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THE PREFERENTIAL STRUCTURE OF Co^{2+} SOLVATION IN AQUEOUS AMMONIA SOLUTION DETERMINING BY MONTE CARLO SIMULATION

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ABSTRACT

A Monte Carlo simulation was performed for Co^{2+} in 18.6 % aqueous ammonia solution at a temperature of 293.16 K, using ab initio pair potentials and three-body potentials for $Co–H_2O–H_2O$, $Co–NH_3–NH_3$ and $Co–H_2O–NH_3$ interactions. The first solvation shell consists average of 2.9 water and 3.2 ammonia molecules, and the second shell of 10.4 water and 11.2 ammonia molecules. The structure of the solvated ion is discussed in terms of radial distribution functions, angular distributions and coordination number.

Keywords: Molecular simulation, Monte Carlo simulation, solvation, ab initio

INTRODUCTION

Theoretical studies of mixed solvents by Monte Carlo or molecular dynamics simulations have been used extensively to obtain information about solvent-solvent interactions such as in methanol-water [1], *t*-butyl alcohol-water [2], DMSO-water [3], ammonia-water [4], acetone-water [5], hYdroxYlamine-water [6] and formamide-water [7] mixtures. On the other hand, some works about interaction solute and solvent in multicomponent have also been the subject of numerous studies in solution chemistry, both experimental [8] and theoretical methods [9], e.g. for Na^+ [10], Li^+ [11], Cu^{2+} [12,13] and Mg^{2+} [14] in ammonia–water system.

The behaviour of ions in mixed solvents has been interpreted in terms of preferential solvation, as it is an interesting phenomenon playing an important role in solubility and kinetics. The solvent exchange raction is one of the most basic chemical reactions of metal ions in solution, and its mechanism has been widely investigated in order to characterise the reactivities of the metal ion. Akesson's group has been studying water exchange reactions for metal ions of the first [15,16] and second [17] transition period. Structures of the transition states and intermediates formed in the water exchange of metal hexaaquo ions of the first transition series were treated theoretically by Rotzinger [18,19].

Simulations for aqueous solutions of divalent metal ions based on Monte Carlo method always give overestimated coordination numbers for the first shell, if they are performed classically with pair potentials only, i.e. neglecting three-body and higher interactions terms, especially when transition metal ions such as Fe^{2+} [20], Zn^{2+} [21], Ni^{2+} [22], Cu^{2+} [12,13] or Co^{2+} are involved. By using the assumption of pairwise additive intermolecular potentials and thus neglecting the higher interactions, Monte Carlo simulations for some mono- and divalent metal ions have led to structural result in agreement with those achieved experimentally [9-14,20-22]. In most cases concerning divalent and trivalent ions, however, this simplification of the ion-solvent interaction results in overestimated structural and energetic properties of the solution. It was found that in aqueous solution, the assumption of pairwise additivity leads to an error of interactions energies in cation-water systems of at least 10%, 15% and 20% for mono-, di- and trivalent ions, respectively.

In order to simulate Co^{2+} in aqueous ammonia solution, we had to include three different three-body correction function for cation–ligand interaction, i.e. $Co–H_2O–H_2O$ [23], $Co–NH_3–NH_3$ [24] and $Co–H_2O–NH_3$ three-body potentials. The first two correction functions were taken from literature [23,24] and the third one had to be newly developed for the present work.

In this study, the focus of interest is put on the solvation structure around the Co^{2+} in order to see how ammonia and water ligands are preferentially bonded to the ion in its first and second solvation shell. Energetic and structural properties were evaluated on the basis of Monte Carlo statistical simulations.

EXPERIMENTAL SECTION

Three-body potential for Co^{2+}-water-ammonia system

The quantum chemical calculations were performed at the Unrestricted Hartree-Fock (UHF) level using the basis sets of LANL2DZ/ECP for cobalt and 6-31G* for water and ammonia molecules. The first basis set for cobalt was taken from literature [23] whereas 6-

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31G* basis set was provided by Gaussian98 program. The experimental gas-phase geometry of the ammonia [25] (N–H distance at 1.0124 Å and H–N–H angle of 106.67) and water [26] (O–H distance of 0.9601 Å and H–O–H angle of 104.47°) were kept rigid throughout the calculations. All *ab initio* calculations were carried out using Gaussian98 program [27].

