

A New Group Contribution Method For The Estimation Of The Surface Tension Of Non- Electrolyte Organic Compounds

By

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Abstract

Surface tension is an important property in the design of some unit operations such as extraction and distillation. Surface tension affects liquid-liquid phase separation, interfacial surface and mass transfer and the wetting of the column packing/walls strongly influencing tray/packing efficiency which ultimately determines the height of the column. Current estimation and correlation methods [1; 2; 3; 4; 5; 6] require critical property data, molar volumes or experimental data to regress the model parameters which makes them less generally applicable. It is for this reason that the objective of this work is to develop a model whose parameters can be estimated from molecular structure (via group contributions) or are simple to acquire via measurement or estimation.

In group contribution methods the molecule is fragmented into functional groups. Each of these functional groups contributes to the value of the property being calculated e.g. surface tension. The Thermodynamics Research Unit at the University of KwaZulu-Natal and the Industrial Chemistry Group at the Carl von Ossietsky University have developed several successful group contribution methods for the normal boiling point [7; 8], critical properties [9], vapour pressure [10; 11] and liquid viscosity [12] as part of an ongoing collaboration between the two Universities.

The model development in this work will follow a route similar to that of the previously developed methods, and will be based on data from the Dortmund Data Bank [13] which contains about 22000 surface tension data points for over 2200 compounds. A critical examination of other available methods will be performed, and the performance of the new model will be compared to existing models.

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Nomenclature

A	Surface Area, Parameter in Equation	$m^2, -$
a	Parameter in Equation	-
B	Parameter in Equation	-
b	Parameter in Equation	-
c	Parameter in Equation	-
d	Parameter in Equation	-
e	Parameter in Equation	-
f	Parameter in Equation	-
G	Gibbs Free Energy	J
g	Parameter in Equation	-
H^σ	Surface Enthalpy	J/m^2
HA	The hydrogen acceptor dependent hydrogen donor surface area descriptor	-
M_W^R	Molar Mass	g/mol
N_C^R	Number of carbon atoms	-
N_O^R	Number of oxygen atoms	-
N_N^R	Number of Nitrogen atoms	-
[P]	Parachor	
P_C	Critical Pressure	bar
P_C^*	Critical Pressure from Equation	bar
S^σ	Surface Entropy	J/m^2
T	Temperature	K
T_b	Normal Boiling Temperature	K
T_C	Critical Temperature	K
T_C^*	Critical Temperature from Equation	K
T_{rb}^*	$= \frac{T_b}{T_C^*}$	-
T_r, \tilde{T}	Reduced Temperature $= \frac{T}{T_C}$	-
T_{rb}	Reduced boiling point $= \frac{T_b}{T_C}$	-
T_{ref}	Reference Temperature in Equation	K
T_P	Arbitrary Reference Temperature	K
v_L	Liquid molar volume	mol/m^3
\tilde{v}_L	Reduced liquid molar volume	-
x	Stiel polar factor	-
α_c	Riedel Factor	-

${}^3\chi^v$	Third order Kier and Hall Index	-
Δh	Latent heat of vaporization	J/mol
$\Delta\tilde{h}$	Reduced latent heat of vaporization	-
η_l	Liquid Viscosity	Pa.s
η_v	Vapour Viscosity	Pa.s
ρ_c	Molar density at the critical Point	mol/m ³
ρ_l	Liquid molar density	mol/m ³
ρ_v	Vapour Molar density	mol/m ³
σ	Surface Tension	N/m or J/m ²
σ_0	Parameter in Equation	N/m or J/m ²
$\tilde{\sigma}, \sigma_r$	Reduced Surface Tension	-
ω	Acentric factor	-

1. Introduction

Surface tension is an important property in the chemical process industry. Surface tension data is used in many engineering applications such as mass transfer operations including distillation, liquid-liquid extraction, adsorption and absorption [14]. Accurate and reliable values of surface tension are necessary for the optimal design of equipment, this leads to better operation and ultimately a reduction in costs.

Several predictive and correlative equations are available for surface tension. Correlative equations are usually only applicable in the range for which they were fitted and cannot be confidently extrapolated to further temperature ranges. Predictive and correlative equations usually require additional properties of the substance that may not be readily available. Another drawback of the predictive equations is that they might only be applicable to a small family of compounds.

The Dortmund Data Bank [13] contains over 23000 surface tension data points for over 2200 components. This represents only a fraction of the chemicals that are in use today. A lot of the literature data covers only a limited temperature range. Experimental measurement of all the available chemical compounds covering large temperature ranges is time consuming and expensive. It is for this reason that accurate reliable predictive methods are being sought.

Group contribution methods are popular for the prediction of thermophysical properties. In group contribution methods the component of interest is broken down into its structural groups (e.g. CH₃, CH₂, OH etc...). The contributions of these individual groups are then combined to describe the molecule's behaviour as a whole. Group contribution methods exist for numerous properties such as critical properties, boiling point, vapour pressure and heat capacity. Several methods do exist for the prediction of surface tension but are generally not very satisfactory.

Cordes and Rarey [7], Nannoolal et al. [8; 9; 10; 12] and Moller et al. [11] have previously published work on the prediction of the normal boiling point, critical properties, vapour pressure and viscosity of non-electrolyte organic compounds. The aim of this work is to build on the foundation they have laid to develop a method for the prediction of surface tension for non-electrolyte organic compounds.

2. Theory and Literature Review

Surface tension is a property that arises at the vapour-liquid interface due to unbalanced forces acting on the molecules in the liquid surface layers (see Figure 1). The molecules at the interface interact with the other interface molecules and with the bulk molecules, interaction with the molecules in the vapour phase is much smaller than the liquid phase interactions. As a result the molecules are attracted sidewise and towards the bulk liquid, but experience little attraction from the vapour phase. This causes the surface layer to be in tension, and to contract to the smallest allowable area [15]. The units for surface tension are N/m or J/m². Surface tension is numerically equivalent to the surface free energy and is merely a more convenient form of expressing this surface energy.

