Surface Tension of Pure Hydrocarbons[1]

A. Romero-Martínez[2] and A. Trejo[2,3]

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[2] Instituto Mexicano del Petróleo

Subdirección de Transformación Industrial

Gerencia de Investigación Aplicada de Procesos

Eje Lázaro Cárdenas 152, 07730, México, D.F., México.

[3] Author to whom correspondence should be addressed.

ABSTRACT

A new correlation scheme for the surface tension of homologous series of pure liquid hydrocarbons, as a function of molecular weight and temperature, is presented. Using orthobaric surface tension data from literature for four homologous series of hydrocarbons, i.e. n-alkanes, 1-alkenes, cycloalkanes and aromatics, the adjustable parameters for two new surface tension equations are obtained individually for each series. The agreement between experimental values and those calculated with the two new generalized surface tension equations is very good, i.e. the temperature and molecular weight dependences of surface tension are well reproduced.

KEY WORDS: alkanes; alkenes; aromatics; correlation equations; cycloalkanes; hydrocarbons; molecular weight; surface tension; temperature.

1. INTRODUCTION

Surface tension of pure and mixed liquids is an important thermophysical property for almost every separation process involving mass transfer between vapor and liquid phases. For the oil industry, thermophysical and phase equilibria properties of hydrocarbons are of the utmost importance for the design, operation and optimization of chemical and separation processes for both refinery and petrochemical needs. Also, the surface tension has been part of the systematic analysis carried out to understand the asymptotic behaviour of different physical properties. Nonetheless, an examination of the literature shows that experimental data of surface tension in a large temperature range are lacking even for pure components, thus there exists a clear need for models or empirical methods to obtain a good representation of the experimental behavior.

In this work we have developed two empirical equations to correlate surface tension data in a large temperature range for pure components. The experimental surface tension data for n-alkanes (n-pentane to n-eicosane), 1-alkenes (1-pentene to 1-eicosene), cycloalkanes (cyclopentane to cyclooctane) and aromatics (benzene to n-butylbenzene) were correlated to obtain optimized values for the parameters considered in the two proposed equations. The agreement between the experimental values and those calculated with the two new generalized surface tension equations is evaluated through the standard deviation.

2. EQUATIONS TO CORRELATE SURFACE TENSION DATA FOR PURE COMPOUNDS

Many are the equations proposed to correlate and predict surface tension data of pure compounds, mainly to relate surface tension of a single compund with temperature. Considering that most of the experimental surface tension determinations for pure components cover a limited temperature range most of such equations are linear or cuadratic in temperature, in the best case [1]. Equations which relate surface tension data to some pure component property have also been reported and include the well known methods proposed by McLeod [2], Sudgen [3], Hildebrand and Scott [4] and others.

Le Grand and Gaines reported an empirical equation to correlate surface tension data for liquid polymers [5] and homologous series of organic liquids [6] as a linear function of their molecular weight, at a given temperature, which has the following form:

$$\gamma = \gamma_{\infty} - \frac{k}{M^{2/3}} \qquad (1)$$

where γ is the surface tension, γ_{∞} is the surface tension for a component, within the homologous series, with infinite molecular weight, k is the slope in a plot of γ vs $M^{-2/3}$ and M is the molecular weight of the pure component.

These authors showed that a linear dependence of γ on $M^{-2/3}$ holds with good generality, also tested by Siow and Patterson [7] through a corresponding states method,

and reported the corresponding values of the parameters γ_∞ and k of Eq. (1) at each temperature at which they found orthobaric surface tension data for alkanes (0 and 60 ^oC), 1-alkenes (0 and 60 ^oC) and other alkane derivatives (30 ^oC).

More recently, Grigoryev et al. [8], arrived to an equation, derived from critical power laws, which relates the surface tension, individually, of four n-alkanes as a function of temperature, from their triple point up to the vapor-liquid critical temperature. Their equation represents the surface tension data reported to within about ±0.3 $mN \cdot m^{-1}$. The original equation can be reduced to the following form:

$$\gamma = \gamma_0 \tau^{1.26} + \gamma_1 \tau^{1.76} \qquad (2)$$

Grigoryev et al. used γ_1 as an adjustable parameter, while γ_0 was obtained through power laws relationships for each one of the four alkanes studied, and τ is the reduced temperature difference 1-T/Tc; Tc being the vapor-liquid critical temperature of the pure component.

