Experimental attempts to observe vibrational frequencies of aquolithium ions are mostly focused to the totally symmetric stretching mode (ν_1). There are some conflicting interpretations in the assignment of this mode. Nash et al. [17] assigned a band at 440 cm^{-1} to this mode of the tetraaquolithium ion. Michaelian and Moskovits [18] and Kameda et al. [19] claim that it should be 190 cm^{-1} and 192 cm^{-1}, respectively. Rudolph et al. [14] report the assignment of the band at 255 cm^{-1} to ν_1.

We chose to adopt $\nu_1 = 255$ cm^{-1} by Rudolph et al. [14]. This is partly because their value best fits to the prediction of Kanno [20] that is based on the correlation among the symmetric stretching mode of metal ion-oxygen of water and the charge on the metal ion and metal-oxygen distance. Another reason is that their value seems most widely accepted. Our present calculations yield 248 cm^{-1} for the $Li^+(H_2O)_4$ species (**F4**).

In their MO calculations on $Li^+(H_2O)_n$ ($n = 1, 2, 3, 4, 8,$ and 12), Pye et al. [13] stated that a model of the secondary solvation sphere containing only four waters, *i.e.*, $Li^+(H_2O)_8$ with D_{2d} symmetry, seems to be closer to reality. That is, our **F8-2** structure best represents the lithium ion in the solution phase. The totally symmetric stretching frequency is calculated as 266 cm^{-1}. Thus, the scale factor in this case is $255/266 = 0.959$.

In general, Hartree-Fock level calculations overestimate vibrational frequencies [21]. Our ν_1 value is 248 cm^{-1} for $Li^+(H_2O)_4$, which is smaller than the experimental value of 255 cm^{-1}, and is 266 cm^{-1} for $Li^+(H_2O)_8$, which is larger than the experimental value. We thus decided to use 0.959 (more accurately, 0.95829) as the value of the scale factor in the calculations hereafter.

3.3. Reduced Partition Function Ratios and Equilibrium Constants of Lithium Isotope Exchange Reactions

The RPFR value of each of the optimized structures at 25 °C is calculated using (4) with the corrected frequencies, and all the results are summarized in the sixth column of Table 1. All the calculations are made with ^1H, ^{12}C, ^{16}O, and ^{32}S.

3.3.1. RPFR of the lithium ion in the solution phase

In general, there is more than one optimized structure for a given $Li^+(H_2O)_n$ species, and the number of these structures is expected to rapidly increase with in-

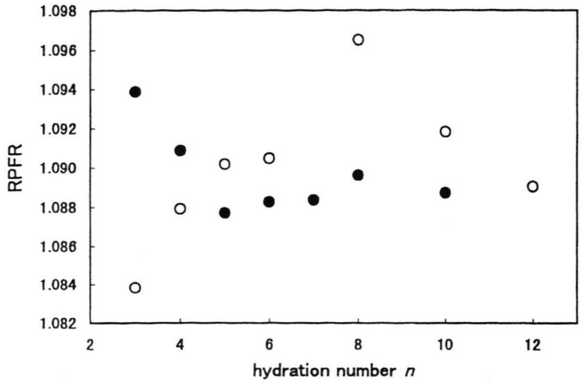

Fig. 3. Plot of RPFRs against the hydration number, *n*. ○ for $Li^+(H_2O)_n$ and ● for $Li^+MeS^-(H_2O)_n$.

creasing *n*. The most appropriate RPFR value of a given species may be obtained first by finding all the structures at global and local minima of the potential energy surface and calculating their RPFRs and then by averaging those RPFRs weighted by respective populations based on the Boltzmann distribution. It is, however, impractical or may be impossible to obtain all the optimized structures, especially for a large *n*. Instead of laboring to complete the collection of optimized structures for a given species, we chose to find a few typical structures and calculate the RPFR of the species as the average of the RPFRs of those typical structures weighted by their respective populations. The results are summarized in the "RPFR of the species" column of Table 1 and plotted against *n* in Figure 3.

The RPFR value of $Li^+(H_2O)_n$ thus obtained increases with increasing *n* up to $n = 8$ and turns to decrease for *n* beyond 8. This indicates that, while the hydration number up to four in the secondary hydration sphere contributes to the increase in sum of the forces acting on the lithium ion, the opposite is the case with that number beyond four. It is also seen in Fig. 3 that no abrupt change in the RPFR is observed between $n = 4$ and 5 where the secondary hydration sphere begins to be formed.

3.3.2. RPFR of the lithium ion in the resin phase

In the present study, the methyl moiety of MeS^- serves as the organic framework of strongly acidic cation exchange resin which is expected to be nearly vibrationally immobile regardless of vibrational motion of the lithium ion. This immobility is better presented when the atoms in the methyl moiety are given fictitiously large weights. Table 2 summarizes changes in RPFR values when atomic weigths of the methyl moiety are changed. As is seen in the table, the RPFR values are nearly independent of the masses of the atoms in the methyl moiety except that of **R3**. Based on this observation, the isotopes of hydrogen, carbon, oxygen and sulfur were confined to ^1H, ^{12}C, ^{16}O, and ^{32}S, respectively, in other calculations (*vide supra*).

In general, there are two types of interaction between the lithium ion and $-SO_3^-$ of MeS^- (**type-A** and **type-B**), and **type-B** structures are more stable than **type-A** structures (*cf*: Section 3.1.2). Thus, we only consider RPFRs of **type-B** structures here. The RPFRs of $Li^+MeS^-(H_2O)_n$ species are listed in the last column of Table 1 and plotted against *n* in Figure 3. The RPFR value of $Li^+MeS^-(H_2O)_n$ decreases with increasing hydration number of up to $n = 5$, and beyong $n = 5$ it becomes nearly constant.

