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Chemical reactivity of hypervalent silicon compounds: The local hard and soft acids and bases principle viewpoint

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Abstract. The silicon atom may increase its coordination number to values greater than four, to form pentacoordinated compounds. It has been observed experimentally that, in general, pentacoordinated compounds show greater reactivity than tetracoordinated compounds. In this work, density functional theory is used to calculate the global softness and the condensed softness of the silicon atom for SiH_nF_{4-n} and $SiH_nF^{1-}_{5-n}$. The values obtained show that the global and condensed softness are greater in the pentacoordinated compounds than in the tetracoordinated compounds, a result that explains the enhanced reactivity. If the results are analysed through a local version of the hard and soft acids and bases principle, it is possible to suggest that in nucleophilic substitution reactions, soft nucleophiles preferably react with $SiH_nF^{1-}_{5-n}$, and hard nucleophiles with SiH_nF_{4-n}.

Keywords. Density functional theory; hard and soft acid and bases principle; hypervalent silicon compounds.

1. Introduction

The silicon atom may increase its coordination number to values greater than four, to form pentacoordinated compounds.[1] It has been observed, experimentally, that, in general, pentacoordinated compounds show greater reactivity than tetracoordinated compounds.[2a] The first explanations of this behaviour attributed the enhanced reactivity to the pentavalent silicon atom, by noting that its positive character increases when the coordination increases.[2b] However, later on, Deiters and Holmes[3] performed ab-initio calculations (HF/6-31+G* level) that led them to conclude that the enhanced reactivity is associated with an increase in the leaving group ability of the reactive ligand, and not with a significant change in the positive character of the silicon atom accompanying increased coordination at silicon.

The object of the present work is to make use of the hard and soft acids and bases (HSAB) principle[4–9] and of its local version,[10–12] and density functional theory (DFT)[13,14] to analyze the global behaviour of hypervalent silicon compounds, and the role of the silicon atom in the reactivity of tetra and pentacoordinated species in nucleophilic substitution reactions. That is, rather than studying the leaving group ability of the ligand and the charge of the silicon atom, we will focus on the global softness,[13,15] and on the softness of the silicon atom in the molecule[10] to rationalize the inherent reactivity of these chemical species. Such procedure has already been used to explain some aspects of the inherent reactivity of several molecules.[16] Thus, in the present work we will discuss first the basic aspects of the local HSAB principle (§2), and then we will present results for SiH_nF_{4-n} and $SiHnF^{1-}_{5-n}$ (§3).

2. Global and local HSAB principles

The HSAB principle,[8,9] has been interpreted as the result of two opposing tendencies, one related to the charge transfer process, and the other one related to the reshuffling of the electronic density. This interpretation is the result of making the assumption that the interaction energy between two chemical species A and B, may be divided into two steps which can be taken as happening in succession, that is

$$\Delta E_{int} = \Delta E_v + \Delta E_m, \tag{1}$$

where

$$\Delta E_v = \frac{-(m_A - m_B)^2 (S_A S_B)}{2(S_A + S_B)}, \tag{2}$$

*For correspondence

$$\Delta E_m = -\frac{l}{2(S_A + S_B)}. \quad (3)$$

m_A and m_B are the chemical potential of A and B, S_A and S_B are their global softness, and l is a constant[11,17] related to an "effective number of valence electrons" that participate in the interaction between A and B.

The first step, ΔE_v, corresponds to the charge transfer process between A and B arising from the chemical potential equalization principle[18] at constant external potential $v(\mathbf{r})$. The second step, ΔE_m corresponds to a reshuffling of the charge distribution, and it is basically a manifestation of the maximum hardness principle[16a] and it takes place at constant chemical potential m.

Through this procedure it has been possible to establish a local version of the HSAB principle by assuming that these tendencies are dominated by the local properties rather than by the global properties of the molecule.[10–12] Thus, in general analysis of the inherent chemical reactivity of the sites of a given species A and B, it has been shown that the interaction energy between two species A and B, at the kth and lth atomic sites of A and B is given approximately by

$$\Delta E_{\text{int}} = -\frac{(m_A - m_B)^2 (S_{Ak} S_{B1})}{2(S_{Ak} + S_{B1})} - \frac{l}{2(S_{Ak} + S_{B1})}, \quad (4)$$

where S_{Ak} and S_{Bl} are the condensed softness of the kth and lth atoms in A and B respectively.

