

## Application of topological indices to froth-flotation of an uranium ore

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**Topological indices, namely Wiener index, Randic's connectivity index and the information index based on distances are used to describe the molecular structure of a series of alkylcupferrons used as mineral collectors in the beneficiation of a Canadian uranium ore. There is a linear relation between any of these topological indices and the separation efficiency of the alkylcupferrons considered. The data fit into two separate curves, differentiating the alkylcupferrons into two subclasses, one with rigid rod-like methyl substituents and the other with flexible alkyl substituents.**

THE process of froth-flotation is used to separate a mineral or solid particulate matter from a mixture of finely divided solids suspended in an aqueous solution using dispersed gas bubbles. It involves attachment of hydrophobized mineral particles to air bubbles and bringing the aggregate to the surface of the dispersion in the form of froth, called concentrate. Usually the valuable minerals separate in the froth. A chemical called *collector* is used to render a mineral selectively hydrophobic and rise to the surface of the dispersion. A collector renders a mineral hydrophobic either by physisorption or by chemisorption on its surface. Several chelating agents have been tested as mineral collectors and shown to be better selective than conventional collectors such as petroleum sulphonates.

A chelating collector's molecule may be considered to comprise two parts, viz. the hydrocarbon part and the functional chelating part. The chelating part is hydrophilic while the hydrocarbon part is hydrophobic. It is the chelating group that bonds with the cations in a mineral present on the wet host (ore) particle and thus attaches the collector molecule to the mineral by chemisorption. Otherwise the hydrophobic part made up of the carbon skeleton of the molecule does not participate directly in bonding with the minerals.

In a homologous series of chelating collectors, the hydrocarbon part changes over the series but the chelating part remains the same. Because the chelating group is the same, and it is bonding with the cations in the mineral lattice, there can be no noticeable change in the nature or strength of bonds formed by the chelating group of the

members of a homologous series with the cations in the mineral lattice<sup>1</sup>. Relative flotation efficiencies of various homologues will therefore depend primarily on the nature of the hydrophobic hydrocarbon part of the homologues, and its peculiarities.

In order to express the dependence of separation efficiency of a collector on its carbon skeleton, it is essential to represent the carbon skeleton as a numerical quantity. *Carbon number*, i.e. the number of carbon atoms in the carbon backbone of the molecule, may be used for this purpose. However, carbon number may not be an actual measure of the length of the carbon chain for branched alkyl-chains. The limitation in using carbon number was realized in a detailed study<sup>2</sup> done for uranium flotation to determine the dependence of separation efficiencies of alkylcupferrons (cupferron is ammonium salt of *N*-nitrosophenylhydroxylamine, Figure 1) on their carbon numbers.

A literature review showed that topological indices are extensively used as descriptors of a compound's molecular structure. Topological indices are used in predicting gas chromatographic (GC) retention indices<sup>3-5</sup>. The basic principle of GC is the relative adsorption (followed by elution) of different compounds on the column material of the chromatogram. It may be noted that the unit operation of mineral flotation involves the same adsorption phenomenon as is encountered in a GC column. Because the topological indices enable an accurate prediction of retention indices in GC, it was thought that the limitation of the use of carbon number as molecular descriptor perhaps could be overcome.

Molecular topology, otherwise known as the chemical graph theory, is an extension of graph theory, which falls in the domain of mathematics. In the chemical graph theory a graph, also referred to as the *molecular graph* (*G*), is the hydrogen-suppressed skeleton structure of a molecule in which the atoms are depicted as points (*vertices*) and the bonds connecting them as straight lines (*edges*). The actual three-dimensional shape of the molecule and various bond lengths and bond angles are not considered in sketching the molecular graph<sup>6</sup>. The molecular graph of 2,2-dimethylbutane is shown in Figure 2. A *subgraph* is the designated portion of a graph. The subgraphs are normally of four types, namely *path*, *cluster*, *path cluster* and *circuit* as shown in Figure 3.

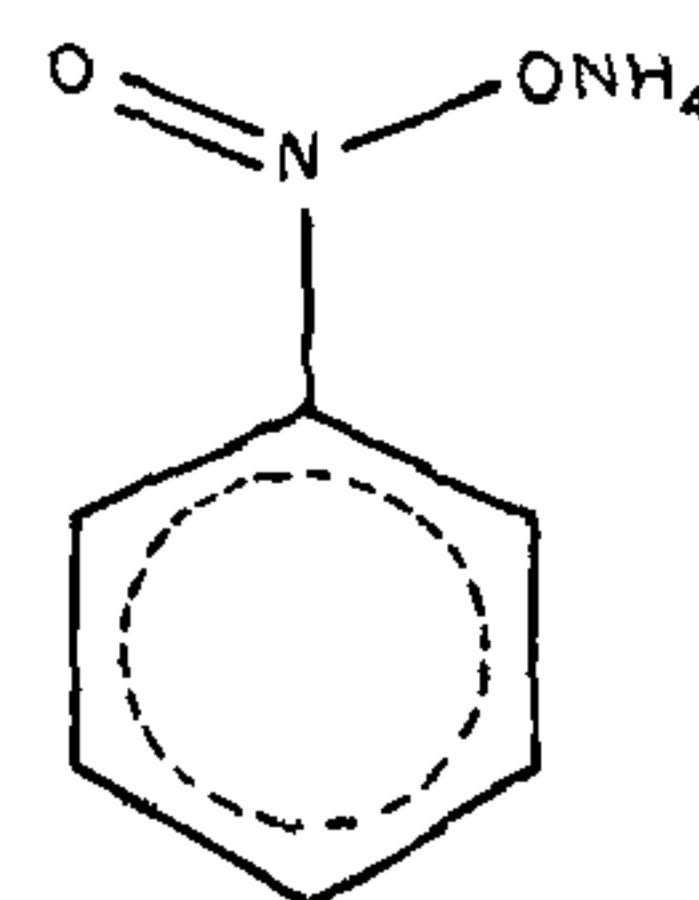


Figure 1. Structure of cupferron.

