MOLECULAR DESCRIPTION OF COPPER (I) OXIDE AND COPPER (II) OXIDE

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Recebido em 14/03/2018; aceito em 30/05/2018; publicado na web em 12/07/2018

The topological index of a molecular structure correlate certain physicochemical properties such as boiling point and stability of that molecular structure. Recently several topological indices have been introduced and studies have shown their association with certain physical and chemical properties of other molecules. Specifically, Zagreb, Atom-bound connectivity (ABC) and Sanskruti indices have been correlated with extent of branching, enthalpy and entropy of some organic molecules. In this study we have calculated Zagreb, Atom-bound connectivity (ABC) and Sanskruti indices (S) for Copper (I) oxide and Copper (II) oxide CuO. Additionally, from the experimentally available data, we calculated entropy and enthalpy per unit cell for both the oxides and compared with Atom-bound connectivity and Sanskruti indices. It appears that these indices have very poor relation with these physical properties in both oxides of copper and they may need some modifications to show considerable compliance as reported in other organic molecules.

Keywords: molecular graphs; zagreb indices; atom-bound connectivity index; sanskruti index; copper oxide.

INTRODUCTION

“A graph that shows constituents of a molecule and their connectivity is known as molecular graph and such representation is usually referred as topological representation of molecule.” Molecular graphs are usually characterized by different topological indices for correlation of chemical structure of a molecule with biological, chemical or physical properties. Studies have reported several applications of different topological indices in quantitative structure-activity relationship (QSAR) and quantitative structure-property relationship (QSPR), virtual screening and computational drug designing.

“So far, many different topological indices have been developed, and most of them are only graph descriptors.” Only a few indices have shown their correlation with biological, chemical or physical chemical properties of certain molecules. For example, Zagreb indices \((M_1 & M_2)\) were first reported by Gutman and Trinajestic for the correlation of chemical structure with \(\pi\) electrons. However, later \(M_1\) and \(M_2\) were associated with extent of branching in a molecule. They are described by equation (1) & (2) for a graph \(G \equiv (V,E)\), where \(V\) to be the vertex set and \(E\) to be the edge set of \(G\). The degree \(d_p\) of the vertex \(p\) is the quantity of edges of \(G\) incident with \(p\). The length of most limited path in a graph \(G\) is a distance \(d(p,q)\) amongst \(p\) and \(q\).

\[
M_1(G) = \sum_{pq \in E} (d_p + d_q) \tag{1}
\]

\[
M_2(G) = \sum_{pq \in E} (d_p \cdot d_q) \tag{2}
\]

“Another topological index is atom-bound connectivity (ABC) that was introduced by Estrada et al.” Later, studies have reported its exceptional correlation with thermodynamic properties of organic molecules, specifically with heat of formation of alkanes. This index is characterized by Equation (3) considering the graph similar to Zagreb indices

\[
ABC(G) = \sum_{pq \in E} \sqrt{\frac{d_p + d_q - 2}{d_p \cdot d_q}} \tag{3}
\]

“Another molecular descriptor that was correlated with thermodynamic properties is Sankruti index. This index was introduced in 2016 by S. M. Hosamani and it shows considerable correlation with entropy of some organic molecules. It is characterized as equation (4) considering the above mentioned graph conditions

\[
S(G) = \sum_{pq \in E} \left( \frac{s_p \times s_q}{s_p + s_q - 2} \right)^3 \tag{4}
\]

“This study is designed to calculate Zagreb, ABC and Sanskruti indices for two oxides of \(\text{CuO}\). It will allow us to compare these indices with the experimentally determined entropy, enthalpy and other physical properties of \(\text{CuO}\) and \(\text{Cu}_2\text{O}\).”

