Free Solvation Energy of aqueous Aluminium (III) species

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INTRODUCTION

Thermodynamics studies in condensed phase are important to comprehension of many chemical processes. For example, the *p*Ka of species in solution can be estimated from thermodynamics cycles[1]; however, in this methodology, the calculation of $\Delta_{solv}G$ is a challenge. The shell solvation theory developed by Pliego[2] considers explicit solvent molecules, placed via molecular dynamics, and continuum method, to evaluate long range effects. In this work we have studied the $\Delta_{solv}G$ of $[Al(H_2O)_6)]^{3+}$, $[Al(OH)(H_2O)_5)]^{2+}$, $[Al(OH)_2(H_2O)_4)]^{+}$ and $Al(OH)_3$ speciation in aqueous medium.

METHODS

The $\Delta_{solv}G$ was estimated using eq. (1)

$$\Delta\Delta_{Solv}G = \frac{1}{2}\langle U\rangle + \langle \Delta_{Solv}G^{A^{+}(H2O)_n} - \Delta_{Solv}G^{(H2O)_n}\rangle \quad \textbf{(1)}$$

on the right hand side, the first term accounts the specific iterations between solute and solvent, while the second term and third terms add the long range contribution. Molecular dynamics (MD) were carried out in deMonNano package from which 4000 structures of a water box were obtained, whereas each structures contains about 54 explicit waters molecules. The solvation free energy were estimated using different number of explicit water molecules. The first term of eq. (1) was averaged from 500 equally spaced structures selected from MD. DFT calculation were carried out at PBE/6-31++G** level to evaluate the interaction between the solute and the explicit solvent molecules. The second and third terms were averaged from 50 equally spaced structures using the PCM/HF/6-31++G** method. All calculations were carried out in the software GAUSSIAN09.

RESULTS AND DISCUSSION

By Eq. 1, was calculated the free solvation energy of all species. In a previews analysis, was determinate that the value of $\Delta_{solv}G$ converge between 2 Kcal mol^{-1} for 30 explicit solvent molecules, as shown in Figure 1. Thus, was obtained a $\Delta_{solv}G$ around -420.4, -216.7, -90.0 and -73.4 Kcal mol^{-1} for the species $[Al(H_2O)_6)]^{3+}$, $[Al(OH)(H_2O)_5)]^{2+}$, $[Al(OH)_2(H_2O)_4)]^{+}$, and $Al(OH)_3$ respectively.

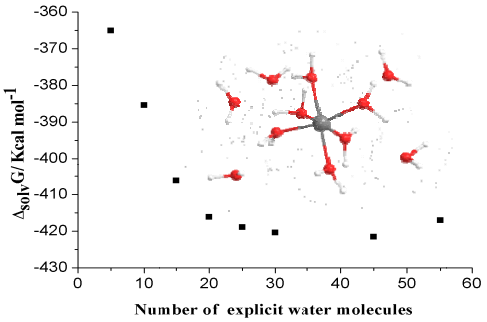

Figure 1. Convergence of $\Delta_{solv}G$, for $[Al(H_2O)_6)]^{3+}$.

CONCLUSIONS

The results indicate that the shell solvation energy method in combination with the SCC-DFTB method is adequate for estimating the free solvation energy of aqueous metal species.

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