

Surface Tension for Silanes, Refrigerants, and Carboxylic Acids: Simple Corresponding State Correlations versus DIPPR Data

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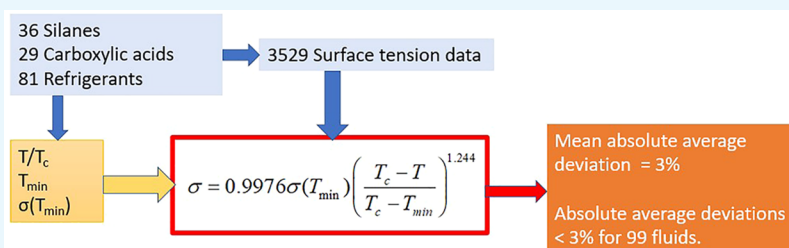
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ABSTRACT: A simple corresponding state-based correlation, whose analytical expression contains just one term with an exponential function, is proposed to calculate the surface tension of 36 silanes, 29 carboxylic acids, and 81 refrigerants as a function of temperature. This correlation only requires critical temperature, maximum value of surface tension, and its corresponding temperature in the DIPPR database as inputs for each liquid considered. The correlation allows us to calculate the accepted DIPPR data for silanes with a mean absolute average deviation (AAD) of 2.75%, 2.42% for acids, and 3.32% for refrigerants. Moreover, it gives AADs below 3% for 99 fluids. The mean deviation for the 146 fluids is 3.0%, which is practically equal to the results obtained when two terms are used in the analytical expression.

1. INTRODUCTION

Surface tension is an essential property of fluid for the study of industrial applications.^{1,2} In recent years, interest in surface tension has increased because this property plays a fundamental role in the study of phase transition and technical processes such as gas absorption and refrigeration.^{1–5} Many correlation models have been proposed to try to predict the surface tension for various kinds of fluids.^{2,6–16} Some of them are based on the corresponding state principle (CSP) to show a possible universal behavior of different kinds of fluids.^{2,10–20} Other possibility is the use of specific empirical correlations that require to obtain several adjustable parameters for each fluid.^{6,21–23} For example, the van der Waals model⁶ contains two parameters whose values have to be obtained for each fluid using the available data. Similarly, it has been shown that the Weibull model, a well-known probability distribution function that uses only two adjustable coefficients with certain mathematical meaning, can be used to correlate the surface tension values of liquids.²³ Other possibilities have been also explored by our research group, but always including at least one adjustable coefficient for each fluid.^{21–23}

In comparison to CSP models, the specific correlation models give better results (as they include adjustable coefficients for each fluid). As a counterpart, the CSP models are more general and can be used for different fluids using the same coefficients.

In the last few years, some attention has been paid to study the surface tension of mixtures,^{24–26} but models for mixtures

require in-depth knowledge of the values for pure components. Nevertheless, the available CSP models for pure components are not always accurate enough or applicable to different kinds of fluids. Because of this, our attention is focused on the development of a new model for the surface tension that can be applied to at least three different families of pure substances.

By applying the corresponding states principle, it is possible to obtain a relationship between surface tension and temperature through an analytical expression. This expression can include different properties of the fluids (as temperature, volume, or pressure at the critical point; acentric factor; boiling temperature; etc.) and several constant coefficients, which are obtained usually for a set or family of fluids on the basis to a fit to the available data. As the surface tension is defined as zero just at the critical point, the analytical expression is commonly expressed in terms of $(1 - T/T_c)^n$, where T is the temperature, T_c is the critical-point temperature, and n is an adjustable coefficient. If the n exponent is adequately determined, then the behavior of the surface tension in the range of high temperatures, i.e., near the critical point, can be reproduced.

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Table 1. Comparisons of the Reduced Methods in Different Correlations Based on the Corresponding State Principle

