# New corresponding-states correlation model for the surface tension of refrigerants

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ABSTRACT

A new corresponding-states correlation model for the calculation of the surface tension of refrigerants is proposed. The main difference with respect to other models available in the literature is that this includes the temperature and surface tension values at the triple point as input properties to define the reduced (non-dimensional) properties, and therefore it is applicable to the entire vapour-liquid temperature range in which this property is defined. The model uses the critical point and the triple point temperature of refrigerant R142b as fixed input parameters and four numerical coefficients obtained by a fitting procedure. The adjustable coefficients were calculated by taking into account the data for 33 selected refrigerants for which the surface tension values at the triple point are known. For each fluid the input variables are the critical point temperature, the triple point temperature, and surface tension at the triple point temperature. To check the model's capacity, we used it to calculate the surface tension values of another 50 refrigerants for which the value of this property is not known at the triple point. To do this, we used as input the lowest temperature at which a value of the surface tension is available. In both cases, correlation and prediction, the calculations were done by considering the most up-to-date database presently available for the surface tension of refrigerants. Averaged absolute deviations below 5% were found for 63 of the 83 fluids considered, and only for 4 of them were they greater than 10%. Results for another four corresponding-states models available in the literature were also obtained. That proposed here gave clearly better overall results.

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## 1. Introduction

Understanding physical properties such as surface tension is of great use for both fundamental research and industrial engineering applications. In particular, in recent years interest in surface tension has increased considerably because this property plays an important role in the design of equipment involving gas-liquid contact in several chemical processes, for instance, gas absorption, distillation, extraction, refrigeration, etc. [1,2]. Within the wide variety of fluids that can be considered, refrigerants are widely used in both domestic and industrial processes of refrigeration, including brewing, meatpacking, food transport, and air-conditioning. Particularly interesting are the so-called third and fourth generation refrigerants, which have zero ozone depletion and also low global warming potential, with RE347mcc being a clear example [3]. This kind of fluids can be used as refrigerants, aerosol propellants, metered dose inhalers, blowing agents for polymer foam, heat transfer media, and gaseous dielectrics.

In particular, the knowledge of surface tension behaviour is essential in the use of refrigerants because it has an influence on the nucleation of bubbles in evaporators and the drainage of condensation from condenser surfaces [4–6].

Many papers have been published about the performance and accuracy of the commonest empirical correlation models for the surface tension when used for various kinds of fluids [1,7–21]. The most frequently used correlations for thermodynamic properties along the saturation curve of fluids are based on the corresponding states principle [22], and they commonly include in the design of the model the critical point temperature as an input. Unfortunately, as some authors have noted [23–30], they do not always give good results far from the critical point, i.e., at low temperatures or near the triple point.

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Following the idea of Torquato et al. [23], several authors have proposed the use of the triple point as an additional reference point [24–30] which would permit one to have good accuracy over the entire temperature range at vapour-liquid equilibrium. In particular, Román et al. [26] and Mulero et al. [30] have proposed specific models based on this idea for the calculation of the surface tension and some other properties of a reduced number of fluids. Despite the good results obtained, the applicability of the models is limited to certain kinds of fluids, so they are difficult to generalize.

Focusing our attention on refrigerants, we find that the most extensive studies about the use of corresponding-states models for their surface tension are those carried out recently by Di Nicola et al. [14,17]. In 2011, those authors [14] proposed a new empirical relationship between the surface tension and temperature. The temperature, volume, and pressure at the critical point, the acentric factor, and the dipole moment were the input variables, and the proposed correlation contained seven coefficients calculated in a fitting procedure. Results were obtained for 26 refrigerants, obtaining average absolute deviations below 5.1% except for R236ea. As indicated by the authors, when compared with previous general correlations, the improvement was greatest in the low temperature range.

In 2013, Di Nicola et al. [17] considered 29 refrigerants and proposed a new five-coefficient corresponding-states based correlation model. An important difference with respect to the previous one is that the critical volume and the dipole moment were excluded as inputs. The empirical correlation proposed is therefore simpler and gives better results than other previous corresponding-states correlations, especially in the low temperature range. No comparison was made with their previous seven-coefficient model, but one can see that these two equations have a similar accuracy, with average absolute deviations greater than 2% for most of the fluids. The overall deviation for the 29 refrigerants was 3.20%, which is an improvement with respect to previous models. In particular, the other model giving a similar result (3.99% of overall deviation) is that proposed by Miqueu et al. [7], which uses as inputs only the critical point temperature and volume, and the acentric factor.

