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A MONTE CARLO STUDY ON THE INFLUENCE OF MACROCYCLIC
COMPOUND ON THE STRUCTURE OF WATER
AND AMMONIA MIXTURE

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ได้ทำการศึกษาสมบัติเกี่ยวกับโครงสร้างของสารละลาย 1,4,7,10 - เตตราอะซาไซโคล-
โดเดเคน (ไซคลีน) ใน 18.45 โมลเปอร์เซ็นต์แอมโมเนียในน้ำโดยวิธีมอนติ คาร์โล โดยใช้ศักย์
ฟังก์ชันระหว่างไซคลีน-แอมโมเนียและไซคลีน-น้ำที่พัฒนาขึ้นมาใหม่ ด้วยการใช้เบสิสเซตชนิด STO-
3G ที่ไม่รวมการแก้ไขของบอยด์-แบนาร์ดี เคานท์เตอร์พอยส์ โดยได้พิจารณาคัดเลือกเปรียบเทียบกับ
เบสิสเซต 3-21G, 6-21G, 6-31G, DZV, DZ และ DZP แล้ว ส่วนศักย์ฟังก์ชันคู่อื่นที่เกี่ยวข้อง
ได้เลือกจากวารสารวิจัย ในการคำนวณครั้งนี้ได้เลือกใช้ค่าตัวแปรและวิธีการต่าง ๆ ดังนี้ รูปร่างทาง
เรขาคณิตสำหรับโมเลกุลแอมโมเนียและน้ำจากการทดลอง ความหนาแน่นของสารละลายแอมโม-
เนียเข้มข้น 18.45 โมลเปอร์เซ็นต์จากการทดลองที่ 298 เคลวิน และ 1 บรรยากาศ โครงแบบเริ่มต้น
ที่ได้จากการสุ่ม เส้นโซ่พรีออดิก บาวนด์ารี และโพเทนเทียล คัทออฟที่ระยะครึ่งหนึ่งของความยาว
กล่องลูกบาศก์ ได้ทำการทดลองจำนวน 35 ล้านโครงแบบ เพื่อที่จะทดสอบลักษณะไดนามิกส์ของ
สารละลาย ผลการศึกษาทำให้สามารถแยกชั้นของการซอลเวชันรอบโมเลกุลไซคลีนได้เป็น 2 ชั้น
อย่างชัดเจน ชั้นซอลเวชันชั้นใน ประกอบด้วยน้ำ 6 โมเลกุล ในจำนวนนี้ 2 โมเลกุล (อัตราส่วนที่พบ
1 และ 2 โมเลกุลน้ำมีค่า 1:2.3 ทำให้ได้ค่าเฉลี่ย 1.7) จะอยู่ใกล้ ๆ โพรงของไซคลีนโดยจะชี้อะตอม
ไฮโดรเจน 1 อะตอมไปที่โพรง ส่วนน้ำที่เหลืออีก 4 โมเลกุลจะอยู่บริเวณใกล้กับหมู่ฟังก์ชัน NH และ
เกิดพันธะไฮโดรเจนกับน้ำ 2 โมเลกุลแรก แต่ไม่เกิดพันธะไฮโดรเจนกับหมู่ NH สำหรับส่วนในของ
ชั้นซอลเวชันชั้นนอก จะประกอบด้วยแอมโมเนีย 3 โมเลกุล ซึ่งยึดอยู่กับน้ำ 6 โมเลกุลในชั้น
ซอลเวชันชั้นในโดยเกิดพันธะไฮโดรเจน ในขณะที่ส่วนนอกของชั้นซอลเวชันชั้นนอกแสดงลักษณะใน
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ซอลเวชันมีส่วนทำให้เกิดปรากฏการณ์แมกโครไซคลิก