The condensed softness, or the softness of an atom in a molecule, may be derived through the chemical potential equalization principle that leads to define the Fukui function of the kth atom in a molecule A with N_A electrons, in the form,[10]

$$f_{Ak}^{+} = q_{Ak}(N_A + 1) - q_{Ak}(N_A), \quad \text{for nucleophilic attack,} \quad (5)$$

$$f_{Ak}^{-} = q_{Ak}(N_A) - q_{Ak}(N_A - 1), \quad \text{for electrophilic attack,} \quad (6)$$

where q_{Ak} is the gross of the kth atom in the molecule A, and it may be determined by several procedures.[19,20] With these definitions the condensed softness becomes

$$S_{Ak}^{+} = S_A^{+} f_{Ak}^{+}, \quad \text{for nucleophilic attack,} \quad (7)$$

$$S_{Ak}^{-} = S_A^{-} f_{Ak}^{-}, \quad \text{for electrophilic attack,} \quad (8)$$

while the condensed hardness, or the hardness of an atom in a molecule is given by

$$h_{Ak}^{\pm} = 1/S_{Ak}^{\pm}. \quad (9)$$

The condensed softness satisfies the sum rule because $\sum_{k=1}^{K} f_{Ak}^{\pm} = 1$, where K is the total number of atoms in A,

$$\sum_{k=1}^{K} S_{Ak}^{\pm} = S_A^{\pm}. \quad (10)$$

Now, according to (4), among two sites in A, each characterized by its own value of S_{Ak}, when S_{Bl} is large, there is a greater stabilization when the interaction occurs at the site with the greater value of S_{Ak}. However, when S_{Bl} is small, there is a greater stabilization when the interaction occurs at the site with the smallest value of S_{Ak}. These results seem to imply that the statement "soft likes soft" and "hard likes hard" may be extended to a local level, and that although the softest atom in a molecule A is, in general, the most reactive site, there may be other sites, not as soft, that may become the most reactive sites, depending on the atomic softness of the reacting molecule B.

3. Results

In order to analyze the role of the silicon atom in the reactivity of tetra- and pentacoordinated species in nucleophilic substitution reactions, in the context of the local HSAB principle, one needs to calculate the condensed softness of the silicon atom by (7). This situation implies that one may perform *ab-initio* calculations to obtain the charges for the reference molecule $q_{Ak}(N_A)$ and its corresponding anion $q_{Ak}(N_A + 1)$ at the minimum of the potential energy surface of the reference molecule. However, because of the difficulties associated with the SCF procedure for the anions of the molecules studied in this work, we also estimate the values of the global and condensed softness through a simpler procedure.

First, one may note that if the relaxation effects associated with the addition of charge are neglected, then[7]