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A *topological index* is a single unique number characteristic of the molecular graph and is mathematically known as the *graph invariant*. The topological index of a molecule is a non-empirical numerical quantity that quantifies the structure and the branching pattern of the molecule. Therefore, the topological analysis of a molecule involves translating its molecular structure into a characteristic unique number (or index) that may be considered a descriptor of the molecule under examination.

The topological indices used in this paper are Wiener number, information theoretic index based on graph distances and Randić's connectivity index. A brief outline and the calculation of each of these topological indices is explained here for the benefit of the general reader.

The pioneer work in the field of chemical graph theory is that of Wiener<sup>7</sup>. He proposed a topological index called the *path number* that might relate the structure to properties of hydrocarbons. The path number is defined as the total number of bonds between all pairs of atoms in the molecular graph. The path number was found to be related to the physical and thermodynamic properties such as boiling point, density, refractive index, surface tension, viscosity and heat of formation, etc.<sup>8-11</sup>, of the parent alkane. The path number was later termed as the Wiener number  $W(G)$ . Hosoya<sup>12</sup> showed that  $W(G)$  was in fact half of the sum of all the elements in the *distance matrix*  $D(G)$  of a molecule. Thus,  $W(G)$  can be expressed as:

$$W(G) = \frac{1}{2} \sum (d_{ij}), \quad (1)$$

where  $d_{ij}$  is the distance between any pair of vertices  $i$  and  $j$ . The sketching of the distance matrix  $D(G)$  and computation of  $W(G)$  for 2,2-dimethylbutane is explained here as an example. The summation in eq. (1) is over all the unique distances between the vertices  $i$  and  $j$  in a

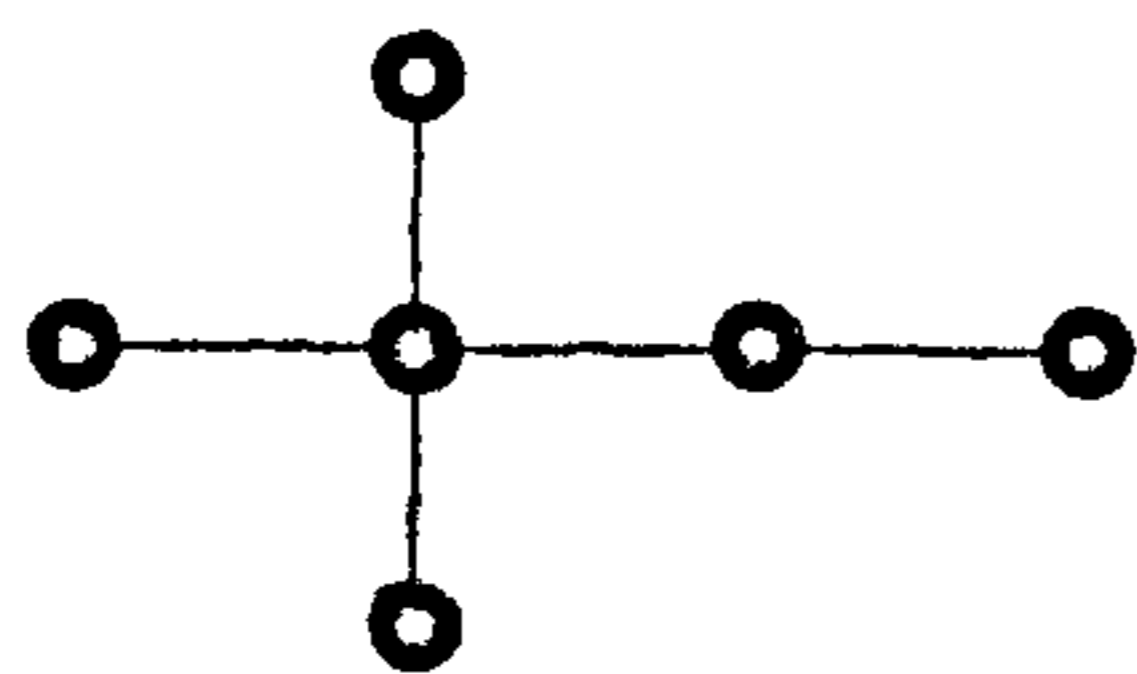


Figure 2. Hydrogen suppressed graph of 2,2-dimethylbutane.

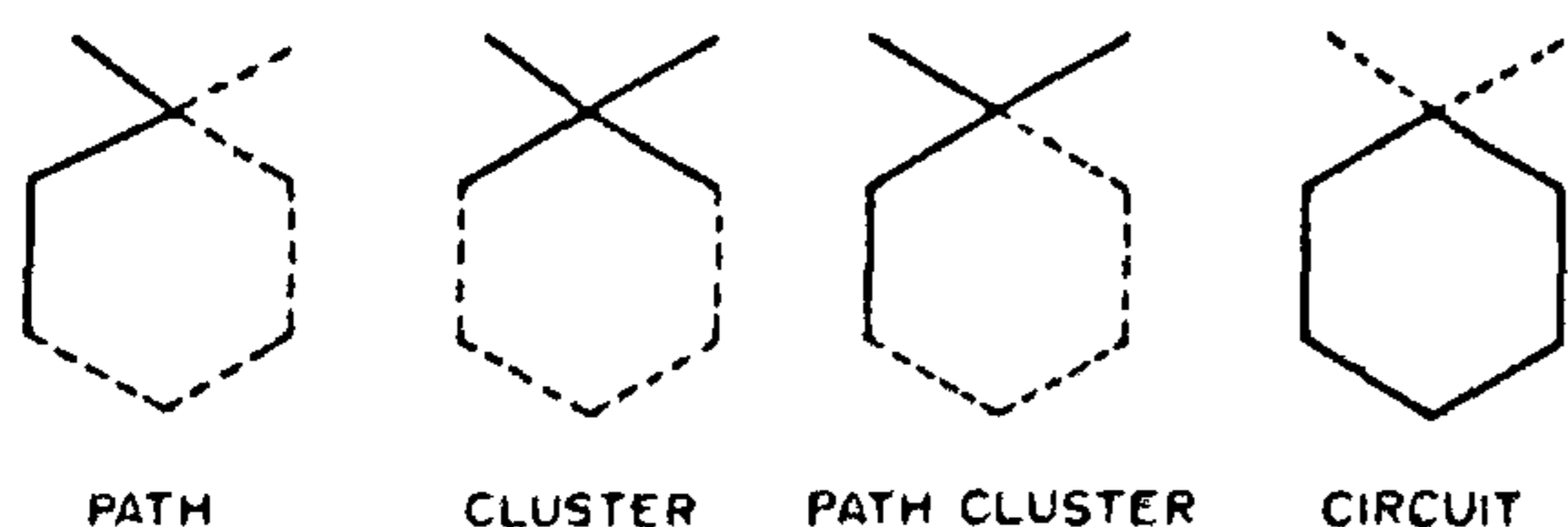


Figure 3. Subgraphs of a cyclic graph.