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ลายมือชื่อนิสิต สรียาพร อุดมทรัพย์
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Structural properties of 1,4,7,10-tetraazacyclododecane (cyclen) in 18.45 mol% aqueous ammonia solution have been studied, based on the Monte Carlo method. The cyclen-ammonia and cyclen-water potential functions have been newly developed. The STO-3G, 3-21G, 6-21G, 6-31G, DZV, DZ and DZP basis sets with and without applying the Boys-Bernardi counterpoise corrections have been considered, and the STO-3G set without the correction has been selected. The other related pair functions were taken from the literature. The following variables and algorithm have been applied: experimental geometries of water and ammonia molecules, experimental density of 18.45 mol% aqueous ammonia at 298. K and 1 atm., random starting configurations, periodic boundary conditions, and potential cutoff at half of the cube length. The simulations were carried out for 35 million configurations, in order to examine dynamic characteristics of the solution. A clear picture of cyclen's solvation sphere has been proposed, consisting of two layers. The *inner solvation shell* contains 6 water molecules; 2 of them (the ratio for having one and two is 1:2.3, leading to an average number of 1.7), are located closely and point one hydrogen atom to cyclen's cavity, and the other 4 water molecules are located near NH groups and bound to those two water molecules via hydrogen bonds, but are not bound to the NH groups. An inner part of the *outer solvation shell* accumulates 3 ammonia molecules, held in place by forming hydrogen bond with the 6 water molecules, while the outer part of this shell shows *ideal* characteristics of bulk water-ammonia solvent. On the basis of obtained data, the *solvation effect* is found to partially explain the existence of the *macrocylic effect*.

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CONTENTS



	Pages
Abstract in Thai.....	iv
Abstract in English.....	v
Acknowledgement.....	vi
List of Figures.....	xi
List of Tables.....	xvi
CHAPTER I INTRODUCTION.....	1
1.1 Ligand solvation: open questions regarding the macrocyclic effect.....	1
<i>enthalpic contribution</i>	1
<i>entropic contribution</i>	2
1.2 Factors influencing the macrocyclic effect.....	3
1.3 The significance of macrocyclic compounds.....	3
1.4 Specification of the model.....	4
CHAPTER II QUANTUM CHEMICAL METHODS.....	5
2.1 The schrödinger equation.....	5
2.2 Molecular orbital theory.....	6
2.3 Self-consistent field procedure.....	8
2.4 Mulliken population analysis.....	11
2.5 Basis set superposition error (BSSE).....	11
CHAPTER III MONTE CARLO METHOD.....	13
3.1 Basic principles of Monte Carlo method.....	14
3.2 Conditions for the calculations.....	15

	Pages
3.2.1 The cubic size.....	15
3.2.2 The constant number of particle.....	15
3.2.3 The starting configuration.....	16
3.2.4 The periodic boundary condition.....	16
3.2.5 The spherical cut-off.....	18
3.2.6 Long-range interactions.....	19
3.3 Steps of calculations.....	19
3.4 Radial distribution Functions and running intergration number.....	22
CHAPTER IV DETAILS OF THE CALCULATIONS.....	23
4.1 Development of interpotential function.....	23
4.1.1 Selection of the geometries the pairs.....	25
4.1.2 Selection of a reliable basis set for theSCF calculations.....	28
4.1.3 Performance of the SCF calculations.....	29
4.1.4 Fitting of the pair interaction energies to a functional form.....	30
4.1.5 Testing the quality of the function.....	31
4.2 Specification of the model system.....	31
4.3 Monte Carlo studies of 1,4,7,10-tetraazacyclododecane in aqueous ammonia.....	32
4.3.1 Characteristics of the simulations.....	32
4.3.2 Defect in the HR potential for cyclen-water interactions.....	34
4.3.3 Development of the cyclen-water potential function.....	35
4.3.4 Monte Carlo simulations with the new cyclen-water function.....	35

	Pages
4.4	BSSE for cyclen-water interactions.....36
CHAPTER V	RESULTS AND DISCUSSION.....37
5.1	Selection of a reliable basis set.....37
5.2	Intermolecular potential function.....39
5.2.1	Cyclen-ammonia potential function.....39
5.2.2	Cyclen-water potential function.....42
	<i>The HR potential</i>42
	<i>The newly developed potential</i>44
	<i>Basis set superposition error</i>46
5.3	Solvation structure of the cyclen molecule in an aqueous ammonia solution.....48
5.3.1	Solvent structure.....50
	<i>Water-water</i>52
	<i>Ammonia-ammonia</i>52
	<i>Water-ammonia</i>52
5.3.2	Water structure around the cyclen molecule.....53
	<i>Overview</i>53
	<i>The solvent exchange</i>56
	<i>Nearest neighbors</i>62
	<i>The hydrogen bond</i>66
	<i>The outer hydration shell</i>71
	<i>Conclusion for the first-order solvation shell</i>73
5.3.3	Ammonia structure around cyclen molecule.....73
CHAPTER VI	CONCLUSIONS AND COMMENTS.....77
6.1	On the basis set.....77
6.2	On the solvent structure.....77
6.3	On the entire solvation shell of cyclen.....78
6.4	On the macrocyclic effect.....78

