Molecular Orbital Estimation of Reduced Partition Function Ratios of Lithium Interacting with Aromatic Hydrocarbons with Condensed Benzene Rings

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Molecular orbital calculations at the B3LYP/6-311G(d) level were carried out to elucidate the lithium isotope effects accompanying chemical insertion of lithium from 1-methoxybutane solution containing lithium and naphthalene to graphite. The lithium atom between the graphene layers of graphite was modeled as lithium atoms in 1:1 complexes of lithium and simple aromatic hydrocarbons with condensed benzene rings. The ^{7}Li-to-^{6}Li isotopic reduced partition function ratio (RPFR) was found to be a decreasing function of the number of benzene rings adjacent to the benzene ring above which the lithium atom was located, and was "saturated" at 1.04570 at 25 °C. The most plausible lithium species in the 1-methoxybutane solution was a lithium atom interacting with a naphthalene molecule and solvated by a 1-methoxybutane molecule in the contact ion pair manner. Its RPFR value was 1.07126 at 25 °C. The two RPFR values gave a single-stage separation factor of 1.024 for the lithium isotopes, which agreed well with the experimental value of 1.023.

Key words: Lithium Isotopes; Graphite; Reduced Partition Function Ratio; Molecular Orbital Calculations.

1. Introduction

Lithium can be chemically and electrochemically intercalated into graphite to form lithium graphite intercalation compounds (Li-GICs) [1]. GICs are layered compounds, in which atomic or molecular layers (intercalate layers) are inserted between graphene layers of host graphite. GICs are characterized by the staging phenomenon, their staged structures being denoted by the stage index, the number of graphene layers between adjacent intercalate layers [2]. Four different staged structures are known for Li-GICs, depending on the concentration of lithium. The maximum concentration corresponds to the formula of LiC_6.

In a previous paper [3], we synthesized Li-GICs by chemical intercalation of lithium and observed lithium isotope effects accompanying chemical intercalation/deintercalation of lithium to/from graphite from/to 1-methoxybutane (Met) solution containing lithium and naphthalene (Nap). The lighter isotope, ^{6}Li, was preferentially fractionated into the graphite phase in every experiment, and a single-stage separation factor, *S*, of 1.023 (average) was obtained at 25 °C for intercalation experiments where staged structures were observed. If only one kind of lithium species exists in each of the Met solution and graphite phases in these experiments, the separation factor is nothing but the equilibrium constant, *K*, of the lithium isotope exchange reaction:

$$^6\mathrm{Li(Met)} + {}^7\mathrm{Li(graphite)} = {}^7\mathrm{Li(Met)} + {}^6\mathrm{Li(graphite)}, \quad (1)$$

where Li(Met) denotes the lithium species in the Met solution and Li(graphite) in the graphite. *K* in (1) may be expressed in terms of the ^{7}Li-to-^{6}Li isotopic reduced partition function ratios (RPFRs), $(s/s')f$, [4] as

$$\ln K = \ln(s/s')f_{\mathrm{metho}} - \ln(s/s')f_{\mathrm{graphite}}, \quad (2)$$

where $(s/s')f_{\mathrm{metho}}$ and $(s/s')f_{\mathrm{graphite}}$ are the RPFRs of lithium in the Met solution and in graphite, respectively. The experimental results [3] indicate that $\ln(s/s')f_{\mathrm{metho}}$ is larger than $\ln(s/s')f_{\mathrm{graphite}}$ by about 0.023 at 25 °C.

The RPFRs can be calculated if all the vibrational frequencies of the isotopic species of lithium involved in the lithium isotope exchange reaction are known. Unfortunately, no lithium-related frequency is reported for the Met solution containing lithium and Nap or for

Table 1. Summary of calculated results on optimized structures of lithium species modeling the lithium atom in graphite.

