



Surface tension of alcohols: A scaled equation and an artificial neural network



Giovanni Di Nicola*, Mariano Pierantozzi

DIISM, Università Politecnica delle Marche, Ancona, Italy

ARTICLE INFO

Article history:

Received 15 September 2014

Received in revised form 8 January 2015

Accepted 12 January 2015

Available online 13 January 2015

Keywords:

Alcohols

Neural network

Radius of gyration

Surface tension

ABSTRACT

This work presents a new formula to calculate the surface tension of alcohols.

As a first step, an analysis of the data available on the surface tension of alcohols was made. A total of 2121 data were collected for *n*-alcohols, aromatic alcohols, cycloaliphatic alcohols, 2-alkanols and methyl alkanols. The data were then regressed with the most reliable semi-empirical correlation methods in the literature based on the corresponding states theory. The scaled equation proposed is very simple and gives noticeable improvement with respect to existing equations.

The same physical parameters considered in the scaled equation were also adopted as input parameters in a multi-layer perceptron neural network, to predict the surface tension of alcohols. The multilayer perceptron proposed has one hidden layer with 29 neurons, determined according to the constructive approach. The model developed was trained, validated and tested for the set of data collected, showing that the accuracy of the neural network model is very good.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

An alcohol is an organic compound in which the hydroxyl functional group (–OH) is bound to a carbon atom. Due to the presence of the hydroxyl functional group, alcohols can hydrogen bond. In addition, because of the difference in electronegativity between oxygen and carbon, they are polar, and therefore hydrophilic, showing the ability of dissolving both polar and non-polar substances. For this reason, between the several uses of alcohols, of particular interest are the fields of solvents and reagents. Other important uses are in fuels, antifreezes, preservatives and beverages. In organic synthesis, alcohols serve as versatile intermediates.

Surface tension is an important fluid property for the study of industrial applications. In particular, it plays a fundamental role in the study of phase transitions and technical processes such as boiling and condensation, absorption and distillation, microscale channel flow processes and detergents. Liquid–vapour interfaces are also important for particular naturally occurring phenomena, such as the performance of biological membranes.

In this paper, the raw surface tension data (experimental, smoothed and predicted) available from DIPPR database [1] were analysed for 117 alcohols. The main advantage of the DIPPR database is that it collects data from a wide range of sources and

evaluates them critically. References, notes, and quality codes for all data points are given [2]. During the data collection, a fluid by fluid analysis was performed and data showing deviations higher than three times the standard deviation were rejected. All the fluids containing the alcohol functional group were considered and divided into the following subfamilies: *n*-alcohols, aromatic alcohols (phenols), cycloaliphatic alcohols and other aliphatic alcohols (2-alkanols and methyl alkanols). Although phenols, whose hydroxyl group is attached to an unsaturated aromatic ring system, are more reactive than alcohols and act more like acids, they were still considered in the data treatment.

Despite there being no surface tension calculation/estimation methods specifically oriented to alcohols, several theories that have been proposed to date can be applied to describe the surface tension of alcohols. It is necessary to emphasise that, because of association, the equations for the surface tension calculation of polar molecules, such as alcohols or acids, often pose serious problems in terms of predictability.

The surface tension σ (mN m^{-1}) of a fluid can be expressed as a function of temperature using an equation similar to that of van der Waals [3]

$$\sigma = \sigma_0 \left(1 - \frac{T}{T_c}\right)^n \quad (1)$$

where T_c (K) is the critical temperature, σ_0 (mN m^{-1}) and n are empirical constants obtained with the least squares method in a fit to the experimental data available on surface tension [4,5].

* Corresponding author. Tel.: +39 0712204277.

E-mail address: g.dinicola@univpm.it (G. Di Nicola).

Nomenclature

<i>b</i>	Network weight
<i>g</i>	Neural network model
G_r	Radius of gyration (Å)
<i>K</i>	Temperature independent constant
K_b	Boltzmann's constant
<i>m</i>	Slope ($\text{mN m}^{-1} \text{K}^{-1}$)
<i>M</i>	Molecular mass (kg kmol^{-1})
<i>n</i>	Number of points
<i>nh</i>	Number of neurons
N_a	Avogadro's number
<i>p</i>	Pressure (bar)
<i>P</i>	Parachor
<i>q</i>	Intercept (mN m^{-1})
<i>Q</i>	Riedel parameter
<i>s</i>	Activation function
S_i	Substance-dependent parameters
<i>T</i>	Temperature (K)
<i>v</i>	Molar volume ($\text{m}^3 \text{kmol}^{-1}$)
<i>w</i>	Network weight
<i>x</i>	Network input
\hat{y}	Network output
<i>Z</i>	Compressibility factor

