STRUKTUR SOLVASI DAN SIFAT DINAMIKA ION Cu^{+} DAN Cu^{2+} DALAM PELARUT AMONIA CAIR DAN LARUTAN AMONIA: SIMULASI DINAMIKA MOLEKUL AB INITIO *QUANTUM MECHANICAL CHARGE FIELD* (QMCF)

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INTISARI

Struktur solvasi dan sifat dinamika ion Cu^{+} dan Cu^{2+} dalam amonia cair pada 235,15 K, dan larutan amonia 18,6% pada 298,15 K telah diinvestigasi menggunakan simulasi dinamika molekul QMCF (DM QMCF). Simulasi ini juga dilakukan untuk mengetahui perbandingan sifat dinamik antara amonia cair model fleksibel dan *rigid* terutama pada kulit solvasi kedua. Preferensial solvasi ion Cu^{+} dan Cu^{2+} terhadap ligan NH_3 atau H_2O diidentifikasi pada sistem larutan amonia 18,6%.

Metode simulasi DM QMCF memiliki dua daerah simulasi, yaitu daerah mekanika kuantum (MK) dan mekanika molekul (MM). Daerah MK diperpanjang dan dibagi menjadi daerah inti (*core*) dan daerah *layer*. Metode perhitungan pada tingkat Hartree-Fock (HF) digunakan pada daerah MK, dengan himpunan basis LANL2DZ-ECP untuk ion Cu^{2+} dan Cu^{+}, dan himpunan basis DZP-Dunning untuk ligan NH_3 dan H_2O.

Sistem ion Cu^{2+} dalam amonia cair dan larutan amonia 18,6% membentuk kompleks oktahedral $[Cu(NH_3)_6]^{2+}$ yang stabil tanpa ada perpindahan ligan NH_3 di kulit solvasi pertama selama proses simulasi berlangsung. Jarak Cu^{2+}-NH_3 pada pelarut amonia cair model fleksibel, model *rigid*, dan larutan amonia 18,6% masing-masing sebesar 2,17 Å; 2,19 Å; 2,19 Å. Pada sistem ion Cu^{+} dalam amonia cair membentuk kompleks berkoordinasi 3 (95,7%) dan 4 (4,3%). Jarak Cu^{+}-NH_3 pada pelarut amonia model fleksibel dan *rigid*, masing-masing sebesar 2,23 Å dan 2,24 Å. Pada larutan amonia 18,6% terbentuk kompleks dengan bilangan koordinasi 3 (5,2%); 4 (83,3%); 5 (10,8%); 6 (0,7%), dan terjadi perpindahan ligan NH_3 dan H_2O di kulit solvasi pertama. Jarak Cu^{+}-NH_3 pada larutan amonia 18,6% sebesar 2,23 Å. Pada ketiga sistem ion Cu^{+} ini, kompleks yang paling stabil adalah $[Cu(NH_3)_4]^{+}$ tetrahedral terdistorsi, meskipun terdapat perpindahan ligan di kulit solvasi pertama. Secara garis besar sifat dinamika solvasi ion Cu^{+} lebih tinggi dibandingkan Cu^{2+}, dan analisis NBO menunjukkan bahwa kekuatan interaksi elektrostatik Cu^{2+}-NH_3 lebih tinggi dibandingkan Cu^{+}-NH_3. Pada sistem pelarut amonia cair, sifat dinamika ligan NH_3 model fleksibel lebih tinggi dibandingkan model *rigid* terutama pada kulit solvasi kedua. Preferensial solvasi ion Cu^{2+} dan Cu^{+} terhadap ligan NH_3 lebih tinggi dibandingkan H_2O pada larutan amonia 18,6%.

Kata kunci: simulasi, DM QMCF, struktur, dinamika, solvasi, Cu^{+}, Cu^{2+}, amonia cair, larutan amonia

SOLVATION STRUCTURE AND DYNAMICAL PROPERTIES OF Cu^{+} AND Cu^{2+} ION IN LIQUID AMMONIA AND AQUEOUS AMMONIA SOLUTION: *AB INITIO* QUANTUM MECHANICAL CHARGE FIELD (QMCF) MOLECULAR DYNAMICS SIMULATION

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ABSTRACT

Solvation structures and dynamical properties of Cu^{2+} and Cu^{+} in liquid ammonia at 235.15 K and 18.6% aqueous ammonia at 298.15 K have been investigated via quantum mechanical charge field molecular dynamics (QMCF MD) simulation. This simulation is also carried out to compare the dynamical properties of flexible and rigid ammonia models was also carried out, especially in the second solvation shell. The preferential solvation of Cu^{+} and Cu^{2+} ions to NH_3 or H_2O ligands was identified in the 18.6% aqueous ammonia solutions.

The QMCF MD simulation method has two simulation regions, namely quantum mechanics (QM) and molecular mechanics (MM). The QM region is extended and divided into core and layer areas. The QM region is treated via ab initio Hartree–Fock (HF), using LANL2DZ-ECP basis set for Cu^{2+} and Cu^{+}, and DZP-Dunning for NH_3 and H_2O ligands.

Cu^{2+} ion in liquid ammonia and 18.6% aqueous ammonia solution formed a stable octahedral complex $[Cu(NH_3)_6]^{2+}$ with the absence of first shell ligand exchange during simulation time. The distance of Cu^{2+}-NH_3 in flexible, rigid ammonia, and 18.6% aqueous ammonia solutions were 2.17 Å; 2.19 Å; 2.19 Å, respectively. Cu^{+} in liquid ammonia formed complexes coordinating 3 (95.7%) and 4 (4.3%). The distances of Cu^{+}-NH_3 in flexible and rigid ammonia were respective 2.23 Å and 2.24 Å. In the 18.6% aqueous ammonia solution, complexes with the coordination number of 3 (5.2%); 4 (83.3%); 5 (10.8%); 6 (0.7%) were formed, with NH_3 and H_2O ligand exchange in the first solvation shell. The distance of Cu^{+}-NH_3 in 18.6% aqueous ammonia solution was 2.23 Å. All of these Cu^{+} ion solvation systems indicated the most stable complex was $[Cu(NH_3)_4]^{+}$ distorted tetrahedral, even though there was a ligand displacement on the first solvation shell. In general simulation, the dynamical properties of Cu^{+} ion was higher than Cu^{2+}, and NBO analysis also showed that electrostatic interaction of Cu^{2+}-NH_3 was higher than Cu^{+}-NH_3. In liquid ammonia solution, the dynamical properties of flexible ammonia model was higher than the rigid model, particularly in the second solvation shell. The preferential Cu^{+} and Cu^{2+} ions to NH_3 ligand was higher than H_2O in 18.6% aqueous ammonia solutions.

Keywords: simulation, QMCF MD, structural, dynamical, solvation, Cu^{+}, Cu^{2+}, liquid ammonia, aqueous ammonia