REFERENCES

1. Cram, D.J., and Cram, J.M. Design of Complexes between Synthetic Hosts and Organic Guests. Acc. Chem. Res. 11 (1978): 8-14.
2. Christensen, J.J., Eatough, D.J., and Izatt, R.M. The Synthesis and Ion Binding of Synthetic Multidentate Macrocyclic Compounds. Chem. Rev. 74 (1974): 351-384.
3. Izatt, R.M., Christensen, J.J., and Hill, J.O. Science 174 (1971): 459.
4. Cabbiness, D.K., and Margerum, D.W. Macrocyclic Effect on the Stability of Copper(II) Tetramine Complexes. J. Am. Chem. Soc. 91 (1969): 6540-6541.
5. Smith, G.F., and Margerum, D.W. Diminution of the Macrocyclic Effect for Nickel(II) Complexes of Thioethers in Nonaqueous Solvents. J.C.S. Chem. Comm. (1975): 807-808.
6. Fabbrizzi, L.,Paoletti, P., and Lever, A.B.P. Relationship between Electronic Spectra and Heat of Formation of Some Copper-Polyamine Complexes and the Macrocyclic Effect. Inorg. Chem. 15 (1976): 1502-1506.
7. Hancock, R.D., and McDougall, G.J. Origin of Macrocyclic Enthalpy. J. Am. Chem. Soc. 102 (1980): 6551-6553.
8. Rode, B.M., Ruangpornvisuti, and Hannongbua, S.V. The Role of Solvation for the Macrocyclic Effect. J. Sci. Soc. Thailand. 13(1987): 47-55.
9. ———, and Hannongbua, S.V. Quantum Chemical Calculation on Structure and Bonding of Macrocyclic Complexes of Li(I) and Na(I). Inorg. Chim. Acta 96 (1985): 91-97.
10. Hinz, F.P., and Margerum, D.W. Ligand Solvation and the Macrocyclic Effect. A Study of Nikel(II)-Tetramine Complexes. Inorg. Chem., 13 (1974): 2941-2949.
11. Fabbrizzi, L., Paoletti, P., and Clay, R.M. Microcalorimetric Determination of the Enthalpy of a Slow Reaction : Destruction with Cyanide of the Macrocyclic (1,4,8,11-Tetraazacyclotetradecane)nickel(II) Ion. Inorg. Chem. 17 (1978): 1042-1046.

12. McDougall, G.J., Hancock, R.D., and Boeyens, J.C.A. Empirical Force-field Calculations of Strain-energy Contributions to the Thermodynamics of Complex Formation. Part1. The Difference in Stability between Complexes containing Five- and Six-membered Chelate Rings. J.C.S. Dalton (1978): 1438-1444.
13. Hannongbua, S.V., and Rode, B.M. Quantum-Chemical Investigations on the Interaction of Alkaline-Earth-Metal Ions with Macrocyclic Compounds. Inorg.Chem. 24 (1985): 2577-2580.
14. Peng, S.M., and Goedken, V.L. **Coordination Chemistry of Macrocyclic Compounds**. New York: Plenum Press, 1978.
15. Hancock, R.D., and McDougall, G.J. Advance in Molecular Relaxation and Interaction Process. 18 (1980): 99.
16. Busch, D.H., Farmery, K., Goedken, V., Katovic, V., Melnyk, A.C., Sperati, C.R., and Tokel, N. Adv. Chem. Ser. 100 (1971): 44.
17. Kodama, M., and Kimura, E. Equilibrium of Complexes Formation between Several Bivalent Metal Ions and Macrocyclic Tri- and Penta-amines. J.C.S. Dalton (1978): 1081-1085.
18. Boys, S.F., and Bernardi, F. The Calculation of Small Molecular Interactions by the Differences of Separate Total Energies. Some Procedure with Reduced Errors. Mol. Phys. 19 (1970): 533-566.
19. Metropolis, N., Rosenbluth, A.W., Rosenbluth, M.N., Teller, A.H., and Teller, E. Equation of State Calculations by Fast Computing Machine. J. Chem. Phys. 21 (1953): 1087-1092; Barker, J.A., and Watts, R.O. Structure of Water; a Monte Carlo Calculation. Chem. Phys. Lett. 3 (1969): 144.
20. Rahman, A., and Stillinger, F.H. Molecular Dynamics Study of Liquid Water. J. Chem.Phys. 55 (1971): 3336-3359; Hydrogen-Bond Patterns in Liquid Water. J. Am. Chem. Soc. 95 (1073): 7943-7948; Ben-Naim, A., and Stillinger, F.H. In R.A. Horn (ed.), **Water and Aqueous Solutions.** New York: Wiley, 1974.
21. Stillinger, F.H., and Rahman, A. Improved Simulation of Liquid Water by Molecular Dynamics. J. Chem. Phys. 60 (1974): 1545-1557.
22. Slater, J.S. Phys. Rev. 34 (1929): 1293.
23. ——— Phys. Rev., 36 (1930): 57.

