DFT Study of the Interaction of Trialkylamines with Ni₄-Clusters

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Abstract
This research studies binding of trialkylamine derivatives to the multiplicity optimized Ni₄-clusters using theoretical approaches. The goal is to understand the interaction behavior on the metal surface and provide some key points important to the corrosion problems. The results show that trialkylamine derivatives are able to establish N–Ni bond through either short or long diagonal of Ni₄-cluster. Of the studied triethylamine, tripropylamine, and tributylamine, the last derivative in series shows highest binding energy. TAAs/Ni₄-cluster complexes with $M = 5$ show special electronic charge transfer that stabilizes the complex. According to this analysis for natural charges, therefore, the nature of metal–ligand (e.g., N–Ni) interactions that underlay TAAs/Ni₄-cluster complexes can be elucidated. Possible correlation between interaction strength, polarizability, nitrogen’s atomic charge and the orbitals energy gaps is also investigated. The results of natural bond orbital analysis explore the strong charge transfer from lone pair of nitrogen atom to $\sigma^*$ and $\pi^*$ orbitals of the clusters. The trialkylamines in this work are weaker corrosion inhibitor on the small nickel cluster than the previously studied aromatic nitrogen containing compounds like pyridine.

Keywords Binding · DFT · Ni₄-clusters · Multiplicity · Trialkylamine · Charge transfer

1 Introduction
The study of transition metal clusters is of essential interest for industrial applications due to their novel geometrical structures, physical, chemical, and electronic properties [1]. Changing physical and chemical properties of the transition metal clusters as a function of size is an attractive point. Among transition metal clusters, nickel clusters have attracted much attention both experimentally and theoretically [2–6]. Nickel clusters exhibit appropriate future in a wide range of applications in chemistry, medical, biological science technology and therefore have a lot of applications because of their quantum size effect and magnetic properties [7–14]. Experimental methods for investigation of the structure of nickel clusters are transmission electron microscopy and X-ray diffraction. Parks et al. have probed the geometrical structure of small nickel clusters Ni₃ to Ni₁₅ via molecular adsorption of nitrogen on their surfaces [15]. However, characterization of small nickel clusters by experimental methods encountered some difficulties. Many theoretical works have been devoted to the studies of the geometry and binding energy of nickel clusters [16]. Goel et al. showed that the rhombic (planar) structure of Ni₄ is the most stable structure by using broken-symmetry density functional theory (DFT) calculations [17]. An empirical many-body potential and molecular dynamics simulation has been used to calculate the equilibrium geometries, relative stabilities, the binding energies and dominant fragmentation channels of Niₙ ($n \leq 23$) clusters [18].

Considering the structural properties of membrane proteins in relevant experiments, i.e., containing amino groups, the research on the interaction between the nickel and the active amino group has become an important biomedical issue [14].

Trialkylamines (TAAs) are interesting group containing organic compounds, which act as corrosion inhibitors by interacting with metal surfaces. Although many amine inhibitors have been studied to date, no detailed interaction mechanism is available in the literature. Among the var-
ious TAAs, the tributylamine is the most interesting one because it is confirmed that it has features of the most favorable corrosion inhibitor [19]. Bastidas et al. reported an inhibition mechanism and selective chemical adsorption for tributylamine on mild steel in hydrochloric acid solution [20]. They analyzed the relation between the chemical adsorption, molecular structure, and inhibition efficiency of tributylamine as corrosion inhibitor. They demonstrated that tributylamine adsorbs on the mild steel, with one tributylamine molecule replacing three molecules of water. The concentration of tributylamine raises as the inhibition efficiency increases. Khaleed et al. [19] have used quantitative structure–activity relationships (QSARs) methods for predicting the corrosion inhibition efficiencies on mild steel surface in hydrochloric acid solution. They pointed out the lowest unoccupied molecular orbital energy ($E_{UL}$) and the molecular volume as important predictive descriptors. The most stable adsorption has been found for tributylamine on mild steel surface. It was claimed that understanding the adsorption phenomena is of key point in corrosion problems.

In our previous investigation [21], we presented the most stable structure and electronic properties of Ni$_4$-cluster, required for exploring the adsorption of an aromatic amine, pyridine, on the metal cluster. An interesting outcome was that rhomboid structure is the most stable form of Ni$_4$-cluster with spin multiplicity ($M$) of 5. The results of these computational studies were in contrast with experimentally claimed exchange between butterfly and rhomboid forms of the cluster [15].