The three body potential Co^{2+}-H_2O-NH_3 was constructed from 2430 configurations that generated by varying the distance and orientation of the ligands in the configuration space around the cobalt ion. Orientation where one of the hydrogen atoms is closer to the ion than the corresponding nitrogen or oxygen, respectively, need not be considered as their highly repulsive two-body interaction energy values prevent the occurrence of such orientation during the simulation process. The three-body interaction energy, ΔE_{3b}, for each configuration was computed by subtracting the two-body interactions, ΔE_{2b}, calculated with the help of the pair potential functions for cobalt-ammonia, cobalt-water and ammonia-water, from the *ab initio* energies in the following way :

$$\Delta E_{3bd} = \{E_{ML_1L_2} - E_M - E_{L_1} - E_{L_2}\} - \{E_{2bML_1}\} - \{E_{2bML_2}\} - \{E_{2bL_1L_2}\} \quad (1)$$

where *M*, *L_1* and *L_2* denote cobalt, water and ammonia, respectively. All three-body data points were fitted to an analytical function to be used as correction for the pair potentials. The form of this correction function is

$$\Delta E_{3bd} = 0.05721[1.00682 + (\pi - \theta_{L_1ML_2})^2]^2 \text{ x } \exp\ (0.963 \text{ x } r^2_{ML_1})$$
$$\text{x } \exp\ (0.8144 \text{ x } r^2_{ML_2}) \text{ x } [(CL^2 - r^2_{ML_1})(CL^2 - r^2_{ML_2})] \quad (2)$$

where *L_1* and *L_2* denote the center of mass of water and ammonia molecule, respectively, $\theta_{L_1ML_2}$ is the H_2O–Co–NH_3 angle and r_{ML_1} and r_{ML_2} are the distance between the center mass of water and ammonia and Co^{2+} respectively. CL represents a cutoff limit to be used in the simulation, beyond which three-body effects can be neglected. In our case CL was set to 6.0 Å.

Monte Carlo simulation

In order to perform the simulation for the system consisting of one Co^{2+} surrounded by ammonia and water molecules, five-pair potentials and three-body potentials were required. For water-water interactions, the CF2 potential of Jansco and Heinzinger [28] was used, and the pair potential of Hannongbua et al. [29] for ammonia-ammonia interactions. Ammonia-water interaction energies were evaluated using the potential function developed by Tanabe and Rode [4] adopting the same scaling factor to obtain better energetic data.

The pair and the three-body potentials for describing Co^{2+}–water and Co^{2+}–ammonia interactions were taken from our previous work [23,24]. The new three-body potential for Co^{2+}–water–ammonia of this work was used in addition.

The simulation box contained one cobalt, 171 water and 39 ammonia molecules corresponding to 18.6% aqueous ammonia solution at the temperature of 6 K. The density of 0.9291 g cm^{-3} for this solution at the specified temperature gives an edge length of 18.951 Å for the elementary box. Periodic boundary conditions and a cutoff at half of this length [30] for exponential terms were employed, and the starting configuration was randomly generated. The Metropolis sampling algorithm [31] was used and structural data were evaluated for 3 million configurations after the system had reached energetic equilibrium after 4 million configurations.

Beside radial distribution functions and their integrations for various pairs of species, the first solvation shell has been the subject of detailed analysis regarding coordination number and angular ligand molecule distributions.

