Ab Initio Molecular Orbital Computation Studies of Ag⁺-C₂H₄ Complexation in the Presence of Water

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ABSTRACT *Ab initio* calculations are done to explore the influence of water on the Ag⁺-C₂H₄ complex formation. The simulated coordination environment of Ag ion is based on the existence of a dynamic equilibrium between the coordination of Ag ion with water and a sulfonate group, the counter ion. Calculated electronic properties reveal that electron delocalization from water molecules and the sulfonate group onto Ag 5s-atomic orbital reduces the ability of Ag ion to accept additional electrons from the C₂H₄ π–orbital. The dissociation of water molecules from the hydrated Ag⁺ is essential for the thermodynamic possibility of the Ag-C₂H₄ complex formation. It is also evident from the electronic structure calculations that the dissociation of water is favorable for the formation of a stable Ag-C₂H₄ complex. In the absence of water, the reaction between Ag ion strongly bound to sulfonate group and C₂H₄ is thermodynamically impossible.

KEYWORDS: *Ab initio* calculations, Ag⁺-C₂H₄ complexation, Ag⁺ hydration, facilitated transport membrane.

INTRODUCTION

Facilitated transport membranes incorporated with Ag⁺ have long been investigated as an approach to augment or replace existing olefin separation technologies.[1] A reversible complexation reaction between Ag⁺ and olefin in the presence of a polar solvent preferentially enhances the olefin flux through the membranes. Water is most used as the solvent for the facilitated olefin transport membranes because of its effectiveness in promoting the reaction and several other advantages. In the absence of water, however, facilitation of olefin is not observed.[2-8] The loss of water from the membrane during the operation consequently diminishes olefin flux and selectivity, limiting membrane lifetimes. The requirement that the membrane be saturated with water makes the membrane technology less competitive compared to other conventional separation processes. A recent approach to the solution of this problem is the development of the membranes that do not require water for the Ag⁺ to complex with the olefin penetrant.[9-10]

Considerable studies have been done to obtain structural and chemical information of Ag⁺ in aqueous solutions and membranes of interest for the facilitated olefin transport. The structure of the primary hydration shell of Ag⁺ in aqueous solutions was investigated by neutron diffraction[11] and ultraviolet absorption.[12] There was good agreement on the primary hydration shell containing four water

molecules. Investigation done by Antonio et al[13] provided some insights about the Ag⁺ environment within the geltype membranes. The membranes were swollen when wet and the water molecules were well-dispersed in a polymer matrix. One of the significant findings was that the Ag⁺ coordinated to three oxygen atoms, irrespective of the types of counterions. However, it was not possible to identify whether the oxygen atoms come from water molecules and/or the membrane matrix material.

Extensive research on the character of water present in perfluorosulfonate ion exchange membrane or Nafion® has provided information about the interaction between cation and SO₃⁻ group.[14-16] It was evident that the sulfonate groups in a fully hydrated membrane were shielded from the nearest counterion by several water molecules. Nevertheless, there was a dynamic equilibrium between strongly associated ion pairs and relatively free ions. In contrast, the number of water molecules in a partially hydrated membrane was inadequate to completely shield cations from sulfonate groups. This resulted in the increasing number of contact ion pairs, and the exchange of ions between the bound and unbound states was unlikely to exist.

To date, however, little attention has been devoted to studying the importance of water to the Ag⁺-olefin complexation. This work intends to computationally study the complex formation between Ag⁺ and C₂H₄ in the presence of water. However, it must be

emphasized that the simulation is performed in a gas phase, while the Ag^+-C_2H_4 reaction in a membrane occurs in an aqueous environment. In an attempt to use the calculation results to throw light on the necessity of water for the complexation in a membrane, hydration effects are taken into consideration. Despite the simplistic approach and the fairly low level of theory used, the present work can to some extent explain the role of water on the complexation. It is hoped that the concept provided by this study has implications for the membrane development.

Ag+-olefin complexation

The olefin-transition metal interaction has been qualitatively elucidated by the most widely accepted model proposed by Dewar.[17] According to the model, the Ag^+-olefin bonding consists of two synergic interactions involving σ-bond and π-bond. The σ-bond originates from the interaction between the π-orbital of olefin and the 5s-orbital of Ag^+, ie the electrons in the π-orbital on the olefin localize onto the empty 5s-orbital on the Ag^+. An unfavorable build-up of negative charge on the Ag^+ is counteracted by the π-bond, the result of the interaction between the π*-orbital of olefin and the 4d-orbital of Ag^+. In this case, the electrons delocalize from the fully filled hybrid 4d-orbital on the Ag^+ onto the initially empty π*-orbital (antibonding) on the olefin.

