Computational Studies of Polyelectrolytes Containing Zeolitic Fragments

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The structures and sodium affinities of a series of zeolitic fragments [$H_3Al(OCH_3)_x(OSiH_3)^-_{1-x}$, 2T, $H_2Al(OCH_3)_x(OSiH_3)^-_{2-x}$, 3T, $Al(OCH_3)_x(OSiH_3)^-_{4-x}$, 5T] that mimic the charge sites in polyelectrolytes are calculated by ab initio molecular orbital methods at different levels of theory. At the HF/6-31G* level, the decrease in the sodium affinity due to the substitution of an OCH_3 group by an $OSiH_3$ group is about 8 kcal/mol in the 2T and 3T systems. In the 5T systems, the replacement of a sodium-coordinated OCH_3 group by an $OSiH_3$ group causes a decrease of 7 kcal/mol in the sodium affinity, while the substitution for a non-sodium-coordinated OCH_3 group results in a 2.7 kcal/mol decrease. The lower sodium affinity indicates a weaker Coulombic interaction, suggesting an enhanced ionic conductivity with the substitution of carbon by silicon, consistent with experimental results. Natural bond orbital (NBO) analyses show that silicon-bonded oxygen atoms have smaller lone-pair dipole moments, resulting in a lower sodium affinity. The substitution of aluminum by boron leads to a higher sodium affinity, although the effect of replacing an OCH_3 group by an $OSiH_3$ group still reduces the sodium affinity. The effect of the sodium cation on the bond angles in these systems is also investigated.

I. Introduction

Solvent-free polymer electrolytes have become the focus of considerable research[1−8] because of their potential in high-energy batteries and electrochemical devices. So far, the design of most polymer electrolytes is based on the mixing of weakly bound salts with poly(ethylene oxide) (PEO), or comb polymers containing ethylene oxide side chains. In polymer electrolytes, both cations and anions are mobile. Measurements[9−11] of the ionic transference number indicate that typically the dominant charge carriers are mobile anions and that the cation transference number is usually only between 0.2 and 0.5. In practical applications, this phenomenon will cause problems due to dc polarization[12,13] in battery devices; the current will decrease gradually and reach a limiting value, leading to a less efficient system.

To avoid the dc polarization, polyelectrolytes,[14−16] in which only one type of ion (usually the cation) is mobile, are attractive materials. Generally, these polyelectrolytes contain charged groups bonded to the polymer. Accordingly, the cation transference number is unity and the dc polarization is avoided. In polyelectrolytes, as in polymer/salt complexes, Coulombic interactions between cations and anions impede the performance of these materials. Hence, rational design of polyelectrolytes having reduced ion pairing between cations and bound anions is important for improving the performance of polyelectrolytes.

Aluminosilicates, used as solid acids and ion exchangers in catalytic applications, possess strong acidity, suggesting that the Coulombic interactions between the anionic density and cations are quite weak.[17] It is then reasonable to design polyelectrolyte materials using aluminosilicate (zeolite) fragments as charge sites. This should enhance ionic conductivity due to the decrease in ion pairing. Previous work in our group[18,19] included the

synthesis of polyelectrolytes containing aluminate (aluminum bonded by four alkoxy groups), semialuminosilicate (aluminum bonded by two alkoxy groups and two siloxy groups), and aluminosilicate (aluminum bonded by four siloxy groups) fragments as charge centers. Experimental results showed that the optimal ionic conductivity at room temperature for alumi-nate-incorporated PEO-based polyelectrolytes is 10^{-8} S cm^{-1}, rising to 10^{-6} S cm^{-1} in semialuminosilicate and aluminosili-cate-incorporated systems. These results indicate that the substitution of carbon atoms by silicon atoms causes a decrease in Coulombic interactions between cations and bound anions, enhancing the ionic conductivity. Understanding the difference in Coulombic interactions between cations (sodium cations) and aluminate and aluminosilicate charge centers is the aim of this paper.

