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A corresponding states principle-based equation for the surface tension of Alkenes

Giovanni Di Nicola · Cristiano Di Nicola · Matteo Moglie · Marco Pacetti

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Abstract This study presents a new formula for the surface tension prediction of alkenes. As a first step, an analysis of the available data of the experimental surface tension data for alkenes was performed. The experimental data were collected, after a careful literature survey, for the following pure fluids: propene, 1-hexene, 1-heptene, 1-octene, 1-decene, 1-tetradecene, and 1-pentadecene. Then, the experimental data were regressed with the most reliable semi-empirical correlating methods based on the corresponding state theory existing in the literature. As a final step, an analysis of the available data of the experimental surface tension data for alkenes was performed starting from the two recently proposed equations for the prediction of the surface tension of refrigerants based on the corresponding states principle. To minimize the deviation between the predicted data and the experimental data and to find the optimal equation coefficients for experimental data regression, a $(\mu + \lambda)$-evolution strategy was adopted. The analysis showed that the equation that gave the best results for the prediction of the surface tension of alkenes was the one with a very limited number of parameters. The finally proposed equation is very simple and gives a noticeable improvement with respect to the existing equations. It is based on the corresponding state principle, containing the acentric factor, the critical temperature, and pressure.

Keywords Alkenes · Corresponding states · Evolution strategy · Surface tension

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G. Di Nicola (✉) · C. Di Nicola · M. Moglie · M. Pacetti
Dipartimento di Energetica, Università Politecnica delle Marche,
Via Brecce Bianche, 60100 Ancona, Italy
e-mail: g.dinicola@univpm.it

Introduction

The surface tension is an important fluid property for correlating and predicting heat transfer during a phase change, in particular playing a fundamental role for the study of phase transitions and of technical processes like boiling and condensation. For these reasons, its prediction starting from a limited number of known parameters and from the well-grounded corresponding states principle is a very attractive task for the refrigeration industry.

To provide a reliable database of surface tensions for alkenes, we first performed a careful literature survey. The list of the alkenes is summarized in Table 1, together with the physical properties and the chemical name of each fluid.

The main goal of this study was to find the coefficients for the recently proposed equations [1, 2] that minimizes the deviations between the predicted data and the experimental data. For this purpose, an evolutionary algorithm has been used. The statistical analysis was based on the $(\mu + \lambda)$-evolution strategy [3], which guarantees the identification of a solution that belongs to a global minimum of the fitness function. Using this algorithm, it is possible to identify the parameters of the proposed equations which guarantee the lowest deviation of the predicted surface tension.

Experimental literature data

In Table 2, the experimental data of surface tension for the alkenes available in the open literature are summarized [4–8]. The table gives the references to the original study, the number of experimental points per data set, the temperature and the surface tension ranges.

From Table 2, it is possible to notice that the measurements were performed over quite wide temperature (from

Table 1 Physical properties for each alkene

	MW/g mol^{-1}	T_c/K	P_c/MPa	T_b/K	ω	V_c/m^3 kg^{-1}	μ
Propene	42.080	364.850	46.000	225.450	0.138	0.00440	0.366
1-hexene	84.159	504.000	32.100	336.630	0.285	0.00414	0.450
1-heptene	98.186	537.400	29.200	366.790	0.343	0.00409	0.629
1-octene	112.213	566.900	26.630	394.410	0.392	0.00414	0.420
1-decene	140.266	616.600	22.230	443.750	0.480	0.00416	0.420
1-tetradecene	196.372	691.000	16.270	524.250	0.650	0.00440	0.510

Table 2 The experimental data of surface tension for alkenes available in the open literature

Alkene	Ref.	T range/K	σ range/N m^{-1}	Number of data
Propene	[4, 5]	193.15–253.10	0.01273–0.02141	12
1-hexene	[6, 8]	133.39–333.15	0.0144–0.038182	12
1-heptene	[4, 6]	154.12–353.15	0.01435–0.036735	19
1-octene	[4, 6]	171.45–373.15	0.0141–0.036024	14
1-decene	[8]	273.15–373.15	0.01681–0.02597	11
1-tetradecene	[7]	273.15–373.15	0.01977–0.02856	11
1-pentadecene	[4]	283.15–373.15	0.02037–0.02817	11

254 to 372 K) and surface tension (from 0.014 to 0.038 N m^{-1}) ranges. Finally, a total of 90 points were considered in the regressions.

Correlating methods based on the corresponding states principle

The surface tension σ(mN m^{-1}), of a fluid can expressed as a function of the temperature through an equation similar to that of Van der Waals [9]:

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

where T_c (K) is the critical temperature, σ_0(mN m^{-1}) and n are empirical constants obtained with the method of least squares as close as possible to the experimental values of surface tension.