In view of the specific characteristics of the above two equations, i.e. Eq. (1) relates the surface tension of homologous series to molecular weight at constant temperature whereas Eq. (2) relates surface tension to temperature for each alkane, we propose here a new two-parameter generalized surface tension equation (GSTE2) to correlate experimental orthobaric surface tension data of homologous series of hydrocarbons, as a simultaneous

function of temperature, in the entire temperature range of the liquid state, and molecular weight. The GSTE2 has the following form:

$$\gamma = a_0 \tau^{1.26} + \frac{a_1 \tau^{1.76}}{M^{2/3}} \tag{3}$$

in this equation, γ is the orthobaric surface tension, a_0 and a_1 are adjustable parameters, τ is the reduced temperature difference, previously defined, and M is the molecular weight of each member of the homologous series considered.

Equation (3), with only two adjustable parameters, is capable of correlating, within experimental error, experimental surface tension data as a function of temperature, from the triple point up to the gas-liquid critical point, for all the members of a homologous series of pure compounds. That is, this equation includes the independent merits of the two mentioned literature equations.

Exploring further the possibility of new forms for a generalized surface tension equation we arrived to another equation, (GSTE4), assuming a linear dependence of a_0 and a_1 in Eq. (3), with molecular weight. Thus, the GSTE4 has four adjustable parameters:

$$\gamma = \left(a_0 + a_1 M\right)\tau^{1.26} + \left(b_0 + b_1 M\right)\tau^{1.76} \tag{4}$$

as above, γ is the surface tension, a_0, a_1, b_0 and b_1 are adjustable parameters, τ is the reduced temperature difference, and M is the molecular weight.

3. CORRELATION SCHEME

In order to correlate the experimental surface tension data available for hydrocarbons of the different homologous series mentioned above, pure component molecular weight and vapor-liquid critical temperature were obtained from different sources [9-14]. Experimental surface tension data were taken from Grigoryev et al. [8] for n-alkanes C_5 to C_8, who report this type of information in a wide temperature range, and from Jasper`s compilation [15] for all the remaining compounds. The correlation was performed using the least squares technique together with the Gauss-Newton method, to minimize the following objective function:

$$F = min \sum_{i=1}^{n} (\gamma_i^{exp} - \gamma_i^{cal})^2 \tag{5}$$

this objective function is fullfilled for each of the homologous series of hydrocarbons with *n* experimenatl data points. The quality of the correlation is evaluated through the standard deviation which includes the sum of squared diffences between experimental and calculated surface tension values, the number of experimental points, *n*, and the number of parameters being adjusted, *m*, according to the following relationship:

$$\sigma_\gamma = \sqrt{\frac{\sum_{i=1}^{n} (\gamma_i^{exp} - \gamma_i^{cal})^2}{n-m}} \tag{6}$$

4. **RESULTS**

In this section, the results of the correlation of experimental surface tension data, using the two new generalized surface tension equations proposed, are presented. In order to carry out a direct comparison with the results of Grigoryev et al.. Table I shows the results of correlating their 94 experimental surface tension points with the present GSTE2 equation for n-pentane, n-hexane, n-heptane and n-octane, in the complete temperature range where these hydrocarbons show liquid-vapor equilibrium.

Table II shows a comparison between the values of the parameters in the equation for surface tension, as a function of temperature, reported by Grigoryev et al., Eq. (13) in [3], and those obtained with our GSTE2 equation. It may be observed that in Eq. (3), a_0 has a constant value for all the n-alkanes considered and is of the same order of magnitud as those a_0 values reported by Grigoryev et al. [3] for each n-alkane. The values for a_1, assumed as an adjustable parameter by Grigoryev et al. [3], can also be compared with those obtained with Eq. (3) from this work. Making the corresponding transformations, they are also of the same order of magnitude, although the values obtained in this work show a more regular behaviour with the size of the n-alkane. The standard deviation obtained in this work from the correlation of 94 experimental points is 0.16 mN m^{-1} , which compares very well with the four individual values reported by Griegoryev et al.