The effect of substituting silicon for carbon on molecular proton affinities has been widely studied.[20−29] Ion cyclotron resonance (ICR) and IR spectroscopy were applied[20−23] to measure the proton affinities and the O−H stretching frequency shift of alkyl alcohols, ethers, and corresponding silicon-substituted compounds. Both experimental and theoretical results showed lower basicity of oxygen atoms upon substitution of carbon by silicon. This conclusion was affirmed by the lack of chelation in β-siloxy/Lewis acid complexes.[24,25] It was first assumed that the mixing of oxygen lone pairs with silicon 3d orbitals contributed to the low basicity of oxygen after silicon substitution.[26] However, this viewpoint was challenged and several other explanations[28,29] were presented for the substitution effect.

In this paper, we apply ab initio methods to study the substitution of silicon atoms for carbon atoms at the zeolitic charge sites of polyelectrolytes. Information about reactivities and structures of molecules can be obtained by theoretical methods based on ab initio molecular orbital calculations.[30] To apply ab initio methods in macromolecular systems, one

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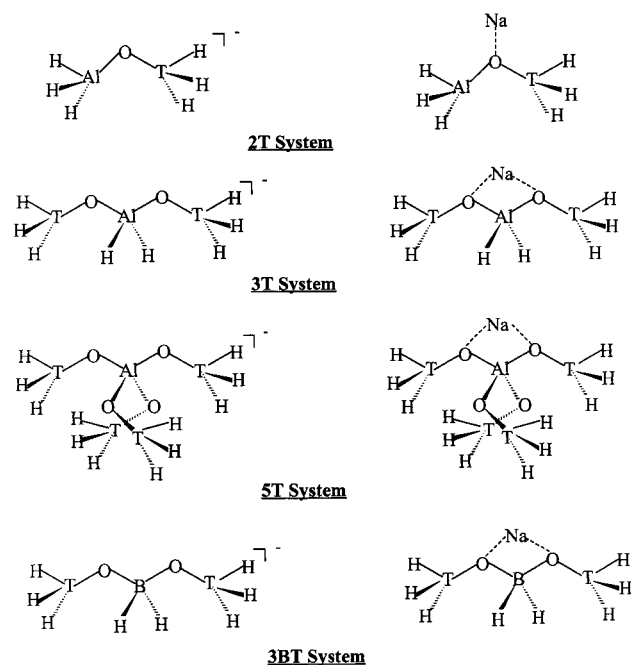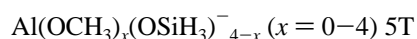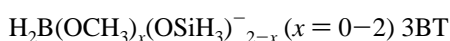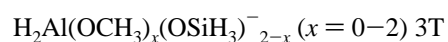[‡] Argonne National Laboratory.

Figure 1. The structures of anions and corresponding sodium salts in each system (T = C or Si).

Figure 2. Na affinities of the 2T systems at different levels of theory. All the anions have C_s symmetry.

effective approach is to use a fragment to mimic the whole structure of charge sites in polyelectrolytes, and to terminate the fragment by hydrogen atoms.[31−34] Although the whole structure cannot be represented perfectly by these clusters, much valuable information can still be obtained. Since the relevant ion-pairing interactions are local, this fragment-based approach seems well justified. In this study, the dependence of sodium affinities on the clusters of charge sites at different levels of theory is examined. These clusters are used to examine the effect of substitution of carbon by silicon on the sodium affinities. The substitution of aluminum by boron is also examined.