$$S_A = (e_A^{L} - e_A^{H})^{-1}, \quad (11)$$

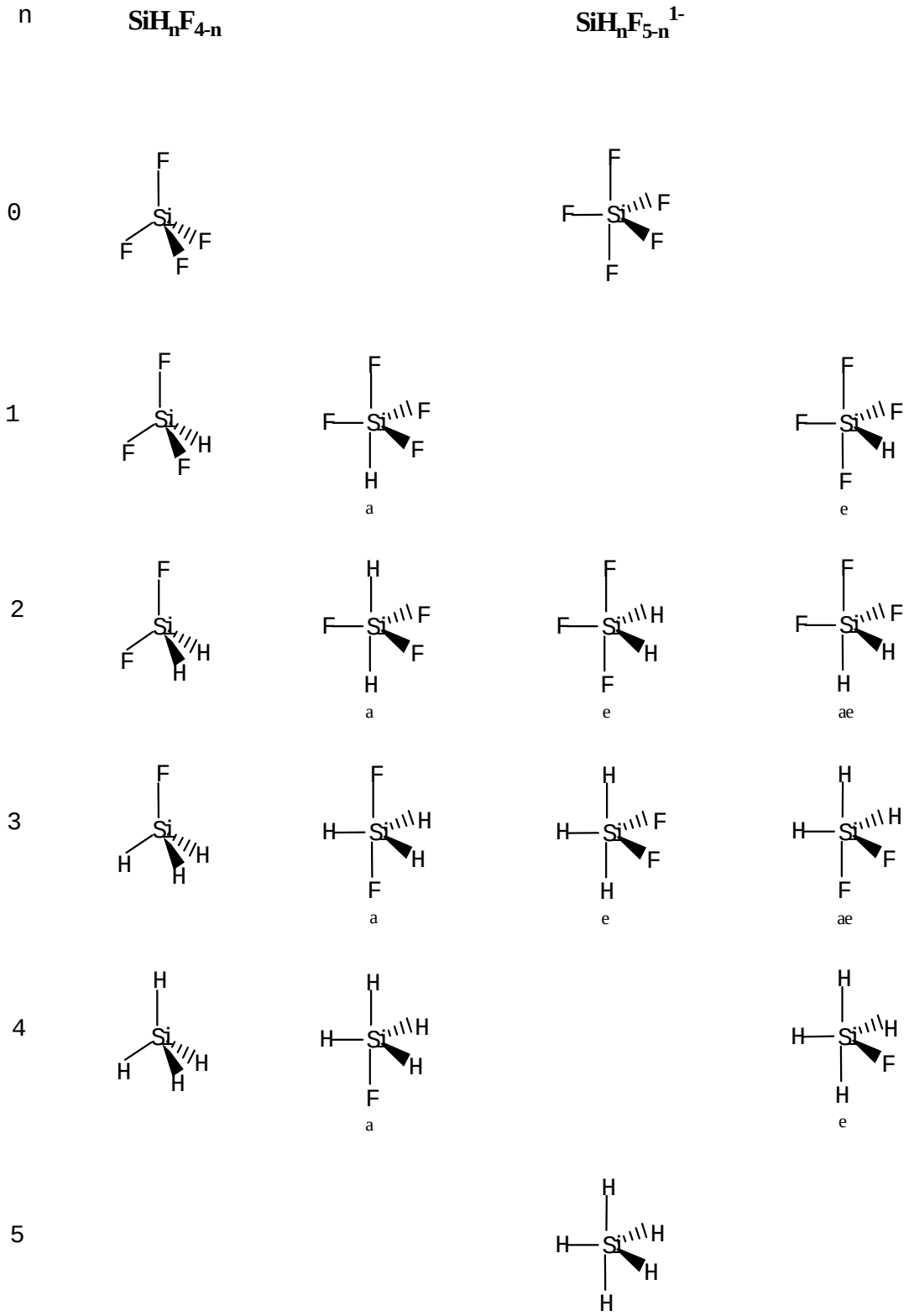

Figure 1. Tetra- and pentacoordinated silicon species; SiH_nF_{4-n} ($0 < n < 4$) and $SiH_nF_{5-n}^{1-}$ ($0 < n < 5$); *a* = apical and *e* = equatorial.

where e_A^L and e_A^H are the eigenvalues of the lowest unoccupied and highest occupied molecular orbitals respectively.

On the other hand, one may approximate the hardness of an atom as a function of the charge through a Taylor series expansion,