Brock and Bird [10] developed the Van der Waals idea for nonpolar liquids and proposed the following correlation:

$$\sigma = P_C^{\frac{2}{3}} T_C^{\frac{1}{3}} Q (1 - T_r)^{\frac{11}{9}} \tag{2}$$

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 [11]:

$$Q = 0.1196\left[1 + \frac{T_{br} \ln\left(\frac{P_C}{1.01325}\right)}{1 - T_{br}}\right] - 0.279 \tag{3}$$

T_{br} (K) is the reduced normal boiling temperature T_b/T_c and T_b(K) is the normal boiling temperature. In some cases, surface tension can be represented in terms of an additional parameter. An example is the so-called acentric factor, ω, initially introduced as an empirical parameter by Pitzer [12] to describe the deviation from the corresponding states principle, as well as defined for noble gases, when applied to larger molecules. The Pitzer relation in terms of T_c (K), P_c (bar) and ω leads to the following corresponding-states relation for σ (mN m^{-1}):

$$\sigma = P_C^{\frac{2}{3}} T_C^{\frac{1}{3}} \frac{1.86 + 1.18\omega}{19.05}\left[\frac{3.75 + 0.91\omega}{0.291 - 0.08\omega}\right]^{\frac{2}{3}} (1 - T_r)^{\frac{11}{9}} \tag{4}$$

For compounds that exhibit hydrogen bonds, Sastri and Rao [13] recently proposed a modified expression for the Brock and Bird correlation. This correlation was extended by the same authors also to all others compounds simply adopting different values of constants, and finally, the equation assumed the following expression:

$$\sigma = 0.158 P_C^{0.5} T_b^{-1.5} T_C 1.85 \left[\frac{(1 - T_r)}{(1 - T_{br})}\right]^{\frac{11}{9}} \tag{5}$$

A new improved scaled equation to represent the surface tension of several substances was also recently proposed [14]:

$$\sigma = kT_C \left(\frac{N_A}{V_C}\right)^{\frac{2}{3}} (4.35 + 4.14\omega) T_r^{1.26} \left(1 + 0.19 T_r^{0.5} - 0.487 T_r\right) \tag{6}$$

In addition, an equation strictly focussed on refrigerants was proposed by our research group [1]:

$$\sigma = 0.813 P_c^{0.565} T_c^{0.364} (1 - T_r)^{1.266} (4.259\omega - 0.645\mu*)^{0.143} \tag{7}$$

where $\mu*$ is the reduced dipole moment.

To test the quality of the most commonly adopted existing equation's prediction, deviations between the experimental surface tension and the ones predicted by Eqs. 2–7, were calculated for the alkenes and are reported in Table 3.

For each equation, the deviations between calculated and experimental σ values are summarized in Table 4.

For the deviations, the following equations were adopted:

$$\mathrm{d}\sigma = \frac{1}{n}\sum_{i=1}^{n}\left(\sigma_{i,\exp} - \sigma_{i,\mathrm{calc}}\right) \tag{8}$$

$$\mathrm{d}\sigma\% = \frac{1}{n}\sum_{i=1}^{n}\left[\frac{\sigma_{i,\exp} - \sigma_{i,\mathrm{calc}}}{\sigma_{i,\mathrm{calc}}}\right]100 \tag{9}$$

$$|\mathrm{d}\sigma\%| = \frac{1}{n}\sum_{i=1}^{n}\left[\frac{\left|\sigma_{i,\exp} - \sigma_{i,\mathrm{calc}}\right|}{\sigma_{i,\mathrm{calc}}}\right]100 \tag{10}$$

where n represents the total experimental points of each fluid. Equation 9 was also adopted as objective function.

New equation

The equation proposed for the prediction of the surface tension has a very limited number of parameters and it is based on the corresponding states principle as follows:

$$\sigma = AP_{\mathrm{C}}^{B} T_{\mathrm{C}}^{C} (1 + \omega)^{D} (1 - T_{\mathrm{r}})^{E} \tag{11}$$

where A, B, C, D and E are the regressed parameters, while P_c (bar), ω, T_c (K), and T_r are the critical pressure, the acentric factor, the critical temperature, and the reduced temperature, respectively. The A, B, C, D, and E parameters were obtained with the evolution strategies (ES).

Every time that a set of data are regressed, the study is oriented toward the identification of the parameters that minimize or maximize a defined fitness function for a better representation of the relationship amongst independent and dependent variables. A possible approach could be the application of the design of experiment approach (DoE) followed by the evolution strategies (ES) [15].