	Pages
6.5 Predictions for other systems.....	79
6.6 On further study.....	80
REFERENCES.....	81
APPENDIXES.....	86
Appendix I Exponents and coefficients for 7 basis sets.....	87
Appendix II Optimized coefficients in the analytical pair potential functions.....	95
Appendix III Programme generates HONDO input/output and calculates stabilization energy and coordinate (FORTRAN).....	97
Appendix IV HONDO input file.....	99
CURRICULUM VITAE.....	100

LIST OF FIGURES

Figures	Pages
3.1 A two-dimensional periodic system.....	17
3.2 The minimum image convention in a two-dimensional system.....	18
3.3 The calculating steps of the Monte Carlo simulations.....	20
3.4 State v' is generated from state v by displacing atom i from r^v to $r^{v'}$	21
3.5 Accepting uphill moves in the MC simulation.....	22
4.1 The <i>alternate form</i> of 1,4,7,10-tetraazacyclododecane.....	25
4.2 The optimized coordination of solvent molecule interacting with 1,4,7,10-tetraazacyclododecane.....	26
4.3 Cyclen-water configurations where a) global minimum and b) the unwanted minima take place.....	34
5.1 The stabilization energies obtained from the STO-3G <i>ab initio</i> calculations (solid line) and from the cyclen-ammonia function shown in equation [4.4] (dashed line) with the fitting parameters given in Table 5.3 versus the N-origin distance (Figure 4.2).....	41

Figures	Pages
5.2	Comparison of the stabilization energies from the STO-3G <i>ab initio</i> calculations, ΔE_{SCF} , and from the cyclen-ammonia potential function, ΔE_{FIT} , shown in equation [4.4] with fitting parameters given in Table 5.3.....42
5.3	Potential energy curves obtained from the HR potential (dashed lines) and from the <i>ab initio</i> calculations using the STO-3G basis set (solid lines) where water molecule lies in: <ul style="list-style-type: none"> a) the optimal direction (Figure 4.3a), b) the direction where the unwanted minimum occurs (Figure 4.3b) and, c) the direction along the N-H bond of cyclen.....43
5.4	The stabilization energies obtained from the STO-3G <i>ab initio</i> calculations (solid line) and from the cyclen-water function shown in equation [5.1] (dashed line) with the fitting parameters given in Table 5.4 versus the O-origin distance (Figure 4.2).....45
5.5	Comparison of the stabilization energies from the STO-3G <i>ab initio</i> calculations, ΔE_{SCF} , and from the cyclen-water potential function shown in equation [5.1] with the fitting parameters given in Table 5.4, ΔE_{FIT}46
5.6	The cyclen-water stabilization energy for the optimal direction (see Figure 4.3a) as a function of the O-origin distance, calculated with (dashed line) and without BSSE (solid line) using <ul style="list-style-type: none"> a) the STO-3G basis set b) the DZP basis set.....48
5.7	The solvent-solvent configurations where global interaction energies (Table 5.6) occur for <ul style="list-style-type: none"> a) water-water, b) ammonia-ammonia and c) water-ammonia interactions.....49

Figures	Pages
5.8 H ₂ O/H ₂ O (top), NH ₃ /NH ₃ (middle) and H ₂ O/NH ₃ (bottom) radial distribution functions obtained from the Monte Carlo simulations of 18.45 mol% of aqueous ammonia solution with a) one cyclen molecule, b) one Li(I), and c) without solute.....	50
5.9 Orientation of the cyclen molecule in the coordinate system, indicating top, side and plane regions.....	53
5.10 Distributions of a) water, b) ammonia and c) both solvent molecules taken from one out of several million configurations of a cyclen molecule in a 18.45 mol% aqueous ammonia solution.....	55
5.11 The E-O (solid line) and E-N (dashed line) radial distribution functions.....	55
5.12 The E-O (solid line) and E-H (dashed line) radial distribution function for the 8th-35th million configurations.....	57
5.13 Distances between the oxygen atom of water and the center of mass of cyclen versus number of configurations for a) W1, b) W2 (for details see text), and c) any water molecules which approach closer than 4.2 Å to the cyclen's cavity.....	60
5.14 Radial distribution functions and corresponding running intergration numbers from O (solid line) and H (dashed line) of water to the centre of mass of cyclen in the following regions: a) entire, b) top, c) side, and d) plane.....	63

