Density Functional Theory Studies on the Reaction Mechanisms of Silver Ions with Ethylene in Facilitated Transport Membranes: A Modeling Study

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Received: April 10, 2001; In Final Form: July 6, 2001

Facilitated olefin transport has been observed through membranes containing $AgBF_4$ dissolved in poly(ethylene oxide) (PEO), but not through ones containing $AgNO_3$ according to the previous studies. The difference in facilitated transport behavior between the two systems was theoretically investigated in terms of the mechanism on facilitated transport, in particular, the interaction of the silver cation with olefin using the density functional theory (DFT) method. It was found that the reaction of silver cation with ethylene occurred through two steps: (i) addition of one ethylene molecule to a silver cation dissolved in PEO, (ii) replacement of the ethylene molecule coordinated on the silver cation with another ethylene molecule. In the two-step mechanism of the addition and replacement reactions, the addition reaction is a nonactivated, preequilibrium process and the replacement reaction occurred through a transition state of two ethylene molecules coordinated to a silver cation dissolved in PEO. It was also found that the PEO/$AgBF_4$ system was energetically more favorable for the facilitated olefin transport than the PEO/$AgNO_3$ system. These results were well accordant with the experimental results.

Introduction

Ethylene and propylene have been used as an important feedstock in chemical industries. Currently, a cryogenic distillation process has mainly separated olefins such as ethylene and propylene from their mixtures with paraffins such as ethane and propane, respectively, which is costly due to similar volatilities of the component. Therefore a more economical separation process is ever demanded. A membrane process using the concept of facilitated transport has been an interesting alternative for separation of an olefin/paraffin mixture.[1−3] In facilitated transport membranes comprising carriers dissolved in a solid matrix, carrier-mediated mass transport occurs in addition to normal Fickian diffusion and therefore the separation efficiency can be improved remarkably.[1]

It has been well-known that silver or copper ions reversibly react with olefins, but not with paraffins. Thus, silver or copper ions can be utilized as a carrier for olefin/paraffin separation. Recently, it has been reported that polymer electrolyte membranes comprising silver salts such as silver tetrafluoroborate, silver triflate, and silver perchlorate dissolved in dry solid matrixes such as poly(2-ethyl-2-oxazoline),[1] poly(*N*-vinyl pyrrolidone), and poly(ethylene oxide),[3] are very effective in facilitated olefin transport, whereas polymer electrolyte membranes containing silver nitrate are not. Thus, it seems that facilitation behavior depends strongly upon the interaction of olefin with silver or copper ion carrier, which can be determined by the interactions of the silver cation with counteranion and with polymeric medium. In particular, it has been reported that the reaction equilibrium and the backward reaction constants of the reaction between a solute and a carrier are crucial in determining the transport properties.[4]

Therefore, in this research, the dissolution of silver salts in poly(ethylene oxide) (PEO) and subsequently the complexation of propylene with silver cation dissolved in PEO will be investigated theoretically using the density functional theory (DFT).[5] On the basis of the complexation energies, a new mechanism will be proposed for facilitated olefin transport through polymer electrolyte membranes containing silver salts. Finally, the distinct transport behavior between polymer electrolyte membranes of $AgBF_4$ and $AgNO_3$ dissolved in PEO will be interpreted in terms of the new mechanism proposed.

Calculations

Ethylene glycol dimethyl ether has been used as a model compound of PEO for simplicity. The electronic energies and structures of stationary species in the gas phase were calculated by full optimization without any geometrical constraint using the DFT method of the Becke's three parameter hybrid functional[6] using the Lee, Yang, and Parr correlation functional[7] (Becke3LYP) with 6-31+G(d) basis set[8] for nonmetallic elements and the effective core potential (ECP) of the LANL2DZ basis[9] set for silver cation. In these calculations, we have used the d-orbitals (6d-Cartesian function) in order to obtain more accurate results, since it is well-known that they are important in species containing a transition metal. The nature of all stationary point species was verified by calculating the vibrational frequencies.[10] The Gibbs Free energy changes (ΔG_g) for the reactions in the gas phase were obtained by correction to the electronic energy for zero-point energy (E_{ZPE}), thermal energy (E_T), *PV*-term, and entropy at 298.15 K and 1.0 atm, eq 1:[11]

$$\Delta G_g = \Delta E + \Delta E_{ZPE} + \Delta E_T + \Delta PV - T\Delta S \qquad (1)$$