Complex	Hydrocarbon	r_{Li-C}(s)Å	r_{Li-C}(a)Å	Chg(Li)	n_b	RPFR
g1	benzene	2.717	2.717	−0.1469	0	1.00511
g2	naphthalene	2.132	2.236	0.4731	1	1.05477
g3	anthracene	2.165	2.229	0.5414	2	1.04945
g4	anthracene	2.143	2.219	0.5036	1	1.05594
g5	phenanthrene	2.121	2.224	0.5319	2	1.05136
g6	phenanthrene	2.145	2.243	0.4678	1	1.05214
g7	pyrene	2.148	2.226	0.5485	3	1.05210
g8	pyrene	2.152	2.215	0.5292	2	1.05534
g9	tryphenylene	2.132	2.373	0.4952	3	1.03390
g10	benzo(a)pyrene	2.136	2.232	0.5729	3	1.04850
g11	perylene	2.232	2.235	0.5909	4	1.04581
g12	perylene	2.155	2.221	0.5390	2	1.05374
g13	benzo(e)pyrene	2.192	2.234	0.5883	4	1.04553
g14	benzo(ghi)perylene	2.218	2.240	0.6029	5	1.04577
g15	coronene	2.241	2.241	0.6192	6	1.04568

Li-GICs. We [5, 6] demonstrated that the vibrational analysis based on the molecular orbital (MO) theory was effective to elucidate and predict isotope fractionations in such systems where no or few vibrational frequency data were available. In this paper we report MO calculations of the RPFRs of lithium atoms interacting with various simple aromatic hydrocarbons with condensed benzene rings, which were intended to model lithium atoms in Li-GICs, and of lithium atoms interacting with Nap and Met molecules, which modeled lithium atoms in Met solution containing lithium and Nap. These calculations were carried out in the hope that the lithium isotope effects observed in [3] may be reproduced and elucidated.

2. Calculations

2.1. Modeling of Lithium in Li-GICs and in the 1-methoxybutane Solution Containing Lithium and Naphthalene

As lithium in Li-GICs, we considered lithium atoms interacting with benzene and various small hydrocarbon molecules with condensed benzene rings, *i. e.*, from benzene to coronene as given in Fig. 1 and Table 1. We only considered 1:1 complexes of a lithium atom and a hydrocarbon molecule with the expectation that even MO calculations on such simple complexes may give some insight into lithium in graphene layers concerning its RPFR value.

It is said that lithium can dissolve in Met solution containing Nap upon forming a lithium-methoxybutane-naphthalene complex [7], although the nature of the complex is not well understood. The existence of Nap (or other aromatic hydrocarbons) is indispensable, because lithium never dissolves in Met solutions without Nap. It has also been pointed out that the complex may be of the solvent separated ion pair type and not of the contact ion pair type [7, 8]. In this paper, we thus considered four lithium species for the estimation of the RPFR of lithium in the Met solution. They were a lithium atom interacting with a Nap molecule (Li-Nap; **m1** (= **g2**)), a lithium atom solvated by a Met molecule (Li-Met; **m2**), a lithium atom interacting with a Nap molecule and solvated by a Met molecule in the contact ion pair manner (Met-Li-Nap; **m3**) and a lithium atom interacting with a Nap molecule and solvated by a Met molecule in the solvent separated ion pair manner (Li-Met-Nap; **m4**).

All the MO calculations were made with a Dell computer using the Gaussian 98W program package [9] at the B3LYP/6-311G(d) level of theory. Although we attempted the HF theory in order for the results of this study to be consistent with our previous HF/6-31G(d) level calculations on the RPFRs of hydrated and solvated lithium ions [5, 10], it did not work well. The choice of the combination of B3LYP and 6-311G(d) was based on the results by Rousseau and Marx [11] on MO calculations on small lithium clusters. They reported that the B3LYP/6-311G(d) level calculations gave reasonable structures and energies of these clusters. We expected that B3LYP/6-311G(d) would yield reasonable results on lithium-hydrocarbon molecules since Li-Li bonds and Li-hydrocarbon bonds are both categorized as weak bonds. The Freewheel program was used for the graphics. Calculated frequencies were used for the RPFR calculations without scaling due to the lack of experimental ones to be referenced. Setting the scale factor value to unity, however, seems a reasonable approximation [12].

All geometry optimizations were conducted without symmetry consideration: For each of the structures considered, the bond lengths, bond angles and dihedral angles were varied independently to achieve the geometry optimization. The isotopes of hydrogen, carbon and oxygen were ^{1}H, ^{12}C, and ^{16}O.