The Ag^+-olefin bonding can be further comprehended by considering the significance of the energy requirements necessary for the formation of Ag^+-C_2H_4 complex. Given the appropriate symmetry to permit a non-zero overlap, the interacting orbitals must be characterized by well-matched orbital energies to provide the thermodynamic driving force for the complexation. The resulting stabilizing effect is inversely proportional to the relative energy difference between the orbitals taking part in bonding. The stabilization energy is large for the bonding molecular orbital generated from the orbitals having a small energy level separation.

Thermodynamic data of Ag^+-olefin complexes are available in the literature.[18-19] The data are quite useful for demonstrating two important aspects of the complex formation. First, the relative stability of the complexes can be obtained by making a comparison of the equilibrium constants. Second, the information can also be used to generalize about the properties of olefin that influence the formation of the complexes. The data however cannot be used to rationalize the importance of solvent in the Ag^+-olefin complexation.

Computational chemistry has been a valuable approach to explore the bonding of C_2H_4 to Ag^+.[20-26] However, there has been disagreement as to whether the bonding is mainly attributed to electrostatic forces or covalent interactions. An early work by Basch[20] described the bonding as being mainly electrostatic. In contrast, Ziegler et al[22] demonstrated that the net positive charge on Ag^+ only partly accounted for the attraction, whereas the σ-donation was the dominant factor for the bonding. Much needed experimental information for the Ag^+-C_2H_4 complex was provided by Guo et al.[23] By using high-pressure mass spectrometry and the calculated entropy changes in combination, the relatively large bond dissociation energy of 33.7 Kcal mole^{-1} was determined. It was inferred that electrostatic forces were not the dominant factors in the complexation. A few years later, Hertwig et al[24] examined Ag^+-C_2H_4 complex by different levels of theory and reported the bond dissociation energy close to the experimental number. Nevertheless, Morokuma's bond-decomposition analysis revealed that electrostatic and covalent contributions were to first order equally important in the Ag^+-C_2H_4 interaction with the π-back-bonding amounted to only one-fifth of all covalent contributions. Recently, Ma[25] proposed a computationally efficient procedure for estimating the Ag^+ affinity for a range of ligands including C_2H_4. Natural population analysis on the Ag^+ complexes suggested that the interaction was predominantly electrostatic in nature while the covalent bonding was also important.

METHODS

Ab initio SCF-MO calculations were performed with the PC Spartan Plus software version 1.5 on IBM compatible personal computer with a Pentium MMX CPU. The HF/3-21G(*) level of theory was used for all calculations as a larger basis set for Ag^+ was not available. The computations were carried out in the geometry optimization modes with the spin-restricted Hartree-Fock (RHF) model to obtain the optimized molecular structures and their electronic properties. The thermodynamic properties were subsequently calculated at the temperature of 298.15 K and the pressure of 1 atm.

RESULTS AND DISCUSSION

The interactions of Ag^+ with counterion and water molecules within the membrane could be deduced from the information provided in the

literature. As mentioned earlier, a cation in a fully hydrated Nafion® is in a dynamic equilibrium between bound and unbound states.[14-16] It was found not long ago that Ag^+ in the gel-type membranes coordinates to three oxygen atoms.[13] On the basis of these findings, it is probable that Ag^+ in a fully hydrated membrane alternately coordinates to oxygen atoms from water molecules and the sulfonate group. On the contrary, the absence of such equilibrium in a dry or partially hydrated membrane implies that Ag^+ coordinates to three oxygen atoms from the sulfonate group.

In this study, *ab initio* molecular orbital calculations were done to elucidate the properties of Ag ion in the dry and hydrated membranes. $[Ag-3H_2O]^+$ was simulated to serve as the simplified model for the coordination of Ag^+ with three water molecules in a fully hydrated membrane. Figure 1 shows the position and orientation of $[Ag-3H_2O]^+$. Completely shielded by water molecules, Ag^+ was presumably unaffected by electron delocalization from the sulfonate group. The charge of the complex was then assigned to be +1. In the absence of water, there was evidence suggesting the formation of contact ion pairs between Ag^+ and the sulfonate groups.[16] In this case, the interaction between Ag^+ and sulfonate group was studied through $[HSO_3-Ag]$ complex. Additional *ab initio* calculations of $[HSO_3-Ag-H_2O]$ and $[HSO_3-Ag-2H_2O]$ complexes were carried out to study the intermediate environment of Ag ion between unbound and bound states.