To obtain the solvation energy in a polymeric medium, the isodensity polarized continuum solvation (IPCM) method[12] with

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10.1021/jp011338y CCC: \$20.00

SCHEME 1

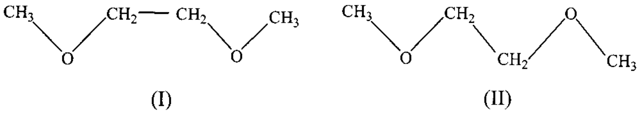


TABLE 1: Calculated Gibbs Free Energies (G in hartree) of (I) Plus Silver Salts, and the Complexation Gibbs Free Energy Changes (ΔG_c in kcal mol^{-1}) in the Gas Phase and in Polymeric Medium at 298 K from Equations 3 and 4

		G	ΔG_c	
X^-	path	gas phase	gas phase	polymeric medium
BF_4^-	eq 3	−879.02	+73.32	+5.06
	eq 4		−17.60	−9.01
NO_3^-	eq 3	−734.86	+93.40	+21.65
	eq 4		−12.52	−5.40

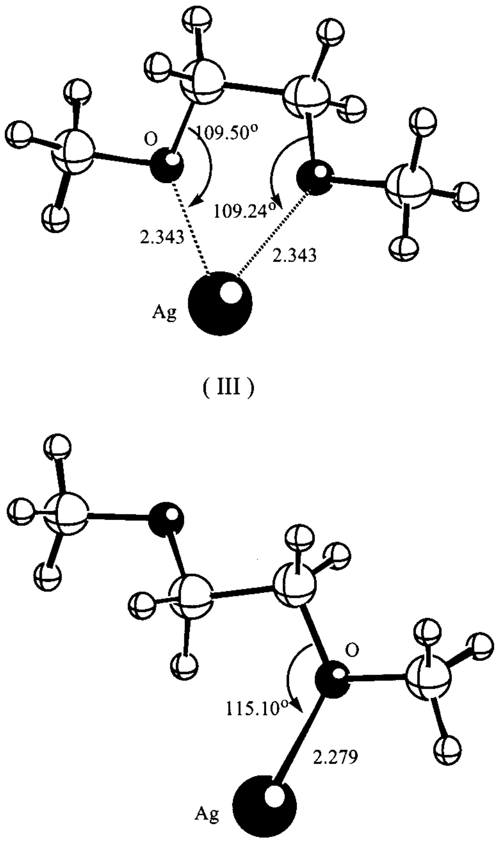
isodensity level of 0.001 a.u. was used. In the IPCM calculation, the dielectric constant (ϵ) of the polymeric medium was assumed to be 5. The gas-phase optimized geometries were used in the IPCM calculation. The solvation free energy changes (ΔG_s) for the respective species were calculated from the energy difference between the IPCM and the gas-phase calculation. Then the Gibbs free energy changes (ΔG_{sol}) for the reactions in the polymeric medium were obtained using eq 2. The Gaussian 94 and 98 program packages were used throughout in this work.[13]

$$\Delta G_{sol} = \Delta G_g + \Delta G_s \tag{2}$$

Results and Discussion

Complexation of Silver Salts in PEO. Two different stable conformers of ethylene glycol dimethyl ether are possible as shown in Scheme 1, i.e., two oxygen atoms in this unit can be located to the cisoid, (I), or transoid type, (II), for the intervening C−C single bond. The conformer (II) was slightly more stable than (I) in the gas phase, but the Gibbs free energy difference ($\delta\Delta G$ at 298.15 K) between two conformers was only 0.47 kcal mol^{-1} at the B3LYP/6-31+G* level. It is reasonable to expect, therefore, that the two conformers will be randomly distributed in a real system.

