

CHAPTER VI

SUMMARY

6.1 Cyclen-Methanol Potential Function

In the first part of this work, detail development of the intermolecular potential function for cyclen and methanol was presented using the STO-3G/SCF calculations. The function was fitted and tested until convergency of standard deviation in the final step of 0.95 kcal/mol for 600 SCF data points was reached.

The final form of cyclen-methanol potential function is

$$\Delta E \text{ (kcal / mol)} = \sum_{i=1}^6 \sum_{j=1}^{32} \left[-\frac{|A_{ij}|}{r_{ij}^7} + \frac{|B_{ij}|}{r_{ij}^{10}} + \frac{q_i q_j}{r_{ij}} \right]$$

where A_{ij} and B_{ij} are fitting parameters. r_{ij} is the distance (in atomic unit) between the i th atom of methanol and the j th atom of cyclen. q_i and q_j are the net charges of the i th atom of methanol and the j th atom of cyclen, respectively.

6.2 Cyclen-Water-Methanol Simulation

In the second part, the Monte Carlo simulation for one cyclen molecule in the mixture of 165 water and 37 methanol molecules has been performed using the newly develop cyclen-methanol potential function together with the water-water, water-methanol, methanol-methanol and cyclen-water functions taken from literatures. The system was performed at 298 K, 1 atm., and the experimental density of 0.96 g/cm³. The resulting solvation structure around ligand can be summarized as :

1) Two water molecules locate unsymmetrically by pointing the O-H bond toward the ligand's cavity. The distances between center of mass of cyclen and the oxygen atom is 2.3-3.4 Å for W1 and 3.4-4.0 Å for W2 above and below the molecular center.

2) Four water molecules lie in the region around NH functional groups of cyclen. They are held in place by forming hydrogen bond with the first two water molecules, but not with the NH groups.

3) The second solvation shell of cyclen still consists mainly of water molecules, i.e., 23-24 water and only one methanol molecules. This methanol molecule is found to form hydrogen bond with W2.

4) An arrangement of solvent molecules around cyclen has been observed up to the third shell, 8-9 Å far from the molecular center, while ideal characters of bulk solvents were not disturbed.

6.3 Suggestions for Future Work

1) As it has already been mentioned in page 22 about the justification of employing STO-3G basis set in this work, it is thought that such justification is still valid for other similar systems that may be topics of further study.

2) In this study it was found that two water molecules are strongly coordinated to the ligand and hydrogen bonding to the donor atoms of cyclen (NH) were not detected which resulted from a weaker ligand-solvent interactions than solvent-solvent interactions. Relative sizes between solvent and solvent, ligand and solvent are responsible for such a nature of interactions thus observed ($\text{CH}_3\text{OH} > \text{H}_2\text{O}$, cyclen \gg CH_3OH , cyclen $\gg\gg$ H_2O). It is therefore thought worthwhile to recommend for future study on systems with the following characters :

- a system where the ligand-solvent interaction is stronger than the solvent-solvent one,
- a system where the ligand cavity is bigger, for example those similar to cyclen but with 5, 6 and 7 donor atoms, and
- a system where the solvent molecules is larger than the previous investigated systems, for example formic acid (HCOOH), acetic acid (CH_3COOH) etc.