2.2. Isotope Exchange Equilibria and Reduced Partition Function Ratios

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

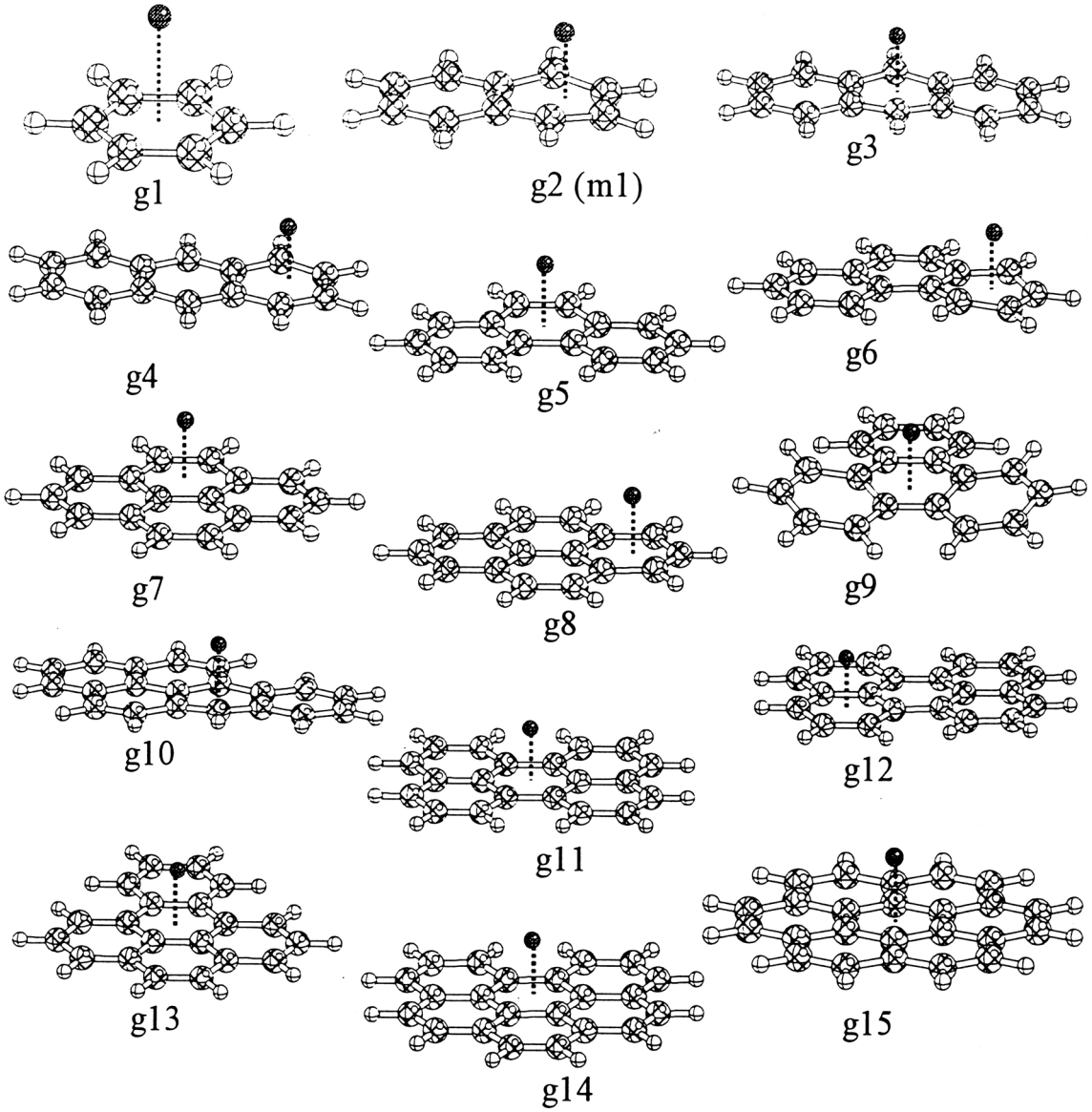

Fig. 1. The optimized structures of 1:1 complexes of lithium and benzene (**g1**) and of lithium and aromatic hydrocarbons with condensed benzene rings (**g2** to **g15**).

concerned [4]. That reaction may be expressed, without losing any generality, as

$$\mathrm{AX} + \mathrm{BX}' = \mathrm{AX}' + \mathrm{BX}, \tag{3}$$

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 (3) (strictly speaking, the equilibrium constant estimated quantum mechanically divided by that estimated classically) can be given as

$$\ln K = \ln(s/s')\, f_{\mathrm{BX}} - \ln(s/s')\, f_{\mathrm{AX}}, \tag{4}$$

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

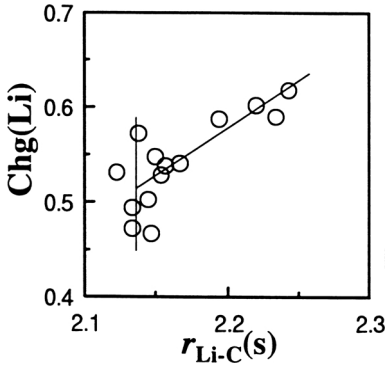

Fig. 2. Plot of chg(Li) against $r_{\text{Li}-\text{C}}$(s) for the 1:1 complexes of lithium and aromatic hydrocarbons with condensed benzene rings (**g2** to **g15**).