RESULT AND DISCUSSION

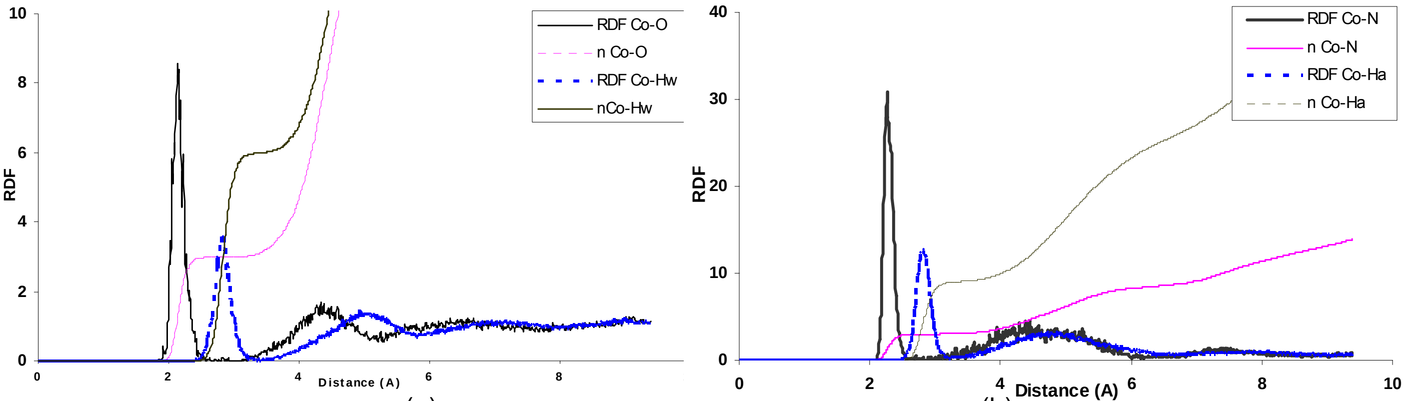
Radial distribution functions

Characteristic values of radial distribution functions for Co^{2+} in 18.6% aqueous ammonia solution are shown in Table 1.

Tabel 1. Characteristic values of the radial distributions functions for the Co(II) in 18.6% aqueous ammonia solution;

α	β	r_{M1}	r_{m1}	$n_{\alpha\beta}(m1)$	r_{M2}	r_{m2}	$n_{\alpha\beta}(m2)$
		Co^{2+}-H_2O					
Co	O	2.08	2.54	2.9	4.32	4.90	10.4
Co	H	2.78	3.16	5.9	4.9	5.92	31.2
		Co^{2+}-NH_3					
Co	N	2.26	2.70	3.2	4.57	5.27	11.21
Co	H	2.72	3.35	9.4	4.62	5.86	44.33

Note : r_{M1} and r_{M2} are first and second maximum in Å; r_{m1} and r_{m2} are the first and second minimum in Å, where $n_{\alpha\beta}(r)$ are the first and second coordination number from the running integration numbers integrated up to r_{m1} and r_{m2}, respectively. α is Co^{2+} and β is the atom of ligand.



(a) (b)

Fig 1. (a) Co-O and Co-Hw radial distribution functions and their running integration numbers obtained from the simulation of Co^{2+} in 18,6 % aqueous ammonia solution; (b) Co-N and Co-Ha radial distribution functions and their running integration numbers obtained from the simulation of Co^{2+} in 18,6 % aqueous ammonia solution

Co^{2+}–O and Co^{2+}–H_W radial distribution functions (RDFs) and their corresponding integration are shown in Fig 1(a). From the graphic in Fig 1a and Table 1, the first maximum (r_{M1}) for the Co^{2+}–O (2.08 Å) is 0.05 Å closer than observed for Co^{2+} in pure water [23]. The average 2.9 water molecules contained in the first shell, $n_{Co\text{–}O}$(m1), are well separated from the second shell as can be seen from the Co^{2+}–O RDF values of zero over quite some distance (2.4–3.3 Å), and little exchange of water molecules between the first and second solvation shell was observed throughout the simulation, as expected for such strong ion–solvent interactions. The Co^{2+}–H_W RDFs shows a sharp peak (r_{M1}) centered at 2.78 Å representing the water hydrogen of the first solvation sphere of Co^{2+}. This peak does not overlap with the Co^{2+}–O RDF, indicating that the first solvation shell structure is rather rigid with the oxygen oriented toward the central ion in dipole moment direction. The average coordination number $n_{Co\text{–}H}$(m1) for hydrogen atom is 5.9 corresponding to the 2.9 water molecules in the first shell within 2.7 Å. The region from ~3.2 Å up to ~4.8 Å corresponds to the second hydration shell with the maximum of the Co–O RDF at 4.6 Å, containing an average number of 10.4 water molecules.