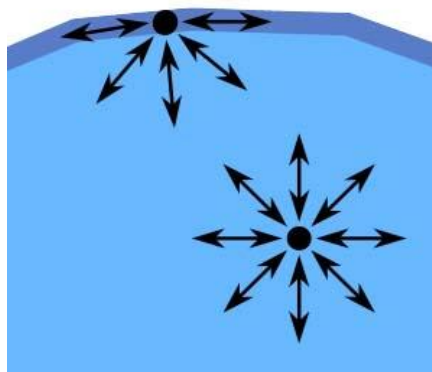


Figure 1. *Forces on molecules in the bulk liquid and surface layers. Image from <http://en.wikipedia.org/wiki/File:Wassermolek%C3%BCleInTr%C3%B6pfchen.svg>*

The surface tension is related to the Gibbs free energy by Equation (2.1) [16].

$$\sigma = \left(\frac{\partial G}{\partial A} \right)_{T,P,n} \quad (2.1)$$

Using Equations (2.2) and (2.3) [17] the surface entropy and surface enthalpy can also be calculated.

$$S^\sigma = -\frac{d\sigma}{dT} \quad (2.2)$$

$$H^\sigma = \sigma - T \frac{d\sigma}{dT} \quad (2.3)$$

The surface tension of a compound is highest at its triple point, and decreases with increasing temperature to reach zero at the critical temperature. The surface tension versus temperature curve is concave and exhibits no maxima or minima (See Figure 2).

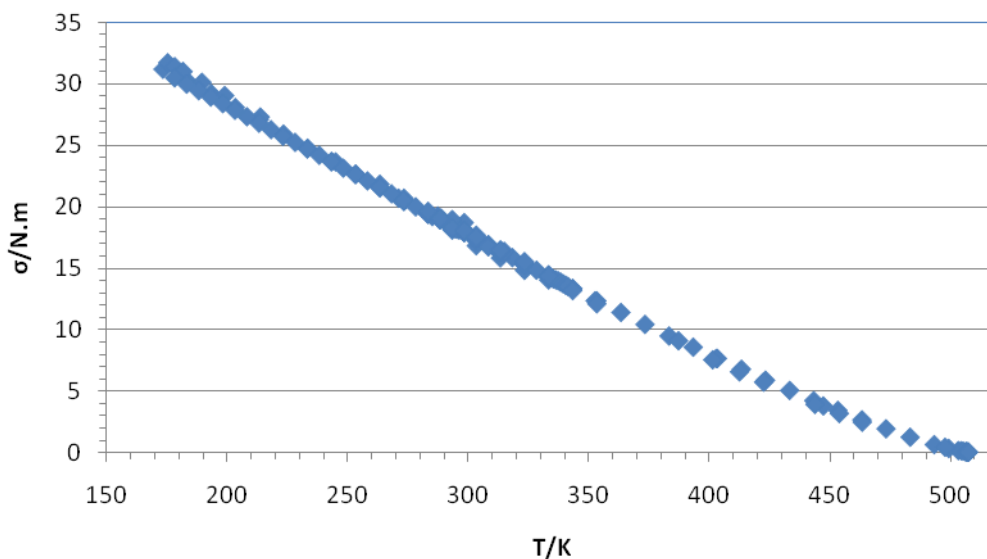


Figure 2. Surface tension of n-Hexane as a function of temperature.

If the surface enthalpy is assumed to be constant then Equation (2.3) can be integrated using the integrating factor technique to yield an expression for surface tension as a function of temperature. Equation (2.4) results from this integration.

$$\sigma = a + bT \quad (2.4)$$

Equation (2.4) is the simplest equation describing surface tension as a function of temperature. It can only be used for small temperature ranges as it cannot model the curvature that occurs when large temperature ranges are considered.

Numerous other correlative and predictive equations have been proposed to model surface tension. And to account for the curvature of the surface tension – temperature curve. These equations are largely empirical.

2.1 Correlative Equations

2.1.1 Guggenheim Equation

Guggenheim [18] suggested Equation (2.5). This equation correctly predicts the behaviour of the surface tension – temperature curve. It has a high value at the triple point and goes to zero at the critical temperature. Numerous other predictive equations are based on Equation (2.5).

$$\sigma = \sigma_0 (1 - T_R)^{11/9} \quad (2.5)$$

2.1.2 Schonhorn Equation

Schonhorn [6] introduced Equation (2.6) as an improvement on the surface tension - viscosity relationship of Pelofsky [19]. It addresses the shortcoming displayed by Pelofsky's equation at the critical temperature by ensuring that the surface tension goes to zero at this point. This is achieved by subtracting the vapour viscosity from the liquid viscosity in the denominator of the exponentiated term.

$$\sigma = A \exp\left(\frac{-B}{\eta_l - \eta_v}\right) \quad (2.6)$$

This equation requires both the liquid and vapour viscosities as functions of temperature, as well as the two correlating parameters. This means that a minimum of six constants need to be known in order to model the surface tension.

2.1.3 Faizullin Equation

There are numerous correlations relating surface tension to the latent heat of vaporization. This is expected as both properties exhibit similar behaviour when moving from the triple point to the critical temperature i.e. they both start at a maximum value at the triple point and go to zero at the critical temperature. Faizullin [20] gave the following relation between the two properties. Faizullin's equation seems fairly popular in literature. Equation (2.7) gives the reduced surface tension in terms of the reduced latent heat of vaporization and reduced molar volume.

$$\tilde{\sigma} = \left(\frac{\Delta\tilde{h}}{\tilde{v}_L}\right)^{2.15} \quad (2.7)$$

The reduced surface tension, reduced latent heat of vaporization and reduced molar volume are given by Equations (2.8), (2.9) and (2.10) respectively.

$$\tilde{\sigma} = \frac{\sigma}{(\sigma)_{\tilde{T}=0.6}} \quad (2.8)$$

$$\Delta\tilde{h} = \frac{\Delta h}{(\Delta h)_{\tilde{T}=0.6}} \quad (2.9)$$

$$\tilde{v}_L = \frac{v_L}{(v_L)_{\tilde{T}=0.6}} \quad (2.10)$$

The drawback of this equation is that both the latent heat of vaporization and the molar volume has to be known as functions of temperature, and the critical temperature has to be known.

2.2 Predictive Equations

2.2.1 Macleod-Sugden Equation

$$\sigma = ([P](\rho_l - \rho_v))^4 \quad (2.11)$$

This equation is based on that of Macleod [1]. It relates surface tension to the equilibrium liquid and vapour densities. The parachor ([P]) was originally introduced by Sugden [21]. Quayle [22] later showed how [P] could be calculated from molecular structure. This equation performs well for most compounds, but is very sensitive to the values of the parachor and density that is used. This is due to the large exponent on the product of the parachor and densities. As a result of this any error in the parachor or densities will be amplified. This correlation has been confirmed through statistical mechanics by Boudh-Hir and Mansoori [23], however their work shows that [P] is a weak function of temperature. More recently Knotts et al. [24] have proposed a QSPR correlation for [P]. Guggenheim [18] suggested that the exponent should be $3\frac{2}{3}$ rather than 4. If the difference between the liquid and vapour densities is expressed as a function of temperature such as Equation (2.12) [18] then Equation (2.11) reduces to the same form as Equation (2.5)

$$\rho_l - \rho_v = \rho_c (1 - T_r)^{\frac{1}{3}} \quad (2.12)$$

2.2.2 Brock and Bird Equation

$$\frac{\sigma}{P_c^{2/3} T_c^{2/3}} = (0.132\alpha_c - 0.279)(1 - T_r)^{\frac{11}{9}} \quad (2.13)$$