The correlation scheme already disscussed was extended to include more members of the n-alkane series, apart from the four compounds already discussed, as well as to other homologous series, such as 1-alkenes, cycloalkanes and alkylaromatics. Thus, Table III shows values for the two adjustable parameters, a_0 and a_1, and the corresponding standard deviation, also included are the range of carbon atoms of the compounds considered in the correlation for the different homologous series and the number of experimental surface tension points considered.

Overall, it may be observed that the quality of the fit is good for the four series of hydrocarbons considered, however, the standard deviation for the aromatic hydrocarbons is outside the experimental error of the data.

Table IV shows the results of correlating simultaneously all the experimental surface tension data for n-pentane, n-hexane, n-heptane and n-octane with the present GSTE4 equation, in the complete liquid range of these hydrocarbons. It is observed that the standard deviation of the fit compares very well with the individual values reported by Griegoryev and given in Table II.

Fig. 1 is a deviation plot for calculated values of the surface tension using Eq. (4). This figure shows that GSTE4 reproduces more than 90 % of the experimental data for the alkanes C_5 to C_8 within ± 0.30 $mN \cdot m^{-1}$. Fig. 2 shows a comparison between experimental

and calculated surface tension for the alkanes C_5 to C_8 in the temperature range 144-569 K. The experimental data, given as points, are well reproduced in the whole range considered.

Table V includes results of the correlation of the experimental data for the same four series of hydrocarbon homologous as above, but now using Eq. (4). It is observed that GSTE4 gives a good representation of the experimental data of the different hydrocarbon homologous series, in a large temperature range, and it is marginally better than Eq. (3), since the standard deviation for each fit is now lower than the values given in Table III.

In order to further test the two equations proposed in this work we carried out a comparison between calculated and experimental surface tension data for n-butane [16] in the range 238-273 K. These experimental data were not included in either of the two correlations. Table VI contains the results of this comparison, it may be observed that both equations yield good predictions, being in this case the GSTE2 slightly superior, according to the deviations shown. Fig. 3 shows the experimental surface tension data of n-butane as points togeteher with continuous lines that represent the values derived from the two equations presented in this work. Considering this comparison it has to be assumed that the two equations developed here are capable of predicting the surface tension behaviour of the different members of the homologous series studied that are not included in the correlation due to lack of experimental data and also to give good surface tension data for the compounds included in the correlation but in a range of temperature outside the one considered for most of the homologues.

4.- DISCUSSION

The decrease of surface tension with decreasing molecular weight and the decreases of surface tension with increasing temperature have been considered in the development of the two equations presented in this work. The experimental behaviour of surface tension for a large number of compounds of four homologous series of hydrocarbons has been well reproduced by the two equations.

We conclude that both the GSTE2 and GSTE4 give a satisfactory representation for the molecular weight and temperature dependence of the surface tension for the homologous series of hydrocarbons studied, although the latter equation with four parameters is more accurate. Further, the two equations give satisfactory predictions of surface tension data either for homologues not included in the correlation scheme or in a temperature range outside the one considered in the present work.

We will continue testing the two equations as surface tension data become available for more homologous series of organic compounds.

5.- ACKNOWLEDGMENTS

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Table I. Results of the correlation of experimental surface tension data for n-alkanes C5-C8 [8] using Eq. (3).

Parameters and standard deviation	Values
a_0/mNm^{-1}	55.42
a_1/mN·m^{-1} (g·mol^{-1})$^{2/3}$	-33.04
σ_γ/mN·m^{-1}	0.16

Table II. Comparison of values of the parameters in Eq. (13) in reference [8] for individual n-alkanes and those derived with Eq. (3), and standard deviation for each individual correlation with Eq. (13) in [8].

n-ALKANE	a_o		a_1		σ_γ/mN·m^{-1}
	Eq. (13) in [8]	Eq.(3)	Eq. (13) in [8]	Eq.(3)	Eq. (13) in [8]
n-pentane	53.94	55.42	-0.0048	-0.0344	0.18
n-hexane	54.78	55.42	-0.0117	-0.0306	0.07
n-heptane	55.49	55.42	-0.0253	-0.0276	0.10
n-octane	54.77	55.42	-0.0114	-0.0253	0.14

Table III. Results of the correlation of experimental surface tension data for different homologous series of hydrocarbons using the GSTE2 equation (Eq. (3)).