correlation and reference	fluids	inputs	T^*	σ^*
eq 1 ¹⁵	normal saturated fluids	T_c, T_v, σ_t	$T^* = \frac{T_c - T}{T - T_t}$	$\sigma^* = \left(\frac{\sigma}{\sigma_t}\right) \left(\frac{T_c - T_t}{T - T_t}\right)$
eq 2 ¹³	refrigerants	(T_c, T_v, σ_t) or $(T_c, T_{\min}, \sigma(T_{\min}))$	$T^* = \frac{T}{T_c - T_t}$	$\sigma^* = \frac{\sigma_t - \sigma}{\sigma_t}$
eq 3 ²⁹	hydrocarbons	T_c, T_v, σ_t	$T^* = \frac{T_c - T}{T_c - T_t}$	$\sigma^* = \frac{\sigma}{\sigma_t}$
eq 4 ¹⁴	carboxylic acids	$T_{\max}, T_{\min}, \sigma(T_{\max}), \sigma(T_{\min})$	$T^* = \frac{T}{T_{\max} - T_{\min}}$	$\sigma^* = \frac{\sigma(T_{\min}) - \sigma}{\sigma(T_{\min}) - \sigma(T_{\max})}$
eq 5 ³¹	carboxylic acids	(T_c, T_v, σ_t) or $(T_c, T_{\min}, \sigma(T_{\min}))$	$T^* = \frac{T}{T_c - T_t}$	$\sigma^* = \frac{\sigma_t - \sigma}{\sigma_t}$
eq 6 ³⁰	silanes	$T_c, T_{\min}, \sigma(T_{\min})$	$T^* = \frac{T}{T_c - T_{\min}}$	$\sigma^* = \frac{\sigma(T_{\min}) - \sigma}{\sigma(T_{\min})}$
eqs 11–12 this work	silanes, carboxylic acids, and refrigerants	$T_c, T_{\min}, \sigma(T_{\min})$	$T^* = \frac{T_c - T}{T_c - T_{\min}}$	$\sigma^* = \frac{\sigma(T_{\min}) - \sigma}{\sigma(T_{\min})}$

However, the accuracy of the model in the low-temperature range, i.e., near the triple point, is not guaranteed.^{13,14,16,27–29} In particular, Román et al.²⁷ have shown that including the triple-point temperature as an input parameter significantly improves the accuracy of models for several thermodynamic properties along the vapor–liquid saturation curve, such as vaporization enthalpy and surface tension.

Following the idea of Román et al.,²⁷ different CSP models have been proposed recently for the surface tension of different kinds of fluids. In all cases, temperature and surface tension at the triple point (T_t, σ_t) or at the lowest temperature for which surface tension is available ($T_{\min}, \sigma(T_{\min})$) are used as input properties together with the critical-point temperature, T_c . First, this kind of model has the advantage of not depending on the properties that could be unknown for some fluids or whose relationship with the surface tension is unknown. Moreover, their analytical expressions can be simpler than those given in classical CSP models.^{13–15,29–31}

All of these new proposals are summarized in Table 1. As usual in CSP models, reduced (nondimensional) temperature, T^* , and reduced surface tension, σ^* , are defined as a function of the selected input properties. The main characteristics and results of each one of the models in Table 1 are given below.

The first model of this kind is developed by Yi and Tian,¹⁵ who proposed a simple correlation for normal saturated fluids as

$$\sigma = 0.99948\sigma_t \left(\frac{T_c - T}{T_c - T_t}\right) - 0.20133\sigma_t \left(\frac{T - T_t}{T_c - T_t}\right) \quad (1)$$

This expression can represent the selected data for 41 normal saturated liquids with a mean absolute averaged deviation (AAD) of 1.26% in the temperature regions considered. For most substances, the temperature covers the range from the triple-point temperature to above the boiling point.

Cachadiña et al.¹³ proposed a similar expression, but in this case, it was specifically designed for refrigerants

$$\sigma = \sigma_t \left[1.242 \left(\frac{T_c - T}{T_c - T_t}\right)^{1.3239} - 0.242 \left(\frac{T_c - T}{T_c - T_t}\right)^{1.6504} \right] \quad (2)$$

For those refrigerants with no available surface tension value at the triple point, eq 2 was applied using $(T_c, T_{\min}, \sigma(T_{\min}))$ as inputs. For 63 of the 83 fluids, the AADs were below 5% and only 4 had AADs above 10%.

The third model of this kind was proposed by Tian et al.²⁹ and applied for saturated hydrocarbons

$$\sigma = \sigma_t \left[3.6313 \left(\frac{T_c - T}{T_c - T_t}\right)^{1.2605} - 2.6313 \left(\frac{T_c - T}{T_c - T_t}\right)^{1.2607} \right] \quad (3)$$

It can reproduce the NIST data³² with AAD less than 5% for 17 out of 19 hydrocarbons.

More recently, by introducing two novel reduced quantities, Yang et al.¹⁴ proposed a correlation specifically designed for carboxylic acid fluids as

$$\sigma = \sigma(T_{\min}) - (\sigma(T_{\min}) - \sigma(T_{\max})) \sum_{i=1}^4 a_i (T^* - 1.008T_{\min}^* + 0.8523)^{4-i} \quad (4)$$

where $\sigma(T_{\max})$ and $\sigma(T_{\min})$ are the surface tension values at the maximum and minimum temperatures available for the acid in the DIPPR database,³³ T_{\max} and T_{\min} , respectively. The correlation can be used for different subfamilies of carboxylic acids and can describe the DIPPR data³³ with AAD < 2% for 20 out of 29 carboxylic acids and with AAD < 5% for all of them. As can be seen, eq 4 is analytically more complex than eqs 1–3. Its main advantage is that it can be used for any temperature range where the extreme values of the surface tension are known, i.e., the critical- or triple-point temperature or surface tensions are not needed.