The equation proposed by Brock and Bird [2] (Equation (2.13)) is based on the same form as Guggenheim's Equation. The surface tension is reduced with the critical temperature and pressure. The Riedel factor, α_c , can be calculated using Equation (2.14) given by Miller [25], which requires the input of an additional parameter namely the normal boiling point.

$$\alpha_c = 0.9076 \left[1 + \frac{T_{br} \ln(P_c / 1.01325)}{1 - T_{br}} \right] \quad (2.14)$$

Equation (2.13) performs well for simple non-polar compounds even though the training set was very limited, but shows large deviations for large molecules, alcohols and carboxylic acids. The required parameters are T_c , P_c and T_b .

2.2.3 Zuo and Stenby Method

Zuo and Stenby [3] used a two fluid reference corresponding states equation to calculate surface tension. T_c and P_c are used as the reducing parameters. The chosen reference fluids are methane and n-octane. The surface tension is reduced with the critical temperature and pressure using Equation (2.15). Equation (2.16) then relates the reduced reference surface tensions to the reduced surface tension of the substance under investigation.

$$\sigma_r = \ln \left(1 + \frac{\sigma}{T_c^{1/3} P_c^2} \right) \quad (2.15)$$

$$\sigma_r = \sigma_r^{(1)} + \frac{\omega - \omega^{(1)}}{\omega^{(2)} - \omega^{(1)}} (\sigma_r^{(2)} - \sigma_r^{(1)}) \quad (2.16)$$

The surface tension for methane is given by Equation (2.17) and that of n-octane is given by Equation (2.18).

$$\sigma^{(1)} = 40.520(1 - T_r)^{1.287} \quad (2.17)$$

$$\sigma^{(2)} = 52.095(1 - T_r)^{1.21548} \quad (2.18)$$

The drawback of this method is the large number of constants that it requires. A total of seven inputs are required by this method to yield a value for the surface tension.

2.2.4 Sastri and Rao Method

Sastri and Rao [26] use a Guggenheim type equation to predict surface tension. The constant K and the exponents of the reducing parameters and the exponent for the reduced temperature take different values for different chemical families to account for the different behaviour of the chemical families. (See Table 1)

$$\sigma = KP_C^x T_B^y T_C^z \left[\frac{1-T_r}{1-T_{rB}} \right]^m \quad (2.19)$$

Table 1. Constants for use in Equation (2.19)

Type of liquid	K	x	y	z	m
Alcohols	2.280	0.175	0.25	0	0.8
Acids	0.125	0.350	0.50	-1.85	11/9
All other liquids	0.158	0.350	0.50	-1.85	11/9

2.2.5 Hakim et al. Method

The equation by Hakim et al. [4] was developed to predict the surface tension of polar compounds as there was not a satisfactory method for this. In order to achieve this goal extra parameters were added to the correlation. The parameters are the acentric factor and the stiel polar factor.

$$\sigma_R = \sigma_R|_{T_R=0.6} \left[\frac{1-T_R}{0.4} \right]^{m(\omega,x)} \quad (2.20)$$

$$m = 1.210 + 0.5385\omega - 14.61x - 32.07x^2 - 1.65\omega^2 + 22.03\omega x \quad (2.21)$$

$$\sigma_R|_{T_R=0.6} = 0.1574 + 0.359\omega - 1.769x - 13.69x^2 - 0.510\omega^2 + 1.298\omega x \quad (2.22)$$

$$\sigma_R = \frac{\sigma}{P_C^{2/3} T_C^{1/3}} \quad (2.23)$$

$$x = \log P_R|_{T_R=0.6} + 1.70\omega + 1.552 \quad (2.24)$$

This method requires a large amount of input parameters. The Stiel polar factor is not known for many compounds and would have to be calculated from experimental data.

2.2.6 Pitzer Method

Poling et al. [15] report the equation given by Pitzer and his co-workers [27; 28] who developed an equation similar to that of Brock and Bird [2] that uses the acentric factor instead of the Riedel factor.

$$\sigma = P_C^{2/3} T_C^{1/3} \frac{1.86 + 1.18\omega}{19.05} \left[\frac{3.75 + 0.91\omega}{0.291 - 0.08\omega} \right]^{2/3} (1 - T_r)^{11/9} \quad (2.25)$$

Equation (2.25) requires three inputs. The acentric factor is available for a large number of compounds, but can also be calculated from vapour pressure data using Equation (2.26).

$$\omega = -1 - \log P_r \Big|_{T_r=0.7} \quad (2.26)$$

2.2.7 CSGC Method

The corresponding states group contribution method of Li et al. [29] gives two different equations for estimating surface tension. The first is based on the Brock and Bird [2] type equation and the second on a Guggenheim [18] type equation. They are denoted CSGC-1 and CSGC-2 respectively. CSGC-1 is given by Equation (2.27). The parameters a to f and the parameters for the T_C^* and P_C^* equations were all determined by fitting experimental surface tension data to Equations (2.27), (2.28), (2.29) and (2.30). This large amount of parameters suggests that some of the parameters will be intercorrelated and that predictions on compounds not included in the training set will most likely be errorneous.

$$\sigma = (P_C^*/101.325)^a (T_C^*)^b (c\alpha_C - d)(1 - T_r^*)^e \quad (2.27)$$

$$\alpha_C = f \left(1 + \frac{T_{br}^* \ln(P_C^*/101.325)}{1 - T_{br}^*} \right) \quad (2.28)$$

$$T_C^* = \frac{T_b}{\left[A_T + B_T \sum_i^M n_i \Delta_{T_i} + C_T \left(\sum_i^M n_i \Delta_{T_i} \right)^2 + D_T \left(\sum_i^M n_i \Delta_{T_i} \right)^3 \right]} \quad (2.29)$$

$$P_C^* = \frac{101.325 \ln(T_b - 273.15)}{\left[A_P + B_P \sum_i^M n_i \Delta_{P_i} + C_P \left(\sum_i^M n_i \Delta_{P_i} \right)^2 + D_P \left(\sum_i^M n_i \Delta_{P_i} \right)^3 \right]} \quad (2.30)$$

$$\sigma = \sigma_{20} \left(\frac{1 - T_r^*}{1 - T_{r,20}^*} \right)^g \quad (2.31)$$

CSGC-2 is given by Equation (2.31). T_r^* for Equation (2.31) is also given by Equation (2.29), but the parameters are different from when it is used in Equation (2.27). CSGC-2 should yield better results as there are fewer terms that were regressed for.