24. Boys, S.F. Proc. Rov. Soc., A207 (1951): 181.
25. Whitten, J.L. Gaussian Expansion of Hydrogen-Atom Wavefunctions.J. Chem. Phys. 39 (1963): 349-352.
26. ——— Gaussian Lobe Function Expansions of Hartree-Fock Solutions for the First-Row Atoms and Ethylene. J. Chem. Phys. 44 (1966): 359-364.
27. Fosdisk, L.D. Methods Comp. Phys. 1 (1963): 245.
28. Kimura, K., and Kubo, M. Structure of Dimethyl Ether and Methyl Alcohol. J. Chem Phys. 30 (1959): 151-158.
29. Dupuis, M., Rys, J., and King, H.F. Evaluation of Molecular Integrals over Gaussian Basis Functions. J. Chem. Phys. 65 (1976): 111-116.
30. Jorgensen, W.L., and Cournoyer, M.E. An Intermolecular Potential Function for the Hydrogen Fluoride Dimer from ab Initio 6-31G Computations. J. Am. Chem. Soc. 100 (1978): 4942-4945.
31. Weast, R.C. **CRC Handbook of Chemistry and Physics**. 64th Edition, Florida: CRC Press, 1983-1984.
32. Lie, G.C., Clementi, E., and Yoshimine, M. Study of the structure of molecular complexes. XIII. Monte Carlo simulation of liquid water with a configuration interaction pair potential. J. Chem. Phys. 64 (1976): 2314-2323.
33. Kim, S., Jhon, M.S., and Scheraga, H.A. Analytic Intermolecular Potential Functions from ab Initio SCF Calculation of Interaction Energies between CH_4, CH_3OH, CH_3COOH, and CH_3COO^- and Water. J. Phys. Chem. 92 (1988): 7216-7223.
34. Jorgensen, W. Structure and Properties of Liquid Methanol. J. Am. Chem. Soc. 102 (1980): 543-549.
35. Udomsub, S. A Monte Carlo Study on the Influence of Macrocyclic Compound on the Structure of Water and Ammonia Mixture., Master thesis (to be published), Chem. Dept., Fac. Science, Chulalongkorn Univ., Bangkok, Thailand (1994).

APPENDIX

1). Potential Function for Water-Water [32]

$$\Delta E\ (\text{kcal/mol}) = 332.052\ q^2\left[\left(\frac{1}{r_{13}}+\frac{1}{r_{23}}+\frac{1}{r_{14}}+\frac{1}{r_{24}}\right)+\frac{4}{r_{78}}-2\left(\frac{1}{r_{28}}+\frac{1}{r_{18}}+\frac{1}{r_{37}}+\frac{1}{r_{47}}\right)\right]$$

$$+ a_1\exp(-b_1 r_{56}) + a_2\{\exp(-b_2 r_{13}) + \exp(-b_2 r_{14}) + \exp(-b_2 r_{23}) + \exp(-b_2 r_{24})\}$$

