DFT studies of the interactions between the $[Ca(H_2O)_5]^{2+}$ cation and monofuctionaloxo, aza, sulfur and phosphorous ligands

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INTRODUCTION

The calcium cation is involved in chemical scaling formation in petroleum industry. The formation of $CaCO_3$ and $CaSO_4$ results in surface blockage that cause decline in the permeate flux, reducing the process efficiency and increasing operational costs.[1]During the past two decades, considerable efforts in the development of chemical additives have been made, which leads to antiscalant molecules like polycarboxylates, polyacrylates and polyphosphonates.[1]

METHODS

All the structures were optimized using quantum chemical calculations with the B3LYP⁄6-311++G(d,p) method and the affinity of the $[Ca(H_2O)_5]^{2+}$cation for several monofunctional ligands were determined. Four sets of ligands were studied: with oxygen, nitrogen, sulfur and phosphorous (phosphine) binding atom (table 1).

RESULTS AND DISCUSSION

Complexes that bind via a double bonded oxygen atom have the strongest metal-ligand interaction shown in table 1, followed by the nitrogen compounds, singly bonded oxygen interacting atom, sulfur ligands and phosphine. The ligand with the strongest interaction, phosphoryl, has an ionic resonance form with a negative charge on the binding oxygen atom that highly contributes to the hybrid geometry, that favors the interaction. The metal-ligand distance, the MerzKollman atomic charges and the HOMO energy of the ligands show high correlation ($r^2> 0.9$) with the interaction strength. The Energy Decomposition Analysis (EDA) of the interaction energy between the $[Ca(H_2O)_5]^{2+}$cation and the ligand shows that the electrostatic term is the major component of the interaction and represents at least 43.7% of the total interaction energy, due to charge attraction. The covalent component represents at least 28.1% of the total interaction energy, due to the ligand

electronic donation effect. Along the set of compounds studied, the electrostatic component varies more than twice the covalent term.

Ligand	ΔH	ΔG^{298}	qL
$O=PH_3$	-18.77	-16.40	0.070
$O=CHNH_2$	-15.97	-13.92	0.053
$O=CHOH$	-14.90	-13.13	0.051
$O=C(CH_3)_2$	-12.49	-12.16	0.045
$O=CH_2$	-9.50	-9.01	0.045
$HN=CH_2$	-8.72	-8.83	0.045
$O(CH_3)_2$	-2.68	-2.09	0.025
$HO-CH_3$	-2.57	-1.88	0.023
$S=CH_2$	2.63	3.73	0.021
PH_3	10.60	11.23	0.005

Table 1.Affinity and charges on the ligand.

CONCLUSIONS

The interaction enthalpy order is: phosphoryl> C=O > C=N > C≡N > C-O > C-N > NH_3> C=S > C-S > PH_3. This interacting order is mainly due to the electronic nature inherent to the atoms that interact with the metal center. The oxygen and nitrogen atoms are small, with a higher electronegativity, favouring polarization to them and increasing the interaction strength with the metal center. In the phosphoryl molecule, which binds more strongly to the cation, a Lewis resonance form with a formal charge on the oxygen atom is the one with the highest contribution to the final hybrid.

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