The Co^{2+}–N and Co^{2+}–H_A RDFs and their corresponding integration are shown in Fig 1(b). The functions are characterised by well-pronounced first solvation shell peak at 2.26 Å, only 0.02 Å further away than for Co^{2+} in pure liquid ammonia [24]. The average coordination number for this first shell is 3.2. Exchange of ammonia molecules between the first and second shells should be slow, since the Co^{2+}–N RDF becomes almost zero over a considerable distance (2.5–3.2 Å). All hydrogen atoms corresponding to the 3.2 NH_3 ligands are placed beyond the Co^{2+}–N RDF and the first Co^{2+}–H_A RDF peak is centered at 2.72 Å, containing 9.4 hydrogen atoms as expected. The second solvation shell of Co^{2+} is represented by a broad peak between 3.3 and 6.3 Å with the maximum of the Co^{2+}–N RDF at 4.6 Å, containing an average number of 11.2 ammonia molecules.

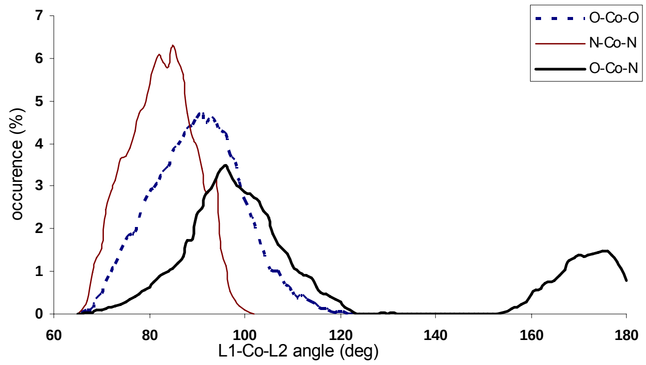


Fig 2. Angular distribution functions for NH_3-Co-NH_3, H_2O-Co-H_2O and H_2O-Co-NH_3 in the first salvation shell obtained from the simulation of Co^{2+} in 18,6 % aqueous ammonia solution

Angular distributions

The structure of ligand around Co^{2+} in the first solvation shell was further analysed with respect to the ligand-ion-ligand angle distribution (Fig. 2). The distribution plots for H_2O–Co–H_2O and NH_3–Co–NH_3 angles show one peak each, centered at 87° and 81°, respectively, meaning that in this complex two water or two ammonia molecules are never located in trans position in each other. This actually means that Co^{2+} is embedded into two hemispheres, one consisting approximately of three water and one approximately of three ammonia molecules. The NH_3–Co–H_2O angle distribution shows two peaks centered at 93° and 173°. The structure of the 6 ligands in the first solvation shell is a distorted octahedron, the 3 water ligands being 0.18 Å closer to Co^{2+} than the three ammonia ligands.

Coordination number distributions

Fig 3 shows the coordination number distribution of the first and second solvation shells of Co^{2+}. The first shell coordination number distribution of Co^{2+}–H_2O and Co–NH_3, shows that the first solvation shell consists approximately of three ammonia and three water molecules. This fact also indicates a slow exchange rate for the first solvation shell ligands.

The second shell coordination number distribution (Fig 3) shows that on average 10.4 water and 11.2 ammonia molecules interact with the molecules in the first shell. Configurations with 10 (25%) water molecules and 12 (44.3%) ammonia molecules dominate. One can see from Fig. 3 that the coordination number for Co–H_2O (8–15) is considerably wider than for Co–NH_3 (8–12). This wider range coordination number reflects a less rigid bonding and thus the majority of second shell ligand exchange processes should involve water molecules. The average solvation structure of Co^{2+} in 18.6% aqueous ammonia solution can thus be characterized by $Co[(H_2O)_{2.9}(NH_3)_{3.2}]\ [(H_2O)_{10.4}(NH_3)_{11.2}]^{2+}$. This means that in this solution, Co^{2+} is preferentially solvated by ammonia ligands in the first solvation shell and even the second solvation shell. This preferential solvation denotes the over-representation of ammonia ligands in the solvation shell compared to their presence in the bulk.

