

QSAR 방법을 이용한 가스 상태의 등온흡착선 예측

Prediction of Gas Phase Sorption Isotherms on The Basis of QSAR Method

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Abstract

Volatile organic compounds(VOC) present in or generated by many sources, can be toxic, mutagenic or even carcinogenic, so that control of such emissions is significant. The 6 chlorinated organic chemicals as VOC were examined in this study. Prediction of the behavior of VOC on activated carbon beds is an important part of control system design. The objective of this study was to predict gas phase sorption isotherms from physical properties and liquid phase isotherms obtained with the same adsorbent and adsorbate. One of the techniques that was investigated was quantitative structure-activity relationships(QSAR)for the prediction procedures. It was possible to estimate sorption isotherms in the gas phase(a_g) using either connectivity index, ${}^2\chi$, and the Henry's law coefficient (H_a) or the solubility and the equilibrium concentration in the gas phase. As a result of study, the predictive equation based on Freundlich model for a_g was $\log a_g = 0.238 {}^2\chi + 0.573 \log H_a + 4.330$ ($r^2 = 0.94$). Finally, this would provide a potentially useful tool to describe and predict sorption capacity without time-consuming tests.

요 지

휘발성 유기물질(VOC)은 많은 경로를 통해 발생되는데, 독성이 있을뿐 아니라 발암물질을 포함하고 있으므로, 이들 물질 제거는 매우 중요하다. 본 연구에서는 휘발성 유기물질 처리를 위해 활성탄을 사용할 경우 처리와 설계를 위해 흡착능력의 연구가 반드시 필요하다. 그러므로, 본 연구에서는 각 화합물에 대한 가스 상태의 등온흡착선을 물리적 특성과 액화상태의 등온흡착선으로 부터 예측하였다. 이를 위해 이용된 방법이 quantitative structure-activity relationships(QSAR) 방법이다. 가스 상태의 등온흡착선을 분자연결계수(${}^2\chi$)와 헨리의 계수, 또는 용해도와 가스 상태의 평형농도에 의해서 예측 할 수 있었다. 연구결과, Freundlich 모델을 근거로한 가스 상태의 등온흡착선은 $\log a_g = 0.238 {}^2\chi + 0.573 \log H_a + 4.330$ ($r^2 = 0.94$)이었다. 결과적으로, 저흡착능력 범위에서 Freundlich 이론을 근거로한 이 방법은 시간소모적 실험을 통하지 않고도 가스 상태의 등온흡착선을 예측할 수 있다는 것을 제시하고 있다.

1. Introduction

The sources of VOC emissions are wastewater treatment plants, sanitary landfills, transportation, industrial processes. In recent years the control of VOC by adsorption onto sorbent materials has increased. Much of the research on adsorption has been concentrated on study of liquid-solid phase sorption. Only limited studies and data on gas-solid sorption isotherms on activated carbon are available. Much of the data are propriety making it difficult to design and evaluate carbon beds is an important part of proper control system design. A multiple regression method for correlating molecular connectivity indices with sorption data was examined. One of the techniques that was investigated was quantitative structure-activity relationships(QSAR) for the prediction procedures.

2. Theory

2.1 Quantitative Structure-Activity Relationships(QSAR)

Quantitative Structure-Activity Relationships (QSAR) is the term applied to methods of quantifying the physical structure of a compound with numerical indices, and then examining the relationship of those indices to chemical or biological activity. One of the first successful applications of the method was suggested by Randic⁽¹⁾ who introduced the effect molecular topology on some physico-chemical properties. The basis of connectivity indices is the molecular skeleton and the order of dissection of the skeleton. For instance, in an organic molecule the first-order connectivity indices are computed from the non-hydrogen atom⁽²⁾. Each atom is assigned a cardinal number and a simple count of adjacently atoms. This count of atoms is used to form the δ_i value of the "ith" atom. The first-order simple χ index, ${}^1\chi$, is computed as:

$${}^1\chi = \frac{1}{\sum(\delta_i * \delta_i)^{0.5}} \quad (1)$$

where the Σ is taken over all adjacent atoms. Similarly, higher order indices can also be formed,

e. g., ${}^m\chi$ where "m" is mth order molecular connectivity index. For methylene chloride(CCl_2H_2), each chloride atom is assigned 1 and the carbon atom has a value of 2, respectively, as δ values. Therefore, the simple ${}^1\chi$ index is calculated as follows:

$$\begin{array}{c} \text{Cl}^1 \\ | \\ \text{H} - \text{C}^2 - \text{H} \\ | \\ \text{Cl}^1 \end{array} \quad \begin{array}{l} {}^1\chi = \sum(\delta_i * \delta_i)^{-0.5} \\ = (1 * 2)^{-0.5} + (2 * 1)^{-0.5} \\ = 1.41 \end{array}$$

On the other hand, in order to distinguish among different heteroatoms, i.e., atoms other than carbon or others having multiple bonds, the superscript "v" is used to denote the valence index from the simple index.