THEORY AND METHODS

Structure of copper (I) oxide (\(\text{Cu}_2\text{O}\))

\(\text{Cu}_2\text{O}\) is a naturally occurring reddish ore that is mainly used in chemical sensors, solar oriented cells, photo-catalysis and batteries. Crystal structure of \(\text{Cu}_2\text{O}\) is composed on small cubic unit cells based on Cu and O atoms (Figure 1a). Analysis of the crystal lattice showed that each Cu atom is linked with two O atoms; in turn every O atom is connected with four Cu atoms (Figure 1b)”
Here, we have considered monolayer of Cu$_2$O for convenience. To determine the indices for Cu$_2$O we choose the settings of this graph as; $G \cong \text{Cu}_2\text{O}[m,n]$ be the chemical graph of Cu$_2$O with $(m \times n)$ unit cells in the plane. More precisely, $m$ represents the number of unit cells in row and $n$ represents the number of unit cells in column. Also for our convenience we represent Cu$_2$O[m,n] as a graph $G$. The Figure 1(b) is representing Cu$_2$O[2,2]. Also Figure 2 represents one sheet view of Copper(I) oxide Cu$_2$O[4,4]. Computational analysis showed that the quantity of vertices and edges of Cu$_2$O[m,n] are $7mn+2m+2n+2$ and $8mn$, respectively. In Cu$_2$O[m,n], the number of zero degree vertices is 4, the number of one degree vertices is $4m+4n-4$, the number of two degree vertices is $6mn-2m-2n+2$ and the number of four degree vertices is $mn$ (Table 1).

**Theorem 1.** “Consider the graph of $G \cong \text{Cu}_2\text{O}[m,n]$ with $m,n \geq 1$, then its first and second Zagreb index is equal to,”

\[
M_1(G) = 40mn-4m-4n+4 \\
M_2(G) = 48mn-8m-8n+8
\]

**Proof.** “Let $G$ be the crystallographic structure of [m, n]. The first Zagreb index is computed as below:”

\[
M_1(G) = \sum_{pq \in E(G)} (d_p + d_q)
\]

“$M_1(G) = (4n+4m-4)(1+2)+(4mn-4n-4m-4)(2+2)+(4mn)(2+4)$

$M_1(G) = 40mn-4m-4n+4.$”

“By using Table 1 and Equation 1 the second Zagreb index are computed as below:”

\[
M_2(G) = \sum_{pq \in E(G)} (d_p \cdot d_q)
\]

“$M_2(G) = (4n+4m-4)(1\times2)+(4mn-4n-4m-4)(2\times2)+(4mn)(2\times4)$

$M_2(G) = 48mn-8m-8n+8.$”

“In the next Theorem, we have computed the exact result of ABC index for the chemical graph Cu$_2$O[m,n].”

**Theorem 2.** “Consider the graph of $G \cong \text{Cu}_2\text{O}[m,n]$ with $m,n \geq 1$, then its ABC index is equal to,”

\[
\text{ABC}(G) = 4\sqrt{2} (mn - 1)
\]

**Proof.** “Let $G$ be the chemical graph of Cu$_2$O[m,n]. Then by using Table 1 and equation (3) the ABC index is computed as below:”

\[
\text{ABC}(G) = \sum_{pq \in E(G)} \sqrt{\frac{d_p + d_q}{2} - \frac{d_y}{2}}
\]

\[
\text{ABC}(G) = (4n+4m-4)\sqrt{\frac{1+2+2}{1\times2}} + (4mn-4n-4m-4)\sqrt{\frac{2+2+2}{2\times2}}

+ 4mn\sqrt{\frac{4+2+2}{4\times2}}

\text{ABC}(G) = 4\sqrt{2} (mn - 1)
\]

“The Table 2 shows partition of edges of the chemical graph Cu$_2$O[m,n] depending on the sum of degrees of the neighbouring vertices of end vertices of each edge.”

“The next Theorem shows the exact value of Sanskruti index of Cu$_2$O[m,n].”