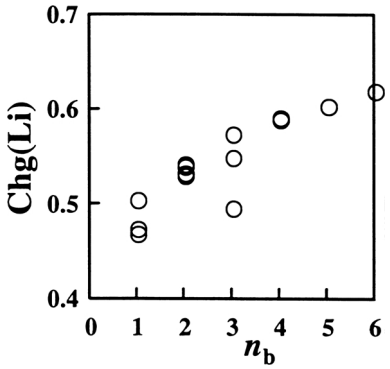

Fig. 3. Plot of chg(Li) against n_b for the 1:1 complexes of lithium and aromatic hydrocarbons with condensed benzene rings (**g2** to **g15**).

$$(s/s')f = \prod_{1}^{f} \frac{u_i \exp(-u_i/2)/\{1-\exp(-u_i)\}}{u_i' \exp(-u_i'/2)/\{1-\exp(-u_i')\}}, \quad (5)$$

where

$$u_i = hc\omega_i/(kT), \quad (6)$$

and

$$u_i' = hc\omega_i'/(kT). \quad (6')$$

Here, f is the degree of freedom of the vibrational motion, h 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. In the present case, $(s/s')f_{\text{AX}} = (s/s')f_{\text{graphite}}$ and $(s/s')f_{\text{BX}} = (s/s')f_{\text{metho}}$.

3. Results and Discussion

3.1. Optimized Structures

Fifteen 1:1 lithium-aromatic hydrocarbon complexes were considered to model lithium atoms between graphene layers of graphite. Their optimized structures are depicted as **g1** to **g15** in Figure 1. No imaginary frequency is obtained for those structures, which means that they are all at the global or local minima of the potential energy surfaces. In every complex, the lithium atom is located right above or nearly right above the center of a benzene ring, which is hereafter denoted as lithium-bonded benzene ring. All the carbon and hydrogen atoms in a complex are nearly coplanar except for **g9**, for which the molecular plane of the tryphenylene molecule is substantially distorted;

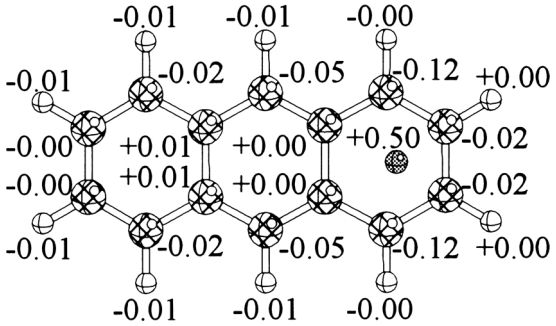

Fig. 4. Changes in atomic charges upon formation of the 1:1 complex of lithium and anthracene: the total atomic charge of the atom in **g4** minus that of the same atom of the system where a lithium atom and an anthracene molecule are separated infinitely from each other.

The largest deviation of 17.2° from 0° in the C-C-C-C dihedral angle of the lithium-bonded benzene ring is observed for **g9** (In passing, the second largest deviation of 13.6° is found for **g6**.). The shortest distance between the lithium and carbon atoms, $r_{\text{Li}-\text{C}}$(s), the average distance between the lithium atom and the six carbon atoms of the lithium-bonded benzene ring, $r_{\text{Li}-\text{C}}$(a), and the total atomic charge on the lithium atom, chg(Li), are summarized in Table 1. The $r_{\text{Li}-\text{C}}$(s) values range from 2.121 Å (**g5**) to 2.241 Å (**g15**) except for **g1**, for which $r_{\text{Li}-\text{C}}$(s) is 2.717 Å, indicating that the overlap of the 2s orbital of the lithium atom and the π orbital of the benzene molecule does not occur effectively. Although the formal charge on the lithium atom is zero in every complex considered, it is actually positively changed between +0.468 (**g6**) to +0.619 (**g15**) except for **g1**. In Fig. 2, chg(Li) is plotted against $r_{\text{Li}-\text{C}}$(s). As can be seen, it is roughly linearly correlated with $r_{\text{Li}-\text{C}}$(s) in the $r_{\text{Li}-\text{C}}$(s) range of