molecular graph. The distance matrix  $D(G)$  of a molecular graph  $G$  is a real  $N \times N$  matrix, where  $N$  is the number of atoms (vertices) in a given graph which contains elements  $d_{ij}$  representing the number of edges (length) between the vertices  $i$  and  $j$  along the shortest path between them. By definition, all the diagonal elements,  $d_{ii}$ , of the distance matrix are taken as zero.

$$D(G) = \begin{bmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ 0 & 1 & 2 & 3 & 2 & 2 \\ 1 & 0 & 1 & 2 & 1 & 1 \\ 2 & 1 & 0 & 1 & 2 & 2 \\ 3 & 2 & 1 & 0 & 3 & 3 \\ 2 & 1 & 2 & 3 & 0 & 2 \\ 2 & 1 & 2 & 3 & 2 & 0 \end{bmatrix}$$

$$W(G) = \frac{1}{2} \text{sum of off diagonal elements} = 28$$

This topological approach of employing  $W(G)$  is very useful in characterizing isomeric acyclic, cyclic and other structures<sup>13</sup>. The various algorithms for calculating  $W(G)$  and its relationship with physical properties are reviewed by Gutman *et al.*<sup>14</sup>.

Information theoretic index based on molecular distances between all possible pairs of vertices  $I_w$  was shown to be better than  $W(G)$  as a molecular descriptor because it can differentiate compounds even with the same Wiener numbers<sup>13</sup>. Information index for the magnitude of distances between all possible pairs of vertices is calculated using the equation:

$$I_w = W(G) \log_2 W(G) - k_i \sum i \log_2 i. \quad (2)$$

Another topological index used extensively is the Randić's *Molecular Connectivity Index*,  $\chi(G)$  (ref. 15). Connectivity index is calculated from the *degree* ( $D$ ) of each vertex, which is defined as the number of vertices (carbon atoms) a particular vertex (carbon atom)  $i$  is connected to in a graph  $G$ . The product of the reciprocals of the square roots of the degrees of the vertices an edge joins,  $(D_i D_j)^{-1/2}$ , is the value of the edge. The sum of all the values of the edges of a molecule is the connectivity index. Thus:

$$\chi(G) = \sum (D_i D_j)^{-1/2}. \quad (3)$$

An illustration for calculating  $\chi(G)$  is given in Figure 4.

The connectivity index calculated using eq. (3) is generally referred to as the *first-order connectivity index* and is denoted as  ${}^1\chi(G)$ . Other indices used occasionally



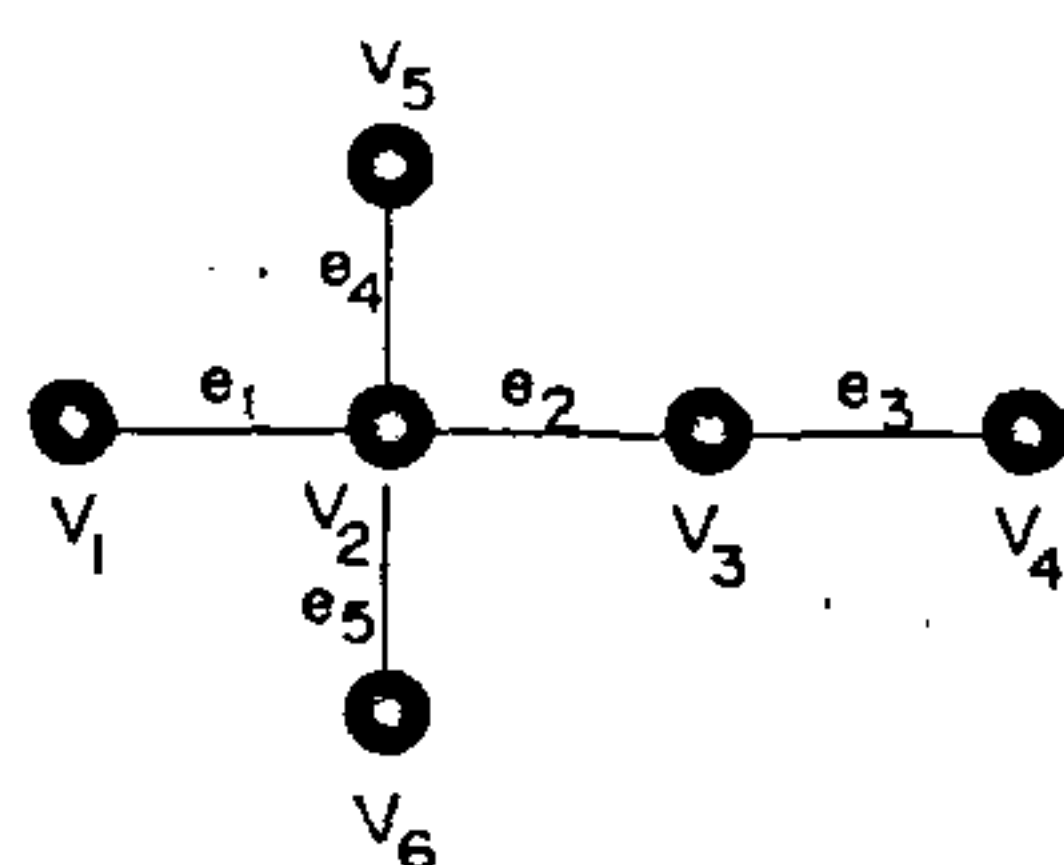
are the *zero-order* ( ${}^0\chi(G)$ ) and the *second-order* ( ${}^2\chi(G)$ ) connectivity indices. The generalized connectivity index can therefore be calculated from the equation:

$${}^h\chi(G) = \sum_{s=1}^t (D_s D_s)^{-1/2}, \quad (4)$$

where  $s$  refers to a single path containing  $h$  edges as its length;  $t$  is the total number of paths, each of length  $h$ , in a graph.