II. Theoretical Method

Four series of anions with different carbon and silicon substitutions were considered in this study:

$$H_3Al(OCH_3)_x(OSiH_3)^-_{1-x} \ (x = 0-1) \ 2T$$

$$H_2Al(OCH_3)_x(OSiH_3)^-_{2-x} \ (x = 0-2) \ 3T$$

$$H_2B(OCH_3)_x(OSiH_3)^-_{2-x} \ (x = 0-2) \ 3BT$$

$$Al(OCH_3)_x(OSiH_3)^-_{4-x} \ (x = 0-4) \ 5T$$
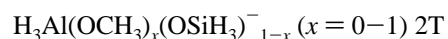
The T refers to either a silicon, carbon, or aluminum atom in the cluster. Figure 1 illustrates the structures of the different anions. For each anion, the corresponding sodium salt in which sodium cation coordinates to Al−O−C(or Si) bridging oxygens is shown in Figure 1. The ion-pairing energy, i.e., sodium affinity of each cluster above, is defined as the energy of the following reaction:

$$NaZ \rightarrow Na^+ + Z^- \qquad \Delta E$$
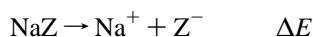
where Z^- is one of the clusters described above.

In this study, the sodium affinities were calculated as the differences in electronic energies, not including zero-point energies. Initially, all of the calculations were performed at the Hartree−Fock (HF) level. The split-valence 3-21G and split-
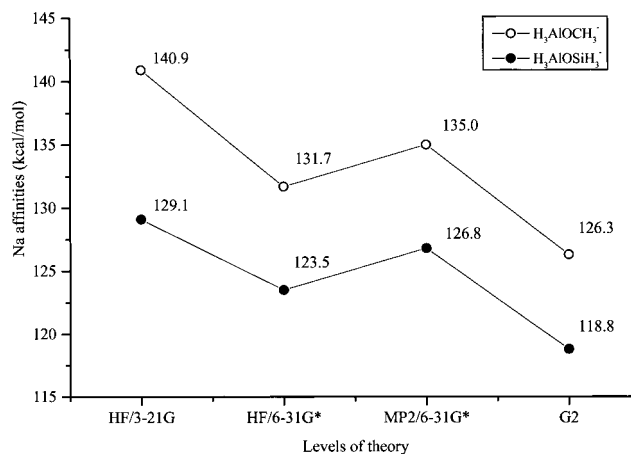
valence plus polarization 6-31G* basis sets were used. Correlation was included by Møller−Plesset perturbation theory to second order (MP2)[35,36] in calculations on the 2T, 3T, and 3BT systems. A higher level of theory, G2 theory,[37,38] was used to perform accurate calculations on the 2T clusters. G2 theory is effectively at the QCISD(T)/6-311+G(3df, 2p) level. Local minima were obtained by full geometrical optimizations, and all of the structures had all positive frequencies. The ab initio calculations are carried out using the computer program Gaussian-94.[39]

III. Results and Discussions

Figure 2 shows the sodium affinities of $H_3AlOCH_3^-$ and $H_3AlOSiH_3^-$ calculated at different levels of theory. The differences between the sodium affinities of $H_3AlOCH_3^-$ and $H_3AlOSiH_3^-$ are reasonably similar at different levels of theory: HF/3-21G(11.8 kcal/mol), HF/6-31G*(8.2 kcal/mol), MP2/6-31G* (8.2 kcal/mol), and G2(7.5 kcal/mol). The latter three methods give differences that agree to within 1 kcal/mol. This indicates that the sodium affinities calculated at the HF/6-31G* level are reasonably reliable, and we have chosen to use this level of theory for most of the calculations in this work.

Dependence of the Sodium Affinities on Silicon Substitution in the 2T and 3T Systems. From Figure 2, it can be observed that $H_3AlOSiH_3^-$ has a lower sodium affinity than $H_3AlOCH_3^-$ (123.5 vs 131.7 kcal/mol at the HF/6-31G* level), indicating a weaker Coulombic interaction in the former case. Thus, the substitution of an OCH_3 group by an $OSiH_3$ group indeed reduces the ion pairing.