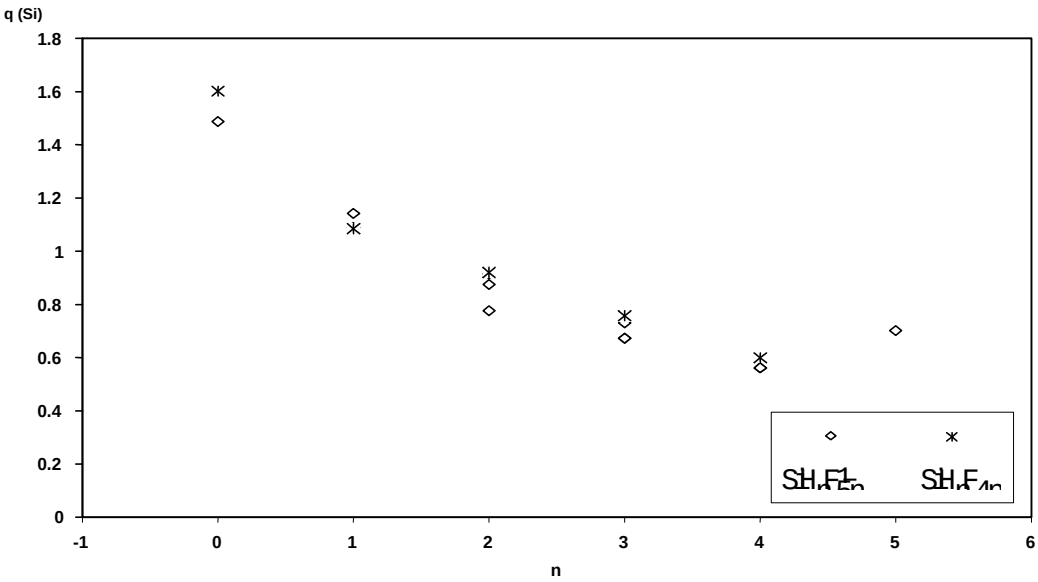

Figure 2. Atomic silicon charge as a function of the number of hydrogen atoms in the molecules SiH_nF_{4-n} and $SiH_nF_{5-n}^{1-}$ (obtained by a Mülliken population analysis). The silicon charge values are given in a.u.

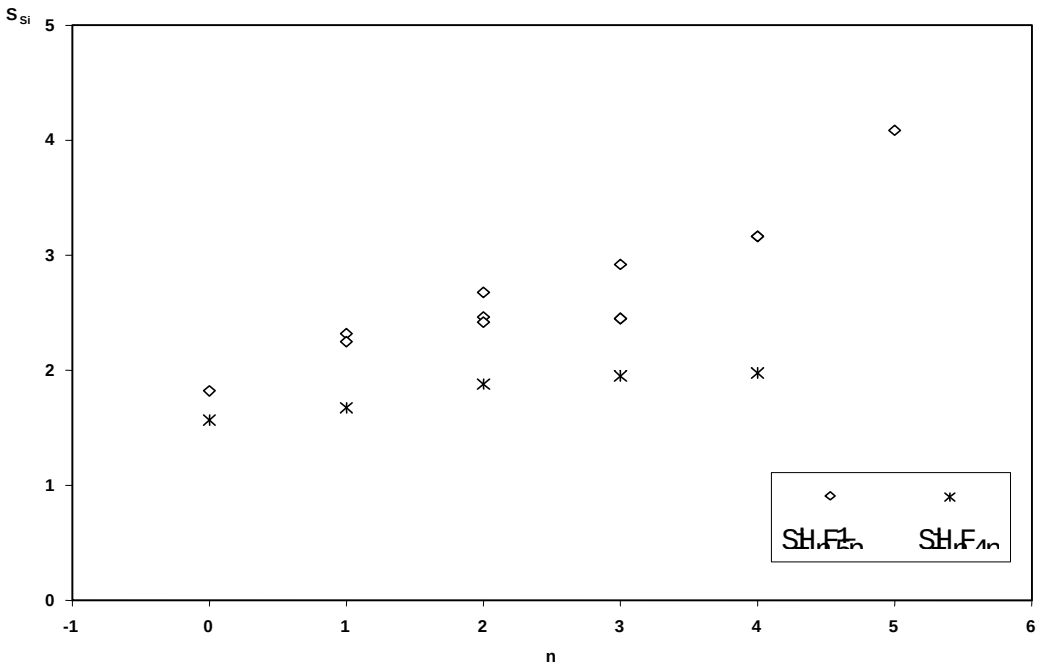

Figure 3. Global softness as a function of the number of hydrogen atoms in the molecules SiH_nF_{4-n} and $SiH_nF_{5-n}^{1-}$ (obtained by $S = I - A)^{-1}$). The global softness values are given in a.u.$^{-1}$

$$h_k(q_k) = h_k^0 - q_k(\partial h_k / \partial N_k)|_{N_k^0}, \tag{12}$$

where h_k^0 is the hardness and N_k^0 is the total number of electrons of the isolated neutral atom k, qk = $N_k^0 - N_k$. Note that

$$\left(\frac{\partial h_k}{\partial N_k}\right)_v\Big|_{N_k^0} = \left(\frac{\partial^2 m_k}{\partial N_k^2}\right)_v\Big|_{N_k^0} = \left(\frac{\partial^3 E_k}{\partial N_k^3}\right)_v\Big|_{N_k^0}. \tag{13}$$

Assuming that the hardness of the kth atom in a molecule may be estimated through (9), substitut-