As in the case of Wiener index, connectivity index has also been correlated with physical properties such as density and heat of vaporization. In addition, connectivity index is also related to some biological properties<sup>16</sup>. The first order connectivity index is also correlated with the limiting organic concentration for third phase formation in solvent extraction<sup>17</sup>. The connectivity indices are extensively used as molecular descriptors in predicting the retention indices in chromatographic analysis of various isomeric aliphatic, aromatic and polycyclic hydrocarbons<sup>3-5</sup>.

Topological indices, namely Wiener index, modified Wiener index and connectivity index are used to discriminate various isomeric alkylcupferrons. In order to test whether these topological indices can be used as molecular descriptors, separation efficiencies ( $E_s$ ) of alkylcupferrons as uranium collectors in the flotation of uranium ore<sup>2</sup> are plotted against the above-mentioned topological indices. Separation efficiency of a collector,  $E_s = R_m - R_g$ , where  $R_m$  and  $R_g$  are % recovery of the valuable mineral (%U recovery in the present case) and that of the gangue mineral into the float concentrate<sup>18</sup>. In the case of *low-grade* ores, the amount of metal even at 95% recovery will be quite small and the major mass will be that of the gangue minerals. Hence, separation efficiency can be defined as  $E_s = \% \text{ metal recovery} - \% \text{ mass recovery}$ . The uranium ore used in the present study is a low-grade ore and  $E_s = \% \text{ uranium recovery} - \% \text{ mass recovery}$ .



Values of edges

$$e_1 = \left( \frac{1}{\sqrt{1}} \times \frac{1}{\sqrt{4}} \right), e_2 = \left( \frac{1}{\sqrt{4}} \times \frac{1}{\sqrt{2}} \right), e_3 = \left( \frac{1}{\sqrt{2}} \times \frac{1}{\sqrt{1}} \right)$$

$$e_4 = \left( \frac{1}{\sqrt{4}} \times \frac{1}{\sqrt{1}} \right), e_5 = \left( \frac{1}{\sqrt{4}} \times \frac{1}{\sqrt{1}} \right)$$

Connectivity index  $\approx 2.56$

Figure 4. Calculation of connectivity index of 2,2-dimethylbutane.

$W(G)$  of cupferron and its sixteen alkyl-derivatives synthesized and used as uranium collectors are calculated from their distance matrices using eq. (1) and are listed in Table 1. In calculating  $W(G)$ , the entire chelating group,  $-\text{N}(\text{NO})\text{O}^-$ , is considered as a single vertex because isomeric derivatives cannot be differentiated otherwise. For example, *p*-methylcupferron ( $G_3$ ) and *m*-methylcupferron ( $G_2$ ) are found to have the same  $W(G)$ , namely 42, when the chelate group is not considered as a vertex. On the other hand, when it is considered as a vertex, the two isomeric structures are differentiated according to their relative lengths,  $W(G_3)$  being 62 for *p*-methylcupferron ( $G_3$ ) and  $W(G_2)$  being 61 for the *meta*-isomer ( $G_2$ ).

Wiener numbers are found to clearly distinguish isomeric structures in other instances also. The isomeric dimethyl derivatives  $G_4$  and  $G_5$  are not only distinguished amongst themselves ( $W(G_4) = 82$  and  $W(G_5) = 84$ ) but also from the *p*-ethylcupferron,  $G_7$ , ( $W(G_7) = 90$ ). Thus *p*-ethylcupferron ( $G_7$ ) having the longest carbon chain among the three, has the highest  $W(G)$ . Similarly, 2,4,6-trimethylcupferron ( $G_6$ ), *p-n*-propylcupferron ( $G_8$ ) and *p-isopropyl*cupferron ( $G_9$ ) are distinguished by  $W(G)$  according to their chain lengths ( $W(G_6) = 110$ ,  $W(G_8) = 127$ ,  $W(G_9) = 120$ ). In the case of the three *p*-butyl derivatives ( $G_{10}$ – $G_{12}$ ), Wiener indices are found to decrease ( $W(G_{10}) = 174$ ,  $W(G_{11}) = 166$  and  $W(G_{12}) = 152$ ) from the least to the most branched chain, which is the decreasing order of the carbon chain lengths. In all the cases,  $W(G)$  is found to be sensitive to changes in the molecular structures and hence is effective in clearly distinguishing the isomeric structures.

To see if the effect of the chain length of the substituent on the performance of cupferron-derivatives can be predicted by the topological approach,  $E_s$  of each collector is plotted against its  $W(G)$  (see Figure 5). A second-order polynomial fit of the fifteen data points (excluding tests 10 and 11 that deviate a lot) gives a curve with  $R^2 = 0.749$ .  $R^2$  increases to 0.934 for curve A and 0.840