The general expression of δ^v is the ratio of electronic structures⁽²⁾.

$$\delta^v = \frac{Z^v - V}{Z - Z^v - 1} \quad (2)$$

where Z, Z^v , and the number of electrons, the number of valence electrons, and hydrogen atoms suppressed, respectively.

For example, to distinguish chloride atom from carbon atom, the modified δ^v value of chloride ion is,

$$\delta^v = \frac{7 - 0}{17 - 7 - 1} = 0.78$$

For methylene chloride(CCl_2H_2), the first order of valence connectivity index becomes 1.60.

$$\begin{array}{c} \text{Cl}^{0.78} \\ | \\ \text{H} - \text{C}^2 - \text{H} \\ | \\ \text{Cl}^{0.78} \end{array} \quad \begin{array}{l} {}^1\chi^v = \sum(\delta_i * \delta_i)^{-0.5} \\ = (0.78 * 2)^{-0.5} + (2 * 0.78)^{-0.5} \\ = 1.60 \end{array}$$

In this study a variety of connectivity indices were used(${}^0\chi$, ${}^0\chi^v$, ${}^1\chi$, ${}^1\chi^v$, ${}^2\chi$, and ${}^2\chi^v$) to derive proper predictive equation.

2.2 Determination of Solubility Data

Solubility is defined as the concentration of solute in the solvent in two phase equilibrium, e.g.,

water or other components. To obtain the reliable data for chlorinated organic compounds from the previously reported values, multiple regression analysis on the basis of QSAR method was attempted³⁾.

After running redression analyses, the following predictive equation was obtained.

$$\log S = -0.719 \chi^0 + 2.322(r^2 = 0.94) \quad (3)$$

where S is solubility in wt. % and χ^0 is the zeroth-order connectivity index.

2.3 Determination of Henry's Law Coefficient Data

Henry's law is the ratio of vapor pressure of a substance in the atmosphere to its dissolved concentration in the water. Regression equation³⁾ of Henry's coefficient for chlorinated organic chemicals was obtained as below:

$$\log H_a = 0.466 \chi^0 + 0.743 \chi^v - 2.653 \chi^v - 0.119(r^2 = 0.85) \quad (4)$$

where H_a is dimensionless Henry's coefficient.

2.4 Sorption Isotherms in the Gas Phase

Adsorption is commonly distinguished as being one of two types: physical adsorption and chemical adsorption. The simple and well-known equation is the Freundlich model.

$$a = k P^n \quad (5)$$

where a is adsorption capacity, P is partial pressure, and k and n are empirical constants.

2.5 Rationality of Prediction Method

To address the complication of real sorbents, the "potential" theory of sorption was introduced by Polanyi. It postulates a temperature invariant intermolecular potential field, the adsorbed layer, between gas and solid phases.

The adsorption potential, G_{ads} , becomes,

$$G_{ads} = RT \ln \left(\frac{P_s}{P} \right) \quad (6)$$

where R is the universal gas constant, and P_s is the saturation vapor pressure of the adsorbate.

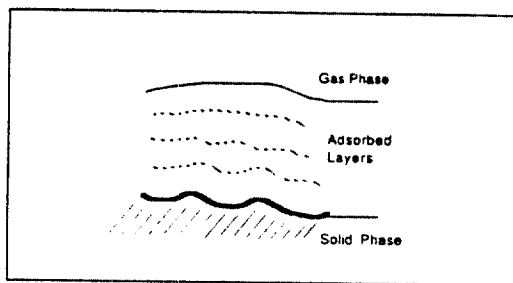


Fig. 1. The structure of the adsorbed phase by the Polanyi theory

Figure (1) illustrates the structure of the adsorbed phase by the Polanyi potential.