In the present work, the interaction of aliphatic amines, TAAs, with Ni$_4$-cluster and their relative structure is explored by means of quantum chemical calculations within the DFT framework. Three different aliphatic amines, triethylamine (TEA), tripropylamine (TPA), and tributylamine (TBA) are employed. We examine features of TAAs interaction with Ni$_4$-cluster at the planar and vertical interaction types. Also, the correlation between interaction strength, polarizability, donor atom electronic charge of Ni$_4$-cluster and TAAs interacting atoms, and their energy gap will be discussed. The nature of bonding between Ni$_4$-cluster and TAAs is explored by means of natural bond orbital (NBO) analysis and donor-acceptor charge transfer.

### 2 Computational Details

Geometries of the TAAs complexes with Ni$_4$-cluster were fully optimized using DFT. The Becke’s three-parameter hybrid functional and the Lee–Yang–Parr correlation (B3LYP) [22–25] functional were used for DFT calculations.

Ni$_4$-cluster was chosen to model the interaction of TAAs on nickel surface [21]. Initially TAAs and Ni$_4$-cluster were optimized separately for electronic and geometrical structures using LANL2DZ [26–28] and 6-311G** [29] basis sets. LANL2DZ basis set uses effective core potential (ECP) of Hay and Wadt for core electrons [28]. 6-311G** is triple-$\zeta$ quality augmented with two sets of polarization functions.

By the use of LANL2DZ basis set, computational time and convergence difficulties were considerably reduced; however, for more precise results we used 6-311G** basis set for Ni$_4$-cluster and TAAs as well as for TAAs/Ni$_4$-cluster complex.

A frequency calculation on the optimized geometries must be done to identify a real stationary point because a geometry optimization alone does not express about the nature of the stationary point that is found. These calculations have been done for all the systems in this research. Within all calculations involving Ni$_4$-cluster, the optimization was performed without imposing any symmetry constraints. Boys–Bernardi’s counterpoise procedure was used to account for the basis set superposition error (BSSE) [30]. The binding energy ($\Delta E_{\text{bind}}$) between TAA and Ni$_4$-cluster was calculated as:

$$\Delta E_{\text{bind}} = [ E(\text{TAA/Ni}_4) - (E(\text{TAA}) + E(\text{Ni}_4)) ] + \text{BSSE}_{\text{bind}} + \Delta \text{ZPVE}$$

where $E(\text{TAA/Ni}_4)$, $E(\text{TAA})$ and $E(\text{Ni}_4)$ are the total energies of TAA/Ni$_4$ complex, TAA, and Ni$_4$-cluster, respectively. BSSE$_{\text{bind}}$ is the basis set superposition error due to the interaction of TAA with Ni$_4$-cluster, and $\Delta \text{ZPVE}$ is the difference between zero-point vibrational energy (ZPVE) of TAA/Ni$_4$ and sum of TAA and Ni$_4$. The NBO analysis [31] was conducted for TAAs/Ni$_4$-cluster complexes in order to understand the nature of bonding involved. The ability of NBO in transforming the delocalized molecular orbitals into equivalent localized molecular orbitals that recover the expected Lewis bond patterns makes it a popular analysis. In order to evaluate the donor-acceptor interaction for the NBO analysis, the second-order perturbation analysis of the Fock matrix [31] is carried out. For each donor NBO($i$) and acceptor ($j$) the stabilization energy $E(2)$ associated with the delocalization $i \rightarrow j$ is estimated as:

$$E(2) = \Delta E_{ij} = \Delta E_{\text{CT}} = \frac{|\langle i | \hat{P} | j \rangle|^2}{\varepsilon_j - \varepsilon_i}$$

where $\varepsilon_i$ and $\varepsilon_j$ are NBO orbital energies and $\hat{P}$ is the Fock operator. As a result, the charge transfer stabilization energy ($\Delta E_{\text{CT}}$) is used to calculate the charge transferred from a donor orbital to an acceptor orbital ($q_{\text{CT}}$) and is estimated by the perturbation theory arguments, which leads to the fol-