At the same time, Cachadiña et al.³¹ proposed a new CSP model for the correlation of the surface tension of organic acids as

$$\sigma = \sigma_t \left[0.323 \left(\frac{T_c - T}{T_c - T_t}\right)^{1.57} + 0.677 \left(\frac{T_c - T}{T_c - T_t}\right)^{1.05} \right] \quad (5)$$

For those fluids for which the surface tension at the triple point is not available, eq 5 is applied using $(T_c, T_{\min}, \sigma(T_{\min}))$ as inputs. The three constant coefficients (the fourth is defined as $1 - 0.323 = 0.677$) were obtained from 608 selected surface tension data for 17 organic acids. For these fluids, the value of the surface tension at the triple point, or at most 1 K higher, is known. The model was then applied to try to predict 379 surface tension values for 12 other organic acids for which experimental values are available, but the lowest temperature considered is not near the triple point. Finally, the model was applied to a set of 70 fluids (1079 data points) for which more than 90% of the data available in the DIPPR database³³ were obtained using the parachor method by Sugden. Overall, AADs

for the three mentioned subsets (containing data for 17, 12, and 70 organic acids) are 2.37, 3.49, and 5.10%, respectively.

In all previous cases, the proposed correlations contain at least two terms. Nevertheless, very recently, Yang et al.³⁰ have shown that it is possible to obtain good results, at least for the family of silane fluids, using just a straightforward term as

$$\sigma = 0.993610\sigma(T_{\min})\left(\frac{T_c - T}{T_c - T_{\min}}\right)^{1.245} \quad (6)$$

where T_{\min} is the lowest temperature at which a value of surface tension is available (for some fluids, it can be the temperature at the triple point) and $\sigma(T_{\min})$ is the corresponding value. AADs between predicted values and those in DIPPR database³³ are below 5% for 33 out of 36 silanes liquids and below 12% for all silanes liquids considered.

Compared to the commonly used CSP correlations that contain other properties as inputs (acentric factor, boiling temperature, critical pressure, etc.), eqs 1–6 use a value of the surface tension as input, instead of these other properties, and they give significantly better results.³⁰ As it is known, some of the drawbacks of CSP models are that the behavior of surface tension at a low temperature is not taken into account and/or that the input properties used are not clearly related to the behavior of the surface tension. The new kind of CSP models, described by eqs 1–6, is a more accurate and straightforward alternative when at least a value of the surface tension is known. This value could be an experimental, smoothed, or predicted value, and even, in some cases, it has no specified origin.

By taking into account the success of eq 6 using just one term in the case of silanes, it seems to be interesting to extend its validity to other kinds of fluids, particularly to refrigerants and carboxylic acids, for which the previously proposed expressions contain at least two terms.

The main aims of this paper are: (i) to check the accuracy of recent previous models developed for silanes, refrigerants, and carboxylic acids when they are applied to the whole set of substances; (ii) to propose an analytical expression similar to eq 6, which can be applied to calculate the surface tension of silanes, refrigerants, and carboxylic acids; (iii) to study if in this kind of CSP correlation the use of two terms is required, i.e., if the results can be significantly improved using an analytical expression with two terms.

In Section 2, two different correlation models based on CSP are proposed for a set of silanes, carboxylic acids, and refrigerant liquids. Results and discussions are presented in Section 3, and the main conclusions are summarized in Section 4.

2. NEW CORRELATIONS

The surface tension data accepted by the recent version of DIPPR database³³ for 36 silanes, 29 carboxylic acids, and 81 refrigerants were collected and analyzed to test the performance of previous correlations and obtain the new CSP model. It has to be noted that these accepted data in the DIPPR database³³ are generally experimental, smoothed by Jasper,³⁴ or predicted with the Sugden method.³⁵ In the case of carboxylic acids and silanes models, experimental, smoothed, and predicted data were used to calculate the fitting parameters. As a comparison, only experimental data for carboxylic acids and experimental and smoothed data for silanes were used by Nicola et al.^{11,12} Apart from this, when

two different values were available for the same temperature, only the one in the most recent reference is considered here.

The number of selected surface tension data for each fluid, with indication of their origin, and the DIPPR values³³ for T_b , T_c , T_{\min} , T_{\max} , and $\sigma(T_{\min})$, are given in Tables S1–S3 in the Supporting Information. As can be seen, 484 data were selected for silanes, 359 for carboxylic acids, and 2686 for refrigerants. Therefore, the total number of data selected for the surface tension was 3529. The number of experimental, smoothed, predicted, and not specified data for each family and for the whole set of fluids are given in Table S4. Thus, 2046 data were experimental, 248 were smoothed, and 774 were predicted. Moreover, there are other 461 data for refrigerants for which DIPPR does not specify their origin.