Dubin and Radushkevich⁴⁾ developed a sorption equilibrium model using Polanyi's ideas as a base and applied it to single component isotherms,

$$a = \left[\frac{W_0 \theta}{MW 10^{-6}} \right] \exp \left[-B \left(\frac{G_{ads}}{\beta} \right)^2 \right] \quad (7)$$

where W_0 is the maximum "adsorption space" of adsorbent, θ is the density of pure solute, MW is the molecular weight of the solute, B is the microporosity constant of adsorbent, and β is the affinity coefficient of adsorbate.

Adsorption isotherms in the gas phase, equation (7), can be rewritten as,

$$\ln a = \ln W_0 - B \left(\frac{G_{ads}}{\beta} \right)^2 + \ln \theta - \ln(MW 10^{-6}) \quad (8)$$

Under the assumption that the affinity coefficient, β , and the pure solute density, θ , depend on connectivity indices, the QSAR approach to predict the sorption isotherm in the gas phase was attempted. Mailhot et al.⁵⁾ reported the relationships between connectivity indices and β or θ .

3. Methodology

Molecular connectivity indices from zeroth to third order for simple (χ^m) and valence (χ^v) were calculated with software (MOLCONN2, 1989) developed by Hall⁶⁾ for an IBM PC computer or compatible. A multiple regression model in the

gas phase was attempted from the physical properties as well as sorption isotherms in the liquid phase. Two methods were used for relating the equilibrium values of sorbed substances onto activated carbon to their concentrations in the gas or liquid phase. One was to assume that a linear model of sorption described the equilibrium at a low fixed value of the total sorptive capacity, e.g., 10mg/g. Alternatively, the other method employed was to use Freundlich parameters to describe the equilibrium sorption data. From the experimentally obtained Freundlich equation the equilibrium concentrations were calculated corresponding to a mass loading of 10 mg/g of adsorption capacity. The 10 mg/g level was selected because it was felt likely to be within the range for which the adsorption isotherm could still be considered approximately linear, and therefore represented by a single constant partition coefficient. This means that the low concentration range

of VOCs was studied. The statistical analysis was performed using the SAS(SAS Institute Inc., 1985) statistical package on a VAX/VMS computer. To choose the best semi-empirical equation for sorption isotherm, the model was determined based on the highest correlation coefficient(r^2) from the multiple regression procedure.

4. Results and Discussion

4.1 Data Review

The adsorption isotherms on activated carbon were obtained using Freundlich's equation and listed in Table(1) and (2)(Dobbs et al.⁽⁷⁾; Stenzel et al.⁽⁸⁾; Rasmuson⁽⁹⁾; Calgon catalog⁽¹⁰⁾; Noll⁽¹¹⁾). Table(1) shows the Freundlich parameters of k and n in the liquid phase. Slopes(or n values) ranged from 0.31 to 1.16 on activated carbon. Also the Freundlich coefficient and correlation coefficient for gas phase sorption are summarized in

Table 1. The Freundlich parameters of solute in the liquid phase

| Solutes | k | n | r^2 | Ref. | Valid range(mg/L) |
|---|--------|------|-------|------|-------------------|
| CCl ₃ H | 8.83 | 0.60 | 0.99 | 8 | 0.03-4 |
| 1,1,1-C ₂ Cl ₃ H ₃ | 28.82 | 0.67 | 0.99 | 8 | 0.03-4 |
| 1,2-C ₂ Cl ₂ H ₂ | 12.96 | 0.55 | 0.99 | 8 | 0.03-4 |
| C ₂ Cl ₃ H | 51.72 | 0.51 | 0.99 | 8 | 0.03-4 |
| C ₂ Cl ₄ | 146.25 | 0.45 | 0.99 | 8 | 0.03-4 |
| CCl ₂ H ₂ | 1.30 | 1.16 | 0.92 | 7 | 0.16-0.58 |
| CCl ₃ H | 2.60 | 0.73 | 0.96 | 7 | 0.03-0.82 |
| 1,1,1-C ₂ Cl ₃ H ₃ | 2.48 | 0.34 | 0.94 | 7 | 0.0035-0.77 |
| 1,1-C ₂ Cl ₂ H ₂ | 4.91 | 0.54 | 0.98 | 7 | 0.0065-0.46 |
| 1,2-C ₂ Cl ₂ H ₂ | 3.05 | 0.51 | 0.98 | 7 | 0.0049-0.60 |
| C ₂ Cl ₃ H | 28.00 | 0.62 | 0.98 | 7 | 0.0052-0.16 |
| C ₂ Cl ₄ | 50.80 | 0.56 | 0.92 | 7 | 0.0070-0.31 |

