DIAMAGNETISM OF SOME ISOELECTRONIC COMPOUNDS

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BHATNAGAR AND CO-WORKERS\(^1\) extended the Langevin's equation to iso-electronic compounds, containing the same number of atoms, which they termed 'electronic isomers' and obtained the following empirical relation for their molecular susceptibility \(X_m\):

\[ X_m = -2 \cdot 832 \cdot K \cdot r_n^2 \]  \hspace{1cm} (I)

in which \(r_n\) is the radius of the molecule, calculated according to Bragg's method\(^2\) of the closest packing of atoms and \(K\) is a constant for a set of such compounds. They showed that the values of \(X_m\) calculated for a large number of inorganic and organic compounds constituting 'electronic isomers' from the average value of \(K\) are in good agreement with the observed values.

In the present paper the validity of the relation I has been tested in the case of (i) SbCl\(_3\), T1CNO and (ii) Bi\(_2\)O\(_3\) and SnBr\(_4\), each set of which separately constitutes iso-electronic compounds containing the same number of atoms. It has been also examined in the case of (i) phenol, aniline, toluene and (ii) \(p\)-hydroxy phenyl, \(p\)-aminophenyl and \(p\)-tolyl arsinic acids. These sets of compounds are separately isoelectronic and contain different numbers of atoms. The nomenclature adopted by Newton Friend\(^3\) for the organo arsenic acids has been used by the author.

**EXPERIMENTAL**

Most of the substances used were of extrapure quality (Merck's or B.D.H.-A.R. quality). \(P\)-Hydroxyphenyl and \(p\)-tolyl arsinic acids were prepared according to the methods described by Bart\(^4\) and Palmer and Adams\(^5\) respectively. A sample of pure \(p\)-amino phenyl arsanic acid was supplied by Dr. T. N. Ghosh of the Bengal Immunity Research Institute, Calcutta. T1CNO was prepared according to Kuhlmann's method\(^6\) and the purity of these substances was established before use, by standard methods of analysis.
The specific susceptibilities \( (X_s) \) of these compounds are given in \(-1 \times 10^{-6}\) cgs. units in column 7 of Table I. Other values are also expressed in the same units. These were measured by means of a modified Gouy's balance in which the usual Paul Bunge balance has been replaced by a Mettler balance, which facilitated the quick weighing of the specimens with the same sensitivity for varying loads. A Mettler balance (semi-micro model) was modified to weigh specimens in and out of a uniform magnetic field as required by the theory of the method. The modifications are shown schematically in Fig. 1 and consist essentially in attaching a pyrex glass fibre assembly to the pan of the balance so as to take up the specimen tube at its lower end.

![Fig. 1](image)

The gravity and equilibrium nuts on the beam of the balance were adjusted for the sensitivity of the balance and to compensate for the extra weight of the attachment. The electromagnet and the specimen tubes, described by Prasad, Dharmatti and Gokhale\(^7\) were used by the author.

The zero reading on the optical scale of the balance was checked and adjusted, if necessary, before each weighing. The empty clean specimen
tube was weighed and the current was switched on while the beam was fully released and the shift, i.e., the decrease in the weight of the tube was determined. The current was switched off and the initial weight of the tube was checked. The weights and shifts of conductivity water \( (\chi_a = 0.720) \) and KCl-A.R. quality \( (\chi_a = 0.516) \) used as the substances of reference for liquids and solids respectively, and of other substances filled in the specimen tube up to an etched mark were determined in the same manner. Packings of solids varying by 3\% of their weight were rejected. The actual weight of the substances and the shifts of the order of a few milligrams were measured with an accuracy of \( \pm 0.02 \text{ mgm} \).

The specific susceptibilities of benzene, cyclohexane, sodium chloride and potassium persulphate of extra pure quality were found to be 0.7020, 0.8001, 0.5080 and 0.3746 respectively. The values agree closely with the values reported in literature by previous workers.\(^8\) A number of determinations of the susceptibilities of standard substances of extra pure quality showed that these measurements could be made with an accuracy of \( \pm 1\% \) with this balance.

**DISCUSSION OF RESULTS**

The specific susceptibilities found by the author for SbCl\(_3\), Bi\(_2\)O\(_3\), SnBr\(_4\), C\(_6\)H\(_5\).OH, C\(_6\)H\(_5\).NH\(_2\) and C\(_6\)H\(_5\).CH\(_3\) are in good agreement with those reported in the International Critical Tables and by other workers. The value for TICNO is in close agreement with the value reported by Trew\(^9\) but is higher than that of Nevgi\(^10\).

The radii \( r_m \) in Å units of the molecules of the several compounds have been calculated according to the method followed by Bhatnagar and co-workers\(^1\) using the latest data of Pauling\(^11\) for the radii of the individual atoms and are given in column 4 of the table. According to Pauling,\(^11\) the single bond covalent radii are so chosen that their sums represent internuclear distances for bonded atoms in molecules and crystals and these are applicable to covalent bonds with considerable ionic character.

