

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

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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 (Macleod 1923; Brock and Bird 1955; Zuo and Stenby 1997) 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 and the Industrial Chemistry Group has developed several successful group contribution methods for the normal boiling point (Cordes and Rarey 2002; Nannoolal *et al.* 2004), critical properties (Nannoolal *et al.* 2007), vapour pressure (Moller *et al.* 2008; Nannoolal *et al.* 2008) and liquid viscosity (Nannoolal *et al.* 2009) as part of an ongoing collaboration between the University of KwaZulu-Natal and the Carl von Ossietzky University.

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 (Gmehling *et al.* 2008) which contains about 22600 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.

Keywords: Surface Tension, Group Contribution.

Literature Overview

Surface tension at the vapour-liquid interface occurs due to unbalanced forces acting on the molecules in the liquid surface layers (see Figure 1). 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 (Poling *et al.* 2004).

The surface tension is related to the Gibbs free energy by Equation(1) (Chunxi *et al.* 2000).

$$\sigma = \left(\frac{\partial G}{\partial A} \right)_{T,P,n} \quad (1)$$

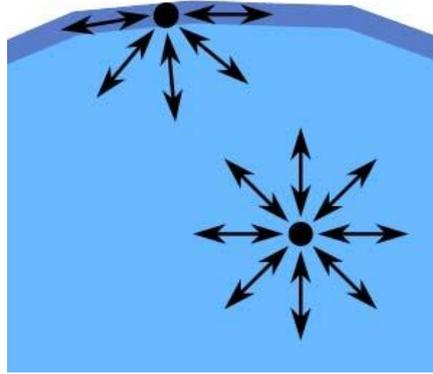


Figure 1. Forces on molecules in the bulk liquid and surface layers. Image from <http://en.wikipedia.org/wiki/File:Wassermolek%C3%BCleInTr%C3%B6pfchen.svg>

Using Equations (2) and (3) (Carvalho *et al.* 2008), the surface entropy and surface enthalpy can also be calculated.

$$S^\sigma = -\frac{d\sigma}{dT} \quad (2)$$

$$H^\sigma = \sigma - T \frac{d\sigma}{dT} \quad (3)$$

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 is concave and exhibits no maxima or minima.

Numerous correlating and prediction equations have been proposed for surface tension. These equations are largely empirical. Several of the most well known equations are outlined below:

1.) Macleod-Sugden correlation

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

This equation is based on that of Macleod (1923) relating surface tension to liquid and vapour densities. The parachor ([P]) was originally introduced by Sugden (1924). 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. 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 (1990), however their work shows that [P] is indeed a function of temperature. More recently Knotts *et al.* (2001) has proposed a QSPR correlation for [P].

2.) Brock and Bird equation

$$\frac{\sigma}{P_c^{2/3} T_c^{2/3}} = (0.132\alpha_c - 0.279)(1 - T_r)^{11/9} \quad (5)$$

The equation proposed by Brock and Bird (1955) is based on that proposed by van der Waals (1895). α_c is usually calculated using the equation given by Miller (1963), which requires the input of an additional parameter. Equation (5) performs well for simple non-polar compounds, but shows large deviations for large molecules and alcohols.

3.) Other corresponding states type equations

There have been numerous modifications of the Brock and Bird equation to attempt a better fit to different classes of compounds. All of the equations can be reduced to the following general equation.

$$\sigma = b(1 - T_r)^n \quad (6)$$

This is the general equation which was first derived by van der Waals (1894). The most significant equations of this type are that of Sastri and Rao (1995) and Zuo and Stenby (1997).

4.) Group Contribution

In group contribution methods the molecule is fragmented into predefined functional groups; each of these groups contributes to the value of the property being calculated. In multifunctional 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. Recently Conte *et al.* (2008) have developed a method to predict surface tensions at 298 K. The method is a Gani type method that uses first, second and third order groups to calculate the surface tension. Sheldon *et al.* (2005) employ existing group contribution schemes to predict surface tension.

5.) 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 (2006) used Equation (7) 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 descriptors.

$$\sigma = -645 + 5660N_C^R + 4840N_O^R + 8309N_N^R + 098M_W^R + 347^3 \chi^v + 0.16HA \quad (7)$$

6.) Equations of state

Recently a number of methods have appeared (Quiones-Cisneros *et al.* 2009, Stefanis *et al.* 2005) 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.