The optimized structures of all complexes revealed that water and sulfonate group are arranged in
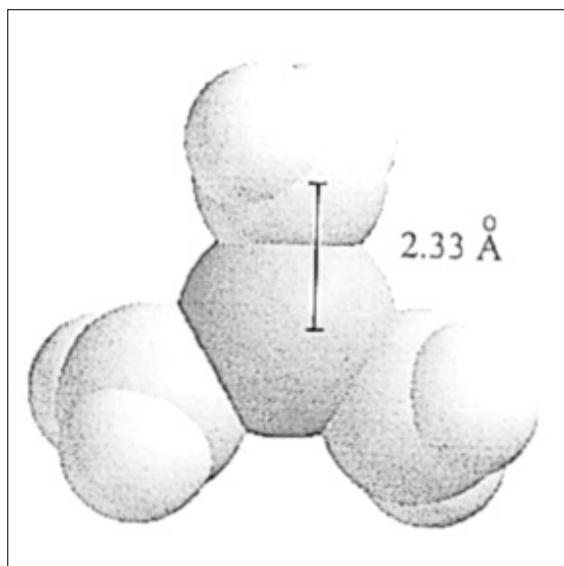
Fig 1. Optimized structure of $[Ag-3H_2O]^+$; Ag^+ is surrounded by H_2O molecules with oxygen atoms pointing towards Ag^+.

a manner that oxygen atoms point to the Ag ion. The average Ag-O distance for the fully hydrated Ag^+ ion was 2.33 Å. Replacement of one water molecule with HSO_3^- did not change the mean distance between Ag ion and the oxygen atoms of water molecules. The distance between Ag ion and the nearest oxygen atom from sulfonate group was 2.39 Å. Within the membrane, Antonio et al (*13*) found from EXAFS (extended X-ray absorption fine structure) data that the Ag-O distance ranged between 2.20-2.26 Å. Apparently, the calculations overestimated the Ag-O interatomic distance by approximately 0.1-0.2 Å.

Martinez et al[26] performed *ab initio* calculations at the MP2 level for $[Ag(H_2O)_n]^+$ clusters placed in a cavity surrounded by a dielectric continuum, which represented the bulk water. For $[Ag(H_2O)_{12}]^+$, with the first shell consisting of 4 water molecules, the $Ag-O_1$ distance was 2.430 Å. The $Ag-O_1$ distance of $[Ag(H_2O)_4]^+$ in gas phase was found to be very close to 2.43 Å which suggested a cancellation between the long-range interactions due to the bulk solvent and the interactions of a second hydration shell.

Effects of water molecules and sulfonate group on electronic properties of Ag ion are shown in Table 1. Upon coordinating with water molecules and/or a sulfonate group, the Mulliken charge was reduced, indicating electron delocalization from the ligands onto the Ag ion. If electrostatic interactions were the major forces that contribute to the stability of the complex, this reduction in the Mulliken charge would essentially mean the weaker bonding between the Ag ion and C_2H_4. Furthermore, the electron delocalization correspondingly caused the Ag 5s-orbital energy to increase. Given the C_2H_4 π-orbital energy of -0.380 au[19], the energy gap between C_2H_4 π-orbital and Ag 5s-orbital was consequently widened, decreasing the potential for the orbitals to overlap. As brought up earlier, the interaction between these two orbitals was substantially important to the complex formation between C_2H_4

Table 1. Effects of Water Molecules and Sulfonate Group on Mulliken Charge and 5s-Orbital Energy of Ag Ion.

Species	Ag-mulliken charge	Ag 5s-orbital energy (au)
free Ag^+	1.0	-0.206
$[Ag-3H_2O]^+$	0.586	-0.073
$[HSO_3-Ag]$	0.610	-0.012
$[HSO_3-Ag-H_2O]$	0.551	0.011
$[HSO_3-Ag-2H_2O]$	0.496	0.033

and Ag ion. Relative to the free ion, the coordinated Ag ion apparently had less favorable electronic environment to complex with C_2H_4. Note that the effects of electron delocalization from three water molecules were slightly greater than those from the sulfonate group. Based on these observations it could be conjectured that water in a fully hydrated membrane did not promote the complexation between Ag ion and C_2H_4 by modifying the electronic environment of Ag ion.