To obtain a new correlation, the reduced properties defined here are very similar to those used in previous models, eqs 1–6, but not identical to any of them (see Table 1). In particular, the reduced surface tension is defined as

$$\sigma^* = \frac{\sigma(T_{\min}) - \sigma}{\sigma(T_{\min})} \quad (7)$$

and the reduced temperature is defined as

$$T^* = \frac{T_c - T}{T_c - T_{\min}} \quad (8)$$

where T_{\min} is the lowest temperature at which a value of surface tension is available and $\sigma(T_{\min})$ is its corresponding value. As a result, σ^* takes the value 0 at the lowest temperature and 1 at the critical-point temperature.

The curves of σ^* versus T^* for all of the silanes, refrigerants, and carboxylic acids are shown in Figure 1. All of the values

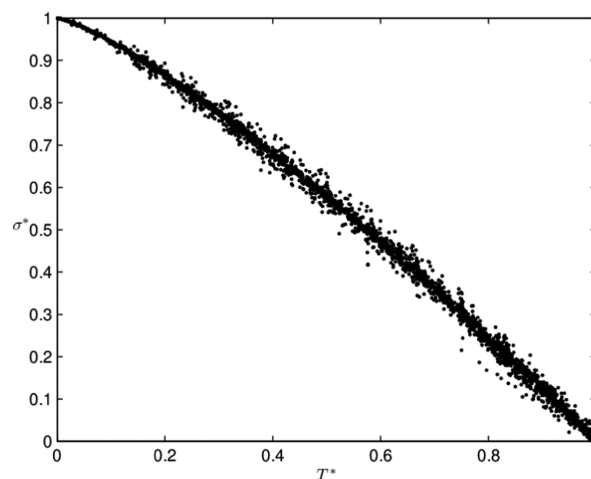


Figure 1. Curves of σ^* versus T^* for silanes, refrigerants, and carboxylic acids.

shown were taken from DIPPR database.³³ As can be seen, when these reduced units are used, the data are very homogeneous, regardless of the kind of substance selected. In fact, all of the selected data almost collapse into a single curve, which can be fitted to the following expression (one term)

$$\sigma^* = 1 - 0.9976\left(\frac{T_c - T}{T_c - T_{\min}}\right)^{1.244} \quad (9)$$

or the following expression (two terms)

$$\sigma^* = 1 - 0.9987 \left(\frac{T_c - T}{T_c - T_{\min}} \right)^{1.234} - 0.0013 \left(\frac{T_c - T}{T_c - T_{\min}} \right)^{7.287} \quad (10)$$

Constant coefficients in eqs 9 and 10 were obtained using all of the data available for the 36 silanes, 29 carboxylic acids, and 81 refrigerants. The method used was the Levenberg–Marquardt curve fitting method³⁶ in MATLAB software.³⁷

Using eqs 7, 9, and 10, the final correlation models proposed for the temperature-dependent surface tension of silanes, refrigerants, and carboxylic acids liquids in real units can be simply written as

$$\sigma = 0.9976 \sigma(T_{\min}) \left(\frac{T_c - T}{T_c - T_{\min}} \right)^{1.244} \quad (11)$$

and

$$\sigma = \sigma(T_{\min}) \left[0.9987 \left(\frac{T_c - T}{T_c - T_{\min}} \right)^{1.234} + 0.0013 \left(\frac{T_c - T}{T_c - T_{\min}} \right)^{7.287} \right] \quad (12)$$

As can be seen, eq 11 is very similar to the one designed for silanes²⁵ (eq 6). This fact means that the results obtained with these two expressions will be very similar, although eq 11 was obtained using data for three families of fluids. On the other hand, the coefficients for the first term of eq 12 are similar to those in eq 11, whereas the coefficients in the second term are clearly different from those proposed in eqs 2 and 5, for instance.

Due to the fact that the surface tension takes values very near to zero at high temperatures, it is considered here as more appropriate to study the accuracy of each model by taking into account the relative percentage deviations. In fact, very little absolute deviations could be obtained in the high-temperature range, but this could be wrongly interpreted as good accuracy, which is not correct. Because of this, the accuracy of each correlation is determined by calculating the AAD(%) of a fluid as

$$\text{AAD} = \frac{1}{N} \sum_{i=1}^N |\text{PD}_i| \quad (13)$$

with

$$\text{PD}_i = (\sigma(T_i) - \sigma_i) / \sigma_i \cdot 100 \quad (14)$$

where $\sigma(T_i)$ is the surface tension value at T_i given by each correlation, (T_i, σ_i) is the data point from the DIPPR database,³³ N is the corresponding amount of data of the fluid considered, and PD is the percentage deviation.