On the other hands, the Gibbs free energy change (ΔG_c) for the formation of the complex (III) from Ag^+ and (I) was much more stable by 13.82 kcal mol^{-1} than that of the complex (IV) from Ag^+ and (II) in the gas phase. In the polymeric medium ($\epsilon = 5$), ΔG_c for the (III) formation was also preferred by 7.15 kcal mol^{-1} compared to that for the (IV) formation. This was caused by the differences in the number of stable interactions between the silver cation and oxygen atoms. The complex (III) is structurally bi-dentate ligand type whereas the complex (IV) is mono-dentate ligand type as represented in Figure 1. The bond lengths (d_{O-Ag}) between two oxygen atoms and Ag^+ in (III) were nearly identical, and the d_{O-Ag} in (III) was somewhat longer than that in (IV). Thus the complex (III) could be more stable than (IV). Of course, the possibility that one silver ion binds to two oxygen atoms of two PEO molecules could not exclude. However, it could be expected that the effects on energetics as well as stereochemistry are very similar to the complex (III), since the silver ion has sp^3-hybrid orbitals to make coordination bonds with oxygens in PEO and anion (vide infra). Therefore we have chosen the complex (III) in further discussion.

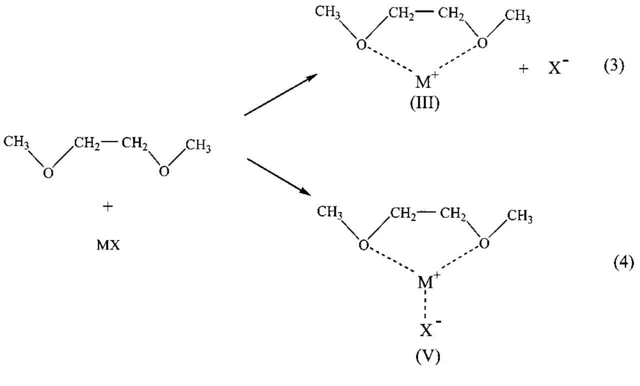


(III)

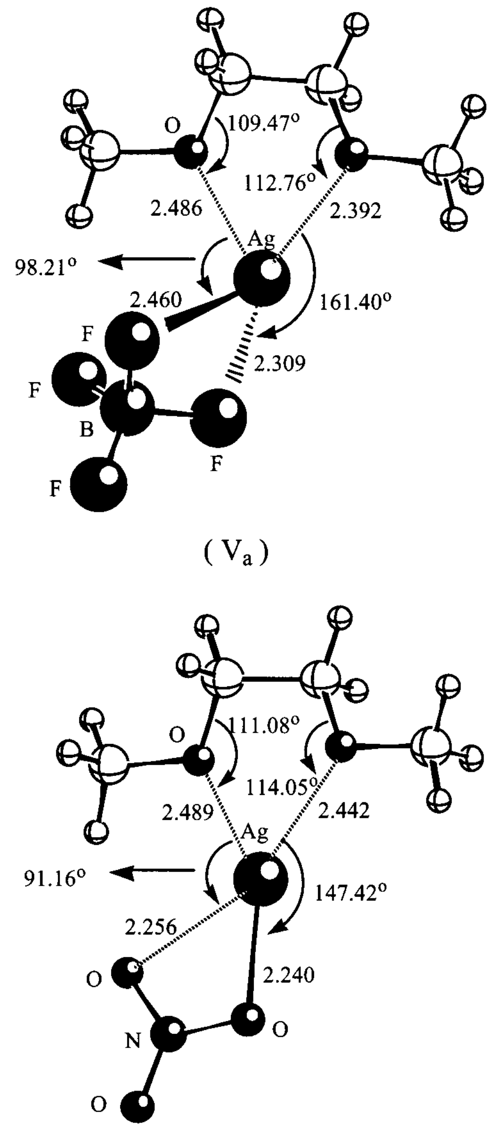
(IV)

Figure 1. Optimized structures of the complexes (III) and (IV) formed between (I) and Ag^+, and between (II) and Ag^+, respectively. Bond lengths are in Å, and bond angles are in degree.