Table 2. The Freundlich parameters of solute in the gas phase

| Solutes | k | n | r^2 | Ref. | Valid range(ppm) |
|---|--------|------|-------|------|------------------|
| CCl ₂ H ₂ | 3.96 | 0.60 | 0.99 | 9 | 0.6-112.3 |
| CCl ₂ H ₂ | 9.86 | 0.38 | 0.99 | 10 | 6.8-10000 |
| CCl ₃ H | 55.11 | 0.24 | 0.99 | 10 | 5.4-10200 |
| C ₂ Cl ₃ H | 164.48 | 0.16 | 0.96 | 11 | 84-4155 |
| C ₂ Cl ₃ H | 180.38 | 0.15 | 0.96 | 11 | 84-4155 |
| 1,1,1-C ₂ Cl ₃ H ₃ | 191.34 | 0.14 | 0.99 | 8 | 6.8-6800 |
| C ₂ Cl ₂ H ₂ | 33.87 | 0.28 | 0.99 | 8 | 6.8-6800 |
| C ₂ Cl ₃ H | 129.87 | 0.18 | 0.98 | 8 | 6.8-6800 |
| C ₂ Cl ₄ | 289.73 | 0.11 | 0.97 | 8 | 6.8-6800 |

Table 3. The various connectivity indices, the calculated solubility and Henry's law coefficient

| Compound Name | Connectivity Indices | | | | | | log S | log H _a |
|------------------------------------|----------------------|-----------------|----------------|-----------------|----------------|-----------------|--------|--------------------|
| | ⁰ χ | ⁰ χ' | ¹ χ | ¹ χ' | ² χ | ² χ' | | |
| CCl ₂ H ₂ | 2.71 | 2.97 | 1.41 | 1.60 | 0.71 | 0.91 | 0.374 | -0.894 |
| CCl ₃ H | 3.58 | 3.98 | 1.73 | 1.96 | 1.73 | 2.23 | -0.252 | -0.693 |
| CCl ₃ -CH ₃ | 4.50 | 4.90 | 2.00 | 2.20 | 3.00 | 3.63 | -0.913 | -0.218 |
| CClH=CClH | 3.41 | 3.42 | 1.19 | 1.64 | 1.00 | 0.76 | -0.130 | -0.340 |
| CClH=CCl ₂ | 4.28 | 4.48 | 2.27 | 2.08 | 1.80 | 1.62 | -0.755 | -0.314 |
| CCl ₂ =CCl ₂ | 5.15 | 5.54 | 2.64 | 2.52 | 2.49 | 2.42 | -1.318 | -0.288 |

Table(2) and the slopes varied from 0.11 to 0.6.

Table (3) summarized the various connectivity indices⁽⁶⁾, the calculated solubility, and Henry's law coefficient data using QSAR method from equation(3) and (4).

4.2 Relationships of Adsorption Isotherms

Assuming that gas, liquid, and adsorbent surfaces are in equilibrium with one another, an attempt was made to find a relationship between sorption isotherms of the liquid and gas phases. Figure (2) illustrates the basic assumption of partitioning behavior among three different phases.

For low surface coverage, linear isotherm behavior was expected for both phases.

$$a_1 = k_1 C_{e, l} \quad (9)$$

$$C_{e, l} = k_2 C_{e, g} \quad (10)$$

$$a_g = k_3 C_{e, g} \quad (11)$$

where a_1 is the adsorption capacity in the liquid

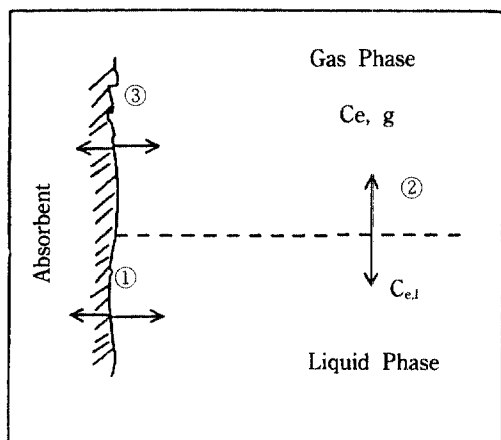


Fig. 2. Partition states at equilibrium

phase, mg/g, $C_{e, l}$ is equilibrium concentration in the liquid phase, ppm, and all k_i are coefficients of proportionality.

