LITERATURE REVIEW

Molecular clearly implies some connection with the molecules. Molecular modeling would therefore appear to be connected with the ways to mimic the behavior of molecules and molecular system (Leach A., 1996). Today, molecular modeling is invariably associated with the computer modeling, but it is quite feasible to perform some simple molecular modeling studies using mechanical models or a pencil, paper and hand calculator. Nevertheless, computational techniques have revolutionized molecular modeling to the extent that most calculations could not be performed without the use of a computer. This is not to imply that a more sophisticated model is necessarily any better than a simple one, but computers have certainly extended the range of models that can be considered and the systems to which they can be applied.

The model that most chemists first encounter is molecular models. These models enable three-dimensional representations of the structures of molecules to be constructed. An important advantage of these models is that they are interactive, enabling the user to pose “what if…” or “is it possible to…” questions. These structural model continue to play an important role both in teaching and in research, but molecular modeling is also concerned with more abstract models, many of which have a distinguished history. An obvious example is quantum mechanics, the foundations of which laid many years before the first computers were constructed.

Ramirez et al. (1996) had built the model of membrane for determining membrane potential and ionic flux in weak amphoteric polymer membranes. They presented model calculations concerning the membrane potential and ionic fluxes in weak amphoteric polymer membranes. They mentioned that the results were compared with experimental data obtained with a membrane which contained succinyl chitosan as ampholyte and poly(vinyl alcohol) as supporting matrix. The ion transport through the membrane had been described with the aid of the Nernst-Planck equations, and the result obtained explained satisfactorily the observed experimental trends in broad ranges of pH and electrolyte concentration. Also, the model predictions concerning the membrane isoelectric point might be useful for the analysis of future experiments.

Majerz et al. (1997) studied the proton transfer and correlations between the C-O, O-H, N-H and O…N bond lengths in amine phenolates. They investigated a relationship between the geometrical parameters of the O-H…N bridge based on the results of X-ray diffraction studies of a number of amino-phenol hydrogen- bonded complexes covering a broad $\Delta\rho$Ka range from -3.91 to 5.93 are proposed. The analysis shows that the shortest bridges are realized when the proton transfer degree, reflected in the C-O bond length, reaches about 50%. The position of the hydrogen atom is then close to the center of the bridge.

Zhou (1999) reported the results of ab initio self-consistent-field and density functional theory calculations of the gas-phase structure, acidity (free energy of deprotonation, ΔGo) and aromaticity of 1,2-dithio-3,4-diselenosquaric acid (3,4-diselenyl-3-cyclobutene-1,2-dithione, $H_2C_2S_2Se_2$). The optimized geometrical parameters resulted in an equalization of the bond lengths compared with the reference compounds cyclobutandithione and cyclobutenediselenol. The computed aromatic stabilization energy and diamagnetic susceptibility exaltation were negative, indicating that 1,2-dithio-3,4-diselenosquaric acid was aromatic. Thus, 1,2-dithio-3,4-diselenosquaric acid fulfilled the geometrical, energetic and magnetic criteria aromaticity.

Jeong and Kwon (2000) applied ab initio and density functional theory methods to investigate the molecular structure and conformational nature of tetrabromoformaldazine. They found that the calculations including the effects of the electron correlation at the B3LYP and MP2 levels with the basis set 6-311 +G(d) could reproduce the experimental geometrical parameters at the skew conformation. The N-N bond torsional angle Φ calculated at the MP2/6-311 +G(d) level was found to be closest the observed angle. The scanning of the potential energy surface suggested that the anti-conformation was at a saddle point corresponding to the transition state.

Valdes and Sordo (2000) indicated that the most stable structure of the pentamenthylene sulfide…HCl potential energy surface was two chair-like complexes involving axial and equatorial hydrogen bonds. An ab initio, using MP2/6-31G(d,p) and MP2/cc-pVDZ levels of theory, were used for the determination. Their computed geometrical parameters and rotational constants were in good agreement with the experimental ones. They found that the basis set superposition error was crucial in giving the equatorial conformer as the most stable structure in accord with the experimental observation. Both the high barrier to interconversion between the axial and equatorial conformers and their low energy difference explained why the intensity ratio experimentally observed for them remains unchanged when different carrier gases were employed.