The calculated complexation Gibbs free energies (ΔG_c) for the formation of the complexes (III) and (V) as shown in eqs 3 and 4 were summarized in Table 1. The structural difference between (III) and (V) is that the salt is in free ions for (III) and contact ion pairs for (V).



As can be seen in Table 1, eq 4 is much more favorable compared to eq 3 in the gas phase as well as in the polymeric medium. From these results, it is expected that the complex (V) is predominantly produced when the silver salts are dissolved into the PEO medium. The bond strength of the ion pair dissolved in PEO is weakened compared to that in a solid salt state. This expectation is well accordant with our theoretical calculations,[14] i.e., the "free" ion formation in the dissolving process of metallic salts is unfavorable compared to the ion-pair formation. For example, the Gibbs free energies (ΔG_d) for dissolving $AgBF_4$ and $AgNO_3$ salts into free ions are higher by 21.51 and 37.76 kcal mol^{-1}, respectively, than those into contact ion pairs in a polymer medium. Therefore it might be reason-



(V$_a$)

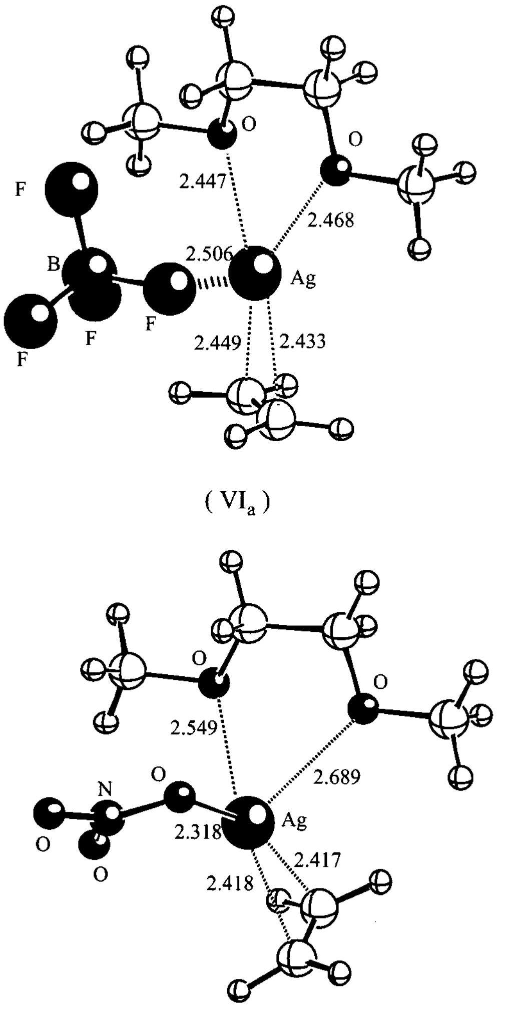
(V$_b$)

Figure 2. Optimized structures of the complexes (V$_a$) and (V$_b$) formed between (I) and AgBF$_4$, and between (I) and AgNO$_3$, respectively. Bond lengths are in Å, and bond angles are in degree.

able to predict that (V) is more a probable complex in PEO than (III).

The structures of the complexes containing AgBF$_4$, (V$_a$), and AgNO$_3$, (V$_b$), dissolved in PEO were represented in Figure 2. The silver ion has sp^3-hybrid orbitals to make coordination bonds with oxygens in PEO and anion. These structures could be rationalized from the fact that the silver cation has the coordination number of 4 using vacant 5s- and 5p-orbitals, since the electron configuration of the silver cation is [core]-4s^{2}4p^{6}4d^{10}. Note that the O−Ag bond lengths $d_{\mathrm{O-Ag}}$s in (V) were longer than those in (III). This indicates that the interaction between PEO and Ag$^+$ is stronger in (III) than (V), since the cationic character of the silver ion decreases due to the charge transfer from the anion ligand in the case of (V).