3. RESULTS AND DISCUSSION

As the three families of fluids considered were silanes, carboxylic acids, and refrigerants, AAD values were obtained for each fluid using the previously proposed equations for refrigerants, carboxylic acids, and silanes, eqs 2, 5, and 6,

respectively, and the new proposals, eqs 11 and 12. Results for each fluid and each model are listed in Tables S5–S7 in the Supporting Information. The mean AAD values for each family of fluids and correlation are summarized in Table 2. The overall mean AAD for the whole set of fluids is also given.

Table 2. MAPDs (Mean of AADs, %) for Each Correlation and Family of Fluids

fluids	eq 2 refrigerants	eq 5 acids	eq 6 silanes	eq 11	eq 12
36 silanes	2.89	3.70	2.76	2.75	2.81
29 acids	2.52	2.24	2.61	2.42	2.28
81 refrigerants	3.22	7.68	3.36	3.32	3.55
silanes, acids, and refrigerants	3.00	5.62	3.06	3.00	3.12

As can be seen in Table 2, the worst overall results are obtained when eq 5, designed for acids, is used for other fluids, especially in the case of refrigerants. Surprisingly, eq 2 and 6, designed for refrigerants and silanes, respectively, also give good overall deviations for acids. As expected, eqs 6 and 11 give very similar results, being the new eq 11 only a little more accurate in general. Also surprisingly, eq 12, containing two terms, gives worse overall results than eqs 6 and 11, which are simpler and contain just one analytical term. As eqs 2, 6, 11, and 12 give similar overall AADs, around 3%, it is clear that two temperature terms are not needed to obtain good overall results for the surface tension of silanes, carboxylic acids, and refrigerants.

An alternative perspective about the accuracy of each expression can be obtained by seeing at the number of fluids with AADs lower or greater than a given value. These numbers are given in Tables S8–S11 (Supporting Information) and shown graphically in Figures 2 and 4–6. Tables S8–S10 show the results for each family of fluids separately, whereas Table S11 does for the whole set of fluids.

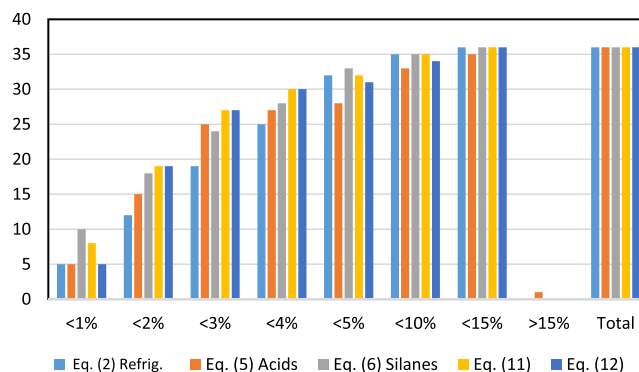


Figure 2. Number of silanes in different AAD (%) ranges for different correlations. Data are given in Table S8 in the Supporting Information.

As shown in Table S8 and Figure 2, eq 6 can reproduce the DIPPR data³³ for 10 silanes with AAD below 1%, which is an expected result. Equation 11, which is very similar to eq 6, and eq 12 also give accurate results. In both cases, the AADs are below 4% for 30 out of the 36 silanes. Nevertheless, eq 12 gives AADs below 1% only for five silanes, despite being analytically more complex than eqs 6 and 11.

Unfortunately, none of the models analyzed here can reproduce the DIPPR available data for ethyl trichlorosilane with AADs below 10%, as shown in Table S5. From Figure 3, it

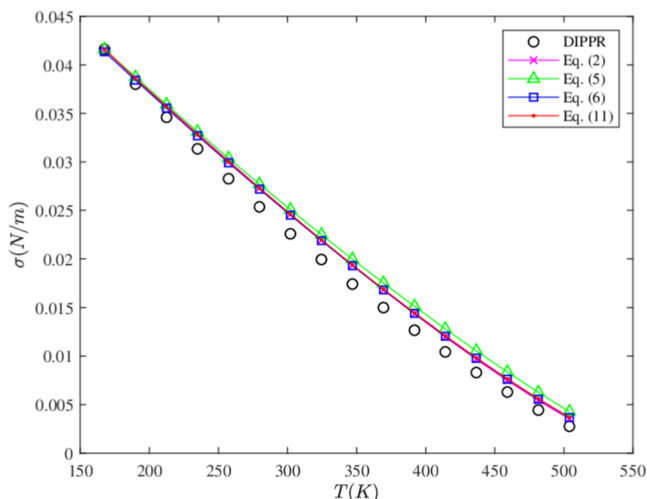


Figure 3. Surface tension values for ethyl trichlorosilane as given by DIPPR database³³ (circles) and different correlation models.

can be seen that the curvature of the DIPPR data³³ is not well represented by any of the models that use $\sigma(T_{\min})$ as a reference value. This one is the only silane that seems not to follow the general behavior of CSP models. The origin of this lack of agreement could be in some particular molecular behavior of this fluid, or better in the lack of thermodynamic consistency in the data selected by DIPPR.³³ In particular, the data in DIPPR were obtained using the parachor method by Sugden³⁵ with an estimated uncertainty of 5%. So, for this fluid, this method could not be appropriate.