Ennari et al. (2001) had used polymer software to gain a greater understanding of the behavior of the conduction mechanisms and to predict the conductivity of new Poly (ethylene oxide), PEO, -based proton conducting membranes suitable of PEM fuel cells. The understanding of conduction mechanism was very important when developing new material. As experimental and theoretical methods faiedl to give insight into these mechanisms, Ennari and coworkers turned to molecular modeling techniques that showed the structure of a material as a function of time and, therefore, should offer insight into conduction mechanism. He studied three different mechanisms: the hopping mechanism, where the proton hopped from one water molecule to another; the classical diffusion mechanism, where the hydronium ions were diffusing; and a mechanism where the cation (proton or hydronium ion) moved inside the helix of the PEO from one EO to another. To predict the conductivity, the diffusion coefficients were calculated. The diffusion coefficients were calculated using molecular dynamics methods. It could be seen that the protons were the most mobile ions in material 1, containing 90 wt% water. In material 2, containing only 35 wt% water, both the hopping mechanism and the classical diffusion mechanism were important, and hence the behavior of protons and hydronium ions would have a great influence on the electrolyte's performance. Thus, the amount of the water had a significant effect on the conduction mechanism. These discoveries increased the understanding of the behavior of protons and hydronium ions through the electrolyte, which would, in turn, lead to design of improved electrolytes and better fuel cell performance. They said molecular modeling had been shown to be an efficient tool used to gain a mechanistic understanding, which could not be easily obtained theoretically or experimentally. In the future, simulations would play a vital role in the design of new materials.

Krajewska (2001) had investigated diffusion of metal ions gel chitosan membranes. He found that the diffusive permeability of 15 metal ion (alkali, alkali earth and transition) were measured for water-swollen gel chitosan membranes: for an unreacted chitosan membranes and four chitosan membrane crosslinked with glutaraldehyde of concentrations between 0.01 amd 1% and coated with a protein, and also for comparison for a commercial Cuprophan membrane. The results were compared with those of nonelectrolytes in terms of the capillary pore and free volume models of solute diffusion through gel membranes While for Cuprophanthe permeability coefficients of the metal ions obeyed the models, those for chitosan membranes were found lower than predicted, the largest deviation being for the transition metal ions. The order of their permeability coefficients: Cu<Ni<Zn<Mn<Pb<Co<Cd<Ag corresponds to the metal ion-chitosan affinity series, which proves that chelation of these ions by chitosan is responsible for the deviation. Mg,Ca and Ba ions were also found to be retained by chitosan membranes, though to a lesser degree, whereas KNH_4, Na and Li ions exhibited minor deviations from the models, attributed to electrostatic interactions. The diffusive properties of chitosan membranes towards metal ions offer potential for protection chitosan-based biological system against destructive effects of heavy metal ions.

Smith et al. (2002) used molecular dynamics simulations to perform a model polymer-nanoparticle composite (PNPC) consisting of spherical nanoparticles in a bead-spring polymer melt. They determined the polymer-mediated elective interaction (potential of mean force) between nanoparticles was determined as a function of polymer molecular weight and strength of the polymer-nanoparticle interaction. For all polymer-nanoparticle interactions and polymer molecular weights investigated the range of the matrix-induced interaction was greater than the direct nanoparticle-nanoparticle interaction employed in the simulations.

Wan et al. (2002) had investigated the ion conductivity of chitosan membrane. The chitosan membranes with the various degrees of deacetylation and deifferent molecular weights (MW) were prepared by film casting with the aqueous solutions of chitosan and acetic acid. Ultraviolet (UV) spectrometry and infrared (IR) spectrometry were used to determine the degree of deacetylation (DDA) of chitosan. The viscosity-average MW of chitosan was measured in an aqueous solvent system of 0.25 M CH_3COOH/0.25 M CH_3COONa. The intrinsic ionic conductivities of the hydrated chitosan membranes were investigated using impedance spectroscopy. It was found that the intrinsic ionic conductivity was as high as 1024 S cm^2 after hydration for 1 h. The tensile strength and breaking elongation of the membranes were evaluated according to standard ASTM methods. The crystallinity and swelling ratio of the membranes were examined. A tentative mechanism for the ionic conductivity of chitosan membranes was also suggested.