When compared between (V$_a$) and (V$_b$), the $d_{\mathrm{O-Ag}}$ in (V$_a$) were slightly shorter than those in (V$_b$). This implies that both the cationic character of Ag$^+$ and the interaction between Ag$^+$ and PEO are higher in the BF$_4^-$ complex than in the NO$_3^-$ complex. This is confirmed by the natural population analyses (NPA),[15] i.e., the charge densities of the silver cation are +0.879 and +0.797 for the BF$_4^-$ and NO$_3^-$ complexes, respectively, since the charge transfer from BF$_4^-$ and NO$_3^-$ to Ag$^+$ are 0.058 and 0.137 e, respectively. The relatively larger charge transfer from NO$_3^-$ compared to that from BF$_4^-$ may be resulted from the narrower energy gap between the lone-pair orbital of the oxygen atom bound to Ag$^+$ in NO$_3^-$ and the LUMO of Ag$^+$. As expected, the energy levels of the lone-pair orbitals by the natural bond orbital (NBO) analyses[16] obtained at NBO-HF/6-31+G*//B3LYP/6-31+G* level were −10.86 and −16.00 eV for NO$_3^-$ and BF$_4^-$, respectively. Therefore the second-order charge-transfer stabilization energies (ΔE_{ct}) between the HOMO and LUMO are much larger in the NO$_3^-$ complex than that in the BF$_4^-$ complex, and hence the bond strength between Ag$^+$ and NO$_3^-$ becomes stronger than that between Ag$^+$ and BF$_4^-$. This relatively stronger bond strength between Ag$^+$ and NO$_3^-$ agrees well with our previously work,[17] i.e., the estimated lattice energies of AgNO$_3$ salt is much larger than that of AgBF$_4$.



(VI$_a$)

(VI$_b$)

Figure 3. Optimized structures of the complexes (VIa) and (VIb) formed between (V$_a$) and ethylene molecule, and between (V$_b$) and ethylene molecule. Bond lengths are in Å and bond angles are in degree.

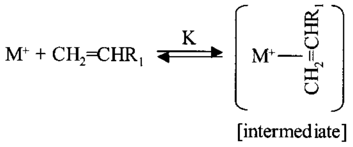
Coordination of Silver Salt Dissolved in PEO with Olefin. When one ethylene molecule was added to the complex (V$_a$) or (V$_b$), a new complex (VI$_a$) or (VI$_b$) was formed by substituting one site of the anion ligands with an ethylene molecule via reaction 5 as shown in Figure 3. This process is a diffusion-controlled type without an activation and the ΔG values (Table 2) for the formation of (VI$_a$) and (VI$_b$) in the polymeric medium

TABLE 2: Calculated Gibbs Free Energies (G in hartree) of (V) Plus Ethylene in Gas Phase and the Gibbs Free Energy Changes (ΔG in kcal mol^{-1}) for the Formation of (VI) in PEO at 298 K

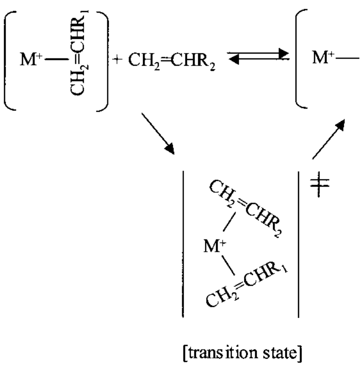
X^-	G_g	ΔG_g	ΔG_s	ΔG_{sol}[a]
BF_4^-	−957.61	+0.69	−1.55	−0.86
NO_3^-	−813.44	+3.36	−1.30	+2.06

[a] $\Delta G_{sol} = \Delta G_g + \Delta G_s$.

were −0.86 and +2.06 kcal mol^{-1}, respectively. Thus the equilibrium constants (K) at 298 K calculated using the relation $\Delta G = -RT \ln K$ were ca. 4.3 and 3.1×10^{-2} M^{-1} for (VI_a) and (VI_b), respectively. It indicates that (VI_a) is more favorable by ca. 140 times in K than (VI_b). In other words, the substitution of one ligand site by an ethylene molecule is more difficult in (V_b) than in (V_a), since the bond strengths in $AgNO_3$ are stronger than those in $AgBF_4$ due to a larger charge transfer from NO_3^- to Ag^+ ion compared to that from BF_4^- as discussed above.