**Theorem 3.** “Consider the graph $G \cong \text{Cu}_2\text{O}[m,n]$ with $m,n \geq 2$, then its Sanskruti index $S(G)$ is equal" 

\[
S(G) = 64mn - \frac{185892m}{1331} - \frac{185892n}{1331} + \frac{185892}{1331}
\]

**Proof.** “Let $G$ be the crystallographic structure of Cu$_2$O[m,n]. Then by using Table 2 and equation (4) the Sanskruti index $S(G)$ is computed as follows:”

\[
S(G) = \sum_{pq \in E(G)} \left( \frac{s_p \times s_q}{s_p + s_q - 2} \right)^3
\]
Molecular description of copper (I) oxide and copper (II) oxide

Structure of copper(II) oxide (CuO)

The crystal structure of Copper(II) oxide (CuO) is composed on monoclinic unit cells (Figure 3a). Here we have considered monolayer of CuO for convenience. To find the indices we choose the settings of this graph as; let \( G \cong CuO[m,n] \) be the chemical graph of CuO with \((m \times n)\) unit cells in the plane. The Figure 3b is representing the lattice of CuO[4,4].

Computational analysis showed that number of vertices and edges of \( CuO[m,n] \) are \( 8mn+2m+2n \) and \( 12mn \), respectively. In \( CuO[m,n] \) the number of one degree vertices are \( 2n \), the number of two degree vertices are \( 2mn+4m+2n \), the number of three degree vertices are \( 4mn-2n \) and the number of four degree vertices are \( 2mn-2m \).

In the next Theorem, we have computed the exact value of first and second Zagreb index for the chemical graph CuO[m, n].

**Theorem 4.** “Consider the graph of \( G \cong CuO[m,n] \) with \( m, n \geq 1 \), then its first and second Zagreb index is equal to,”

- \( M_1(G) = \sum_{pq \in E(G)} (d_p + d_q) \)
- \( M_2(G) = \sum_{pq \in E(G)} (d_p \cdot d_q) \)
- \( M_1(G) = (2)(1 + 2) + (2n + 2)(1 + 4) + (2n + 2)(2 + 2) + (4mn + 8m - 6)(2 + 3) + (8mn - 8m - 4n + 4)(3 + 4) \)
- \( M_1(G) = 76mn - 16m - 10n + 2 \)
- \( M_2(G) = (2)(1 \times 2) + (2n + 2)(1 \times 4) + (2n + 2)(2 \times 2) + (4mn + 8m - 6)(2 \times 3) + (8mn - 8m - 4n + 4)(3 \times 4) \)
- \( M_2(G) = 120mn - 48m - 32n + 16 \)

Proof. “Let G be the crystallographic structure of \( CuO[m, n] \). The first Zagreb index is computed as:

\[
M_1(G) = \sum_{pq \in E(G)} (d_p + d_q)
\]

\[
M_1(G) = (2)(1 + 2) + (2n + 2)(1 + 4) + (2n + 2)(2 + 2) + (4mn + 8m - 6)(2 + 3) + (8mn - 8m - 4n + 4)(3 + 4)
\]

\[
M_1(G) = 76mn - 16m - 10n + 2
\]

In the next Theorem, we have computed the exact result of ABC index for the chemical graph \( CuO[m,n] \).”

**Theorem 5.** “Consider the graph of \( G \cong CuO[m,n] \) with \( m, n \geq 1 \), then its ABC index is equal to”

\[
ABC(G) = \sqrt{2} + \frac{(2n - 2)\sqrt{3}}{2} + \frac{(2n + 2)\sqrt{2}}{2} + \frac{(4mn + 8m - 6)\sqrt{2}}{2}
\]

\[
\frac{(8mn - 8m - 4n + 6)\sqrt{15}}{6}
\]

Proof. Let G be the chemical graph of CuO[m, n]. Then by using Table 3 and equation (3) the ABC index is computed as below:

\[
ABC(G) = \sum_{pq \in E(G)} \sqrt{d_p + d_q - 2}
\]

