# พลศาสตร์โมเลกุลเชิงควอนตัมของสารละลายแคลเซียม-แอมโมเนียเหลว ที่ความเข้มข้นสูงโดยใช้ข้อแก้ไขแบบสามวัตถุ

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# QUANTUM MOLECULAR DYNAMICS OF HIGHLY CONCENTRATED CALCIUM-LIQUID AMMONIA SOLUTIONS USING THREE-BODY CORRECTIONS

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พิมพ์ต้นฉบับบทคัดย่อวิทยานิพนธ์ภายในกรอบสีเขียวนี้เพียงแผ่นเดียว

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ได้ทำการจำลองแบบโดยวิธีพลศาสตร์โมเลกุลของสารละลายแคลเซียม-แอมโมเนียเหลวที่อุณหภูมิเฉลี่ย ๒๔๐ เคลวิน โดยใช้แบบจำลองของแอมโมเนียชนิดยืดหยุ่นได้ อันตรกิริยาระหว่างอนุภาคที่การจำลองแบบได้อธิบายโดยทางตรงและทางอ้อม อันตรกิริยาทางตรงแทนด้วยฟังก์ชันศักย์คู่และข้อแก้ไขแบบสามวัตถุซึ่งได้พัฒนาขึ้นใหม่โดยใช้การคำนวณทางเคมีควอนตัมโดยใช้เบซิสเซตที่มีคุณภาพระดับทวิคูณของเซตาพร้อมด้วยฟังก์ชันเชิงขั้ว อันตรกิริยาทางอ้อมซึ่งอธิบายการเปลี่ยนแปลงของอันตรกิริยาส่วนตรงเนื่องจากการปรากฏของอิเล็กตรอนอิสระที่ละลายอยู่ในสารละลาย การคำนวณนี้จะมีพื้นฐานอยู่บนทฤษฎีศักย์เทียม การจำลองแบบได้กระทำกับสองระบบ ได้แก่ ระบบที่ประกอบด้วยไอออนแคลเซียม ๑ ไอออนกับโมเลกุลของแอมโมเนีย ๒๑๕ โมเลกุลและ ไอออนแคลเซียม ๑๘ ไอออนกับโมเลกุลของแอมโมเนีย ๒๑๕ โมเลกุล

พบว่าข้อแก้ไขแบบสามวัตถุมีความจำเป็นต่อการจำลองแบบระบบดังกล่าว เนื่องจากมีผลกระทบทำให้เลขโคออดิเนชันอันดับแรกของไอออนแคลเซียมในสารละลายเจือจางมีค่าลดลงจาก ๘ เป็น ๘ ขนาดของชั้นซอลเวชันอันดับแรกเพิ่มขึ้น ๐.๓๓ อังสตรอม และชั้นซอลเวชันอันดับสองหายไป ศักย์เทียมได้ส่งผลกระทบที่น่าสนใจมากในสารละลายเข้มข้น สังเกตุพบว่าโมเลกุลของแอมโมเนียถูกดึงเข้าไปรวมกันและกลายเป็นกลุ่ม นอกจากนี้ยังปรากฏโพรงซึ่งไม่มีโมเลกุลของแอมโมเนียอยู่สลับกับกลุ่มของโมเลกุลแอมโมเนีย ไอออนแคลเซียมนั้นเองก็ปรากฏอยู่เฉพาะในโพรงนี้และสามารถเคลื่อนที่ไปได้ภายในโพรงโดยมีการจัดเรียงตัวคล้ายคลึงกับพันธะโลหะ

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ปีการศึกษา 2540 ลายมือชื่ออาจารย์ที่ปรึกษาร่วม .....

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KEY WORD: MOLECULAR DYNAMICS SIMULATIONS / METAL-AMMONIA SOLUTION / PSEUDOPOTENTIAL / WIWAT SIDHISORADEJ: QUANTUM MOLECULAR DYNAMICS OF HIGHLY CONCENTRATED CALCIUM-LIQUID AMMONIA SOLUTIONS USING THREE BODY CORRECTIONS. DISSERTATION ADVISORS: DAVID RUFFOLO, Ph.D. ASSO. PROF. SUPOT HANNONGBUA, Ph.D. 103 pp. ISBN 974-638-623-9.

Molecular dynamics simulations of calcium in liquid ammonia solutions have been performed at an average temperature of 240 K using a flexible ammonia model. Interactions between the simulation atoms were described by the direct and indirect potential. The former includes pair potential and three-body correction functions newly developed using quantum chemical calculations with the basis sets of double zeta quality plus a polarization function. The second part, which represents the changes of the direct interaction due to the presence of free electrons dissolved in the solution, has been evaluated based on pseudopotential theory. The two simulated systems comprise either 1 or 18 calcium ions and 215 ammonia molecules.

It has been found that the three-body correction is necessary for this system as it leads to the reduction of the first shell coordination number of Ca(II) in dilute solution from 9 to 8, the increase of the size of the solvation shell by 0.33 Å, and the disappearance of the second solvation shell. The pseudopotential has an amazing effect in the concentrated solution; ammonia molecules were drawn together and cluster formation was observed. In addition, there are ammonia-free cavities interspersed with the ammonia-filled clusters. Calcium ions are only found in the cavities, where they are movable and are evenly spaced in a form of metallic bonding.

ภาควิชา ฟิสิกส์ ลายมือชื่อนิสิต W. Sidhisoradej

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