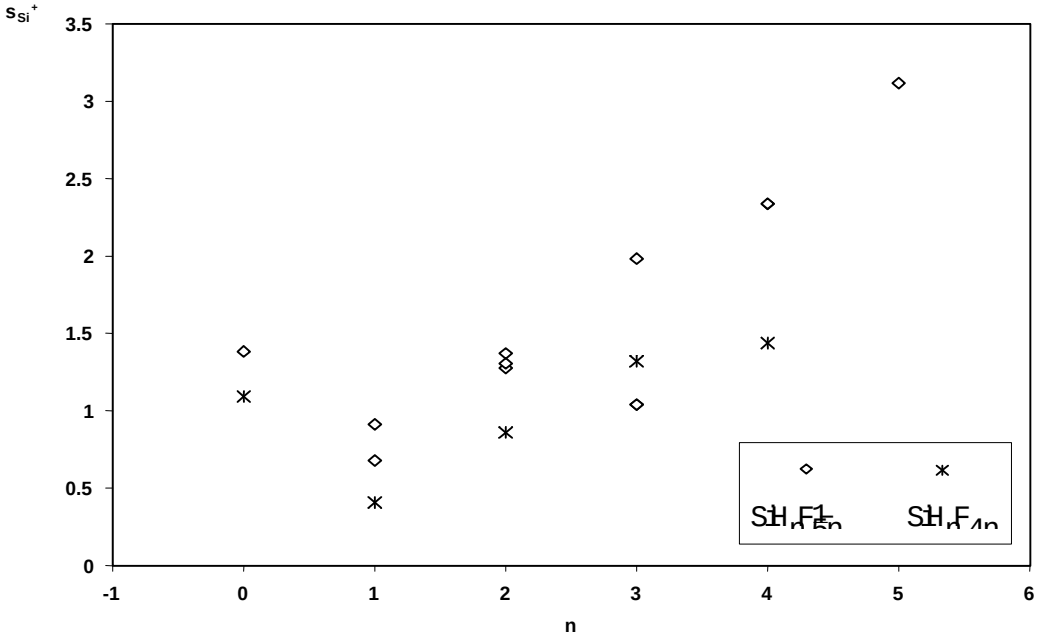

Figure 4. Nucleophilic condensed softness of the silicon atom as a function of the number of hydrogen atoms in the molecules SiH_nF_{4-n} and $SiH_nF_{5-n}^{1-}$ (obtained by $S_{Ak}^+ = S_A^+ f_{Ak}^+$). The condensed softness values are given in a.u.$^{-1}$

ing in this equation the hardness of an atom as a function of the charge of the *k*th atom of the molecule A (12), we find that

$$S_{Ak} = (e_A^L - e_A^H)^{-1} \frac{[h_k^0 - q_k(\partial h_k / \partial N_k)|_{N_k^0}]^{-1}}{\sum_{k=1}^{k}[h_k^0 - q_k(\partial h_k / \partial N_k)|_{N_k^0}]^{-1}}, \tag{14}$$

where (10) and (11) have been used. This procedure allows us to avoid the calculation of the (N_A + 1) electron molecule, because we one only need the isolated atom values[21] of h_k^0 and $(\partial h_k/\partial N_k)_v|_{N_k^0}$, and the molecular values of e_A^L and e_A^H, and q_{Ak} of the N_A electron system.

Thus, we have done *ab-initio* calculations[22] of the molecules SiH_nF_{4-n} ($0 < n < 4$) and $SiH_nF_{5-n}^{1-}$ ($0 < n < 5$) at the BHHLYP/6-311++G** level (figure 1). In figure 2 we present the behaviour of the charge of the silicon atom in the molecule (obtained from a Mülliken population analysis) as a function of the number of hydrogen atoms (*n*). We can see that in general the positive charge of the silicon atom is slight higher in the tetracoordinated molecules than in the pentacoordinated molecules.

In figure 3 we present the behaviour of the global softness as a function of n for the tetracoordinated and the pentacoordinated compounds (calculated by $S = (I - A)^{-1}$). We can see that the global softness of the pentacoordinated species is larger than the global softness of the tetracoordinated species, and the difference increases as *n* increases. Since, in general, the larger the values of the softness, the greater the reactivity, these results imply that, globally, the pentacoordinated species shows an enhanced reactivity, and they also imply that the reactivity diminishes when the number of fluorine atoms increases. Calculations of the chemical potential values show that $m_{SiH_nF_{n-5}^{1-}} > m_{SiH_nF_{n-4}}$ and *m* increases when *n* increases.