The values of \( K \) have been calculated from equation 1 from the observed molecular susceptibilities \( \chi_m \), and are given with the mean values for the isoelectronic organic compounds in columns 5 and 6 respectively. The values of \( \chi_m \) calculated therefrom are given in column 9 of the table.

It will be seen from the table that values of \( K \) vary widely in each set of the inorganic compounds and as such a mean value of \( K \) cannot be obtained to satisfy relation 1. This observation is in line with that of Prasad and co-workers,\(^7\) who found that in several sets of isoelectronic compounds,
containing the same number of atoms, the relation does not hold. This may be due to the fact that in extending the Langevin's equation of a monatomic system to a polyatomic one, Bhatnagar and co-workers did not take into account factors, such as the nature of the chemical binding existing in the molecules and the differences in the solid and liquid states of the inorganic compounds.

The only remarkable feature of their relation appears to be its applicability to isoelectronic organic compounds. It is seen from Table I that the values of $K$ are nearly the same in each set of the organic compounds. The values of $\chi_m$, calculated from the corresponding average values of $K$ are in good agreement with the observed ones.

The author feels grateful to Dr. T. N. Ghosh of the Bengal Immunity Research Institute for supplying $p$-aminophenyl arsinic acid and to Dr. Mata Prasad for the facilities and his encouraging guidance throughout this work.

### Table I

<table>
<thead>
<tr>
<th>Substances</th>
<th>No. of atoms</th>
<th>No. of electrons</th>
<th>$r_n$ Å units</th>
<th>$K$ Mean</th>
<th>$\chi_a$</th>
<th>$\chi_m$ cal</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) SbCl$_3$</td>
<td>4</td>
<td>102</td>
<td>1.878</td>
<td>9.183</td>
<td>...</td>
<td>0.2540</td>
</tr>
<tr>
<td>TICN0</td>
<td>4</td>
<td>102</td>
<td>1.621</td>
<td>7.454</td>
<td>...</td>
<td>0.2251</td>
</tr>
<tr>
<td>(ii) Bi$_2$O$_3$</td>
<td>5</td>
<td>190</td>
<td>1.921</td>
<td>7.670</td>
<td>...</td>
<td>0.1700</td>
</tr>
<tr>
<td>SnBr$_4$</td>
<td>5</td>
<td>190</td>
<td>2.054</td>
<td>12.990</td>
<td>...</td>
<td>0.3542</td>
</tr>
<tr>
<td>(i) Cs$_n$H$_m$OH</td>
<td>13</td>
<td>50</td>
<td>1.473</td>
<td>9.91</td>
<td>...</td>
<td>0.6480</td>
</tr>
<tr>
<td>Cs$_n$H$_m$NH$_2$</td>
<td>14</td>
<td>50</td>
<td>1.486</td>
<td>10.24</td>
<td>...</td>
<td>0.6860</td>
</tr>
<tr>
<td>Cs$_n$H$_m$CH$_3$</td>
<td>15</td>
<td>50</td>
<td>1.507</td>
<td>10.43</td>
<td>...</td>
<td>0.7119</td>
</tr>
<tr>
<td>(ii) $p$-H$_2$C$_6$H$_4$.As: O(OH)$_2$</td>
<td>18</td>
<td>108</td>
<td>1.803</td>
<td>12.30</td>
<td>...</td>
<td>0.5390</td>
</tr>
<tr>
<td>$p$-H$_2$N,C$_6$H$_4$.As: O(OH)$_2$</td>
<td>19</td>
<td>108</td>
<td>1.811</td>
<td>12.61</td>
<td>...</td>
<td>0.5560</td>
</tr>
<tr>
<td>$p$-H$_2$C$_6$H$_4$.As: O(OH)$_2$</td>
<td>20</td>
<td>108</td>
<td>1.859</td>
<td>12.71</td>
<td>...</td>
<td>0.5400</td>
</tr>
</tbody>
</table>

### Summary

The magnetic susceptibilities of (a) isoelectronic compounds containing the same number of atoms such as (i) SbCl$_3$, TICN0; (ii) Bi$_2$O$_3$, SnBr$_4$ and (b) of isoelectronic compounds containing different number of atoms, such as (i) phenol, aniline, toluene and (ii) $p$-hydroxyphenyl, $p$-aminophenyl, $p$-tolyl arsinic acids were measured on a new type of Gouy’s balance in which a modified Mettler balance has been employed. The essential modifications have been indicated.
Diamagnetism of Some Isoelectronic Compounds

The validity of the empirical relation $\chi_m = -2.832Kr_n^2$ deduced by Bhatnagar and co-workers for isoelectronic compounds with the same number of atoms, has been examined in the case of the above compounds. It has been shown that the relation, does not apply to the inorganic compounds belonging to category (a) but applies to the organic compounds belonging to category (b).

REFERENCES

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