In the 3T systems, two OTH_3 groups are attached to the aluminum atom and the sodium affinities of three different systems ($T_1 = T_2 = C$; $T_1 = C$, $T_2 = Si$; $T_1 = T_2 = Si$) are calculated. In these systems, the sodium cations are coordinated by two oxygen atoms. Figure 3 shows the sodium affinities of the three molecules at different levels of theory. At the HF/6-31G* level, the sodium affinity decreases from 143.1 kcal/mol in $H_2Al(OCH_3)_2^-$ to 133.8 kcal/mol in $H_2Al(OCH_3)(OSiH_3)^-$, and to 126.5 kcal/mol in $H_2Al(OSiH_3)_2^-$. The first substitution of carbon by silicon causes a decrease of 9.3 kcal/mol in the sodium affinity and the second substitution causes a further decrease of 7.3 kcal/mol. The difference between the sodium affinities of $H_2Al(OCH_3)_2^-$ and $H_2Al(OSiH_3)_2^-$ is 16.6 kcal/mol, roughly twice the difference of the sodium affinities in the 2T systems.

Sodium Affinities in the 5T Systems. In the 5T systems, the aluminum atom is coordinated by four oxygens and two

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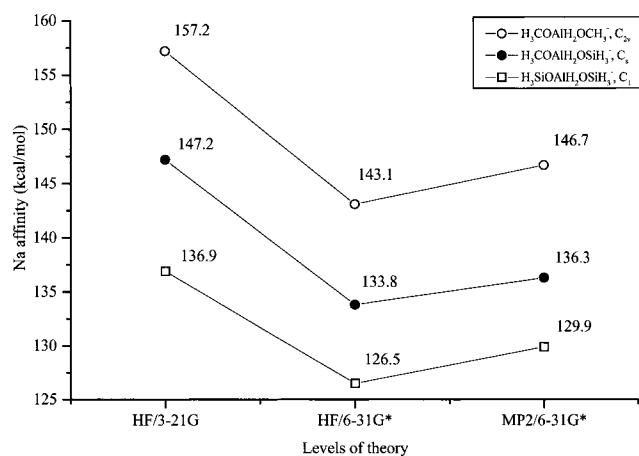*J. Phys. Chem. B, Vol. 103, No. 31, 1999* **6447**

Figure 3. Na affinities of the 3T systems at different levels of theory. The symmetries are indicated.

TABLE 1: Na Affinities at Different Coordination Sites in the 5T Systems

molecule	symmetry	site of Na^+ [a]	HF/3-21G	HF/6-31G*
		Na afffinity (kcal/mol)		
$Al(OCH_3)_4^-$	C_1	2O(C)	161.7	139.7
$Al(OCH_3)_3(OSiH_3)^-$	C_1	2O(C)	158.5	137.1
	C_1	1O(C), 1O(Si)	152.0	132.7
$Al(OCH_3)_2(OSiH_3)_2^-$	C_1	2O(C)	155.9	133.9
	C_1	1O(C), 1O(Si)	148.9	130.0
	C_1	2O(Si)	142.1	125.6
$Al(OSiH_3)_3(OCH_3)^-$	C_1	1O(C), 1O(Si)	141.4	126.9
	C_1	2O(Si)	138.7	122.8
$Al(OSiH_3)_4^-$	C_1	2O(Si)	135.2	120.1

[a] Location of Na^+. For example, 2O(C) means the Na^+ cation is coordinated by two carbon-bonded oxygen atoms.

oxygen atoms coordinate to each sodium cation. Table 1 lists the sodium affinities at different coordination sites in the 5T systems. The sodium affinity order is $Al(OCH_3)_4^- > Al(OCH_3)_2$-$(OSiH_3)_2^- > Al(OSiH_3)_4^-$, predicting that a lower ionic conductivity would be obtained in the aluminate polyeletrolyte compared with semialuminosilicate and aluminosilicate polyelectrolytes, consistent with the experimental results.[19]

