



## Surface tension of silanes: A new equation<sup>☆</sup>

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### ABSTRACT

This work presents a new formula to calculate the surface tension of silicon based molecules.

As a first step, the raw surface tension data of silanes (experimental, smoothed and predicted) accepted by DIPPR database were collected. After the data analysis, only the experimental and smoothed data were considered for the calculations. The selected data were regressed with a scaled equation based on four input parameters: radius of gyration, critical density, critical temperature and acentric factor 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 selected data also were analyzed with the most reliable semi-empirical correlating methods in literature based on the corresponding states theory. The proposed equation is very simple and gives noticeable improvement with respect to existing equations (AAD = 3.7%).

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### 1. Introduction

Silanes are versatile materials used in a wide range of applications including adhesion promoters, crosslinking agents, dispersing agents, coupling agents, and surface modifiers.

Surface tension of silanes is particularly important, because of a growing number of applications that involves silanes in controlling the interaction of water with a surface, such as hydrophobicity and hydrophylicity.

Several models that have been proposed to date can be applied to describe the surface tension, but none of them was specifically oriented to silanes.

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

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

where  $T_c$  (K) is the critical temperature,  $\sigma_0$  ( $\text{mN m}^{-1}$ ) and  $n$  are empirical constants obtained with the least square method in a fit to the experimental data available on surface tension [2,3].

Another easy and empirical formula was proposed by Macleod [4]:

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

The formula suggests the existence of a simple relationship between surface tension and the difference between the densities of the liquid and of its vapor;  $K$  is a temperature independent constant characteristic of each substance. One year later, Equation (2) was modified by Sudgen [5]:

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

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 [6] using experimental surface-tension data. Parachor property can be related to the critical properties of compounds including critical temperature and molar volume as follows [7,8]:

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

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.

Equation (3) may be considered as an equation of state [9] 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 [10],

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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 [11] and Guggenheim [12] 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 [13] developed this concept for non-polar liquids and proposed the following formula applicable to the range of temperature far from the critical point:

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

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,  $\omega$ , 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 [14] relation in terms of  $T_c$  (K),  $P_c$  (bar), and  $\omega$  leads to the following corresponding state relationship for  $\sigma$ :

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

For compounds that exhibit hydrogen bonds, Sastri and Rao [15] 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.

To underline the work done in this research field, other recent equations have been proposed. Miquieu et al. [16] 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  $k$ ,  $N_A$ ,  $V_c$ ,  $\omega$  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 [17]. These equations describe the surface tension for non-polar, polar hydrogen-bonding, and associating substances. The equations represent the surface tension well, but they are also slightly more complex compared with previous equations, since they have a large number of parameters, including the aspherical factor.

Recently, Di Nicola et al. [18,19] proposed two equations

specifically aimed at refrigerants. Furthermore, Di Nicola and Pierantozzi [20] issued an equation to predict the surface tension of binary refrigerant systems. A new scaled formula to calculate the surface tension of ketones [21] and alcohols [22] was also presented by the same authors. The scaled formula for alcohols was as following:

$$\frac{\sigma}{\sigma_0} = A \cdot (1 - T_r)^B \cdot (1 + \Phi^C)^D \quad (10)$$

where  $\sigma$  is the surface tension (N/m),  $\sigma_0$  is a scaled factor  $= (k \cdot T_c) / G_r^2$ ,  $T_r$  is the reduced temperature,  $k$  is Boltzmann's constant (J/K),  $G_r$  is the radius of gyration (m),  $\Phi$  is an adimensional term  $= N_a \cdot \rho_c \cdot G_r^3$ ,  $N_a$  is Avogadro's number ( $\text{mol}^{-1}$ ),  $\rho_c$  is the critical density ( $\text{mol m}^{-3}$ ).

In this paper, to predict the surface tension of silanes, a modified version of equation (10) is presented.

## 2. Data analysis

In this paper, the raw surface tension data (experimental, smoothed and predicted) accepted by DIPPR database [23] were collected and analyzed. 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 [23]. During the data collection, a fluid by fluid analysis was performed.

In the DIPPR database in its more recent version, the surface tension of 36 silanes are reported. The silanes are divided in the following subfamilies: 3 silanes, 13 chlorosilanes, 5 cyclosiloxanes, 6 linear siloxanes and 9 are classified by DIPPR database under the voice "other", that can be considered as 8 Alkyl alkoxysilanes and 1 silazane.

In Table 1, a summary of the range of data collected for surface tension and temperatures together with the number of points (experimental, smoothed and predicted) and the four fluid parameters adopted during the regressions are reported. The surface tension of silanes are generally predicted by DIPPR database with the Sudgen equation [5] and smoothed by Jasper [24].

In Fig. 1, all the collected from DIPPR data and calculated surface tension data are reported, split in experimental, predicted and smoothed. For the calculations, the more recent equation and better performing literature equation is considered [16]. Deviations produced by equation (9) are also reported in Table 1.

From the figure and the Table analysis, it is evident that the data showing higher deviations values are generally the predicted ones. In a fact, deviations much higher than 10% were achieved for the following silanes: Methyl Chlorosilane (AAD = 18.5%), Hexadecamethylcyclooctasiloxane (AAD = 18.3%), [3-(2,3-epoxypropyl) trimethoxy Silane (AAD = 35.3%), Bis[3-(trimethoxysilyl) propyl]disulfide (AAD = 23.9%), Dimethyl-dimethoxy Silane (AAD = 22.5%), Gammaaminopropyltriethoxy Silane (AAD = 28.6%) and Methyl Silane (AAD = 46.6%).

Going into deeper, the histogram of the predicted, experimental and smoothed data are reported in Fig. 2. From the histogram, it is evident that the predicted data contribution to databank is particularly relevant at extreme surface tension values. However, from 5 to 40  $\text{mN m}^{-1}$  the surface tensions are well represented by the experimental data. In addition, always considering Fig. 1, the surface tension data smoothed by Jasper [24] generally gave quite low deviations. For these reasons, in this paper only the experimental and smoothed data were considered for the further calculations.

Among numerous physical parameters, the fluid parameters most likely to influence experimental surface tension of silanes were identified using factor analysis [25,26]. The factor analysis

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