Table 1. Topological indices of alkylcupferrons

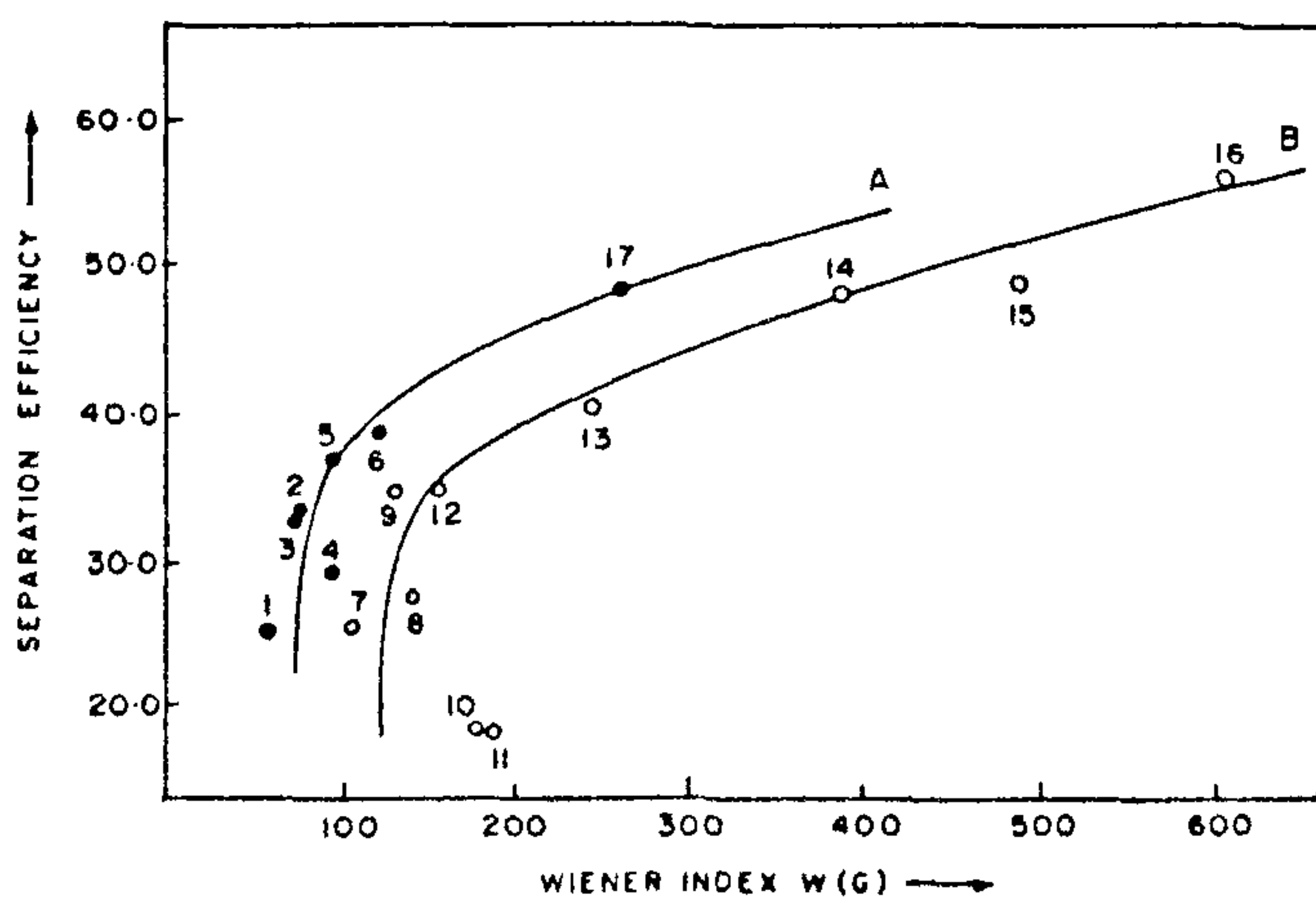
Substituent	Molecular graph	$W(G)$	$I_w$	$\chi(G)$	$E_s$
Nil	$G_1$	42	178.7	2.40	27.2
3-methyl	$G_2$	61	284.5	2.80	36.5
4-methyl	$G_3$	62	288.3	2.89	36.3
2,6-dimethyl	$G_4$	82	413.0	3.31	32.5
3,5-dimethyl	$G_5$	84	432.2	3.38	40.7
2,4,6-trimethyl	$G_6$	110	588.5	3.80	44.8
4-ethyl	$G_7$	90	448.8	3.43	27.2
4-propyl	$G_8$	127	971.1	3.93	30.0
4- <i>i</i> -propyl	$G_9$	120	936.7	3.80	37.4
4-butyl	$G_{10}$	174	965.8	4.43	20.1
4- <i>i</i> -butyl	$G_{11}$	165	917.7	4.29	19.2
4- <i>t</i> -butyl	$G_{12}$	152	851.0	4.10	37.3
4-pentyl	$G_{13}$	232	1392.4	4.93	43.5
4-heptyl	$G_{14}$	385	2399.4	5.93	52.3
4-octyl	$G_{15}$	482	3055.6	6.43	51.7
4-nonyl	$G_{16}$	594	3928.3	6.93	58.7
4-phenyl	$G_{17}$	252	1529.7	5.46	52.4



for curve B. The better fit of the points into two distinct curves indicates that the alkylcupferrons may be classified into two subclasses. The first group includes the compounds corresponding to the graphs  $G_1$ – $G_6$  and the diphenyl compound  $G_{17}$  which are rigid planar molecules containing methyl groups directly attached to the benzene ring. The methyl group(s) may be considered to act as rigid rod-like structures. The phenyl group can also be considered as a rigid planar substituent. The compounds of the second group on the other hand, have their substituents in the form of a flexible alkyl chain attached to the *para* position with respect to the chelating group. Hence  $W(G)$  clearly distinguishes the two types of collector molecules. However, there are some significant deviations such as presented by compounds corresponding to the graphs  $G_4$ ,  $G_6$ ,  $G_{10}$  and  $G_{11}$ .

The two curves in Figure 5 have pronounced curvatures which are reminiscent of the curves obtained by Wiener in the correlation of boiling points of hydrocarbons against  $W(G)$ <sup>5</sup>. These curvatures are due to the higher sensitivity of  $W(G)$  towards the structural changes in the molecules as opposed to that of their separation efficiencies. When the natural logarithms of separation efficiencies are plotted against that of  $W(G)$  of the compounds, the curvature is not found and linear plots are obtained (see Figure 6), except for the two deviant cases. A linear regression analysis excluding the two deviant cases gives a correlation coefficient of 0.827. When the data points are grouped as indicated above, the correlation coefficient improves to 0.900 for line A (7 data points) and 0.957 for line B (8 data points).