Thermodynamic aspect of the complexation between Ag^+ and C_2H_4 was then studied. Two diverse cases were examined in this work. First, Ag^+ was fully hydrated and coordinated to three water molecules, while the sulfonate group presented in the outer sphere and was not considered. Second, Ag ion strongly associated with the sulfonate group in the absence of water. For the hydrated Ag^+, the complexation with C_2H_4 involved an underlying assumption that the water molecules dissociated from Ag^+, as shown by equation 1. The dissociation of water accompanying the complexation will be discussed later. On the other hand, Ag ion in a dry membrane had very limited mobility. The complexation therefore rested on the postulation that Ag ion was simultaneously coordinated with the sulfonate group and C_2H_4 as shown by equation 2.

$$[Ag\text{-}3H_2O]^+ + C_2H_4 \rightleftharpoons [Ag\text{-}C_2H_4]^+ + 3H_2O \quad (1)$$

$$[HSO_3\text{-}Ag] + C_2H_4 \rightleftharpoons [HSO_3\text{-}Ag\text{-}C_2H_4] \quad (2)$$
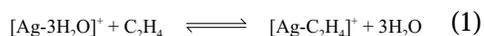
Table 2 lists the calculated thermodynamic data of the proposed reactions. A negative free energy change of reaction (1) suggested the thermodynamic feasibility of the displacement of water molecules with C_2H_4. In contrast, strongly associated with a sulfonate group, Ag ion was incapable of reacting with C_2H_4 as indicated by a positive free energy change. Both the entropy and enthalpy terms were unfavorable for the $[Ag\text{-}C_2H_4]^+$ complex formation. It was evident that water enabled Ag^+ to form a complex with C_2H_4 complex formation by shielding Ag^+ from sulfonate group.

In order to obtain meaningful information from the calculations, the fact that the complex reaction

in the membrane took place in a solution phase had to be considered. Unlike the reaction in gas phase, the dissociated water molecules within the membrane were not free, but have interactions with the surrounding water molecules. Specific interactions such as hydrogen bonding could significantly reduce the entropy change. In addition, as C_2H_4 is an uncharged ligand, the reaction with Ag^+ would not result in a reduction in the number of ions, nor a neutralization of charge. It is probable that the ligational entropy change was not significant. As a consequence, the favorable enthalpy change could be a key factor in the thermodynamic feasibility of the complexation in the membrane.

The hypothesis of the water dissociation upon the Ag^+-C_2H_4 complex formation was investigated through the reactions with differing number of leaving water molecules. An addition of C_2H_4 to the hydrated Ag ion without any loss of water molecule was represented by reaction (3). The other reactions involved the replacement of water molecules with C_2H_4. Reactions (4) and (5) presented the Ag ion-C_2H_4 complex formation taking place with the loss of one and two water molecules, respectively. Thermodynamic data of each case, together with that of the C_2H_4 coordination in place of three expelled water molecules, are listed in Table 3.

$$[Ag\text{-}3H_2O]^+ + C_2H_4 \rightleftharpoons [Ag\text{-}3H_2O\text{-}C_2H_4]^+ \quad (3)$$

$$[Ag\text{-}3H_2O]^+ + C_2H_4 \rightleftharpoons [Ag\text{-}2H_2O\text{-}C_2H_4]^+ + H_2O \quad (4)$$

$$[Ag\text{-}3H_2O]^+ + C_2H_4 \rightleftharpoons [Ag\text{-}H_2O\text{-}C_2H_4]^+ + 2H_2O \quad (5)$$
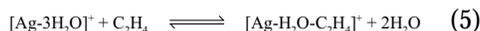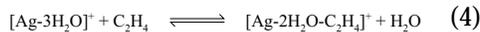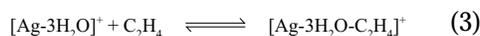
Based on the free energy changes, the water molecules were expected to dissociate from Ag ion upon the formation of $[Ag\text{-}C_2H_4]^+$ bonding. Note that the partial dissociation was also possible for the hydrated Ag^+ to complex with C_2H_4. The origin of water dissociation could be comprehended by separately considering the contribution of enthalpy and entropy components to the free energy change.

The enthalpy change in aqueous solution is a heat change that accompanies the replacement of water

Table 2. Calculated thermodynamic data for reactions (1) and (2).