Dividing equation (11) by equation (9) gives,

$$\frac{a_g}{a_1} = \frac{k_3 C_{e, g}}{k_1 C_{e, l}} \quad (12)$$

$$\frac{C_{e, g}}{C_{e, l}} = H \quad (13)$$

where H is Henry's law coefficient in $m^3\text{-atm./g}$. After taking the logarithm of both sides, equation (12) can be rewritten as shown below:

$$\log a_g = \log a_1 + \log H + \log(k_3/k_1) \quad (14)$$

or from equation(11),

$$\log a_g = \log C_{e, g} + \log k_3 \quad (15)$$

4.2.1 Prediction of adsorption isotherm assuming a linear model

In this study, only 9 data points for 6 different solutes at 25°C were available for gas phase sorption on activated carbon. First, a value of 10mg/g of sorption capacity in the liquid and gas phases was assumed, and then simple linear partition equations(equation (9) and (11)) and Henry's law (equation(13)) were used in order to compute the equilibrium concentration in the liquid($C_{e, l}$) and gas($C_{e, g}$) phases corresponding to the loading. In calculating the k_i coefficients(k_1 and k_3), difficulty was encountered because k_i values varied depending on the equilibrium concentration or the sorption capacity. At low adsorption capacity in the aqueous phase, e.g., less than 1% by weight except for tetrachloethene for which a value of about 3% weight was used, average k_i values were used for the

Table 4. k_i values in the liquid and gas phases

| Solutes | In the liquid phase | | In the gas phase | |
|-----------------------------|---------------------|----------------------|------------------|----------------------|
| | k_i | sorption range(mg/g) | k_3 | sorption range(mg/g) |
| CCl_2H_2 | 1.1 | 0.1 - 0.7 | 2.4 | 2.5 - 35.1 |
| CCl_3H | 4.3 | 0.2 - 1.9 | 28.7 | 40.5 - 83 |
| CCl_3-CH_3 | 82.5 | 0.4 - 2.4 | 25.0 | 240.0 - 300 |
| $\text{CClH}=\text{CClH}$ | 18.3 | 0.2 - 2.1 | 4.4 | 60.0 - 103 |
| $\text{CClH}=\text{CCl}_2$ | 138.7 | 0.9 - 8.7 | 3.9 | < 327 |
| $\text{CCl}_2=\text{CCl}_2$ | 208.4 | 3.4 - 35.8 | 24.8 | 340.0 - 500 |

regression analysis. However, for adsorption capacity in the gas phase, the corresponding range of sorption capacity varied from 0.2 up to 50% by weight because no low range data were available. Table (4) shows the range of sorption capacity and the mean values of k_i used for kinetic model.

After several attempts of regression analysis using solubility, $C_{e, g}$, and various connectivity indices, the following predictive equation was obtained for sorption capacity in the gas phase ($r^2=0.88$).

$$\log a_g = 2.125 \log C_{e, g} - 1.946 \log S - 1.672 \quad (16)$$

where S is the calculated solubility. This equation shows a similar expression of equation(15) and was replaced $\log k_3$ with $\log S$ and constant. In other words, the gas phase sorption capacity depends on the gas phase equilibrium concentration, approximately as the square, and is also affected by the solubility of the compound. Figure (3) shows the results of regression analysis.

The solid line in the figures indicates the "ideal" 45° line if the correlation was perfect ($r^2=1.0$). Most compounds except trichloromethane were observed to yield a good agreement between the two values.

4.2.2 Prediction of adsorption isotherm assuming Freundlich model

Because it was difficult to calculate k_i values using the linear assumption, Freundlich's equation was also used as an alternative method to relate the liquid/solid adsorption capacity to the liquid and gas concentrations at equilibrium and subsequently for prediction of sorption capacity. The coefficients for the Freundlich model was summa-