Information theoretic indices based on molecular distances are calculated for the alkylcupferrons using eq. (2).  $I_w$  differentiates the compounds better because the variation in  $I_w$  among the isomers is larger than that of their  $W(G)$  values. For example, the isomeric *m*-methyl- and *p*-methyl-cupferrons have  $W(G)$  values of 61 and 62,

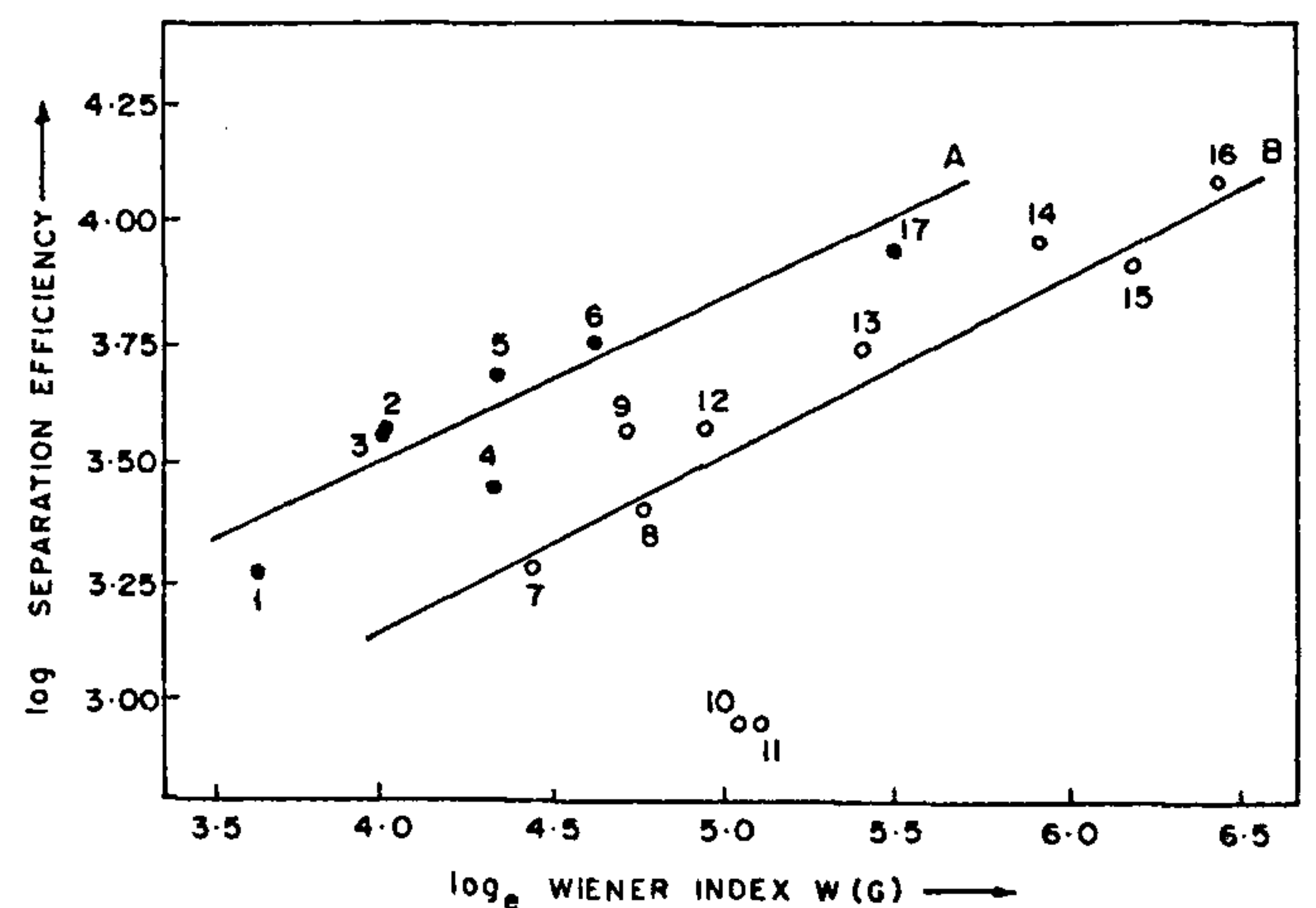


Note: Refer Table 4 for details of test numbers

Figure 5. Dependence of separation efficiency on Wiener number.