The five models selected reproduce the DIPPR data³³ for carboxylic acids with AADs below 10%, as shown in Table S9 and Figure 4. As expected, eq 5, explicitly developed for acids,

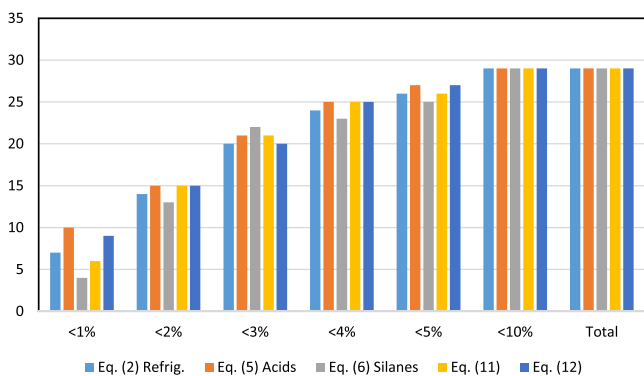


Figure 4. Number of carboxylic acids in different AAD (%) ranges for different correlations. Data are given in Table S9 in the Supporting Information.

obtains the highest number of AADs below 1%. In any case, the distribution of the number of fluids versus AAD ranges is not significantly different for the other four models. In particular, results in Table S9 and Figure 4 show that eq 2, designed for refrigerants, can be applied to carboxylic acids without a significant loss of accuracy. Finally, it is important to consider that eq 11 allows us to reproduce the DIPPR data³³

for 25 acids with AADs below 4%, and it is simpler than the other mentioned models.

The results in Table S10 and Figure 5 show that eq 6, designed for silanes and simpler than eq 2, which was designed

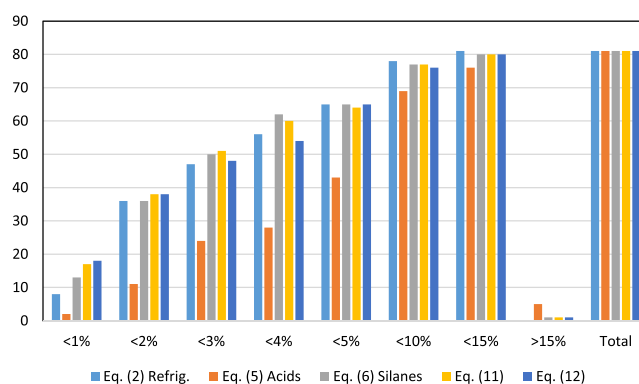


Figure 5. Number of refrigerants in different AAD (%) ranges for different correlations. Data are given in Table S10 in the Supporting Information.

for refrigerants, can give AADs below 1% for 13 refrigerants, whereas eq 2 obtains this result only for 8 of them. On the other hand, the new proposed model, eq 11, gives AADs below 1% for 17 refrigerants and below 3% for 51. The two-term eq 12 produces practically the same results, but it gives a slightly higher mean AAD value (see Table 2).

Finally, Table S11 and Figure 6 show the results for the whole set of 146 fluids. Here, it can be seen that eq 11 is very

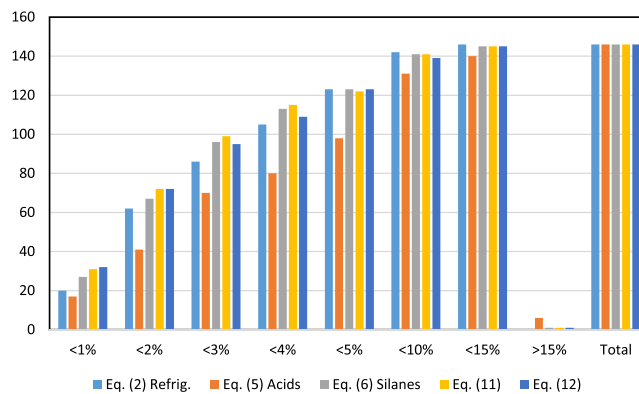


Figure 6. Number of fluids silanes, refrigerants, and carboxylic acids in different AAD (%) ranges for different correlations. Data are given in Table S11 in Supporting Information.

accurate for 99 fluids, giving AADs below 3% for them. As expected, at higher AAD values, it behaves similarly to eq 6. It is also appreciated that the use of two terms in eq 12 does not improve the results given by eq 11, as was already shown in view of the overall AAD values given in Table 2.

