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A new equation for the surface tension of carboxylic acids

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ABSTRACT

This work presents a new formula to calculate the surface tension of the important organic family of carboxylic acids.

As a first step, the raw surface tension data of acids (experimental, smoothed and predicted) accepted by DIPPR database were collected. After the data analysis, only the experimental data were considered for the calculations. The selected data were regressed with a scaled equation based on three input parameters: radius of gyration, critical density and critical temperature as fluid constants. Particularly relevant is the introduction of the radius of gyration as fluid parameter, that is a noticeable difference with respect to other previous literature methods.

The entire dataset was split into two groups, according to their chemical characteristics and acidity. The proposed equation was regressed for the two groups, separately.

The ability of the model to predict the surface tension of new acids was tested for 5 acids for which only one datum point was present in the database and that were not considered during the regression. To check the behavior of the model also at higher reduced temperatures, 6 data for ethanoic acid were also kept for validation. The validation gave satisfactory results.

The selected data also were analysed with the most reliable semi-empirical correlating methods in the literature based on the corresponding states theory. The proposed equation is very simple and gives noticeable improvement with respect to existing equations.

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1. Introduction

As a general definition, an acid is a substance, which donates hydrogen ions. The most common organic acids are the carboxylic acids, compounds that contain a −COOH group.

Organic acids are used as food additives, in medicines and in the manufacture of various chemicals. Acetylsalicylic acid and ibuprofen are carboxylic acids, a form of vitamin C is called ascorbic acid and is a carboxylic acid. Biological systems create many complex organic acids that contain carboxyl groups, like amino acids and nucleic acids. Amino acids are very important because combinations of amino acids make up the proteins. Surface tension appears to be a critical factor in the stabilization of proteins [1]. Higher fatty acids are used in the manufacture of soaps. Soaps and detergents help the cleaning by lowering the surface tension of the water so that it more readily soaks into pores and soiled areas. Many carboxylic acids are present in the foods and drinks (malic acid, tartaric acid, oxalic acid, lactic acid). Acetic acid is used as vinegar. Sodium salts of some organic acids are used as preservatives. Additives or preservatives have also been found to have varying effects on the surface tension of aqueous foods and beverages, which usually results from a decrease in pH. Simple organic acids are used at high temperature for oil and gas well stimulation treatments. Low surface tension is needed to reduce the capillary forces that otherwise reduce the gas production [2]. To correlate and predict the phase transitions of acids and for the description of other technical processes like boiling and condensation, the knowledge of the surface tension is also of fundamental importance.

The physical properties of the carboxylic acids are strongly related to their ability to form hydrogen bonds, that can occur between two molecules of acid creating a dimer and doubling the size of the molecule. As a consequence, the Van der Waals dispersion forces of the dimers are increased, influencing the physical properties (i.e., higher boiling point temperature).

Organic acids do not dissociate completely in water. In the presence of water, the dimerization does not occur. Instead, hydrogen bonds are formed between water molecules and

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Nomenclature

Latin letters

G_r	Radius of Gyration (m)
k	Coefficient of the Sastri and Rao equation
K	Temperature independent constant
K_b	Boltzmann's constant ($J \cdot K^{-1}$)
m	Coefficient of the Sastri and Rao equation
n	Empirical constant of the Van der Waals equation
N	Number of points
N_a	Avogadro's number (mol^{-1})
p	Pressure (bar)
P	Parachor
pH	Acidity or basicity of an aqueous solution
pKa	Acidity constant
Q	Riedel parameter
T	Temperature (K)
V	Molar volume ($m^3\ kmol^{-1}$)
x	Coefficient of the Sastri and Rao equation
y	Coefficient of the Sastri and Rao equation
z	Coefficient of the Sastri and Rao equation

Greek letters

ρ	Density ($mol \cdot m^{-3}$)
σ	Surface tension ($N \cdot m^{-1}$)
ω	Acentric factor

Subscripts/Superscripts

b	boiling point
c	critical point
calc	calculated
exp	experimental
l	liquid
r	reduced
v	vapor

Acronyms

AAD	Average Absolute Deviation
AD	Average Deviation
DIPPR	Design Institute for Physical PRoperties
MAAD	Maximum Average Absolute Deviation

individual molecules of acids. Lower molecular mass organic acids are miscible in water, but higher molecular mass acids are generally insoluble. On the other hand, most organic acids are very soluble in organic solvents.

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

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

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

Macleod proposed another easy and empirical formula [6]:

$$\sigma = K(\rho_l - \rho_v)^4 \tag{2}$$

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, Sudgen [7] modified Equation (2):

$$\sigma = [P(\rho_l - \rho_v)]^3 \tag{3}$$

Where $K = P^4$, suggesting that the parameter P was temperature dependent; he called this parameter parachor. Quayle [8] calculated Parachor values of various compounds using experimental surface tension data. Parachor property can be related to the critical properties of compounds including critical temperature and molar volume as follows [9,10]:

$$P = 0.324 \cdot T_c^4 \cdot V_c^{7/8} \tag{4}$$

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

Equation (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 suggested [12], its good performance and extremely easy analytical form have made Equation (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 the range of temperature far from the critical point:

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

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,

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

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 (K), p_c (bar), and ω leads to the following corresponding state relationship for σ:

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

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

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