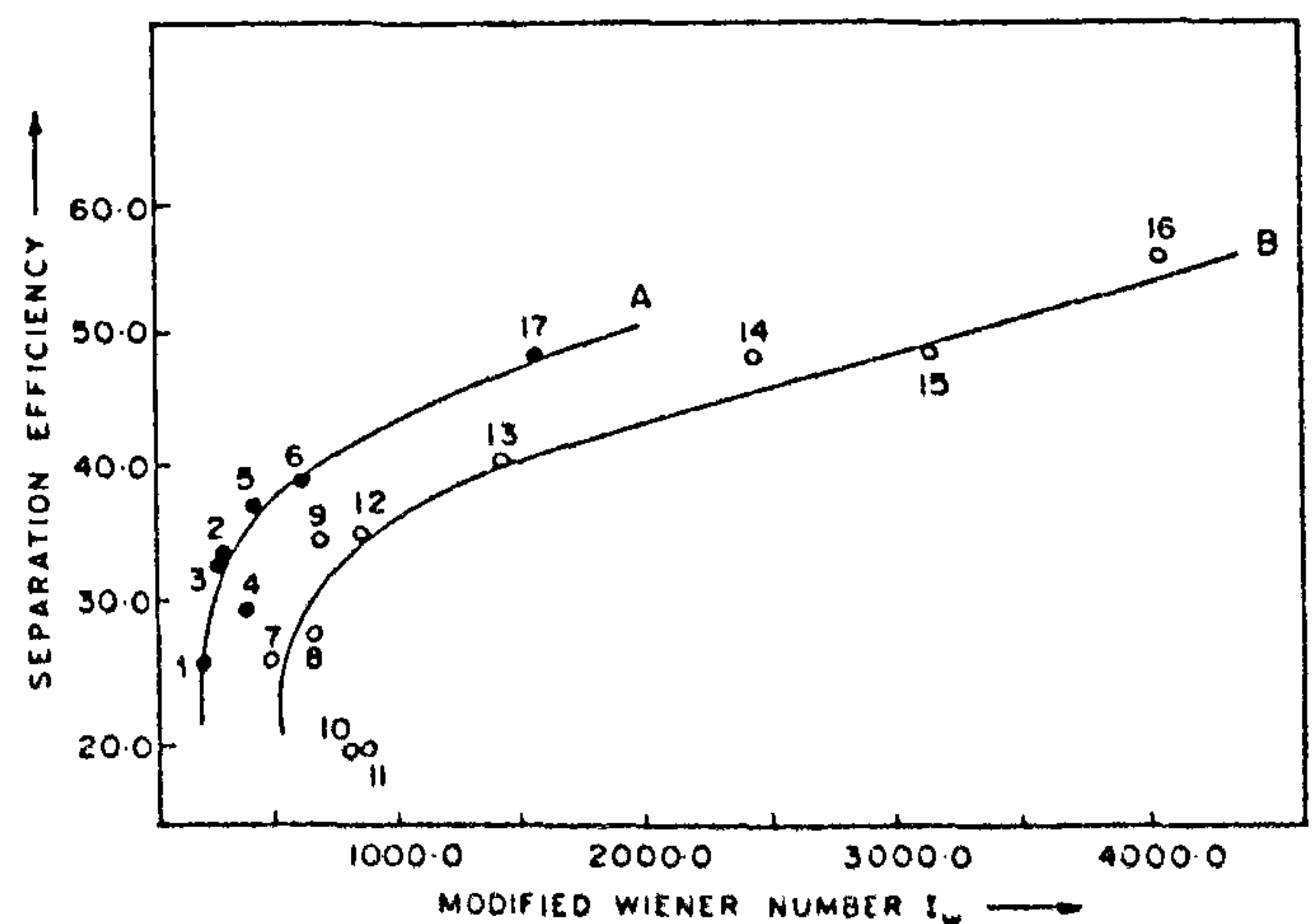
respectively, whereas their  $I_w$  values are 284.5 and 288.3, respectively. Similarly, the difference between the  $W(G)$  values of the two isomeric di-methylcupferrons ( $G_4$  and  $G_5$ ) is only 2, whereas it is 9.2 between their  $I_w$  values. It is interesting to note that the plot of information theoretic index  $I_w$  vs separation efficiencies  $E_s$  of cupferron derivatives (Figure 7) is similar to that of Wiener index graphs, and the curvatures are not removed. However, as seen in Figure 7, use of  $I_w$  appears to be better than that of  $W(G)$  because the anomalies are clearly identified. In this plot also the value of  $R^2$  for a second-order polynomial fit improves from 0.710 (for 15 points) to 0.927 for curve A (7 points) and 0.867 for curve B (8 points).

Randic's molecular connectivity indices based on the path cluster for all the cupferron-derivatives listed in



Note: Refer Table 4 for details of test numbers

Figure 6. Logarithmic plot of separation efficiency against Wiener number.



Note: Refer Table 4 for details of test numbers

Figure 7. Dependence of separation efficiency on information index of distances.