Now, from a local point of view, figure 4 shows that the silicon atom is softer in the pentacoordinated species than in the tetracoordinated species (obtained from (7)). These results also imply that the pentacoordinated species shows an enhanced reactivity with respect to the tetracoordinated species. It should be noted that the condensed softness of the silicon atom diminishes when the number of fluorine atoms increases and, therefore, from a local point of view, we may conclude that when *n* decreases the reactivity decreases.

In figure 5, we present the behaviour of the condensed softness of the silicon atom calculated from (14), we can see that the condensed softness increases as the coordination number and the hydrogen atoms increase. Therefore, the tests that were carried out in

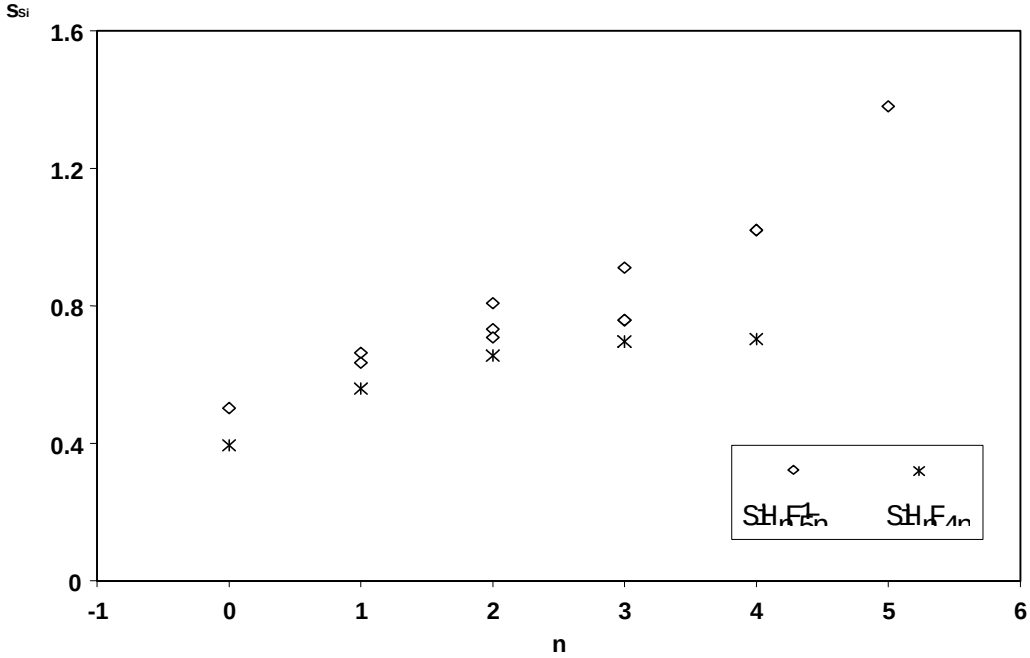

Figure 5. Condensed softness of the silicon atom as a function of the number of hydrogen atoms in the molecules SiH_nF_{4-n} and $SiH_nF_{5-n}^{1-}$ (obtained by (14)). The condensed softness values are given in a.u.$^{-1}$

SiH_nF_{4-n} and $SiHnF_{5-n}^{1-}$ showed that (14) reproduces qualitatively the same trends as (7). Therefore, if we invoke the local HSAB principle, these results seem to imply that soft nucleophiles preferably react with $SiHnF_{5-n}^{1-}$ compounds, and hard nucleophiles with SiH_nF_{4-n} compounds.

It is important to note that although, in general, the behaviour of the global softness of the systems presented in this work is quite similar to the behaviour of the condensed softness of the silicon center, the subtle differences may be very important to describe the inherent chemical reactivity of these species. Indeed, we believe that the local values provide a better representation of the chemical behaviour of a molecule, and therefore it is predicted that pentacoordinated species will be, in general, more reactive than the tetracoordinated species.

3. Conclusions

In summary, it has been shown that the softness of the silicon atom in the molecule seems to be a useful and perhaps unifying concept, to rationalize the inherent reactivity of these chemical species. Thus, we hope that this work will motivate experimental research that may provide information about the role of the condensed softness of the silicon atom as a function of the nucleophile softness, through the study of the interaction between several hypervalent silicon compounds and several nucleophiles. Calculations of the interaction energy through (4) using some examples of soft and hard nucleophiles are in progress.

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