Another recent general correlation model for the surface tension of fluids is that proposed by Gharagheizi et al. [13]. The gene expression programming strategy is applied to present two corresponding states models to represent/predict the surface tension of about 1700 compounds (mostly organic) from 75 chemical families at various temperatures drawn from the DIPPR database. The most accurate model includes the critical point temperature, volume, and pressure, and the normal boiling point temperature as inputs. The overall deviation obtained is 18%, this high value being due to the large number of values included in the calculations. No specific results for refrigerants were given in the paper.

More recently, Cachadiña et al. [31] have proposed specific correlations for the surface tension of 83 refrigerants. They contain from 2 to 6 adjustable coefficients for each fluid, and are valid exclusively for the temperature range for which data are available. This kind of correlation is accurate, but a general model cannot be defined from it and neither can it be used for predictions outside the temperature range in which it holds nor, obviously, for other similar fluids.

In sum, there is currently no adequate general corresponding-states method that allows the surface tension of a large number of refrigerants to be calculated over the entire vapour-liquid temperature range and with good accuracy. Moreover, the presently available models require as input some values that might not be available for a particular fluid. For instance, the boiling temperature cannot be measured for several refrigerant fluids, $CO_2$ being a well-known example. For other fluids the pressure or volume at the critical point can be difficult to measure. Apart from this, previous models were constructed using only a small number of data for each fluid or data from just single database as the only reference.

In this work, we initially considered the database created by Cachadiña et al. [31] which includes data from different sources (including papers published in 2015), which we update with the addition or replacement of new recently published data, as will be explained in Sec. 2. Despite the method being applied here only to refrigerants, it could be used for other families of fluids following the same procedures. A comparison is made with previous correlation models by Miqueu et al. [7], Di Nicola et al. [14,17] (two different models), and Gharagheizi et al. [13].

## 2. The new Corresponding-States method and model

The procedure proposed here to obtain a corresponding-states model is to use reduced variables for the surface tension and temperature. They include the values of the critical temperature $T_c$ (where the surface tension is zero by definition), and the surface tension and temperature just at the triple point, $T_t$ and $\sigma_t$. We define these reduced (non-dimensional) variables as follows:

$$T^* = \frac{T}{T_c - T_t} \tag{1}$$

$$\sigma^* = \frac{\sigma_t - \sigma}{\sigma_t} \tag{2}$$

As can be seen, the reduced value $\sigma^*$ is 0 at the triple point and 1 at the critical point.

It is clear that these reduced variables can only be calculated for those fluids for which these three properties used as inputs ($T_c$, $T_t$, $\sigma_t$) are known. Nevertheless we will consider here the possibility of replacing the input ($T_t$, $\sigma_t$) by ($T_{min}$, $\sigma(T_{min})$), where $T_{min}$ is the lowest temperature at which a value of the surface tension is available.

Initially, we considered the database that we created in 2015 [31] which contains data for 86 refrigerants. We discarded here three of them (R10B1, R114B2, and R1130) for which the data are very disperse so that they do not follow any trend that can be adequately reproduced by a correlation model. We updated this database by adding or replacing new recently published data [32–36]. For R1243zf, the values in the DIPPR database [37] have been replaced by 11 recent experimental data values of Kondou et al. [32] which follow a different trend from that of the DIPPR data. For R161, Bi et al. [33] published 43 new data which to some extent agree with those of Fan et al. [4] considered in Cachadiña et al. [31]. The available DIPPR data [37] for this refrigerant were discarded because they are in clear disagreement with the other two sources. For rE-347mcc (or HFE-7000), 11 new data have been published by Rausch et al. [34]. They are in good agreement with the previous 31 data used by Cachadiña et al. [31], so both sets are considered here. Cui et al. [35] give 7 new experimental data for R32, which agree well with those considered previously by Cachadiña et al. [31], so these have also been added. For R1216 here we use the critical temperature provided by the DIPPR database [37] instead the value used by Cachadiña et al. [31], because all the data for this fluid come from this database. Finally, the value of the critical point temperature for R225ca was also updated with the value given by Sato et al. [36]. After these changes, the updated database used here contains 4160 data for 83 refrigerants. To know the details of the data used for other refrigerants, detailed Supplementary Material can be obtained from Ref. [31].

Table 1 lists all the refrigerants considered, including the number of data and the temperature range for which they are available, and values of the input properties used in our correlation model. We have to remark that for 22 of the refrigerants included here, those marked with an "s" in the third column of Table 1, at least