2.2.8 Method of Conte et al.

The method of Conte et al. [30] is a group contribution method that can be used to calculate surface tension at 298 K. This method uses first, second and third order groups, as well as connectivity indices to calculate the surface tension. The surface tension is given by

$$\sigma = \sum_i N_i C_i + F(\sigma^*) + w \sum_j M_j D_j + z \sum_k O_k E_k \quad (2.32)$$

$F(\sigma^*)$ is a term that is calculated from the connectivity indices, an N, M and O are the frequencies of the first, second and third order groups respectively, and C, D and E are the contributions for those groups.

2.2.9 Method of Sheldon et al.

The method of Sheldon et al. [5] can be used to estimate surface tension at 298 K. The surface tension is calculated by relating it to the Hildebrand solubility parameter. The solubility parameter is given by Equation (2.33).

$$\delta = \left[\frac{\Delta H_{vap} - RT}{V_m} \right]^{0.5} \quad (2.33)$$

When there are no OH, COOH or aromatic COH groups present the surface tension is calculated by Equation (2.34) in all other cases Equation (2.35) is used.

$$0.01707 \delta^2 V_m^{1/3} \quad (2.34)$$

$$0.0068 \delta^2 V_m^{0.45} \quad (2.35)$$

ΔH_{vap} in Equation (2.33) is calculated using the method of Constantinou and Gani [31] and V_m is calculated using the method of Constantinou et al. [32].

2.2.10 QSPR

Numerous QSPR methods are available for the prediction of surface tension, these methods share the same deficiency as that of the group contribution methods in that estimation is only available at a single temperature. Another downfall of QSPR is that a large number of molecular descriptors are needed in order for a prediction to be made. Some of these descriptors can be deduced from the molecular structure, but others have to be calculated or determined by experimentation. Delgado and Dias [33] used Equation (2.36) to predict surface tension at 298 K. They use 6 molecular descriptors of which only 4 can be directly determined from the molecular structure. Other QSPR equations employ even more molecular descriptors.

$$\sigma = -645 + 5660N_C^R + 4840N_O^R + 8309N_N^R + 098M_W^R + 347^3 \chi^v + 0.16HA \quad (2.36)$$

2.2.11 Equations of state

Recently a number of methods have appeared (Quiones-Cisneros et al. [34], Panayiotou et al.[35]) that calculate surface tension using an equation of state. These calculations are very complex requiring the use of complex mathematical operations. The equations of state used to predict surface tension require additional properties as input, such as critical properties and the acentric factor.

2.3 Group Contribution

In group contribution methods the molecule is fragmented into pre-defined functional groups, each of these groups contributes to the value of the property being calculated. In multi-functional compounds the groups aren't always additive in a straight forward manner and group interaction parameters have to be introduced for some of the functional groups. Group contribution methods may require an extra input, but this input is usually widely available. There are a limited number of group contribution estimation techniques available for surface tension; a number of "hybrid" equations are also available that employ group contributions together with the corresponding states principle. The biggest weakness of the current group contribution methods is that estimation is only available at a single temperature. When surface tensions at temperatures far from this point are needed, another estimation method has to be used.

3. This work

3.1 Data Storage and Handling

The surface tension data obtained from the DDB is stored in a Microsoft Access Database for convenient storage and easy viewing. All operations performed on the data are done in Microsoft Visual Basic for Applications (VBA). The data is loaded into a recordset in VBA from the access database using Structured Query Language (SQL). SQL is a set of commands that enable communication between the VBA front end and the access database.

3.2 Proposed Model

The proposed model for the group contribution scheme is a modification of Equation (2.5) given by Equation (3.1).

$$\sigma = \left(a + b \left(1 - \frac{T}{T_{ref}} \right) \right)^{11/9} \quad (3.1)$$

The exponent $\frac{11}{9}$ is retained as it was found to fit the data well. The reference temperature can be any convenient reference temperature, in this work two temperatures were investigated namely 298.15 K and the normal boiling point. Both of these temperatures carry with them their advantages and disadvantages. 298.15 K makes a convenient reference temperature as there are lots of data available at this temperature. However, the trend for different sized molecules in a homologous series is difficult to model. As such, the normal boiling point is used as it follows a simple trend for compound in a homologous series, and hence is simpler to model. These trends can be seen in Figure 3 and Figure 4. Using the normal boiling point as a reference temperature gives a more evenly distributed spread of data with the “reduced temperature” as opposed to the narrow band that is present when 298.15 K is used as the reducing temperature. See Figure 5 and Figure 6.

Using the normal boiling point as a reference temperature is convenient as it is widely available for numerous compounds. The use of the normal boiling point will simplify the group contribution scheme for the calculation of the a and b parameters.

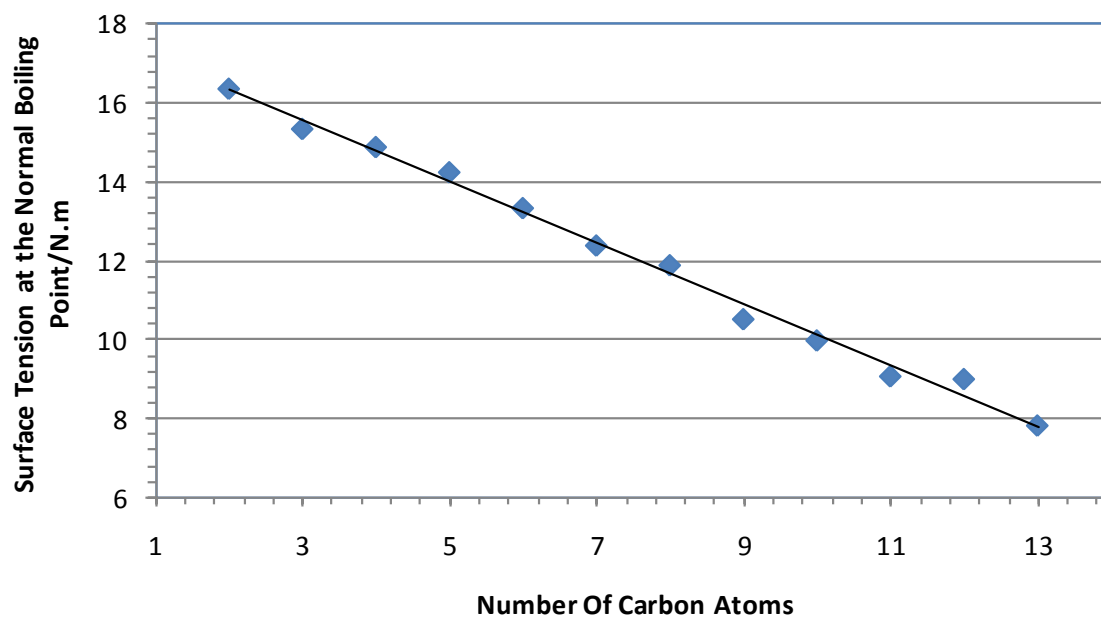


Figure 3. Surface tension of n-Alkanes at the normal boiling point versus number of carbon atoms. Data taken from the DDB.