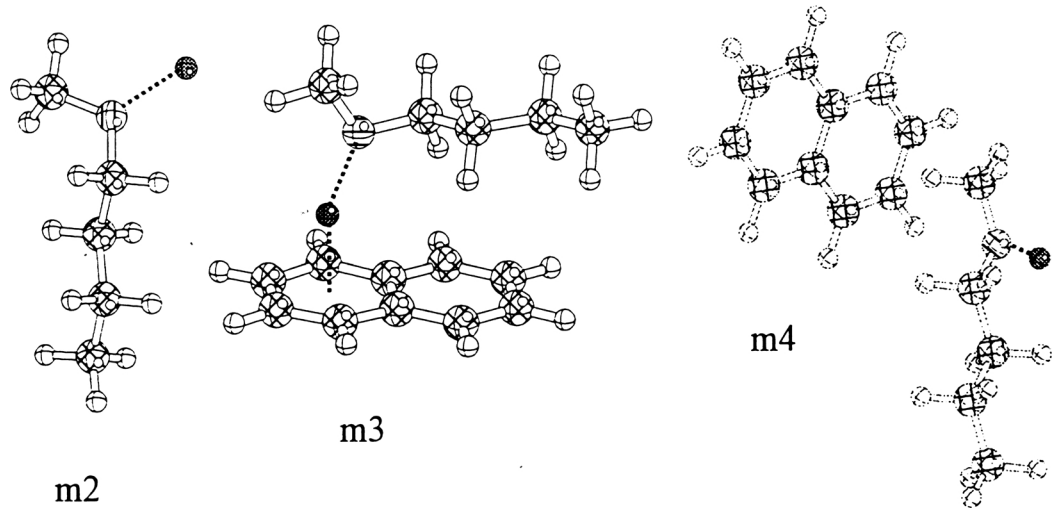

Fig. 5. The optimized structures of **m2** to **m4**.

above about 2.15 Å, and, below that value, it seems independent of r_{Li-C}(s). In Fig. 3, chg(Li) is plotted against the number of benzene rings (n_b) adjacent to the lithium-bonded benzene ring. Figure 3 shows that chg(Li) increases with increasing n_b, probably due to the fact that the negative charge that compensates the positive atomic charge on the lithium atom is dispersed more and more effectively among carbons with increasing n_b. As an evidence for this, the differences in total atomic charges between the atoms in **g4** and the corresponding atoms in an anthracene molecule and a lithium atom separated infinitely from each other are shown in Figure 4. As a whole, it is seen that the changes in atomic charges are largest on the atoms in the lithium-bonded benzene ring and become smaller and smaller for the atoms belonging to the benzene ring that is further away from the lithium-bonded ring. This means that lithium can be charged more positively for the larger n_b, which agrees with the observation found in Figure 3.

The optimized structures of **m1**(=**g2**) to **m4** modeling a lithium atom in the Met solution containing lithium and Nap are depicted in Figs. 1 and 5, and important calculated results are summarized in Table 2. No imaginary frequency was calculated for those structures. In **m1**, the lithium atom is located slightly "outside" the position right above the center of one benzene ring with r_{Li-C}(s) of 2.132Å. In **m2**, the lithium atom is bonded to the methoxy oxygen of a Met molecule with the Li-O bond distance, r_{Li-O}, of 1.896 Å. In **m3**, the lithium atom is sandwiched by a Met molecule and a Nap molecule, and r_{Li-O} and r_{Li-C}(s) are 1.895 Å and 2.198 Å, respectively. Thus, the Li-C bond is slightly lengthened and the Li-O bond distance is nearly unchanged upon the formation of the Met-Li-Nap contact ion pair type complex. In **m4**, the lithium atom is bonded to the methoxy oxygen of the Met molecule that directs its methoxy methyl group towards a benzene ring plane of the Nap molecule with the direction of the hydrocarbon chain of the former and that of the condensed benzene ring of the latter being nearly perpendicular to each other. **m4** does not look like a solvent separated ion pair type complex, but its structure is the only one we could obtain. The shortest distance between an atom (H) on the Met molecule and an atom (C) on the Nap molecule is 3.175 Å, about the same as the sum of the Van der Waals radii of the hydrogen and carbon atoms. Thus, although no imaginary frequency is calculated for **m4**, it is a very weakly bonded complex. The SCF energy calculations show that **m3** is more stable than **m4** by about 80 kJ/mol. Thus, the present MO calculations strongly indicate that the solvent separated ion pair type complex is unlikely to occur in the Met solution containing lithium and Nap. Although the formal charge of a lithium atom is zero in

Table 2. Summary of calculated results on optimized structures of lithium species modeling the lithium atom in 1-methoxybutane solution.