At the HF/6-31G* level, when an OCH_3 group coordinated to the sodium cation is replaced by an $OSiH_3$ group in $Al(OCH_3)_4^-$, the sodium affinity decreases from 139.7 kcal/mol (2 O(C)) to 132.7 kcal/mol in $Al(OCH_3)_3(OSiH_3)^-$ (1 O(C), 1 O(Si)), a decrease of 7.0 kcal/mol. A further substitution of an $OSiH_3$ group for the other sodium-coordinated OCH_3 group in $Al(OCH_3)_3(OSiH_3)^-$ leads to $Al(OCH_3)_2(OSiH_3)_2^-$ (2 O(Si)) with another decrease of 7.0 kcal/mol in the sodium affinity. By the same method, we have calculated the sodium affinity changes in the other 5T systems by replacing the sodium-coordinated OCH_3 groups (see Table 1). An average value about 7.0 kcal/mol is obtained for each substitution. Thus, this substitution effect is slightly lower in the 5T systems than in the 2T and 3T systems.

Second, we examine the sodium affinity changes due to a substitution for an OCH_3 group that does not coordinate to the sodium cation. At the HF/6-31G* level, when the sodium cation is coordinated by two carbon-bonded oxygen atoms, the sodium affinity for this substitution changes from 139.7 kcal/mol in $Al(OCH_3)_4^-$ to 137.1 kcal/mol in $Al(OCH_3)_3(OSiH_3)^-$ and to 133.9 kcal/mol in $Al(OCH_3)_2(OSiH_3)_2^-$. Similar changes in the sodium affinity occur when the sodium cation is in different coordination situations. Considering all of the cases in Table 1, the average decrease in sodium affinity is 2.8 kcal/mol when

an OCH_3 group that does not coordinate to the sodium cation is substituted by an $OSiH_3$ group.

From the results discussed above, it is concluded that the substitution of an OCH_3 group by an $OSiH_3$ group indeed decreases the sodium affinity. A larger decrease in the sodium affinity, 7 kcal/mol, occurs when an $OSiH_3$ group replaces a sodium-coordinated OCH_3 group, compared with a decrease of about 2.8 kcal/mol for the replacement of a non-sodium-coordinated OCH_3 group. Therefore, the sodium affinity change from $Al(OCH_3)_4^-$ to $Al(OSiH_3)_4^-$ can be approximately considered as the replacement of two sodium-coordinated OCH_3 groups, which cause a decrease of 14.0 kcal/mol at the HF/6-31G* level, and of the two non-sodium-coordinated ones, which result in a decrease of 5.6 kcal/mol at the HF/6-31G* level. Under this approximation, the total decrease in the sodium affinity would be 19.6 kcal/mol, consistent with the result obtained directly from Table 1 from the difference in the sodium affinities between $Al(OCH_3)_4^-$ and $Al(OSiH_3)_4^-$.

Population and Natural Bond Orbital (NBO) Analysis of the 3T Systems. To understand the sodium affinity decrease due to the substitution of an OCH_3 group by an $OSiH_3$ group, Mulliken population analysis and natural bond orbital (NBO) analysis[40] were carried out in the 3T systems. First, we examine the energies of highest occupied molecular orbitals (HOMO's) of all the anions in the 3T systems at the HF/6-31G* level. A higher HOMO energy implies a higher basicity of the molecule, and it increases from -5.6 eV in $AlH_2(OSiH_3)_2^-$ to -5.4 eV in $AlH_2(OCH_3)(OSiH_3)^-$ and to -5.0 eV in $AlH_2(OCH_3)_2^-$ in the 3T systems. The trend of basicity from the orbital energies with silicon substitution is the same as the results obtained from sodium affinities in the previous section. The HF/6-31G* wave function shows that the largest coefficient for the Si 3d orbitals in the HOMO is 0.02, indicating less than 0.1% population in this molecular orbital. This suggests little contribution of the silicon 3d orbitals to the lower oxygen basicity observed upon silicon substitution. Table 2 lists the dipole moments of the oxygen lone pairs of all oxygens in the 3T systems at the HF/6-31G* level. Compared with silicon-bonded oxygen atoms, carbon-bonded oxygen atoms have larger lone-pair dipole moments, indicating that they have better coordinating abilities, implying a stronger interaction between the sodium cation and the anion. This explains the reason for the same anion in the 5T systems, a higher sodium affinity is obtained if more carbon-bonded oxygen atoms coordinate to the sodium cation.