7.) Correlations

Numerous correlations exist that correlate surface tension with other properties such as viscosity, heat of vaporisation and number of carbon atoms.

$$\sigma = A \exp\left(\frac{-B}{\eta_l - \eta_v}\right) \quad (8)$$

Equation (8) shows one such example (Schonhorn, 2002). The drawback of these equations are that they have to be fitted to experimental data, and that the correlating property must be known at all the required temperatures and that the parameters must be determined by data regression. As a result the fitted equations have a lot more parameters than a direct surface tension- temperature relationship.

This work

The functional groups in this work are based on those used by Moller *et al.* (2008). For this work the automatic fragmentation procedure developed by Cordes and Rarey (2002) is used to fragment the molecules. 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.

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 Visual Basic for Applications. 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 model used for the surface tension is a modification of Equation (6).

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

The exponent $\frac{9}{11}$ is retained from the Brock and Bird equation, as this 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 it follows a simple trend for compound in a homologous series, and hence is simpler to model. These trends can be seen in Figures 2 and 3.

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 simplifies the group contribution scheme for the calculation of the a and b parameters. At present a simple linear contribution scheme is used to calculate the a and b parameters. This will be modified later to include group contributions if needed.

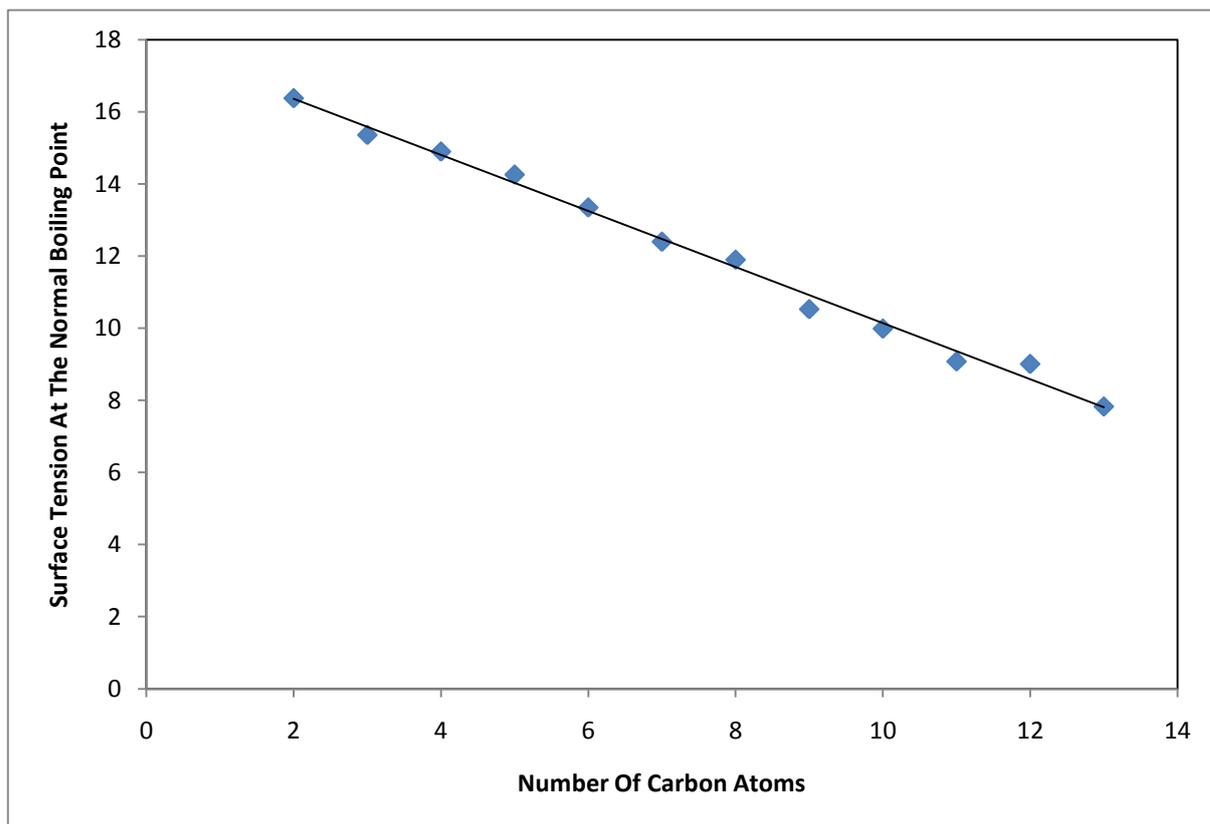


Figure 2. Surface tension of n-Alkanes at the normal boiling point versus number of carbon atoms. Data taken from the DDB.