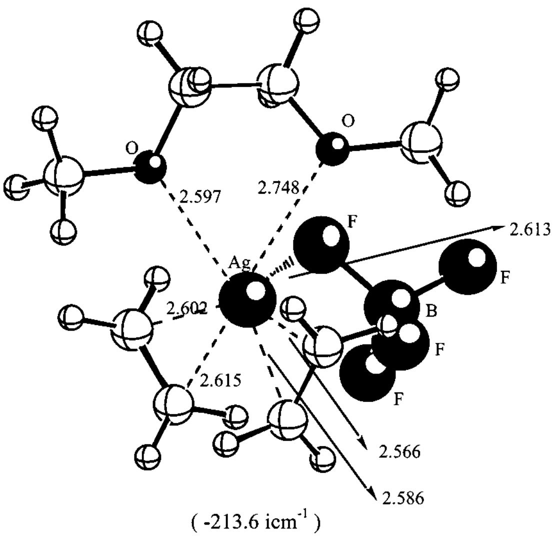


(5)



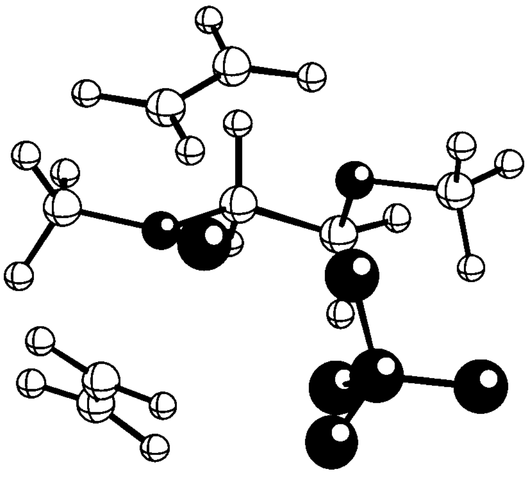
(6)

When another ethylene molecule approaches (VI_a), the ethylene already bonded in the silver cation is substituted with a new ethylene molecule by an activated process through a transition state (TS) of a normal push−pull S_N2 type as written by reaction 6. The Gibbs free energy of the activation ($\Delta G^‡$) in the polymeric medium was 7.07 kcal mol^{-1}. The TS has a typical trigonal bipyramid 5-coordinate (TBP-5C) structure as well-known in common S_N2 reactions. The bond lengths between the silver cation and the carbon of the two ethylenes in the TS were nearly the same (ca. 2.60 Å), which were lengthened by ca. 0.2 Å compared to that of (VI_a). Thus, the reversible reaction mechanism of olefins with silver cations in polymer electrolyte membranes is expressed by eqs 5 and 6. The TS structures of the front- and top-side viewing are presented in Figure 4.



(-213.6 icm^{-1})

(Top view)



(Front view)

Figure 4. Transition state (TS) structure for the replacement reaction of the bound ethylene molecule in (VIa) with another ethylene. Value in parentheses is one imaginary vibrational frequency. Bond lengths are in Å.