Table 3 Deviation of the surface tension for Eqs. 2, 4–7, and 11

	Eq. 2	Eq. 4	Eq. 5	Eq. 6	Eq. 7	Eq. 11
Propene						
$\mathrm{d}\sigma$/mN m^{-1}	0.374	0.887	−0.665	0.206	1.336	0.786
$\mathrm{d}\sigma$ %/%	2.214	5.213	−3.853	1.236	7.913	4.760
$\lvert\mathrm{d}\sigma$ %$\rvert$/%	2.214	5.213	3.853	1.236	7.913	4.760
1-hexene						
$\mathrm{d}\sigma$/mN m^{-1}	0.114	1.084	−0.600	−0.029	0.376	−0.041
$\mathrm{d}\sigma$%/%	0.208	4.452	−2.916	−0.596	1.691	0.140
$\lvert\mathrm{d}\sigma$%$\rvert$/%	0.720	4.452	2.916	1.558	1.691	1.139
1-heptene						
$\mathrm{d}\sigma$/mN m^{-1}	−0.071	0.868	−0.625	−0.325	0.579	−0.350
$\mathrm{d}\sigma$%/%	−0.692	3.163	−2.969	−1.883	2.245	−1.343
$\lvert\mathrm{d}\sigma$%$\rvert$/%	1.418	3.163	2.969	2.392	2.245	1.350
1-octene						
$\mathrm{d}\sigma$/mN m^{-1}	0.602	0.602	0.602	−0.349	0.248	−0.313
$\mathrm{d}\sigma$%/%	2.170	2.170	2.170	−2.341	0.821	−1.532
$\lvert\mathrm{d}\sigma$%$\rvert$/%	2.170	2.170	2.170	3.364	0.905	1.532
1-decene						
$\mathrm{d}\sigma$/mN m^{-1}	−0.067	0.597	−0.721	−0.507	0.737	−0.168
$\mathrm{d}\sigma$%/%	−0.370	2.735	−3.433	−2.453	3.450	−0.732
$\lvert\mathrm{d}\sigma$%$\rvert$/%	0.395	2.735	3.433	2.453	3.450	0.732
1-tetradecene						
$\mathrm{d}\sigma$/mN m^{-1}	0.908	0.965	−0.866	0.173	2.417	0.336
$\mathrm{d}\sigma$%/%	3.641	3.877	−3.709	0.574	9.933	1.349
$\lvert\mathrm{d}\sigma$%$\rvert$/%	3.641	3.877	3.709	1.205	9.933	1.349

Table 4 Summary of deviations for Eqs. 2, 4–7, and 11

Deviations	Eq. 2	Eq. 4	Eq. 5	Eq. 6	Eq. 7	Eq. 11
$d\sigma$/mN m^{-1}	0.350	0.807	−0.590	−0.071	1.151	0.052
$d\sigma$ %/%	1.353	3.449	−2.846	−0.604	5.090	0.438
$\lvert d\sigma$ %$\rvert$/%	1.837	3.449	3.466	1.960	5.102	1.634

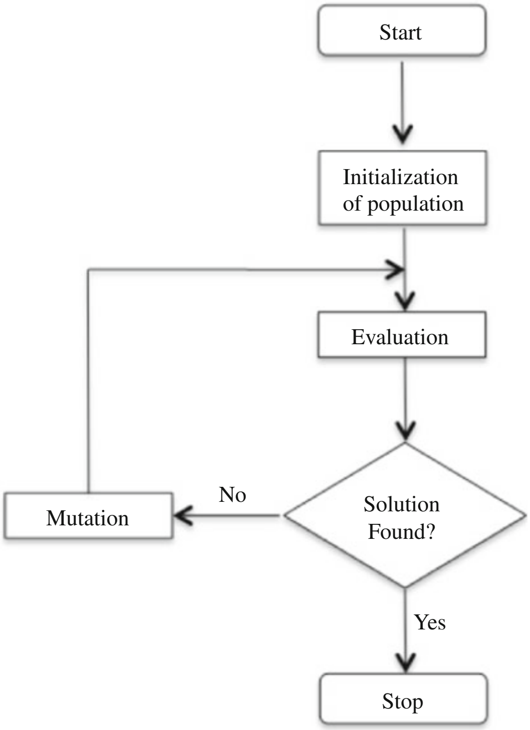

Fig. 1 Flowchart of evolutionary algorithm iteration

Table 5 Range of parameters for the full factorial design and regressed values adopted for Eq. 11

Parameters	Lower values	Higher values	Regressed values
A	0.35	0.7	0.5
B	0.35	0.7	0.55
C	0.2	0.6	0.426
D	0.6	1	0.723
E	1.1	1.5	1.3

Evolution strategies belong to the evolutionary algorithms, which are based on the ideas of evolution and adaptation. The main goal of an ES algorithm is to optimize the objective function with respect to a set of variables and constraints. The iterations followed by the algorithm are as described in Fig. 1, where the initialization of the population is based on the DoE approach and the constraints are related to the maximal value accepted for the defined objective function.