**Table 4.** Edge partition of the graph of CuO[m,n] with \( m, n \geq 2 \)

<table>
<thead>
<tr>
<th>(Sp, Sq)</th>
<th>Frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2, 4)</td>
<td>2</td>
</tr>
<tr>
<td>(4, 5)</td>
<td>4</td>
</tr>
<tr>
<td>(4, 6)</td>
<td>2</td>
</tr>
<tr>
<td>(4, 9)</td>
<td>2n - 2</td>
</tr>
<tr>
<td>(5, 6)</td>
<td>2n + 2</td>
</tr>
<tr>
<td>(6, 6)</td>
<td>12n - 12</td>
</tr>
<tr>
<td>(6, 9)</td>
<td>2n - 2</td>
</tr>
<tr>
<td>(5, 10)</td>
<td>2n - 2</td>
</tr>
<tr>
<td>(6, 10)</td>
<td>4mn - 4m - 4n + 4</td>
</tr>
<tr>
<td>(9, 10)</td>
<td>4n - 4</td>
</tr>
<tr>
<td>(10, 12)</td>
<td>8mn - 8m - 8n + 8</td>
</tr>
</tbody>
</table>

The next Theorem shows the exact value of Sanskruti index of \( CuO[m,n] \).
**Theorem 6.** “Consider the graph \( G \sim CuO[m, n] \) with \( m, n \geq 2 \), then its Sanskruti index \( S(G) \) is equal to:

\[
S(G) = \frac{101843355285146}{137310366375} - \frac{7613496016592n}{7689380517} - \frac{63583488m}{42875} + \frac{700704mn}{343}
\]

**Proof.** Let \( G \) be the crystallographic structure of \( CuO[m, n] \). Then by using Table 4 and equation (4) the Sanskruti index \( S(G) \) is computed as follows:

\[
S(G) = \sum_{p=q \in (m)} \left( \frac{S_m \times S_n}{S_m + S_n - 2} \right)
\]

**RESULTS AND DISCUSSIONS**

“In this section we have compared the first (M1) and second Zegrab (M2) indices of Copper(I) oxide \( Cu_{2O} \) and Copper(II) oxide \( CuO \) which is shown in Table 5. Analysis of the data showed that both the indices are higher in \( CuO \) compared to those of \( Cu_{2O} \). For instance, \( M1(CuO)/M1(\text{Cu}_{2O}) \) for \([1,1]\) cell is 1.44 and the ratio increases to 1.943 for \([7,7]\) and then it decreases to 1.87 for \([10,10]\) cell. On the other hand, \( M2(CuO)/M2(\text{Cu}_{2O}) \) for \([1,1]\) is 1.40 and the ratio gradually increases to 2.413 for \([10,10]\) cell.”

“Comparison of ABC indices for both the oxides of Copper showed higher values for \( CuO \) compared to those of \( Cu_{2O} \) for \([2,2]\) cell is 1.95 and it decreases to 1.44 for \([10,10]\). This shows its decreasing trend with the increase of cells.”

“In the Table 7, we gave a comparison of the Sanskruti indices of Copper(I) oxide \( Cu_{2O} \) and Copper(II) oxide \( CuO \). Analysis of the data showed that host higher Sanskruti index compared to \( Cu_{2O} \). The \( S(Cu_{2O})/S(CuO) \) for \([2,2]\) is 3.825 and it increases to 5.34 for \([10,10]\). This shows its increasing trend with the increase of cells.”

A topological index is a numerical value that is calculate form molecular graph for explaining the relationship of chemical structure with physiochemical properties. So far, several applications of different indices have been reported for organic molecules, such as entropy and enthalpy determination, chirality identification,\(^9\) ZE-isomerism\(^10\) and heterosystem studies.\(^11\) The topological indices can be very helpful for crystalline compounds to correlate their structure with physiochemical properties. Therefore, we have determined Zagreb, ABC and Sanskruti indices for \( Cu_{2O} \) and \( CuO \). Additionally, we compared these indices with the physical properties these oxides as described in Pubchem (https://pubchem.ncbi.nlm.nih.gov/).”