HYDROCARBONS	n-ALKANES	1-ALKENES	CYCLOALKANES	AROMATICS
# CARBON ATOMS	C_5-C_{20}	C_5-C_{20}	C_5-C_8	C_6-C_{10}
# DATA POINTS	260	159	23	48
a_0/mN·m^{-1}	51.01	50.53	55.06	31.90
a_1/mN·m^{-1} (g·mol^{-1})$^{2/3}$	81.3	146.5	281.0	1085.4
σ_γ/mN·m^{-1}	0.25	0.16	0.23	0.68

Table IV. Values of the parameters in Eq. (4) and standard deviation from the correlation of surface tension data for the n-alkanes C_5 - C_8.

a_0	a_1	b_0	b_1	σ_γ/mN·m^{-1}
55.63	-0.010	-3.58	0.032	0.17

Table V. Results of the correlation of experimental surface tension data for different homologous series of hydrocarbons using GSTE4 (Eq.(4)).

HYDROCARBON	n-ALKANES	1-ALKENES	CYCLOALKANES	AROMATICS
# CARBON ATOMS	C_5-C_{20}	C_5-C_{20}	C_5-C_8	C_6-C_{10}
# DATA POINTS	260	159	23	48
a_0/mN·m^{-1}	65.70	75.945	56.246	132.68
a_1/mN·m^{-1} mol·g^{-1}	-0.11436	-0.14964	0.0064	-0.65315
b_0/mN·m^{-1}	-14.07	-28.030	21.560	-64.94
b_1/mN·m^{-1} mol·g^{-1}	0.13846	0.19163	-0.1102	0.64485
σ_γ/mN·m^{-1}	0.14	0.06	0.20	0.36

Table VI. Comparison between experimental [16] and predicted surface tension for n-butane.

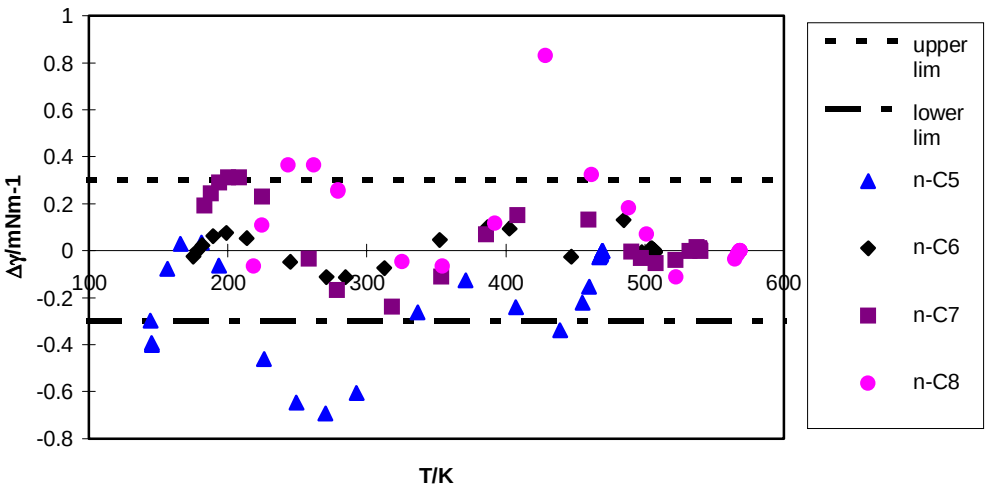
T/K	γ^{exp} mNm^{-1}	γ^{cal} (GSTE2) mNm^{-1}	$\Delta\gamma$(GSTE2) mNm^{-1}	γ^{cal} (GSTE4) mNm^{-1}	$\Delta\gamma$(GSTE4) mNm^{-1}
238.0	19.19	19.59	-0.40	19.59	-0.40
248.3	17.85	18.26	-0.41	18.28	-0.43
253.2	17.37	17.63	-0.26	17.66	-0.29
258.1	16.88	17.01	-0.13	17.04	-0.16
267.8	15.65	15.78	-0.13	15.84	-0.19
273.3	14.97	15.09	-0.12	15.16	-0.19

FIGURE CAPTIONS

Fig. 1 Differences in experimental [8] and calculated with Eq. (4) surface tension values for n-alkanes C_5 to C_8, from their triple point up to their critical temperature.