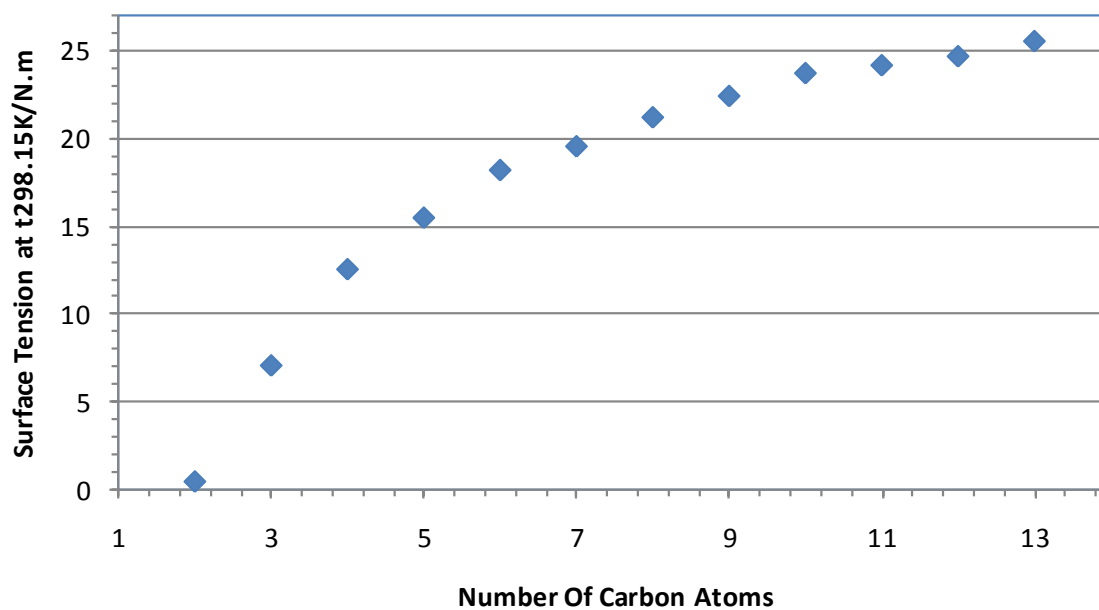


Figure 4. Surface tension of n-Alkanes at 298.15 K versus number of carbon atoms. Data taken from the DDB.

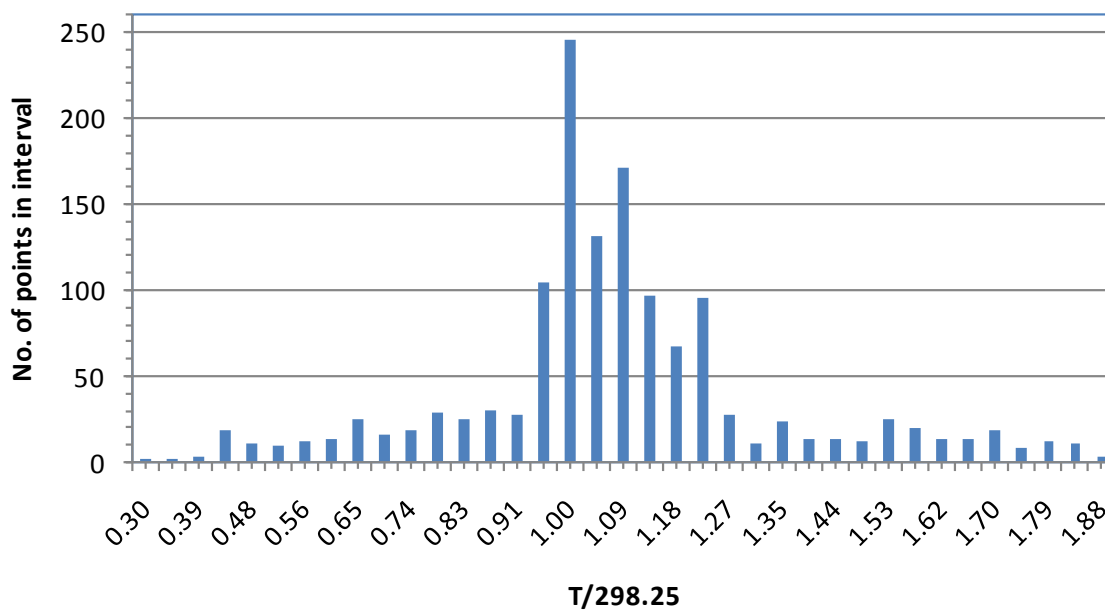


Figure 5. Data distribution of Alkanes as a function of Temperature reduced with 298.15K. Data taken from DDB.

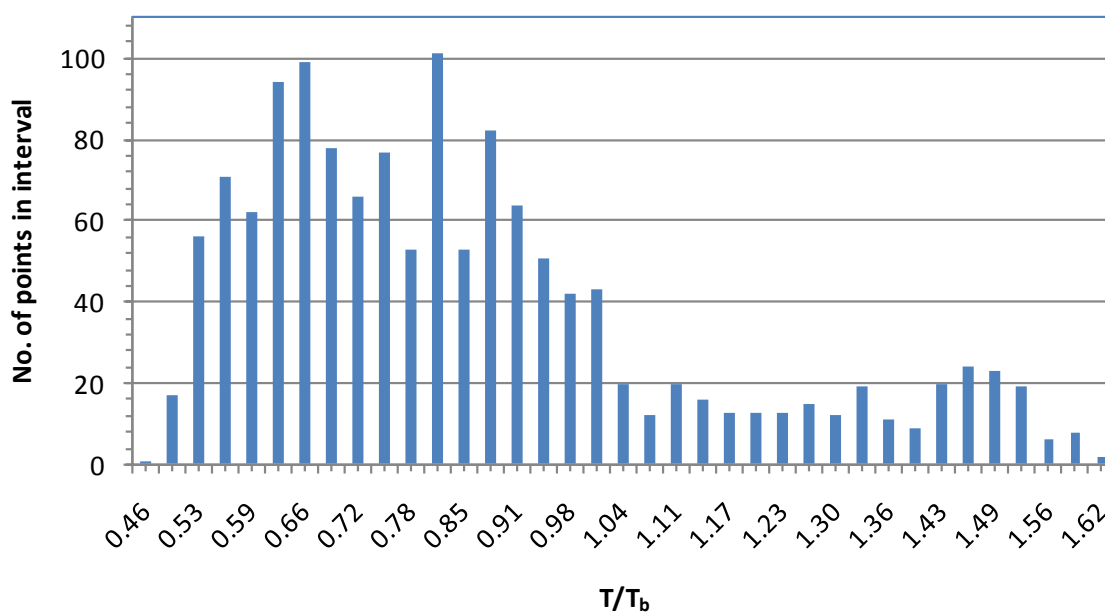


Figure 6. Data distribution of Alkanes as a function of temperature reduced with normal boiling point. Data taken from DDB.