“Zagreb indices (M1 & M2) were initially considered for total energy of \( \pi \)-electrons in organic molecules.\(^12\) However, later they were associated with extent of branching in a molecular graph \([10,11]\). Analyses revealed higher \( M1 \) and \( M2 \) for \( CuO \) compared to those of \( Cu_{2O} \) at any cubic level i.e. at any equal value of \( (m \times n) \) (Table 5). It suggests more branching in \( CuO \) compared to \( Cu_{2O} \). It may cause more compact \( CuO \) (Density: 6.315 g/cm\(^3\)) structure compared to \( Cu_{2O} \) (6.0 g/cm\(^3\)).”
Moreover, higher melting point of CuO (1599 K) compared to that of Cu₂O (1505 K) may also be associated to the higher branching."

"ABC indices of Cu₂O and CuO were calculated at different unit cells as shown in Table 6. Analysis of the data showed higher ABC indices for CuO compared to those of Cu₂O (Table 6). Figure 4 shows that ABC indices increase exponentially with number of cells (m × n) for both the oxides of copper. On the other hand, a linear relation of ABC index was observed with formula units (Figure 5). Since, ABC index has previously been linked with the thermodynamic properties" of different alkanes, 7,11 "therefore, we determined the heat of formation per different units cells of both the oxides from the reported real molar enthalpy of formations (Table 6). For example, experimental molar enthalpy for CuO is -156 kJ mol⁻¹ so for one formula unit it will be -156/6.022×10⁻²³ J. The obtained value then multiplied with the number of formula units present in each cell to get the enthalpy for the cell. Similarly, enthalpy for Cu₂O calculated considering standard molar enthalpy -170 kJ mol⁻¹ (Table 6). Analysis of the data showed that ABC index is not strongly associated with enthalpy of formation for the oxides of copper as reported in case of alkanes. 6,13 Therefore we determined a mathematical relationship, by using equation generator (http://www.1728.org/threepts.htm), between the ABC indices and the heat of formation of both the oxides of copper as below:

Heat of formation for Cu₂O = \[3.045 \times 10^{-6} \times (ABC)^2 + 19.95(ABC) + 112\] × 10⁻²³

Heat of formation for CuO = \[3.75 \times 10^{-4} \times (ABC)^2 + 13.67(ABC) + 60.17\] × 10⁻²³

These equations can be used for the transformation of ABC indices into the approximate heat of formation of the oxides of Cu at any cubic level.

Figure 6 shows a linear relation of Sanskruti indices with number of formula units and analysis showed higher indices for Cu₂O compared to CuO. Previous studies have shown an association of Sanskruti indices with entropy of octane. 15 Here we calculated the entropy of both the oxides at different cells from the standard molar entropy. For instance, standard molar entropy for CuO is 93 J mol⁻¹ K⁻¹ so for one formula unit it will be 93/6.022×10⁻²³ J K⁻¹, and for each cell we just multiplied the obtained value with the no. of formula units present in the cell. Similarly entropy for Cu₂O calculated considering standard molar entropy 43 J mol⁻¹ K⁻¹ (Table 7). Analysis of the data showed a considerable difference between the Sanskruti indices and entropies for the oxides of Cu (Table 7). Therefore, we determined a mathematical relation for the transformation of Sanskruti indices into approximate entropies of both the oxides of copper as below:

Entropy of Cu₂O = \[-2.89 \times 10^{-7} \times (S)^2 + 0.1913 \times (S) + 48.89\] × 10⁻²³

Entropy of CuO = \[-1.081 \times 10^{-6} \times (S)^2 + 0.1819 \times (S) + 70.82\] × 10⁻²³

**CONCLUSIONS**

In conclusion, ABC and Sanskuriti indices of Cu₂O and CuO showed considerable difference with the experimentally reported entropy and enthalpy of these oxides. On the other hand, Zagreb index and all these indices showed exponential increase with the number of unit cells. On the other hand, these indices showed a linear behavior with number of formula units, suggesting that we may need a slight transformation of these indices for better explanation of physical properties of crystalline compounds."
ACKNOWLEDGEMENTS

The authors are grateful to the anonymous referees for their valuable comments and suggestions that improved this paper. This research is supported by the Start-up Research Grant 2016 of United Arab Emirates University (UAEU), Al Ain, and United Arab Emirates via Grant No. G00002233 and UPAR Grant of UAEU via Grant No. G00002590.

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