The number of ligands in the first and second solvation shells of Li^+, Na^+, Mg^{2+}, and Cu^{2+} are compared to those of Co^{2+}. The fully solvated sodium ion in 18.45 % aqueous ammonia can be characterised by $Na[(H_2O)_{2.4}(NH_3)_4]\ [(H_2O)_7(NH_3)_2]^+$ [10], the first solvation being dominated by ammonia and the second shell by water. Li^+ and Mg^{2+} are preferentially solvated by water in both shells. The structure of solvated lithium and magnesium ions can be characterised by $Li[(H_2O)_4(NH_3)_2][(H_2O)_8(NH_3)_4]^+$ [11] and $Mg[(H_2O)_4(NH_3)_3][(H_2O)_9(NH_3)_5]^{2+}$ [14], respectively. While, the solvated Cu^{2+} which can be characterised by $Cu[(H_2O)_3(NH_3)_3]\ [(H_2O)_{11.6}(NH_3)_{10.2}]^{2+}$ [12], shows that it was preferentially solvated by ammonia ligands in both shells. The results for ions with the same charge and similar radius (Mg^{2+}, Cu^{2+} and Co^{2+}) are quite different. The origin of the difference is to be seen in the relative hardness and softness of acids (ions) and bases (ligands) and the involvement of *d* functions of Cu^{2+} and Co^{2+} in ligand binding. This data must be seen with some caution, however, as *n*-body effects have recently been found to be of considerable importance even for mono- and divalent main group metal ions in solution: a molecular dynamics simulation using a mixed quantum mechanical/molecular mechanical (QM/MM) method, gave a tetrahedral structure with 3 water and 1 ammonia ligand for the first hydration shell of Li^+, in contrast to the structure predicted by classical pair potential simulations [32]. In the QM/MM technique, the many-body contributions for the whole first solvation shell are included and lead approximately to quite substantial corrections–although qualitatively most probably correct.

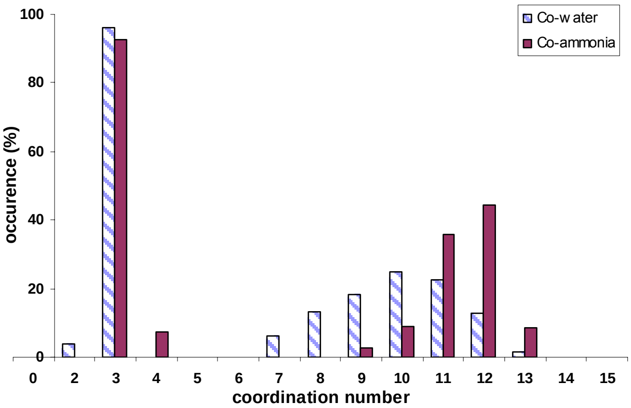


Fig 3. First- and second shell coordination number distribution of Co^{2+}-water and of Co^{2+}-ammonia in 18,6 % aqueous ammonia solution

The result of Monte Carlo simulation would be different if it is simulated in the different concentration, which the higher ammonia concentration the more ammonia ligand would be coordinated around the ion exchanging water molecule. On the other hand, the smaller concentration it would be less ammonia ligand which replacing the water molecule.

CONCLUSION

Our Monte Carlo simulations of Co^{2+} in 18.6% of aqueous ammonia solution using pair potential and three-body correction functions characterise the solvated ion as $Co[(H_2O)_{2.9}(NH_3)_{3.2}]\ [(H_2O)_{10.4}(NH_3)_{11.2}]^{2+}$. Co^{2+} is preferentially solvated by ammonia ligands in both solvation shells and the first shell shows the expected distorted octahedral structure. Preferential solvation phenomena are clearly indicated, strong in favour of NH_3 ligands.

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