Change of Al—O—T Angles. Table 3 lists all of the Al—O—T angles in the 2T and 3T systems. In all optimized anionic structures, the Al—O—C bond angles fall within the range of 120–130°. In the 2T and 3T systems, when the sodium cation is coordinated, the Al—O—C angles decrease about 5° at the HF/3-21G level and 1–2° at the HF/6-31G* level. Compared with the Al—O—C bond angles, the Al—O—Si bond angles are larger and decrease more dramatically when the sodium cation is coordinated. At the HF/3-21G level, Al—O—Si bond angles are almost linear (larger than 170°) in the anion. Similar observations were reported in the literature[41-43] where it was concluded that this basis set does poorly in predicting the Al—O—Si bond angles. At the HF/6-31G* level, the Al—O—Si bond angles are 150–155°. When the sodium cation is coordinated, the Al—O—Si bond angles decrease more than 40° at the HF/3-21G level and about 20° at the HF/6-31G* level. Similar results are also obtained in the 5T systems.

To study the bond angle change due to the coordination of the sodium cation, potential energy curves for variation of Al—O-T and Al—ONa—T bond angles in the 3T systems were

TABLE 2: Natural Bond Orbital (NBO) Analysis of the 3T Systems at the HF/6-31G* Level

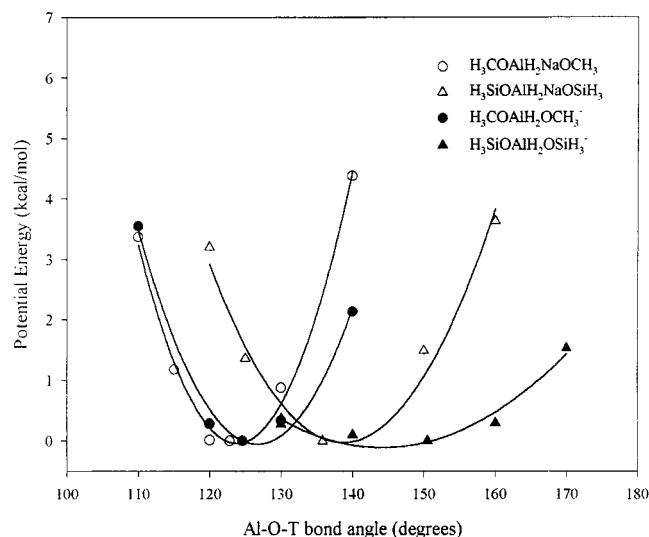| molecule	symmetry		lone pair (LP) dipole moment (in Debyes)		
$H_3COAlH_2OCH_3^-$	C_{2v}	2.77 (LP 1)	0.07 (LP 2)	2.77 (LP 1)	0.07 (LP 2)
		O (C)	O (C)	O (C')	O (C')
$H_3SiOAlH_2OCH_3^-$	C_s	1.78 (LP 1)	0.30 (LP 2)	2.75 (LP 1)	0.48 (LP 2)
		O (Si)	O (Si)	O (C)	O (C)
$H_3SiOAlH_2OSiH_3^-$	C_1	1.67 (LP 1)	0.65 (LP 2)	1.94 (LP 1)	0.12 (LP 2)
		O (Si)	O (Si)	O (Si')	O (Si')

Figure 4. Potential energy curves for the variation of Al−O−T and Al−Ona−T angles calculated at the HF/6-31G* level of theory.