Table 2. Changes in RPFR values of $Li^+MeS^-(H_2O)_n$ with changing atomic weights of the methyl moiety.

Symbol	Isotopes	RPFR	Isotopes	RPFR
R3	$-^{12}C^1H_3$	1.09396	$-^{10000}C^{10000}H_3$	1.09234
RA4	$-^{12}C^1H_3$	1.09202	$-^{10000}C^{10000}H_3$	1.09202
RB4	$-^{12}C^1H_3$	1.09082	$-^{100}C^{100}H_3$	1.09081
			$-^{10000}C^{10000}H_3$	1.09081
			$-^{100000000}C^{100000000}H_3$	1.09081
R5A	$-^{12}C^1H_3$	1.08968	$-^{10000}C^{10000}H_3$	1.08968
R5B	$-^{12}C^1H_3$	1.08749	$-^{10000}C^{10000}H_3$	1.08750
R6A	$-^{12}C^1H_3$	1.09105	$-^{10000}C^{10000}H_3$	1.09104
R6B	$-^{12}C^1H_3$	1.08809	$-^{10000}C^{10000}H_3$	1.08809
R7B-2	$-^{12}C^1H_3$	1.08820	$-^{10000}C^{10000}H_3$	1.08821
R8B	$-^{12}C^1H_3$	1.08949	$-^{10000}C^{10000}H_3$	1.08950

3.3.3. Equilibrium constants of lithium isotope exchange reactions

A comparison of the RPFRs of $Li^+(H_2O)_n$ and $Li^+MeS^-(H_2O)_n$ reveals that the RPFR of $Li^+MeS^-(H_2O)_n$ is larger than that of $Li^+(H_2O)_n$ for $n = 3$ and 4, which is opposite to experimental results [3]. In order for the present calculations to be qualitatively consistent with experiments, it is necessary to take the secondary solvation spheres into consideration both for the solution and resin phases. The hydration in the secondary solvation sphere is thus quite important in elucidating the lithium isotope effects in aqueous ion exchange systems.

It is difficult at the present stage of the research progress to judge which n value best represents the real hydration circumstances around the lithium ion both in the solution and the resin phases. (Of course, the best n value may be different for the two phases.) As Pye et al. [13] suggested, a larger n is not necessarily better. Giving up using a singular species as the hydrated lithium ion in each phase, we chose to consider $Li^+(H_2O)_n$ with $n = 6$, 8, 10, and 12 and $Li^+MeS^-(H_2O)_n$ with $n = 5$, 6, 7, 8, and 10 and calculate RPFR values of the hydrated lithium ions in respective phases as simple arithmetic means of the RPFRs of the species considered. Then, we obtain 1.09195 and 1.08837 as the RPFRs of lithium ions in the solution and resin phases, respectively, and 1.0033 as the K_{Li} value of (1) at 25 °C. This should be compared with experimental value of 1.001 ~ 1.003 [3]. We feel that a fair agreement is obtained.

We do not claim that our present calculations are quite satisfactory. All our calculations are based on HF/6-31G(d), and a more advanced MO theory with a higher level basis set may yield quantitatively better results. The collection of optimized structures of a given species is far from complete, especially for large n values, and accordingly, the present statistical treatments are simplistic. Since the organic framework of a real ion exchange resin has been substituted by the methyl moiety in our calculations, steric hindrance of the lithium ion in the resin phase has not been taken into consideration. In spite of these drawbacks, we would like to emphasize the following. The HF/6-31G(d) level of theory seems to be usable for the study of lithium isotope effects in aqueous systems, and taking hydration in the secondary hydration sphere into consideration is indispensable.

4. Conclusion

To summarize, we make the following statements:

1. Structures of $Li^+(H_2O)_n$ ($n = 3$, 4, 5, 6, 8, 10, and 12) and $Li^+MeS^-(H_2O)_n$ (MeS^- = methyl sulfonate ion; $n = 0$, 3, 4, 5, 6, 7, 8, and 10) species were optimized at the HF/6-31G(d) level of theory. The former and the latter are, respectively, intended as lithium species in the solution and resin phases of ion exchange lithium isotope separation systems. For each of the species considered, at least one structure at the global or local minimum of the potential surface was found.
2. The number of water molecules directly bonded to the lithium ion is four for $Li^+(H_2O)_n$, and additional waters are located in the secondary hydration sphere.
3. In general, there are basically two solvation structures around the lithium ion of $Li^+MeS^-(H_2O)_n$. In one structure, three water molecules and MeS^- form the primary solvation sphere, with the latter being bonded to the lithium ion using one of its three oxygen atoms. In the other type of structure, four waters form the primary hydration sphere and MeS^- interacts with three of the four waters between oxygen atoms of MeS^- and hydrogen atoms of the waters; MeS^- is not directly bonded to the lithium ion. For a given n, the former is generally more stable than the latter.
4. For $n = 3$ or 4, the RPFR value of $Li^+MeS^-(H_2O)_n$ is larger than $Li^+(H_2O)_n$ which is opposite to experimental results. For $n = 5$ or larger, $Li^+(H_2O)_n$ is larger in the relative magnitude of the RPFR value than $Li^+MeS^-(H_2O)_n$, which qualitatively agrees with experiments. Inclusion of the secondary hydration sphere into MO calculations is thus important for better agreement between calculations and experiments.
5. The HF/6-31G(d) level of theory seems to be applicable to the study of lithium isotope effects in aqueous ion exchange systems.

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