Equation (3.1) cannot describe the behaviour of highly polar compounds adequately, and as such a correction term will have to be added in order to describe the compounds that exhibit hydrogen

bonding. According to Horvath [36] surface tension can be split up into a polar part and a non-polar part as shown in Equation (3.2).

$$\sigma = \sigma_{nonpol} + \sigma_{polar} \quad (3.2)$$

Equation (3.1) will represent the non-polar contribution to the surface tension and the correction term will represent the polar contribution to the surface tension. Work is currently underway to determine the polar contribution

3.3 Group Contributions

The functional groups in this work are based on those used by Moller et al. [11]. For this work the automatic fragmentation procedure developed by Cordes and Rarey [7] is used to fragment the molecules into their functional groups. This is achieved by communicating to the Rechenmodul COM Module provided with the DDB from VBA. This makes fragmentation much easier as it reduces the time required for fragmentation, as well as eliminating mistakes in the fragmentation procedure. Having a fast procedure for fragmentation available allows for fast identification of groups that are insignificant, and for easy addition of new groups.

In order for a good prediction to be achieved, the data in the training set must be of good quality. Data analysis is performed graphically by eliminating obvious outlying data points using a user interface developed in VBA (See Appendix A). The data is also tested against other well known methods. This served as a further verification of the available data. Regression of the data and that of the groups are performed using algorithms written in Fortran 90 in order to speed up the regression process. The number of data points available for regression is limited. An average of 10 data points are available for each compound. The critical temperature was included in the regression as a data point (0, T_c) to extend the range covered by the compounds that had mostly lower temperature data points.

At present a simple linear contribution scheme is used to compute the a and b parameters, given by Equations (3.3) and (3.4). (See Appendix B for the group parameters). This will be modified later to include group interaction if needed.

$$a = a_0 + \sum_i v_i a_i \quad (3.3)$$

$$b = b_0 + \sum_i v_i b_i \quad (3.4)$$

3.4 Suggested extension to the critical temperature

As the form of Equation (3.1) suggests, the surface tension close to the critical point will not be predicted correctly. Using a different equation and two mathematical constraints in addition to the critical temperature it will be possible to use the group contributions for the a and b parameters in Equation (3.1) to determine the constants for the new equation. The equation is of the same form as Equation (2.5) and is given by Equation (3.6).

$$\sigma_1 = \left(a + b \left(1 - \frac{T}{T_b} \right) \right)^{11/9} \quad (3.5)$$

$$\sigma_2 = c \left(1 - \frac{T}{T_c} \right)^n \quad (3.6)$$

The mathematical constraints given by Equations (3.7) and (3.8) state that at a temperature T_p say $0.8T_c$ the surface tensions and the slopes given by both equations should be equal. By imposing these conditions the expressions relating c and n to a and b can be obtained.

$$\sigma_1 \Big|_{T=T_p} = \sigma_2 \Big|_{T=T_p} \quad (3.7)$$

$$\frac{d\sigma_1}{dT} \Big|_{T=T_p} = \frac{d\sigma_2}{dT} \Big|_{T=T_p} \quad (3.8)$$

n and c are given by Equations (3.9) and (3.10) respectively.

$$n = \frac{11 T_c}{9 T_b} b \left[\frac{1 - \frac{T_p}{T_c}}{a + b \left(1 - \frac{T_p}{T_b} \right)} \right] \quad (3.9)$$

$$c = \frac{\left(a + b \left(1 - \frac{T_p}{T_b} \right) \right)^{11/9}}{\left(1 - \frac{T_p}{T_c} \right)^n} \quad (3.10)$$

This extension has not been extensively tested as yet, but it is theoretically sound and should be able to extend the method to the critical point.

3.5 Future Work

Future work includes further validation of inconsistent data and elimination of data that exhibits multiple trends. The group contribution schemes for the a and b parameters can be refined to provide a better fit. Group interactions will also be introduced to deal with groups that do not display simple additive behaviour. All the parameters will have to be re-regressed for the new contribution schemes. The extension of the method to the critical temperature will also be tested to see if it can accurately extrapolate to the critical temperature.

3.6 Conclusion

A group contribution method has been proposed to predict the surface tension of non-electrolyte organic compounds using only the molecular structure of the molecule and the normal boiling temperature of the compound. The method performs well for simple non-polar molecules, but prediction of the surface tension of polar compounds is still not satisfactory.