It must be highlighted that there is just one refrigerant for which all of the correlations, except eq 2, give AADs higher than 15%. This fluid is R846 (sulfur hexafluoride) and, as can be seen in Table S7, even eq 2, developed specifically for refrigerants, gives an AAD of 10.35% with respect to the DIPPR data.³³ As shown in Figure 7, there are three DIPPR data³³ at intermediate temperatures that do not follow the same trend as the data at lower and higher temperatures. None of the correlations can reproduce these three values, but as

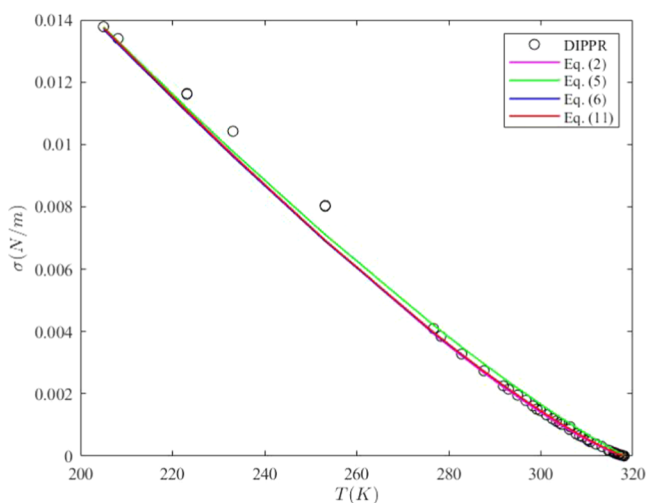


Figure 7. Surface tension values for R846 as given by the DIPPR database³³ (circles) and different correlation models.

shown in Figure 8, the PD values are not excessively high. Therefore, the high AADs are due to much data at

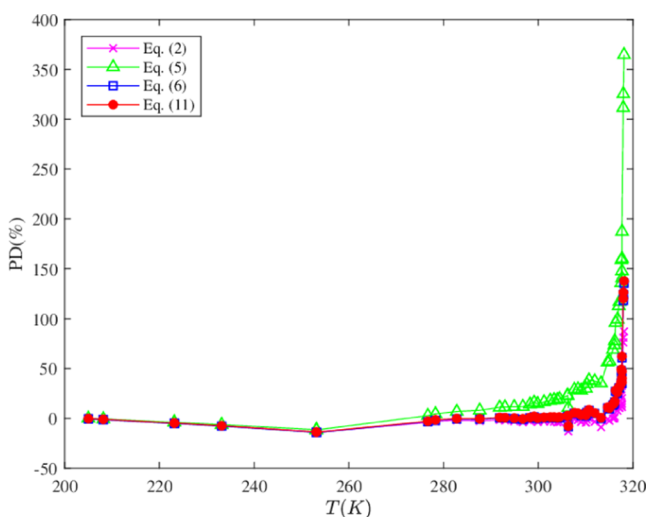


Figure 8. Percentage deviations (PD, %) versus temperature for R846.

temperatures very near the critical point, which takes values very close to zero. Moreover, DIPPR assigned an uncertainty greater than 50% for the surface tension data at high temperatures. In particular, at 316.75 K, the value accepted by DIPPR³³ is $6.89 \times 10^{-5} \text{ N m}^{-1}$, and there are 11 values from this temperature to 318.12 K, which are logically lower. As shown in Figures 7 and 8, the little absolute deviations lead to very high percentage deviations. Only the model represented by eq 2 can reproduce all of the data with PDs below 150%. Experimental data would be necessary to build new models with a better accuracy at high temperatures.

In sum, the CSP correlations cannot reproduce the data for some fluids, such as R846, for which there is much data near the critical point (i.e., very near to zero) and for which DIPPR assigned a great percentage uncertainty. A specific correlation for the fluid, or the high-temperature range, could be used to represent those data analytically more accurately.

There are three refrigerants for which AADs between 10 and 15% are obtained with the proposed eq 11. These are R1216, R13, and R744. In the case of R1216, Table S7 shows that none of the five models studied here can give low AADs. This case is similar to that already commented for ethyl trichlorosilane (Figure 3). The selected models do not reproduce well the curvature of the selected data. It is important to take into account that the DIPPR data for R1216 were predicted ones, and obtained using the Sugden³⁵ method, which could not be appropriate for this fluid. It would be desirable to obtain new experimental data to know if this fluid follows the CSP relationship proposed here or not.