Figures	Pages
5.15 Distribution of angle, β , as defined in the attach, for W1 (dashed line) and W2 (solid line), which are situated in the first nearest neighbor site of cyclen.....	64
5.16 Proposed nearest neighbors of the cyclen molecule in a 18.45 mol% aqueous ammonia solution (values taken from the last million 3 out of 35 million configurations of the solution).....	65
5.17 Calculated atom-oxygen (solid line) and atom-hydrogen (dashed line) radial distribution functions and running integration numbers for a) N and b) H_N atoms of cyclen.....	66
5.18 Distribution of oxygen atoms of water around the following atoms of cyclen, integrated up to r_m of the RDFs, a) N, $r_m = 3.30 \text{ \AA}$ b) N, $r_m = 4.00 \text{ \AA}$ c) H_N , $r_m = 2.70 \text{ \AA}$	67
5.19 Distribution of γ , as defined in the attach, for water molecules lying not further than 3.30 \AA from the N atom of cyclen (solid line), and between 3.30 \AA and 4.00 \AA (dashed line).....	68
5.20 Distribution of angle τ , as defined in the attach, for W3 (see text for details).....	69
5.21 The two favourite configurations of W3 incoordinating, via hydrogen bond, with W1 (taken from one, out of 3 million, configurations).....	70
5.22 Distances and angle between atoms.....	71

Figures	Pages
5.23	Calculated atom-oxygen (solid line) and atom-hydrogen (dashed line) radial distribution functions and running intergration numbers of the (a) C, (b) H _C and (c) H _{C'} atoms of cyclen.....72
5.24	Center-nitrogen (solid line) and center-hydrogen (dashed line) radial distribution functions and corresponding integration numbers.....73
5.25	Distribution of nitrogen atoms of ammonia around center of mass of cyclen, integrated up to the first minimum of 7.00 Å of the g _{EN} (r).....74
5.26	Atom-nitrogen (solid line) and atom-hydrogen (dashed line) radial distribution functions and corresponding integration numbers for the a) N and b) H _N atoms of cyclen.....75
5.27	Atom-nitrogen (solid line) and atom-hydrogen (dashed line) radial distribution functions and corresponding integration numbers for the a) C and b) H _C and c) H _{C'} atoms of cyclen.....75
5.28	One out of 28 million configurations of the solvation shell of cyclen consisting of 6 water and 3 ammonia molecules.....76

LIST OF TABLES

Tables	Pages
4.1	Optimized Cartesian coordinates of 1,4,7,10-tetraaza-cyclododecane (in Angstroms).....27
5.1	Optimal N-origin or O-origin distance (R in Å), dipole moment (μ in Debyes), total energy (E in Hartrees), stabilization energy (ΔE in kcal/mol) and CPU time (minutes) obtained from the SCF calculations with different basis sets.....38
5.2	Number of SCF-data points (N), standard deviation (σ in kcal/mol), number of testing points (N_{test}) and σ_{test} for each optimization step.....39
5.3	Final optimized parameters for the interaction of nitrogen (a) and hydrogen (b) atoms ($q_{\text{N}}=-0.46974$, $q_{\text{H}}=0.15658$) of ammonia with cyclen molecule.....40
5.4	Final optimized parameters for the interaction of oxygen (a) and hydrogen (b) atoms ($q_{\text{O}}=-0.36633$, $q_{\text{H}}=0.18316$) of water with cyclen molecule.....44
5.5	Binding energies with (ΔE_{BSSE}) and without BSSE (ΔE) in kcal/mol at different O-origin distances (R in Å) for the optimal directions of the cyclen-water configuration given in Figure 4.2, calculated using a) the STO-3G basis set, b) the DZP basis set.....47
5.6	The lowest stabilization energy (kcal/mol) and the corresponding distance for each solute-solvent and solvent-solvent.....49

Tables

Pages

- 5.7 Characteristic values of the radial distribution functions for a cyclen molecule in a 18.45 mol% aqueous ammonia solution. R_{M1} and r_{m1} are the distances in Å for the first maxima and minima of $g_{xy}(r)$, respectively. n_1 is the average coordination number integrated up to r_{m1} of the first shell.....51
- 5.8 Characteristic values of the radial distribution functions for a cyclen molecule in 18.45 mol% aqueous ammonia solution. R_{Mi} , r_{mi} are the distances in Å for the i th maxima and minima of $g_{xy}(r)$, respectively. n_i is the average coordination number integrated up to r_{mi} of the i th shell.....62