4. References

- [1] D.B. Macleod, Transactions of the Farady Society 19 (1923) 38-41.
- [2] R.B.B. James R. Brock, AIChE Journal 1 (1955) 174-177.
- [3] Y.-X. Zuo, E.H. Stenby, The Canadian Journal of Chemical Engineering 75 (1997) 1130-1137.
- [4] D.I. Hakim, D. Steinberg, L.I. Stiel, Industrial & Engineering Chemistry Fundamentals 10 (1971) 174-175.
- [5] T.J. Sheldon, C.S. Adjiman, J.L. Cordiner, Fluid Phase Equilibria (2005) 27-37.
- [6] H. Schonhorn, Journal of Chemical & Engineering Data 12 (1967) 524-525.
- [7] W. Cordes, J. Rarey, Fluid Phase Equilibria 201 (2002) 409-433.
- [8] Y. Nannoolal, J. Rarey, D. Ramjugernath, W. Cordes, Fluid Phase Equilibria 226 (2004) 45-63.
- [9] Y. Nannoolal, J. Rarey, D. Ramjugernath, Fluid Phase Equilibria 252 (2007) 1-27.
- [10] Y. Nannoolal, J. Rarey, D. Ramjugernath, Fluid Phase Equilibria 269 (2008) 117-133.
- [11] B. Moller, J. Rarey, D. Ramjugernath, Journal of Molecular Liquids 143 (2008) 52-63.
- [12] Y. Nannoolal, J. Rarey, D. Ramjugernath, Fluid Phase Equilibria 281 (2009) 97-117.
- [13] J. Gmehling, J. Rarey, J. Menke, Dortmund Data Bank, Oldenburg, 2008.
- [14] M.G. Freire, P.J. Carvalho, A.J. Queimada, I.M. Marrucho, J.A.P. Coutinho, Journal of Chemical & Engineering Data 51 (2006) 1820-1824.
- [15] B.E. Poling, J.M. Prausnitz, J.P. O'Connell, The Properties of Gases and Liquids, 5th ed., McGraw-Hill, USA, 2004.
- [16] L. Chunxi, W. Wenchuan, W. Zihao, Fluid Phase Equilibria 175 (2000) 185-196.
- [17] P.J. Carvalho, M.G. Freire, I.M. Marrucho, A.n.J. Queimada, J.A.P. Coutinho, Journal of Chemical & Engineering Data 53 (2008) 1346-1350.
- [18] E.A. Guggenheim, The Journal of Chemical Physics 13 (1945) 253-261.
- [19] A.H. Pelofsky, Journal of Chemical & Engineering Data 11 (1966) 394-397.
- [20] M.Z. Faizullin, Fluid Phase Equilibria 211 (2003) 75-83.
- [21] S. Sugden, Journal of the Chemical Society 125 (1924) 1177-1189.
- [22] O.R. Quayle, Chemical Reviews 53 (1953) 439-589.
- [23] M.E. Boudh-Hir, G.A. Mansoori, The Journal of Physical Chemistry 94 (1990) 8362-8364.
- [24] T.A. Knotts, W.V. Wilding, J.L. Oscarson, R.L. Rowley, Journal of Chemical & Engineering Data 46 (2001) 1007-1012.
- [25] D.G. Miller, G. Thodos, Industrial & Engineering Chemistry Fundamentals 2 (1963) 78-80.
- [26] S.R.S. Sastri, K.K. Rao, The Chemical Engineering Journal and the Biochemical Engineering Journal 59 (1995) 181-186.
- [27] R.F. Curl, K. Pitzer, Industrial & Engineering Chemistry 50 (1958) 265-274.

- [28] K.S. Pitzer, *Thermodynamics*, 3rd ed., McGraw-Hill, New York, 1995.
- [29] P. Li, P.-S. Ma, J.-G. Dai, W. Cao, *Fluid Phase Equilibria* 118 (1996) 13-26.
- [30] E. Conte, A. Martinho, H.A. Matos, R. Gani, *Industrial & Engineering Chemistry Research* 47 (2008) 7940-7954.
- [31] L. Constantinou, R. Gani, *AIChE Journal* 40 (1994) 1697-1710.
- [32] L. Constantinou, R. Gani, J.P. O'Connell, *Fluid Phase Equilibria* 103 (1995) 11-22.
- [33] E.J. Delgado, G.A. Diaz, *SAR and QSAR in Environmental Research* 17 (2006) 483-496.
- [34] S.E. Quinones-Cisneros, U.K. Deiters, R.E. Rozas, T. Kraska, *The Journal of Physical Chemistry B* 113 (2009) 3504-3511.
- [35] C. Panayiotou, M. Pantoula, E. Stefanis, I. Tsivintzelis, I.G. Economou, *Industrial & Engineering Chemistry Research* 43 (2004) 6592-6606.
- [36] A.L. Horvath, *Molecular Design - Chemical Structure Generation from the Properties of Pure Organic Compounds*, Elsevier, Amsterdam, 1992.

Appendix A: Graphical User Interface

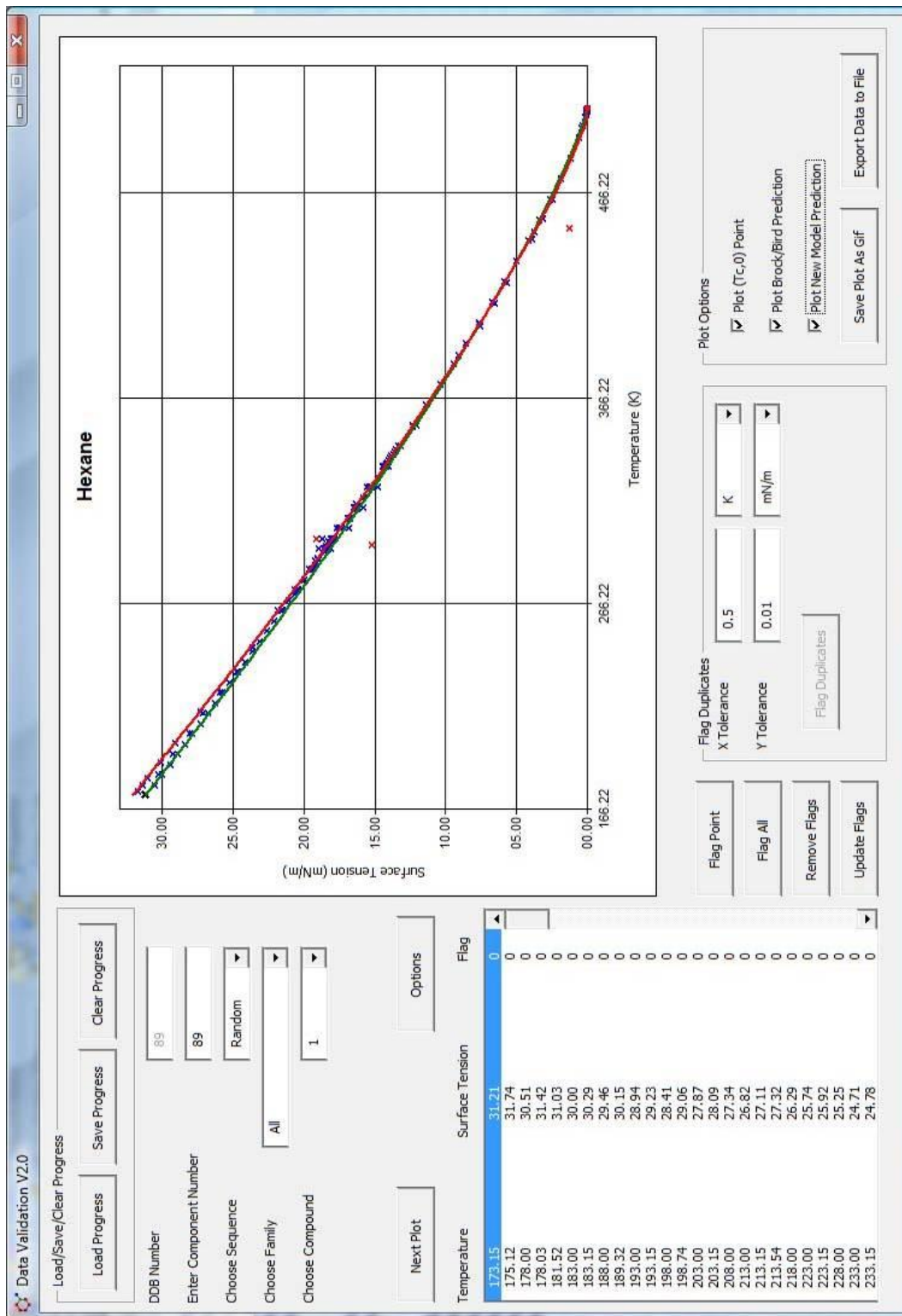


Figure 7. Graphical User Interface for Data Validation.