$$+ a_3\{\exp(-b_3 r_{16}) + \exp(-b_3 r_{26}) + \exp(-b_3 r_{35}) + \exp(-b_3 r_{45})\}$$

$$+ a_4\{\exp(-b_4 r_{16}) + \exp(-b_4 r_{26}) + \exp(-b_4 r_{35}) + \exp(-b_4 r_{45})\}$$

where r_{ij} denote the distances (in atomic unit) between the ith atom and the jth atoms of the first and the second water molecules, respectively.

R_{OH} = 0.9572 Å, HÔH = 104.5°
a_1 = 1088213.2 kcal/mol
a_2 = 666.3373 kcal/mol
a_3 = 1455.427 kcal/mol
a_4 = 273.5954 kcal/mol
b_1 = 5.152712 $Å^{-1}$
b_2 = 2.760844 $Å^{-1}$
b_3 = 2.961895 $Å^{-1}$
b_4 = 2.233264 $Å^{-1}$
and q = 0.717492e (positive charge situated on each hydrogen atom).

The hydrogen atoms are labelled 1-4 and the oxygen atoms are labelled 5 and 6 for the first and second water molecules, respectively. The labels 7 and 8 refer to a point charges situated in the axis of the diploe-moment vector of the two water molecules.

2). Potential Function for Water-Methanol [33]

$$\Delta E \text{ (kcal / mol)} = \sum_{i=1}^{3} \sum_{j=1}^{6} \left[\frac{A_{ij}}{r_{ij}^{12}} + \frac{B_{ij}}{r_{ij}^{4}} + 332.072 \frac{q_i q_j}{r_{ij}} \right]$$

where A_{ij} and B_{ij} are the fitting parameters. r_{ij} are the distances (in angstrom) between the ith atom of water and the jth atom of methanol molecules, respectively. q_i and q_j are the atomic net charges of the ith atom and the jth atom obtained from the population analysis of isolated molecules.

water : $q_O = -0.792$, $q_H = 0.396$
methanol : $q_C = -0.128$, $q_O = -0.736$, $q_{Ho} = 0.398$, $q_H = 0.181$, $q_{H'} = 0.143$
atoms : i = water ; j = methanol

i - j	A_{ii} (kcal.Å^{12}/mol)	B_{ii} (kcal.Å^{4}/mol)
O-C	183804.8130	-314.5004
O-O	631722.1250	-533.0015
O-H_O	353.7631	18.0778
O-H_C	110900.2420	73.4145
H-C	2553.5139	78.9566
H-O	0.0096	39.8765
H-H_C	659.9979	5.4744
H-H_C	235.6463	-10.5887

3). Potential Function for Methanol-Methanol [34]

The methanol-methanol function is the five-center model. The sites are the oxygen atom, the hydroxyl hydrogen, the two pseudo-lone pairs placed tetrahedrally on the oxygen, and the methyl group which was treated as a unit centered on the carbon.

$$\Delta E \text{ (kcal / mol)} = \sum_{i<j}^{4} \frac{q_i q_j}{r_{ij}} + \sum_{i<j}^{3} \left[\frac{A_{ij}}{r_{ij}^{6}} + \frac{B_{ij}}{r_{ij}^{12}} \right]$$

where A_{ij} and B_{ij} are the fitting parameters. r_{ij} are the distances(in angstrom) between the ith atom and the jth atom of the first and the second methanol molecules, respectively. q_i and q_j are the atomic net charges of the ith atom and the jth atom obtained from the population analysis of isolated molecules.

For the Coulombic term, charges were placed on the lone pairs, the hydrogen and carbon. The second sum which represents the short-range interactions is over pairs of atoms (H_O, O, methyl (Me)) with types i and j in the different monomers.

methanol : $q_{Me} = (2.007585)^a$, $q_L{}^b = -2.716198$, $q_H = 3.424811$
$R_{OL} = 0.7547260$ Å.

