ABSTRACT

Variation of Electronegativity with Oxidation State

With Emphasis on Atomic Charges

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The main objective was to determine if electronegativity, χ, varies with oxidation state. This was achieved via the calculation of atomic charges.

The atomic charges for selected compounds of sulphur and nitrogen were calculated using a revised Lewis Langmuir (LL_A) atomic charge equation assuming constant electronegativity and these were compared with results obtained from Natural Population Analysis (NPA) segment of the Gaussian 98W programme. LL_A gives atomic charges which are determined by the Formal Charge (FC) of an atom and the electronegativity of the atom and those atoms bonded to it, whereas NPA is *ab initio*.

Graphical plots were constructed with the data obtained from these two methodologies to ascertain what kind of correlation results. To further check if electronegativity varies with oxidation state, LL_A atomic charges were also calculated using valence state dependent χ values to determine whether there was an improvement in correlation with NPA values.

Analysis indicated that the atomic charges computed using a constant electronegativity showed a relatively high correlation coefficient to Weinhold's NPA atomic charges.

When the electronegativity of the central atom was varied according to its oxidation state, it was discovered that there was a worsening of the correlation between the two variables.

Based on these findings, the data suggest that the electronegativity of the central atom does not vary with changes in the oxidation state.