Greek letters

σ	Surface tension (mN m^{-1})
ρ	Density (mol m^{-3})
ω	Acentric factor
θ	Vector of parameters

Subscripts/superscripts

<i>b</i>	Boiling point
<i>c</i>	Critical point
calc	Calculated
exp	Experimental
<i>l</i>	Liquid
<i>r</i>	Reduced
<i>v</i>	Vapor

Acronyms

AAD	Average absolute deviation
ANN	Artificial neural network
DIPPR	Design Institute for Physical Properties
MLP	Multi-layer perceptron
RMSE	Root-mean-square error

Another easy and empirical formula was proposed by Macleod [6]:

$$\sigma = K(\rho_l - \rho_v)^4 \quad (2)$$

The formula suggests the existence of a simple relationship between surface tension and the difference between the densities of the liquid and of its vapour; *K* is a temperature independent constant characteristic of each substance. One year later, Eq. (2) was modified by Sudgen [7]:

$$\sigma = [P(\rho_l - \rho_v)]^3 \quad (3)$$

where $K = P^4$, suggesting that the parameter *P* was temperature dependent; he called this parameter parachor. Parachor values of various compounds were calculated by Quayle [8] using

experimental surface-tension data. The parachor property can be related to the critical properties of compounds including critical temperature and molar volume as follows [9,10]:

$$P = 0.324 \times T_c^4 \times v_c^{7/8} \quad (4)$$

where *T* is the temperature (K), *v* is the molar volume ($\text{m}^3 \text{kmol}^{-1}$) and the subscript *c* denotes the critical value.

Eq. (3) may be considered as an equation of state [11] of the interface because it has been shown to be a good predictor of surface tension if equilibrium densities and experimental data for the parachor are used. As Escobedo and Mansoori [12] suggested, its good performance and extremely easy analytical form have made Eq. (3) a very popular method for calculating surface tension, but it has some shortcomings, as the percent deviation in predicting surface tension increases with increasing complexity of the molecular structure.

Ferguson and Kennedy [13] and Guggenheim [14] used the corresponding states principle to correlate the surface tension in the low temperature range; this decision was justified under the assumption that, since the corresponding states principle was derived from an equation of state, surface tension is also expected to follow the same principle. Brock and Bird [15] developed this concept for non-polar liquids and proposed the following formula applicable to temperatures far from the critical point:

$$\sigma = p_c^{2/3} T_c^{1/3} Q (1 - T_r)^{11/9} \quad (5)$$

where p_c (bar) is the critical pressure, T_r is the reduced temperature, T/T_c . *Q* is the Riedel parameter developed in terms of p_c and T_{br} according to the Miller suggestion,

$$Q = 0.1196 \left[1 + \frac{T_{br} \ln(p_c/1.01325)}{1 - T_{br}} \right] - 0.279 \quad (6)$$

T_{br} is the reduced normal boiling temperature, T_b/T_c , and T_b is the normal boiling temperature (K).

In some cases, the surface tension can be represented in terms of an additional parameter. One example is the so-called acentric factor, ω , initially introduced as an empirical parameter by Pitzer to explain the deviation from the corresponding states principle, as defined for noble gases, when applied to larger molecules. Pitzer's [16] relation in terms of T_c , p_c (bar), and ω leads to the following corresponding state relationship for σ :

$$\sigma = p_c^{2/3} T_c^{1/3} \frac{1.86 + 1.18\omega}{19.05} \left[\frac{3.75 + 0.91\omega}{0.291 - 0.08\omega} \right]^{2/3} (1 - T_r)^{11/9} \quad (7)$$

For compounds that exhibit hydrogen bonds, Sastri and Rao [17] proposed a modified expression for the Brock and Bird correlation:

$$\sigma = K p_c^x T_b^y T_c^z \left[\frac{1 - T_r}{1 - T_{br}} \right]^m \quad (8)$$

where p_c is in bar. Coefficients were regressed for different families separately, including alcohols.

To underline the work done in this research field, other recent equations have been proposed. Miqueu et al. [18] proposed the following:

$$\sigma = k T_c \left(\frac{N_a}{V_c} \right)^{2/3} (4.35 + 4.14\omega) t^{1.26} (1 + 0.19t^{0.5} - 0.487t) \quad (9)$$

where $t = 1 - T/T_c$, and *k*, N_a , V_c , ω are Boltzmann's constant, Avogadro's number, the critical volume, and the acentric factor, respectively. This equation represents the surface tension for 31 substances up to the critical point with an average absolute deviation of less than 3.5%.

Other relevant equations, again based on the corresponding states principle, were recently proposed by Xiang [19]. These

Download English Version:

<https://daneshyari.com/en/article/201954>

Download Persian Version:

<https://daneshyari.com/article/201954>

[Daneshyari.com](https://daneshyari.com)