Ogawa et al. (2003) had studied to crystal structures of two polymorphs of chitosan, tendon (hydrated) and annealed (anhydrous) polymorphs, had been reported. In both crystals, chitosan molecule taked up similar conformation (Type I form) to each other, an extended two-fold helix stabilized by intramolecular O(3)-O(5) hydrogen bond, which was also similar to the conformation of chitin or cellulose. Three chitosan conformations other than Type I form had been found in the crystals of chitosan-acid salts. In the salts with acetic and some other acids, called Type II salts, chitosan molecule taked up a relaxed two-fold helix composed of asymmetric unit of tetrasaccharide. This conformation seems to be unstable because no strong intramolecular hydrogen bond like Type I form. Type II crystal changed to the annealed polymorph of chitosan by a spontaneous water-removing action of the acid. Chitosan molecule in its hydrogen iodide salt prepared at low temperature takes a 4/1 helix with asymmetric unit of disaccharide. The fourth chitosan conformation was found to be a 5/3 helix in chitosan salts with medical organic acids having phenyl group such as salicylic or gentisic acids. Similar conformation of chitosan molecule in the aspirin (acetylsalicylic acid) salt was suggested by a solid-state NMR measurement.

Yamamoto (2003) applied molecular dynamics simulation to investigate the molecular pathways of polymer crystallization and the structure of crystal-melt interfaces. He adopted a simplified molecular model for polymethylene-like chains; the chain was made of CH_2-like beads connected by harmonic springs, and the lowest energy conformation was a linear stretched sequence of the beds with slight bending stiffness being imposed.

Arab et al. (2003) set up molecular dynamics calculations of hydrated zinc ion to show the formation of a stable octahedral hydration shell around the Zn^{2+} ion. They found that the bond lengths of OH in the octahedral molecules were longer than outside the shell by 0.02 A. They also analyzed the density of vibrational states in terms of motions of the building entities and proposed a description of the dynamics of $Zn(H_2O)^{2+}$ 6 octahedron. Finally, the compared the results with the experimental data and found that they are in good agreement.

Gallant (2003) presented a simple model of single- and multicomponent protein adsorption in a spherical particle. The model included radial diffusion of salt and protein in the liquid phase coupled to adsorption by ion-exchange mechanism described by the steric mass action isotherm. The molecular diffusivities of the protein and salt were reduced in the model by a factor which accounts for the tortous nature of the pores and pore constrictions. The model parameters were selected from published values in the chromatographic literature. Of particular interest were the observations of induced salt gradients during protein adsorption and of multicomponent displacement displacement when more that one protein was adsorbed simultaneously. These results could not be predicted on the basis of the traditional Langmuir isotherm or other currently available descriptions of adsorption. The use of such a model during stationary phase design was discussed.

Mazeau and Rinaudo (2004) mentioned that molecular modeling was a convenient technique to predict the behavior of polymers in solution as well as in the solid state; also, interaction with water and other small molecules could be examined. In their article, the main techniques used for molecular modeling of polysaccharides were briefly recalled and applied to different systems for which the chemical structure was known (allowing valuable description of the molecule). They indicated that experimental determination of the local conformation by NMR or of the global dimension of galactomamnan and chitosan chains by light scattering were compared with the corresponding predicted parameters with good agreement; interaction of amylase with water was studied by thermogravimetry and DSC and strongly interacting water were localized by molecular modeling. At end, modeling of crystalline and amorphous solids together with surface interaction was presented. For the first time, this article demonstrated from a series of data obtained in their laboratory the validity of the molecular modeling approach proposed to predict the behavior of polysaccharide in solution or solid state.

Mukoma et al. (2004) investigated the proton conductivity of chitosan membrane used for the membrane of Proton Exchange Membrane fuel cell (PEMFC). Chitosan membranes cross-linked in sulfuric acid were evaluated for their thermal stability, water absorption. They mentioned that Chitosan membranes were found to be more hydrophilic than Nafion 117 in water uptake experiments. Chitosan membranes absorbed about 60% water on average compared with the 30% for Nafion 117. Preliminary TGA/DSC thermal stability studies showed that after the initial weight loss due to water, chitosan membranes decomposed in three stages with the final stage beginning at about 300 ^{o}C. Chitosan membranes proton conductivities under various temperature and humidity conditions were reported and compared with that for the commercial membrane Nafion 117. Partially-hydrated chitosan membranes at ambient temperature displayed a proton conductivity of about 0.005 S cm-1 as opposed to 0.08 S cm-1 for Nafion 117 under the same conditions. At 60 ^{o}C (full hydration) Nafion 117 membranes had a conductivity of about 0.12 S cm^{-1} and chitosan membranes have 0.02 S cm^{-1}.