Complex	r_{Li-C}(s)Å	r_{Li-O}Å	Chg(Li)	RPFR
m1 (g2)	2.132	—	0.4731	1.05477
m2	—	1.896	−0.1053	1.02651
m3	2.198	1.895	0.5012	1.07126
m4	—	1.897	−0.0984	1.02693

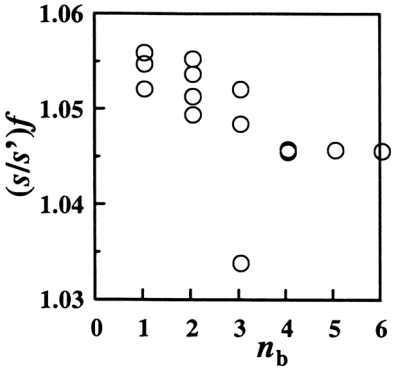

Fig. 6. Plot of RPFR against n_b for the 1:1 complexes of lithium and aromatic hydrocarbons with condensed benzene rings (**g2** to **g15**).

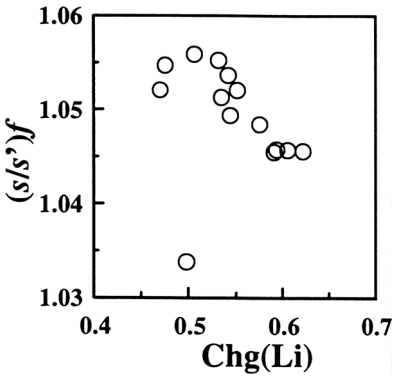

Fig. 7. Plot of RPFR against chg(Li) for the 1:1 complexes of lithium and aromatic hydrocarbons with condensed benzene rings (**g2** to **g15**).

the Met solution, Table 2 shows that it is actually positively charged in **m1** and **m3**, where the lithium atom directly interacts with the Nap molecule.

3.2. Reduced Partition Function Ratios

The RPFR values of the 1:1 lithium-aromatic hydrocarbon complexes at 25 °C are listed in the last column of Table 1. They range from 1.03390 (**g9**) to 1.05594 (**g4**) except for **g1**, whose RPFR value is substantially smaller. In general, vibrational motions that are accompanied by certain frequency shifts upon ^{7}Li/^{6}Li substitutions and consequently contribute to the RPFRs to some extent or more, are those in which lithium atoms vibrate perpendicularly or parallel to the condensed benzene ring planes of the hydrocarbons in the complexes, and the motions that contribute to the RPFRs most are the vibrational motions of lithium atoms perpendicular to the condensed benzene ring planes. In **g3**, for instance, the vibrational motions of the lithium atom perpendicular to the condensed benzene ring plane of the anthracene molecule observed at 450.6 cm^{-1} and at 484.9 cm^{-1} for the heavier lithium isotope, which respectively yield the frequency shift of 16.6 cm^{-1} and 14.7 cm^{-1} upon the ^{7}Li/^{6}Li substitution, account for 28.4% and 26.7% of the logarithm of the RPFR, respectively. The largest frequencies that shift more than a couple of wavenumbers upon ^{7}Li/^{6}Li substitutions are calculated at around 510 cm^{-1} for ^{7}Li, and vibrational motions with frequencies higher than that make practically no contributions to the RPFRs.

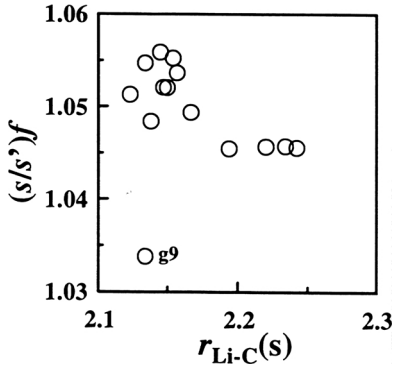

Fig. 8. Plot of RPFR against r_{Li-C}(s) for the 1:1 complexes of lithium and aromatic hydrocarbons with condensed benzene rings (**g2** to **g15**).