TABLE 3: Al−O−T Angles in the 2T and 3T Systems

molecule	symmetry	HF/3-21G	HF/6-31G*	MP2/6-31G*
		2T Systems		
$H_3AlOCH_3^-$	C_s	127.9	123.6	118.3
$H_3AlONaCH_3$	C_s	123.4	122.4	119.1
$H_3AlOSiH_3^-$	C_s	179.7	153.9	138.5
$H_3AlONaSiH_3$	C_s	136.7	134.9	131.3
		3T Systems		
$H_3COAlH_2OCH_3^-$	C_{2v}	128.2	124.6	118.7
$H_3COAlH_2ONaCH_3$	C_{2v}	124.7	122.8	119.5
$H_3COAlH_2OSiH_3^-$	C_s	Si 176.6	Si 152.4	Si 130.6
		C 129.5	C 125.1	C 120.7
$H_3COAlH_2ONaSiH_3$	C_s	Si 139.2	Si 136.1	Si 133.1
		C 124.7	C 122.7	C 119.2
$H_3SiOAlH_2OSiH_3^-$	C_1	180.0	153.6	137.6
$H_3SiOAlH_2ONaSiH_3$	C_{2v}	139.0	135.8	132.7

calculated at the HF/6-31G* level of theory and are shown in Figure 4. The bond angles were varied in 10° increments, and the remaining geometrical parameters were optimized. From Figure 4, we observe that the Al−O−Si bond angles have shallow potential energy surfaces, indicating the flexibility of the Al−O−Si bond angle. After the coordination of the sodium cation to the anion, oxygen atoms in the Al−O−T bond become more sp²-like and results in a decrease in the Al−O−T bond angle. In addition, the potential energy curves become much stiffer after the sodium cations are coordinated. The flexibility of the Al−O−Si bond angle explains the dramatic decrease in the Al−O−Si bond angle upon the interaction with the sodium cation.

Dependence of Sodium Affinities on the Substitution of Aluminum by Boron. In the 3BT systems, we substitute boron atoms for aluminum atoms and compare the sodium affinities with those in the 3T systems. Figure 5 shows the sodium affinities of all molecules at different levels of theory in the 3BT systems, and the values are listed in Table 4. At the HF/
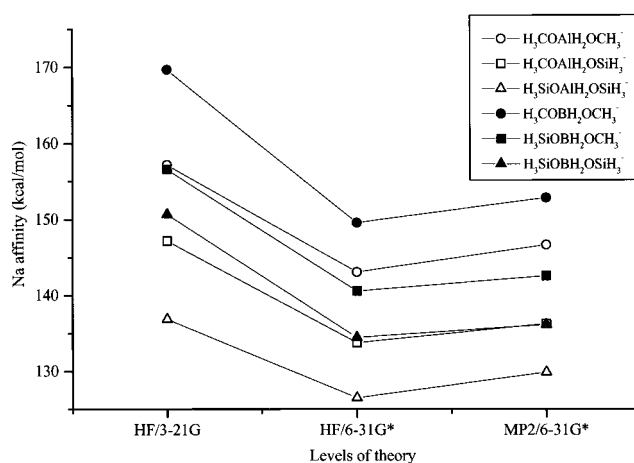

Figure 5. Na affinities of the 3T and 3BT systems at different levels of theory.

TABLE 4: Na Affinities in the 3BT Systems at Different Levels of Theory

molecule	symmetry	Na affinity (kcal/mol)		
		HF/3-21G	HF/6-31G*	MP2/6-31G*
$H_3COBH_2OCH_3^-$	C_{2v}	169.7	149.6	152.9
$H_3COBH_2OSiH_3^-$	C_s	156.6	140.6	142.6
$H_3SiOBH_2OSiH_3^-$	C_{2v}	150.7	134.5	136.2