Reaction	ΔG (Kcal/mole)	ΔH (Kcal/mole)	ΔS (Kcal/mole.K)
1	−19.16	-5.12	0.0471
2	9.45	2.20	-0.0243

Table 3. Calculated thermodynamic data for reactions (1), (3), (4) and (5).

Reaction	ΔG (Kcal/mole)	ΔH (Kcal/mole)	ΔS (Kcal/mole.K)
3	10.13	1.26	-0.0298
4	1.50	-0.39	-0.0063
5	-10.27	-2.63	0.0256
1	−19.17	-5.12	0.0471

by other ligands. When water molecules coordinated to Ag ion, there was an electrostatic repulsion among them against which work has to be done. As a consequence, the influence of water dissociation to the heat term could be expected to favor the ethylene substitution.

The contribution of entropy change could be explained in terms of an increase of randomness associated with a concomitant increase in entropy. The dissociation of water molecule from Ag ion resulted in a greater number of independent components and the disorder within the system. However, due to the interactions on the dissociated water molecules, the entropy change in a solution or within a water-swollen membrane could be substantially less than in a gas phase. The entropy change generated by the release of water molecules may have only little effect on stability of the complex.

Electronic structure calculations also showed evidence that the dissociation of water molecules upon the formation of Ag^+-C_2H_4 bonding increased stability of the complex. Stabilization energy originated from the σ–bonding was determined by the degree to which the π–orbital energy of C_2H_4 was decreased. As shown in Table 4, a complete water dissociation from Ag ion provided the lowest π–orbital energy which corresponded to the highest stabilization energy. Stability of the complex was less for a partial dissociation of water or a simple addition of C_2H_4 to the hydrated Ag ion.

Even though the present work is able to give thought on how the presence of water may promote the Ag^+-C_2H_4 complex formation, a re-evaluation based on a more advanced theory is desirable. It is also possible that the presence of sulfonate group, either in the first or second coordination sphere, affects the reaction between hydrated Ag^+ and C_2H_4. Consequently, possible complex formation involving the counter ion should be explored in more detail.

Table 4. π-orbital energy of free-C_2H_4 and complexed-C_2H_4 (a.u.) and the complex stabilization energy (a.u.)

Species	C_2H_4-π orbital energy (a.u.)	stabilization energy (a.u.)
Free-C_2H_4	-0.380	-
$[Ag\text{-}3H_2O\text{-}C_2H_4]^+$	-0.513	0.133
$[Ag\text{-}2H_2O\text{-}C_2H_4]^+$	-0.534	0.154
$[Ag\text{-}H_2O\text{-}C_2H_4]^+$	-0.562	0.182
$[Ag\text{-}C_2H_4]^+$	-0.581	0.201

CONCLUSIONS

Electronic and thermodynamic effects of water on Ag^+-C_2H_4 complexation were studied through *ab initio* molecular orbital computations. The calculations were done based on the postulation of a dynamic equilibrium between bound and unbound states of Ag^+. In a fully hydrated membrane, the unbound-Ag^+ coordinated to three water molecules. In the bound state, Ag ion formed a contact ion pair with sulfonate group. Such dynamic equilibrium however did not exist in a dry membrane, and Ag ion permanently bound to a sulfonate group. While it is not possible to rely upon the precise values of the calculated data reported by this study, certain findings are apparent.

Coordinated to water molecules and/or sulfonate group, the potential for Ag ion to form a complex with C_2H_4 was diminished. The coordination led to the electron localization onto Ag^+ as evidenced by a decrease in Ag-mulliken charge. The increase in the electron density of Ag ion caused the energy difference between Ag 5s-orbital and C_2H_4 π–orbital to be widened. A large energy gap between these two orbitals was however unfavorable for the complex formation. This suggested that the presence of water did not electronically promote the Ag^+-C_2H_4 complexation.

Thermodynamic aspect of the Ag^+-C_2H_4 reaction was studied. It was hypothesized that water molecules forming a hydration shell around Ag ion were replaced by C_2H_4. The thermodynamic possibility of the reaction was indicated by a negative free energy change. The complex formation became thermodynamically less favorable when the extent of water dissociation decreased. In the absence of water, Ag ion lost its ability to react with C_2H_4 as suggested by a positive free energy change of the HSO_3-Ag-C_2H_4 formation.

Electronic structure calculations also suggested that the dissociation of water accompanying the complexation was favorable for the formation of a stable Ag-C_2H_4 complex. The highest stabilization energy originated from the s-bonding was obtained when water completely dissociated from Ag^+ ion.

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