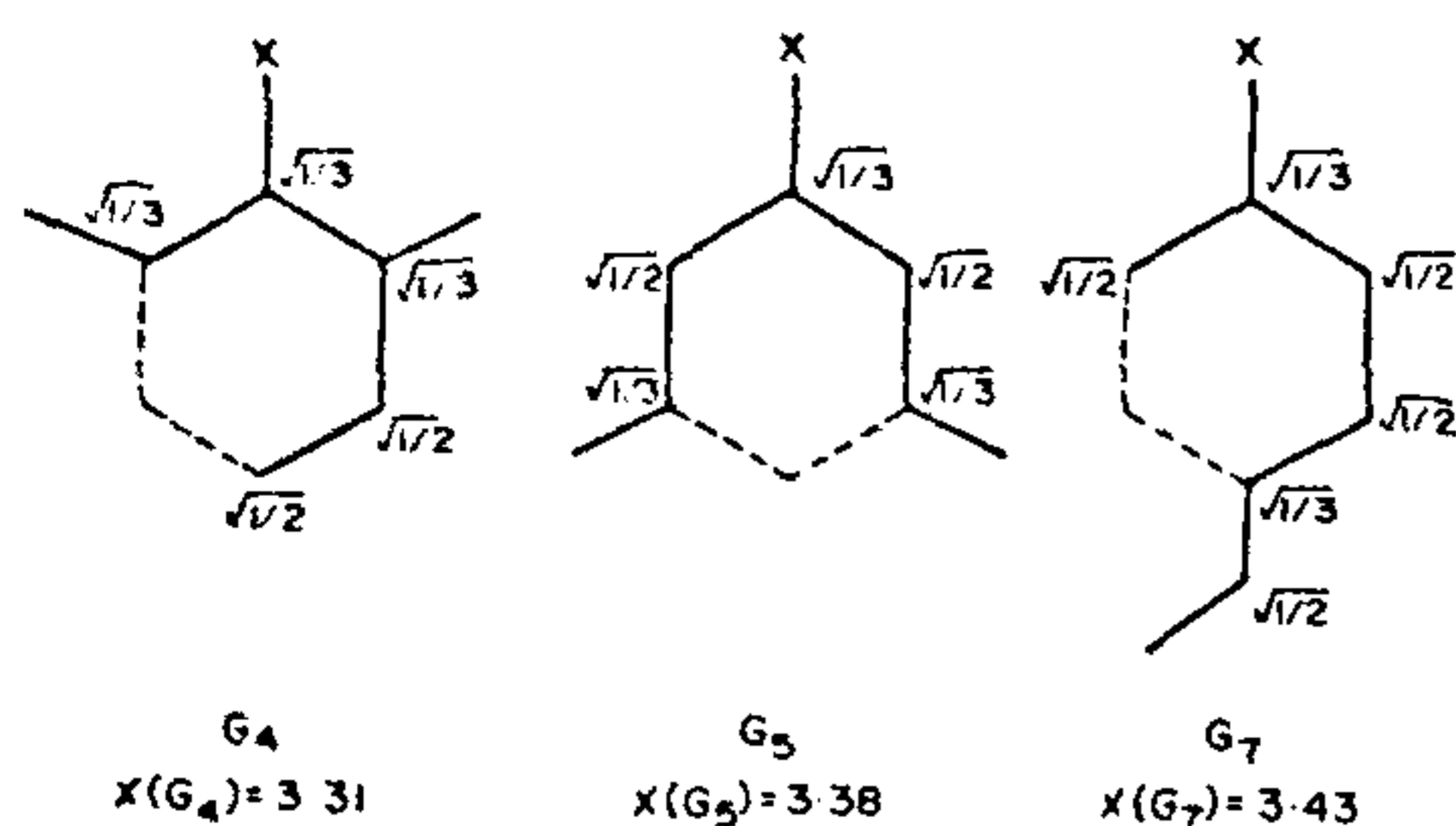
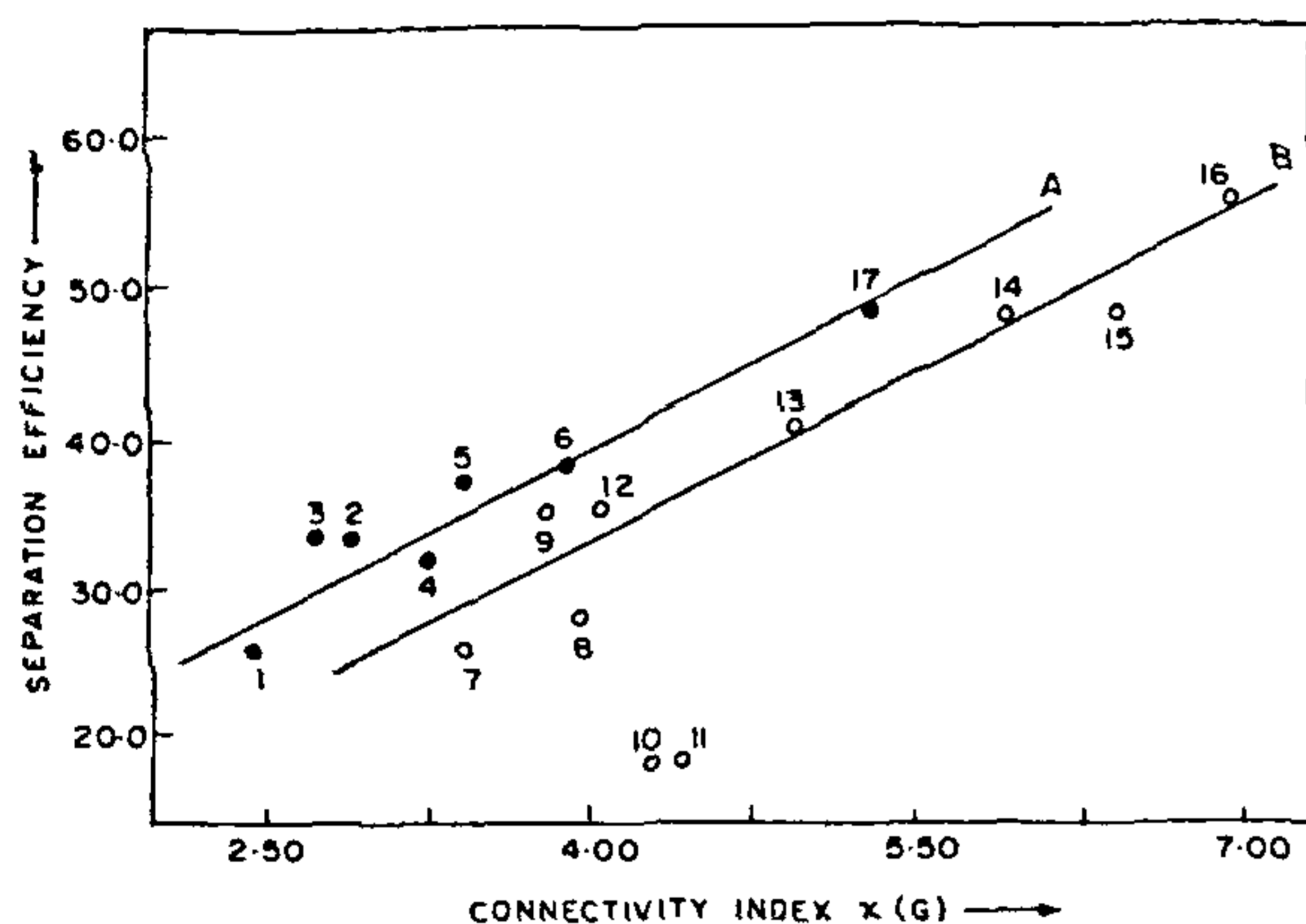


Figure 8. Calculation of  $\chi(G)$  for some isomeric cupferron derivatives.



Note: Refer Table 1 for details of test numbers

Figure 9. Dependence of separation efficiency on Randić's connectivity index.

Table 1 are calculated using eq. (3). Calculation of  $\chi(G)$  for some isomeric cupferrons from their path clusters is shown in Figure 8. As in the case of Wiener numbers, connectivity indices of cupferron derivatives are also found to be proportional to molecular size. However, 2,4,6-trimethylcupferron ( $G_6$ ) and *p*-isopropylcupferron ( $G_9$ ) have the same  $\chi(G)$  value of 3.80 and  $\chi(G)$  is not able to differentiate these two isomers. Separation efficiencies of the cupferron-derivatives are plotted against the path cluster connectivity indices  $\chi(G)$ . It is seen in Figure 9, that two distinct linear lines are obtained even on normal rectangular coordinates. It may be noted that such a linear relation was obtained only on a log-log plot of  $W(G)$  vs  $E_s$  (Figure 6). As in the previous graphs the

correlation coefficient increases from 0.878 for a single line to 0.943 and 0.966 for the two separate lines A and B, respectively.

$W(G)$ ,  $I_w$  and  $\chi(G)$  differentiated the cupferron-derivatives into two groups. Reasonably good fitting of the data in the two curves clearly indicates the existence of a relation between collector efficiency and the molecular structure represented by a topological index. This structural analysis based on topological indices is conceptually simple and may lead to a wide use of topological indices as molecular descriptors of mineral collectors used in ore-beneficiation. This can be considered as the first step towards developing a Quantitative Structure Activity Relation (QSAR) for flotation collectors.

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