Appendix B: Group Contributions

Table 2. Group Contributions for the a and b parameters of Equation 3.1

Group Number	Description	a parameter contribution	b parameter contribution
0	Constant	14.54404	22.06514
1	-CH3	-2.377035	-2.430659
2	-CH3	-1.685591	-1.916038
3	-CH3	-1.843349	-1.907685
4	-CH2-	-0.356352	0.1098599
5	>CH-	1.599048	2.15467
6	>C<	4.729692	1.503607
7	-CH2-	-0.4584482	-0.06244333
8	-CH<	1.319214	1.604808
9	>C<	2.74078	3.433721
10	-CH2-	-0.7013355	-0.3420913
11	>CH-	0.2035391	-0.2568289
12	>C<	0.9111392	3.541861
13	-C=C<	0.6540704	4.4777
14	>CH-	0.3884063	0.4248077
15	>C<	1.69715	2.329672
16	-CH(a)<	-0.5786189	-0.3116263
17	>C(a)<	0.5648264	1.399608
18	>C(a)<	0.5431945	1.616813
19	=C(a)<	0.387203	1.462729
20	-CH=C-	-0.1453209	0.3053877
21	>C=C<	-0.5831358	-0.5531622
22	-CtC-	-0.05634498	1.215687
24	-CH2(r)-en	-0.4861165	-0.4948983
25	CH#	-1.5279	-2.002801
26	CH2=	-2.146469	-3.050385
27	-C=C-	1.479959	2.492158
29	-CH3	-1.630801	-2.796137
32	>C=C-C=C<	-1.633354	-1.911895
33	>C=C-C=C<	0.8896643	1.046446
35	F-	-0.5223321	-0.7951348
37	F-C(a)	-1.284553	-1.851298
38	F-C-1Halo	-1.544486	-1.638635
39	F-C-2Halo	-2.177809	-2.320772
40	Cl-	-0.6871372	0.02185282
41	Cl-C(a)	-1.11423	-1.346589

42	Cl-C=	-1.429883	-0.9207008
43	Cl-C-1Halo	-1.24721	-1.041556
44	Cl-C-2Halo	-1.568841	-1.336313
45	Br-	-0.587754	0.2883377
46	Br-C(a)	-0.7609029	-1.186219
47	I-	0.2043802	0.8617393
48	C(a)-COOH	-1.213171	3.209285
49	-OH (n=<4)	-0.6617996	-0.1645418
50	C(a)-OH	0.2147823	-0.7821009
51	-O-	0.04344435	1.105568
52	-O-	0.12054	1.722006
53	-COOH (n=<9)	-2.023935	-0.6154714
54	-COO -	-0.2044424	2.221181
55	-COO -	-1.289914	0.05686781
57	>C=O	0.5473037	3.009468
58	>C=O	0.4309959	1.568156
59	-CHO	-0.8248828	-0.2233988
60	-CHO	0.1148275	-0.3514498
61	O=C(-O-)2	-0.2344128	3.279727
62	-CO-O-CO-	0.8446514	3.154368
64	>(OC2)<	-0.2139141	1.115941
69	-OCON<	0.3243382	1.073352
70	-CONH<	1.22702	3.119194
71	-CONH<	-0.08191957	1.931592
72	-CONH<	0.8369331	4.126
74	ONC-	-0.1733937	0.4408585
75	NO2-	-1.486813	-0.4407344
76	NO2-	0.08554778	1.302723
77	NO2-	-1.822169	-1.804773
79	NO3-	-0.9837441	0.5153994
80	NH2-	-0.2410543	-0.2415515
81	NH2-	0.1135555	1.692346
82	-NH-	0.1916631	2.123074
84	-N<	2.313049	1.713515
87	=N-	0.8245888	2.859569
88	=N-	0.6063488	1.251721
89	-CtN (n=<12)	-1.285494	0.6100526
91	C#N-	-1.238862	-2.208074
92	-N<	1.917238	4.265195
93	-NH-	0.3237377	1.644321
94	-NH-	1.302032	0.8332131

95	P(O)O3-	1.645884	5.968338
96	>P<	0.4166668	2.678812
97	PO3-	1.457981	2.052291
98	-S-S-	1.084598	3.566849
99	-SH	-0.6020778	-0.3646695
100	-S-	0.6153792	2.579021
101	-S-	-0.3001855	-0.01429169
102	-SO2-	0.9485883	4.500032
103	>SO4	0.6624537	4.244516
105	>S=O	0.2984812	6.692647
106	SCN-	-0.06602307	1.349289
107	>SO3	-1.40861	8.479561
111	B(O-) ₃	0.8066189	4.374774
112	>Al<	2.167881	8.490407
113	COCl-	-1.110943	-0.0242909
115	>Ge<	3.5424	9.971751
117	Cl-Si<	-2.195109	-1.559151
123	>Si<	3.791163	5.058092
125	>Si<	3.252792	2.599729
128	SiH	1.583126	-0.2017524
129	CH3-Si	-2.23361	-1.94885
130	>N-N<	1.572427	2.863907
131	>CH(r) - C(r)<	-0.04952952	0.1363417
132	C(a)-C(r) <	0.552527	1.551834
133	C(a)-C(a)	0.6303381	1.363896
134	>C(r)=C(k)	0.3604649	-0.742883
138	C(a)-C=	0.5313349	2.080671
140	C2-N-C(r)	4.070315	0.3015497
141	-OCN(a)	0.317691	0.08209886
143	N-N_C	-2.307652	0.3358266
144	Br-C-1Halo	-0.5868368	0.3706948
145	Br-C-2Halo	-0.7851267	-0.4923757
149	Cl-C=(1 Halo)	-1.394635	-1.466118