In Fig. 6, the RPFR value is plotted against n_b except for **g1**. Except for one point (**g9**), the RPFR decreases gradually with increasing n_b and seems to become constant for the n_b value of 4 or larger. The simple arithmetic mean of the four data (**g11**, **g13**, **g14** and **g15**) is 1.04570. The correlations found between r_{Li-C}(s) and chg(Li) and between chg(Li) and n_b suggest that RPFR is also correlated with those parameters. In Figs. 7 and 8, RPFR is plotted against chg(Li) and r_{Li-C}(s), respectively. It is seen in those figures that the RPFR is "saturated" for the large chg(Li) and r_{Li-C}(s). Within the limit of the present model, the RPFR value of a lithium atom between graphene layers of graphite is thus estimated to be 1.04570 at 25 °C.

The RPFRs of the model lithium species in the Met solution are listed in the last column of Table 2. The RPFRs of the complexes in which a lithium atom directly interacts with a Nap molecule (**m1** and **m3**) are substantially larger than those of the complexes where there is no direct interaction between a lithium atom and a Nap molecule (**m2** and **m4**). Since the lighter iso-

tope is experimentally preferentially fractionated into the graphite phase rather than into the Met solution phase [3], the RPFR in the former phase (1.04570) must be smaller than that in the latter phase. **m2** and **m4** are then incompatible with the experimental results. The existence of the solvent separated ion pair type complex is thus denied both from the SCF energy and RPFR considerations. Although the RPFR of **m1** (**g1**) is slightly larger than 1.04570, it is not large enough to explain the degree of the isotope fractionation experimentally observed [3]. **m3** yields an *S* value of 1.024 (= 1.07126/1.04570) that agrees well with the experimental value of 1.023. Thus, the present MO calculations lead to the conclusion that lithium dissolves in Met solution by forming a contact ion pair type complex with Nap, and that the assumption of this complex can well reproduce the *S* value experimentally obtained between graphite and Met solution.

The HF/6-31G(d) level calculations yield RPFR values of lithium at 25 ℃ of 1.09195 and 1.07818 for the hydrated lithium ion in water [5] and for the solvated lithium ion in mixed solution of ethylene carbonate (EC) and methylethyl carbonate (MEC) [10], respectively. The RPFR value of lithium in the Met solution in the present study is small compared with those values. This difference in the RPFR may indicate that lithium is less stable in the Met solution than in aqueous and EC/MEC mixed solutions, although the comparison of the results from the different levels of MO calculations should be made very carefully.

4. Conclusion

To summarize, we make the following statements:

1. Structures of 1:1 complexes of lithium and simple aromatic hydrocarbons with condensed benzene rings modeling a lithium atom between graphene layers of graphite were optimized at the B3LYP/6-311G(d) level of theory, and the RPFRs were calculated for the optimized structures. The RPFR was found to be a decreasing function of the number of benzene rings adjacent to the benzene ring above which the lithium atom was located, and was "saturated" at 1.04570 at 25 ℃. This was the RPFR value of lithium in graphite within the framework of the present study.

2. The contact ion pair type complex, *i. e.*, the lithium-naphthalene complex solvated by a 1-methoxybutane molecule was the most plausible lithium species in the 1-methoxybutane solution containing lithium and naphthalene. The RPFR value of this species (1.07126 at 25 ℃) coupled with the value estimated for the lithium atom in graphite yielded the separation factor 1.024 (=1.07126/1.04570) that agreed well with the experimental separation factor of 1.023 [3].

Although the experimentally obtained separation factor is reproduced quite well by the present MO calculations, we do not claim that they are satisfactory and complete. A lithium atom between graphene layers of graphite has been substituted by the lithium atom in 1:1 lithium-simple aromatic hydrocarbon complexes, and the largest hydrocarbon molecule considered has been limited to coronene. The existence of a second lithium atom has not been taken into consideration. The largest drawback of the present calculations may be that a lithium ion sandwiched by two aromatic hydrocarbon molecules with condensed benzene rings, which is expected to better model lithium in graphite, has not been considered. In spite of these drawbacks, we would like to emphasize that the B3LYP/6-311G(d) level calculations seem usable for the lithium isotope effects in systems where lithium atoms are weakly bonded and that we have modeled lithium in graphite in the right way.

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