For R13, DIPPR³³ gives many data at high temperatures, which take values very near to zero and lead to high PDs. Despite this, eq 2, specifically designed for refrigerants, gives an AAD of 4.70%, whereas the here proposed eq 11 increased this value to 11.15% (Table S7).

Finally, for R744, the DIPPR database³³ includes 106 surface tension values ranging from the triple point to very near the critical point (Table S3). Moreover, there are much data at high temperatures taking values very near to zero. The situation is similar to that already commented for R846 (Figures 7 and 8) and R13. High PDs are obtained for the five models at high temperatures. As shown in Table S7, eq 2 gives an AAD of 4.14%, but 11.34% is obtained with the proposed eq 11 for this fluid.

In sum, eq 11 shows the highest AADs for those fluids with much data at high temperatures (such as R846, R13, and R744). On the other hand, high AADs are found for ethyl trichlorosilane and R1216, for which the curvature of DIPPR data, as predicted using the Sugden method, cannot be reproduced by any of the CSP models studied. This could mean that the Sugden method is not adequate for these two fluids.

4. CONCLUSIONS

By taking into account the aims of this work and the results obtained, the following conclusions can be made.

- (i) The use of the critical-point temperature, the triple-point temperature, or the minimum temperature at which a surface tension value is available, together with this last value, allows us to define reduced units and to propose a new kind of CSP correlations that makes it possible to reproduce the available surface tension data for different families of fluids.
- (ii) This new kind of correlation can contain just one term or two added terms. According to the results obtained, one term is enough to reproduce most of the DIPPR data³³ available for silanes, carboxylic acids, and refrigerants accurately.
- (iii) The correlation proposed by Cachadiña et al.¹³ for refrigerants, eq 2, contains two terms and can also be applied to silanes and carboxylic acids, the mean AAD being 3%.
- (iv) The correlation proposed by Cachadiña et al.³¹ for acids, eq 5, contains two terms, and it gives poor results for refrigerants. It could be applied with accuracy only for some silanes but not in all cases.
- (v) The correlation proposed by Yang et al.³⁰ for silanes, eq 6, contains just one term and can be applied with accuracy for the three kinds of fluids mentioned. In

particular, it obtains AAD values very similar to those given by eq 2, which contains two terms.

- (vi) A new CSP correlation model is proposed here, eq 11, which is very similar to eq 6, but it has been obtained by taking into account the most recent 3529 DIPPR data³³ available for 36 silanes, 29 carboxylic acids, and 81 refrigerants. The reduced units used are slightly different from those considered in previous models (see Table 1) and allows us to apply the correlation from the whole temperature range for which surface data are available in the DIPPR database.³³ It gives a mean AAD of 3% and AADs below 3% for 99 fluids.
- (vii) The results obtained with the correlation represented by eq 12, which contained two terms, and was obtained following the same procedure used for eq 11, does not improve the results obtained with this last. This confirms the idea that a very simple and accurate correlation can be obtained if the reduced properties are defined adequately.
- (viii) There are two fluids (ethyl trichlorosilane and R1216) out of the 146 studied here for which the surface tension DIPPR data³³ are not in agreement with the general behavior predicted by the CSP applied here. The origin of this disagreement could be in the source used for DIPPR, Sugden method, and new experimental value would be needed to obtain a definite conclusion about this.
- (ix) The CSP models studied or proposed here must be used with caution when the surface tension takes values very near to zero, i.e., for temperatures very near the critical point. In these cases (such occurs for the refrigerants R846, R13, and R744), the high-temperature data could be fitted accurately only using a specific correlation for the fluid or the high-temperature range.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.1c00913>.

Name of fluids of each family, number of selected data, the origin of the data, and DIPPR values³³ for T_v , T_c , T_{min} , T_{max} , and $\sigma(T_{min})$ (Tables S1–S3); number of experimental, smoothed, predicted, and not specified data for each family and for the whole set of fluids (Table S4); AAD obtained for each fluid using each one of the correlations studied (Tables S5–S7); number of fluids of each family for which the obtained AADs take values in a defined range (Tables S8–S11) (PDF)

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Notes

The authors declare no competing financial interest.

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■ NOMENCLATURES

T , temperature (K)
 T^* , reduced temperature
 T_c , critical-point temperature (K)
 T_v , triple-point temperature (K)
 T_{min} , minimum temperature (K)
 T_{max} , maximum temperature (K)
 σ , surface tension ($\text{N}\cdot\text{m}^{-1}$)
 σ^* , reduced surface tension
 σ_v , surface tension in T_t ($\text{N}\cdot\text{m}^{-1}$)
 $\sigma(T_{min})$, surface tension in T_{min} ($\text{N}\cdot\text{m}^{-1}$)
 $\sigma(T_{max})$, surface tension in T_{max} ($\text{N}\cdot\text{m}^{-1}$)

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