Parameters for methanol-methanol function ;

i-j	A (kcal.Å^6/mol)	B (kcal.Å^{12}/mol)
O-O	-457.0440	504358.3000
H_O-H_O	95.7027	621.4455
Me-Me	3097.0090	670395.2000
O-H_O	-201.9707	1286.5600
O-Me	-966.8230	772968.9000
H_O-Me	290.1323	35961.2400

[a] Value determined from neutrality. [b] Two-point charges (L) are placed on the COH bisector at distances of R_{OL} from the oxygen and with ∠LOL = 109.47°.

4). Potential Function for Cyclen-Water [35]

$$\Delta E\ (\text{kcal/mol}) = \sum_{i=1}^{3}\sum_{j=1}^{32}\left[-\frac{|A_{ij}|}{r_{ij}^{6}} + \frac{|B_{ij}|}{r_{ij}^{12}} + \frac{C_{ij}}{r_{ij}^{4}} + q_i q_j \left\{ \frac{1}{r_{ij}} + \frac{1}{r_{ij}^{2}} \right\} \right]$$

where A_{ij} , B_{ij} and C_{ij} are the fitting constants. r_{ij} are the distances between the ith atom of water and the jth atom of cyclen in angstrom. q_i and q_j are the atomic net charges of the ith atom of water and the jth atom of cyclen obtained from the population analysis of isolated molecules.

water : $q_O = -0.366$, $q_H = 0.183$,
cyclen : $q_N = -0.315$, $q_C = -0.005$, $q_{H_N} = 0.141$, $q_{H_C} = 0.033$, $q_{H'_C} = 0.059$

Parameters for N, C, H_N, H_C, and H'_C atoms for cyclen interacting with ;

(a) oxygen atom of water

Atom	A (kcal.Å^6/mol)	B (kcal.Å^{12}/mol)	C (kcal.Å^4/mol)
N	0.018104	231435.875	-33.023247
C	90.884262	2070439.25	-40.530121
H_N	846.894897	319998.125	6.073781
H_C	0.015756	2212.004395	-8.644856
H'_C	0.042105	773.339661	-20.269018

(b) hydrogen atoms of water

Atom	A (kcal.Å^6/mol)	B (kcal.Å^{12}/mol)	C (kcal.Å^4/mol)
N	30.807240	78.845123	-17.557161
C	105.299133	59179.027344	-15.969069
H_N	0.222827	4776.553711	20.378920
H_C	0.004503	0.338516	17.222708
H'_C	0.010923	1573.516113	15.751525

5). STO-3G Basis Set

Atom	*Shell*	*Exponent*	*s-coefficient*	*p-coefficient*
N				
	S	99.106169	0.154329	
		18.052312	0.535328	
		4.885660	0.444635	
	SP	3.780456	-0.099967	0.155916
		0.878497	0.399513	0.607684
		0.285714	0.700115	0.391957
O				
	S	130.709321	0.154329	
		23.808866	0.535328	
		6.443608	0.444635	
	SP	5.033151	-0.099967	0.155916
		1.169596	0.399513	0.607684
		0.380389	0.700115	0.391957
C				
	S	71.616837	0.154329	
		13.045096	0.535328	
		3.530512	0.444635	
	SP	2.941249	-0.099967	0.155916
		0.683483	0.399513	0.607684
		0.222290	0.700115	0.391957
H				
	S	3.425251	0.154329	
		0.623914	0.535328	
		0.168855	0.444635	

CURRICULUM VITAE

Miss Bussakorn Pongsai

1970	Born July, 28th in Lopburi, Thailand Father : Mr. Sakol Pongsai Mother : Mrs. Tongpool Pongsai
1982-1987	High School (Pattananikom, Lopburi)
1988-1991	Bachelor of Science (Chemistry), Chulalongkorn University
1992-	Master degree studies at Department of Chemistry, Chulalongkorn University