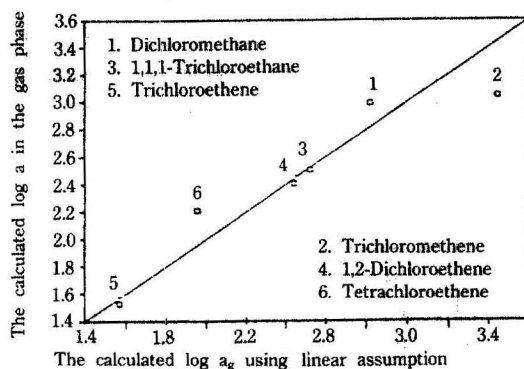


Fig. 3. Comparison of calculated using linear assumption with calculated from regression equation values for adsorption capacity in the gas phase.

riized in Table (1) and (2). The result of the multiple regression analysis is ($r^2=0.94$)

$$\log a_g = 0.238 \chi^2 + 0.573 \log H_a + 4.330 \quad (17)$$

Unlike prediction of solubility, it was observed that prediction of sorption isotherm was closely related to the complicated structure instead of simple molecular skeleton. This means that the consideration of the higher connectivity index, χ^2 , other than lower indices, was regarded as an important factor in prediction of sorption capacity in the gas phase. It can be seen that this regression must only be valid for the assumed liquid phase carbon loading of 10mg/g, which is the reason the $C_{e, g}$ dependence vanished. As illustrated in Figure (4), improved correlation was obtained after using Freundlich's equation to represent the liquid/solid adsorption data instead of a linear isotherm behavior.

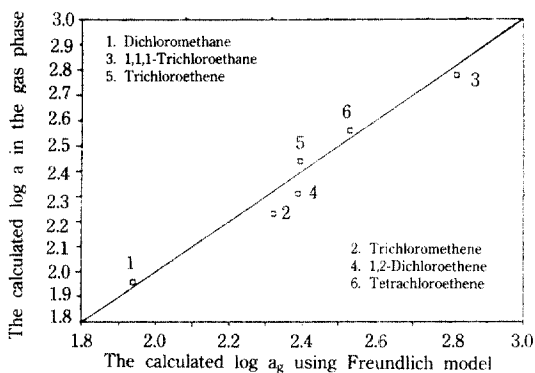


Fig. 4. Comparison of calculated using Freundlich model with calculated from regression equation values for adsorption capacity in the gas phase.

It was presumed that the linear assumption resulted in the apparent difficulty of determination of k_1 values over the higher range of sorption capacity.

5. Conclusions

The QSAR approach was observed to be a useful estimation procedure for correlating adsorption isotherm of individual chlorinated compounds in the gas phase. In addition, the constants suggested in equation(17) would be valid for six chlorinated compounds with the range of 10mg/g of sorption capacity. The following observations are summarized below as a result of this study:

1) It was possible to estimate sorption isotherms in the gas phase(a_g) using either connectivity index, $^2\chi$, and the Henry's law coefficient(H_a) or the solubility and the equilibrium concentration in the gas phase.

2) It was observed that prediction of sorption isotherm in the gas phase was closely related to the complicated structure instead of simple molecular skeleton.

3) Liquid phase sorption data were used for the prediction of gas phase sorption via a regression equation based upon a linear assumption using the QSAR method. However, by using Freundlich description of the liquid phase data, an improved correlation for the gas phase sorption ca-

capacity was developed.

NOMENCLATURES

- a : Adsorption capacity, dimensionless
- a_g : Adsorption capacity in the gas phase, mg/g
- a_l : Adsorption capacity in the liquid phase, mg/g
- B is microporosity of adsorbent
- $C_{e,l}$: Equilibrium concentration in the liquid phase, g/m^3
- $C_{e,g}$: Equilibrium concentration in the gas phase, ppm
- G_{ads} : Adsorption potential, cal/gmole
- H : Henry's law coefficient, $m^3\text{-atm/g}$
- H_a : Henry's coefficient, dimensionless
- k_1 : Coefficients
- MW: Molecular weight, g/gmole
- n : Coefficient
- N : Number of hydrogen atoms
- P : Partial pressure, atm.
- P_s : Saturation vapor pressure, atm.
- R : Universal gas constant, cal/gmole
- S : Solubility, dimensionless
- T : Temperature, $^{\circ}K$
- W_0 : Maximum adsorption space of adsorbent, cm^3/g
- Z : Number of electrons, Z^+ : Number of valence electrons

Greek Symbols

- β : Affinity coefficient
- δ_n : Cardinal number of atoms
- δ^v : δ value for valence index
- θ : Solute density, g/m^3
- ${}^m\chi$: mth-order of simple connectivity index
- ${}^m\chi^v$: mth-order of valence connectivity index

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