TABLE 5: B−O−T Angles in the 3BT Systems at Different Levels of Theory

molecule	symmetry	HF/3-21G	HF/6-31G*	MP2/6-31G*
$H_3COBH_2OCH_3^-$	C_{2v}	115.9	115.5	112.1
$H_3COBH_2ONaCH_3$	C_{2v}	115.5	115.4	112.6
$H_3COBH_2OSiH_3^-$	C_1	Si 122.2	Si 126.3	Si 117.1
		C 118.6	C 116.6	C 114.1
$H_3COBH_2ONaSiH_3$	C_s	Si 124.2	Si 124.0	Si 119.2
		C 115.4	C 115.2	C 112.5

6-31G* level, the sodium affinity decreases from 149.6 kcal/mol in $H_3COBH_2OCH_3^-$ to 140.6 kcal/mol in $H_3COBH_2OSiH_3^-$ and to 134.5 kcal/mol in $H_3SiOBH_2OSiH_3^-$. The first substitution of an OCH_3 group by an $OSiH_3$ group causes a decrease of about 9.0 kcal/mol in the sodium affinity, and the second substitution further reduces the sodium affinity by 6.1 kcal/mol. The decrease in the sodium affinity due to the substitution effect is larger in the 3BT systems than in the 3T systems. From Figure 5, we can see that the sodium affinities in the 3BT systems are larger than those of the 3T systems by about 6 kcal/mol at the HF/6-31G* level. This phenomenon indicates that sodium aluminate/aluminosilicate systems have weaker ion pairing than sodium borate/borosilicate. The carbon-bonded oxygen atoms have larger lone-pair dipole moments than silicon-bonded oxygen atoms and all the lone-pair dipole moments in the 3BT systems are larger than those in 3T systems. This is consistent with the larger sodium affinities in the 3BT system.

Table 5 lists the B−O−T bond angles in the 3BT systems. Compared with the Al−O−T bond angles, the corresponding B−O−T angles are smaller and change slightly when different basis sets are applied. The B−O−C bond angles fall within the

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range of 112−116°. When the sodium cation is coordinated, the angle does not change. The B−O−Si bond angles are larger than B−O−C bond angles by about 10°. Interestingly, the B−O−Si bond angles do not change much (less than 3°) when the sodium cation is added.

IV. Conclusions

We have calculated the sodium affinities of aluminate, semialuminosilicate, and aluminosilicate and borosilicate anions with different sizes (2T, 3T, 3BT, and 5T systems) at different levels of theory. The influence of substitution of an OCH$_3$ group by an OSiH$_3$ group on the sodium affinities has been examined. The following conclusions can be made from this study.

(1) The substitution of an OCH$_3$ group by an OSiH$_3$ group in the zeolitic fragments decreases the sodium affinity. In the 2T and 3T systems, this substitution causes a decrease in the sodium affinity of about 8 kcal/mol. The decrease of sodium affinity due to the substitution effect is slightly lower in the 5T systems; the substitution of a sodium-coordinated OCH$_3$ group by an OSiH$_3$ group causes a 7 kcal/mol drop in the sodium affinity, while the substitution of a non-sodium-coordinated OCH$_3$ group causes a 2.8 kcal/mol decrease. Natural bond orbital (NBO) analyses show that, compared with silicon-bonded oxygen atoms, carbon-bonded oxygens have larger lone-pair dipole moments, resulting in larger sodium affinities. The larger sodium affinity in the aluminate system is consistent with a lower ionic conductivity, found in experimental results.[19,44]

(2) In the 2T and 3T systems, the addition of a sodium cation causes a decrease in the Al−O−C and Al−O−Si bond angles. The decrease in the Al−O−Si bond angle is larger upon the coordination of the sodium cation because the Al−O−Si bond angle is more flexible.

(3) The substitution of boron atoms for aluminum atoms in these zeolitic fragments increases the sodium affinity. In the 3BT systems, the substitution for an OCH$_3$ group by an OSiH$_3$ group also reduces the sodium affinity. The B−O−C and B−O−Si bond angles are smaller than the corresponding ones in the 3T systems.

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