Fig. 2. Plot of surface tension vs temperature for n-alkanes C_5-C_8. Symbols correspond to experimentale values [8] and full lines correspond to values derived with equation (4).

Fig. 3. Comparison between experimental and predicted surface tension data for n-butane. Symbols correspond to the experimental data [16] and the lines correspond to values calculated with the two generalizad equations of this work.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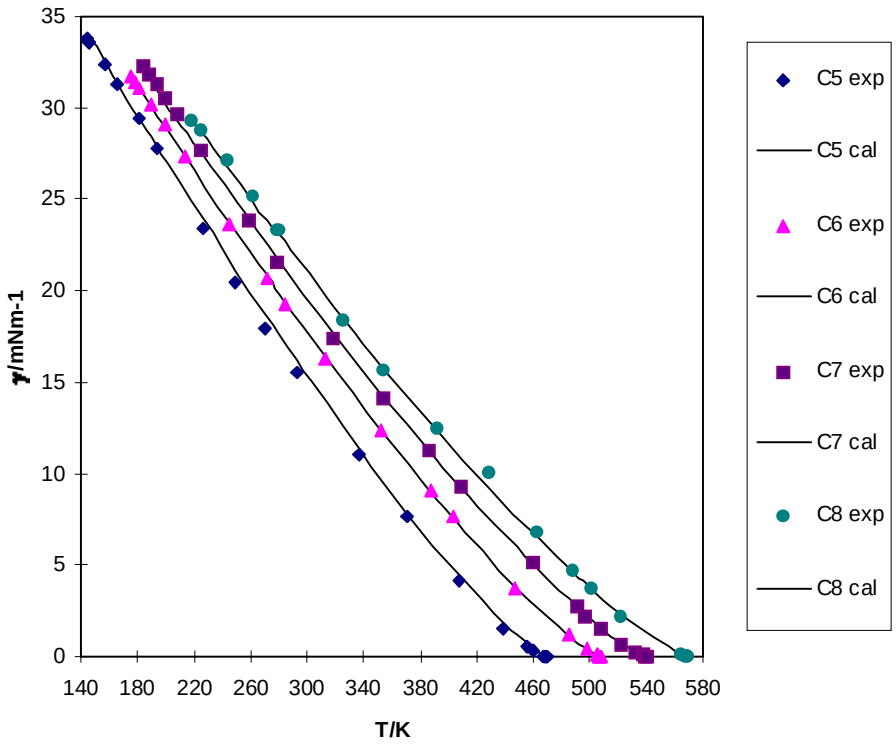
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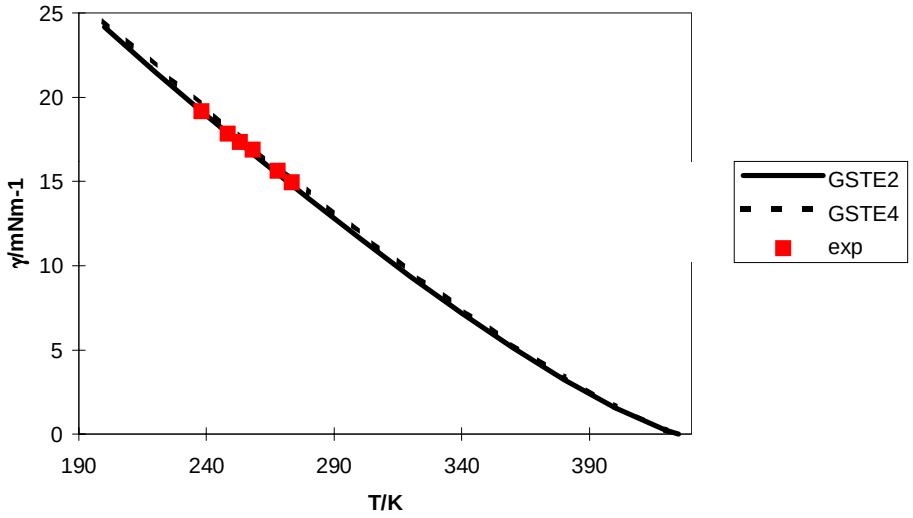
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