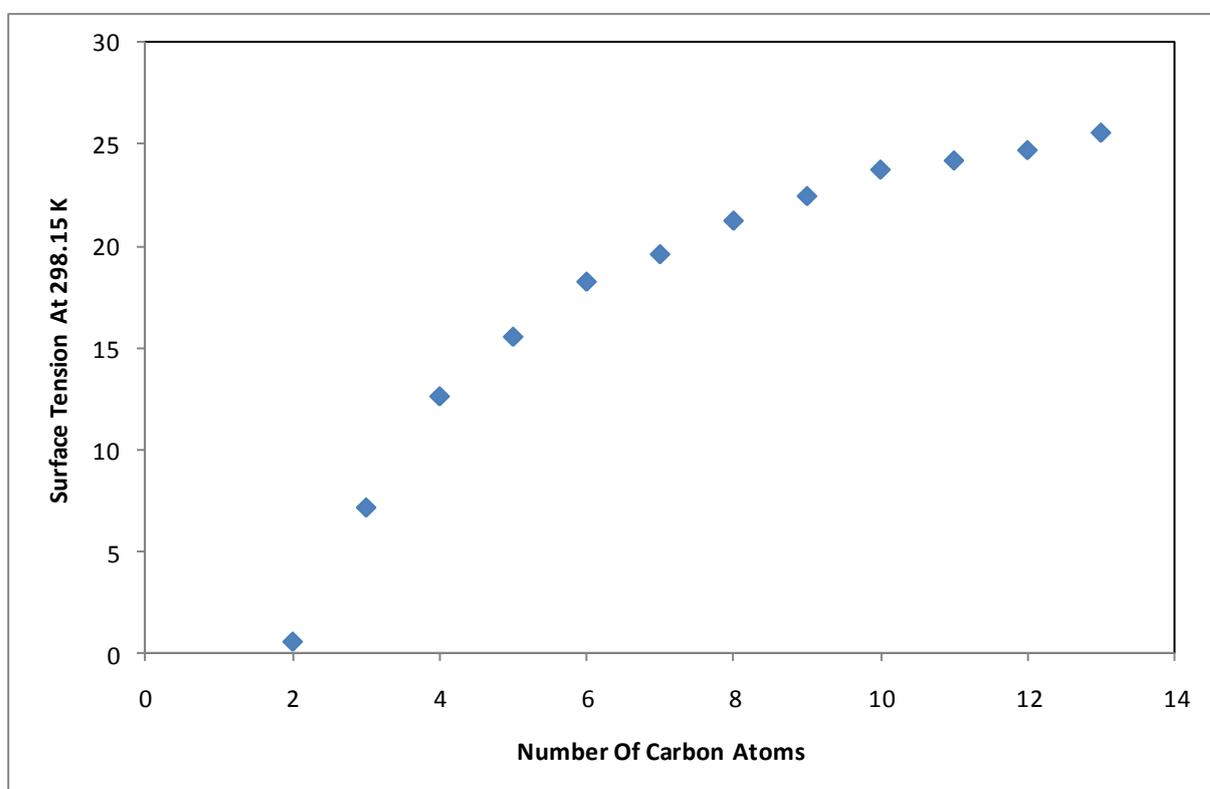


Figure 3. Surface tension of n-Alkanes at 298.15 K versus number of carbon atoms. Data taken from the DDB.

Equation (9) cannot describe the behaviour of alcohols 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 (1992) surface tension can be split up into a polar part and a non polar part as shown in Equation (10).

$$\sigma = \sigma_{nonpol} + \sigma_{polar} \quad (10)$$

As such Equation (9) will represent the non-polar term and the correction will represent the polar term.

Conclusion

A group contribution method has been developed to predict the surface tension of non-electrolyte organic compounds. The inputs required are the molecular structure and the normal boiling point.

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