A TS for the reaction of (VI_b) with a new ethylene molecule was not, however, able to be obtained, since the O−Ag bond was broken during the optimization. This result was rationalized by relatively stronger interaction between Ag^+ and NO_3^- discussed above, i.e., the bond strength between Ag^+ and PEO is stronger in (VI_a) than in (VI_b) due to the larger charge transfer from NO_3^- to Ag^+ compared to that from BF_4^-. This prediction agrees with the O−Ag bond lengths (d_{O-Ag}) in (VI) as can be seen from Figure 3; the d_{O-Ag}'s are shorter by ca. 0.1−0.2 Å in (VI_a) than in (VI_b). Thus the O−Ag bond was broken for the reaction of (VI_b) with a new ethylene molecule, implying that the reaction of (VI_b) with an ethylene molecule is extremely difficult to occur. These results were well accordant with the experimental findings: The polymer electrolyte membrane consisted of $AgBF_4$ dissolved in PEO exhibits the facilitated transport of ethylene but that of $AgNO_3$ does not.

A possible formation of complex of (V_a) or (V_b) with paraffins such as ethane molecules was also considered. The complexation energies of ethane with free Ag^+ (VII) and with silver ion pair (VIII) were calculated. The Gibbs free energy change for the formation of (VII) was −9.14 in the gas phase and +5.78 kcal mol^{-1} in the polymeric medium. This indicates that the formation of (VII) is unfavorable in the polymeric medium. Similarly, the complexation energies of (VIII) in the polymeric medium were also enothermic by +5.50 ($AgBF_4$, (VIIIa)) and +4.23 kcal mol^{-1} ($AgNO_3$, (VIIIb)). Thus it is expected that any complexes containing ethane are not formed in the polymer medium or are produced at most a negligible amount. The optimized structures of (VII) and (VIII) are presented in Figure 5.

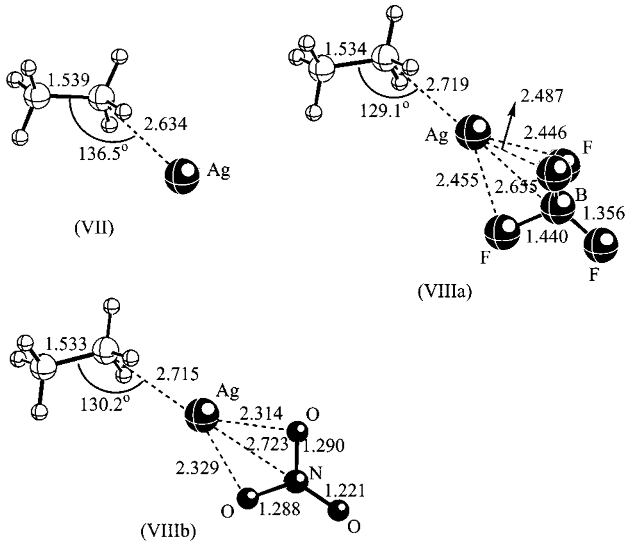


Figure 5. Optimized structures of the complexes (VII) and (VIIII). Bond lengths are in Å and bond angles are in degree.

It is worth noting that the complexation energies between free Ag^+ and ethylene were -27.32 and -9.80 kcal mol^{-1} in the gas phase and in the polymer medium, respectively, and those between silver ion pair of $AgBF_4$ and $AgNO_3$, and ethylene in the polymeric medium were -8.78 and -2.20 kcal mol^{-1}, respectively. The difference in the complexation energy between ethane and ethylene were obviously caused by π-electrons of ethylene. Therefore it may be concluded that the facilitated transfer of ethylene in silver polymer electrolyte membranes is primarily due to the stronger interaction of ethylene with the silver carrier compared to that of ethane.

In summary, it has been suggested that the mechanism of the facilitated transport of olefin through silver polymer electrolyte membranes consists of two stages: (i) one ethylene molecule reacts with a silver ion dissolved in PEO by replacing a ligand site of the anion with an ethylene molecule, (ii) another ethylene molecule pushes the ethylene molecule bound to the silver ion out via the S_N2 type mechanism. Therefore we conclude that the facilitated transport of olefins through membrane will be largely dependent on the extent of the cooperative interaction of the silver ion carrier with matrix polymer, anions, and olefin molecules.

Acknowledgment. The authors gratefully acknowledge the financial support from the Ministry of Science and Technology of Korea through the Creative Research Initiative.

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