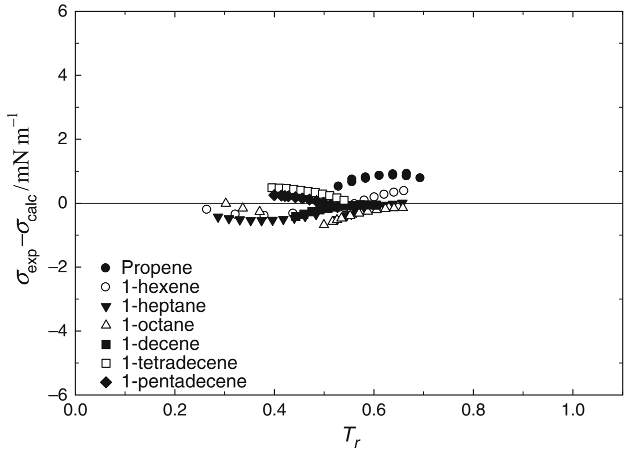

Fig. 2 Deviation between the experimental and calculated surface tension for the Eq. 11

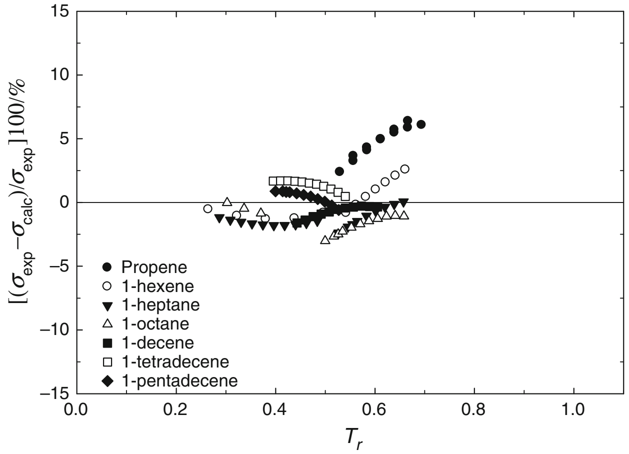

Fig. 3 Percent deviation between the experimental and calculated surface tension for the Eq. 11

In this article, in order to minimize the absolute average deviations between the experimental and the calculated surface tensions of the entire set of alkenes considered, the $(\mu + \lambda)$-evolution strategies algorithm was used. The $(\mu + \lambda)$-ES is an algorithm in which not only one offspring is created in a generation, but $\lambda \geq 1$ descendants, and to keep the population size constant, the λ worst out of all $(\mu + \lambda)$ individuals are discarded [3].

Together with the ($\mu + \lambda$)-ES algorithm, the Full factorial design (FFD) was adopted. The application of the FFD to the proposed equation, requires the identification of the variables and the levels where the variables have to be varied. The FFD adopted here is a two level, and the variables defined are A, B, C, D, and E as listed in Eq. 11, that meant the definition of 2^5 FFD different configurations. The range of levels used for the FFD is summarized in Table 5 together with the optimal values found for the parameters.

Discussion of the results

The deviations obtained with the proposed equation are reported for each alkene in Table 2 and summarized in Table 3 together with values obtained with Eqs. 2, 4, 5, and 7. From this table it is possible to point out that a noticeable improvement was achieved with the proposed equation, together with a relevant simplification of the predictive equation itself.

This is confirmed also from Figs. 2 and 3, where deviation and percent deviation between the experimental and calculated surface tension for all experimental points obtained with Eq. 11 are also shown, respectively. In particular, excluding propene that shows slightly higher deviations, it is clearly evident that there is a general good representation of the surface tension prediction of alkenes, both at high and low reduced temperatures.

Conclusions

After a careful collection of experimental surface tensions for seven alkenes, a survey of the existing literature methods for the surface tension prediction was performed.

Since none of the existing literature methods were specifically oriented to alkenes and their surface tension prediction, in this article a method explicitly oriented to alkenes was developed.

A simple correlation based on the corresponding states principle was proposed. This equation is very simple and it is able to predict the surface tension of the alkenes with an absolute average deviation of 1.63%, improving the predictive ability of existing equations.

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