

A NEW CORRELATIVE MODEL FOR SURFACE TENSION OF MIXTURES: HYDROCARBON MIXTURES

M.L.L. PAREDES, J.M.T. SANTOS and E.S. BEZERRA

State Univ. Rio de Janeiro, Institute of Chemistry, R. São Francisco Xavier, 524, PHLC, 310 – Maracanã - Rio de Janeiro – RJ – 20550-013, Brazil. E-mail: paredes@uerj.br

Abstract — This article presents a new correlative model for surface tension of mixtures. This model is an extension of a predictive model recently proposed by our group. Other correlative models were evaluated and compared to the proposed model. Hydrocarbons mixtures exhibiting chemical nature or shape and chain size asymmetries were chosen as the standard to test the performance of the chosen models at several temperatures. A total of 1433 experimental data was used. All of the correlative models studied showed very good results. However, an F-test study pointed out that there are still opportunities in modeling for describing the studied data within the experimental uncertainties.

Keywords — surface tension, modeling, mixtures, hydrocarbons.

I. INTRODUCTION

Surface tension (ST) is an important physical-chemical property due to its influence on several natural phenomena, as well as industrial applications (Ramírez-Verduzco *et al.*, 2006). The industrial importance can be exemplified through several industrial processes, e.g., chemical reactions that occur in fluid surfaces, distillation, extraction, absorption, electrochemical reactions, operation of biological membranes, flotation, lubrication, and other processes where adhesion and detergency play important roles in the process. ST of liquids and their changes with composition in liquid solutions should be considered in the development of equipments that involve mass transfer (Tahery *et al.*, 2005).

In comparison to other classes of organic compounds, hydrocarbons may be conveniently used to test the performances of models due to the relatively low strength of molecular interactions, as other classes may present strong dipole moment, hydrogen bond, or ionic interactions. Also, the physicochemical properties of hydrocarbons are widely used in the petroleum industry, which deals with heavy oils that contain molecules with more complex structures. In such cases, the models must be able to describe non-idealities due to chain length, shape, and chemical nature asymmetry.

There are classic and empiric methods to estimate the ST for the so-called classic fluids and its mixtures, including hydrocarbons in this category. The most accurate ones are capable of predicting ST of non-aqueous mixtures with a deviation of approximately 3.5% from the experimental data (Poling *et al.*, 2001).

Taking hydrocarbons at room temperature as a reference, ST is typically within the range of (15 to 30) mN m⁻¹. Since experimental uncertainties are typically in

the range between (0.01 and 0.1) mN m⁻¹, the description of mixture ST with deviations comparable to the experimental uncertainties leads to relative deviations ranging from (0.03 to 0.7)%. Then, predictive models found in the literature are not capable of describing mixture ST with such low deviations, even when pure component ST is known.

One demand for ST calculation is on the characterization of petroleum fractions through empiric models (Riazi and Al-Sahhaf, 1995). In this application, the composition of pseudo-components representative of petroleum families is calculated from macroscopic properties of the mixture, e.g., from ST. However, the estimation of ST, given composition and pure components ST, usually lead to smaller errors than the inverse way, when mixture and pure component ST is used to calculate composition. As an example, in Fig. 1 are presented the relative errors when ST is calculated from composition by the molar additive model (Bezerra *et al.*, 2010), and when the inverse calculation is performed. Despite the inaccuracy of the simple model chosen, one can see that the relative errors on composition are much higher than the relative errors on ST. In order to obtain reasonable errors on composition, only very small errors on ST are acceptable.

In a previous paper (Bezerra *et al.*, 2010), we have presented a predictive model for ST performing better than usual predictive references for non-ideal surface thermodynamics, such as the Sprow-Prausnitz model. However, even the better models were not able to predict satisfactorily the ST of many mixtures, especially involving aromatic molecules.

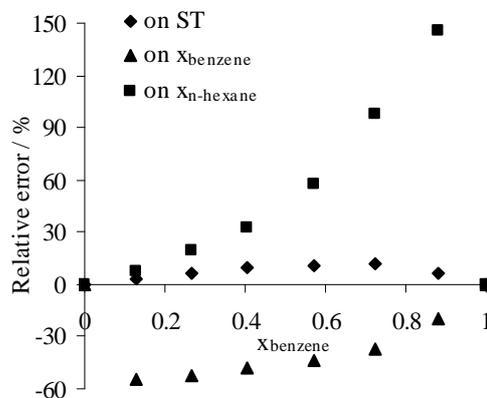


Fig. 1. Relative error on the calculation of ST (given the composition) and compositions (given the ST) using the molar additive ST model for the system benzene/n-hexane (Ridgway and Butler, 1967).

In this context, this paper analyzes and develops correlative mixture ST models using pure component data and composition as entries, evaluating different asymmetries, such as the chemical nature, shape (e.g. paraffinic, naphthenic and aromatic molecules), and chain length, at several temperatures, aiming at obtaining the lowest correlation errors for mixture ST calculation. The proposed models are linear in the parameters, and then no local minima may be found. Besides, this paper performs an F-test using the best models to analyze whether these models are able to correlate ST with errors within experimental uncertainties.

II. MODELS

The main approaches for the calculation of ST are from surface thermodynamics, parachor, and other empiric methods. The methods based on surface thermodynamics consider that a surface layer between the bulk liquid and vapor phases has its own composition, which affects mixture ST. In this sense, these methods estimate this composition in order to obtain the mixture ST (Poling *et al.*, 2001). The second was developed empirically from experimental observations, and is recommended for systems where pure components ST are not so different from each other and the concept of ideal solution applies.

This paper deals with correlative models, which need experimental mixture data to obtain mixture-dependent parameters. While it is convenient to use accurate predictive models, in many cases, correlative models are necessary due to the demand for higher accuracy. The studied models follow.

A. Parachor (P)

The vapor and the liquid phase mixture parachors in Macleod (1923) and Sugden (1924) model were redefined by Hugill and Van Welsenes (1986) aiming at developing a parachor correlative model. In this work the vapor density at low pressures is neglected (Poling *et al.*, 2001).

B. Eberhart and Shereshefsky (ES)

Eberhart (1966) proposed an adjustable-parameter equation for binary liquid mixtures. ST was considered a linear function of surface layer molar fraction:

The equilibrium condition imposed between the surface layer and the bulk of the liquid phase leads to an equality of the chemical potential in both layers. The ratio of the activities for each species in both phases was equaled to temperature-dependent distribution constants. The author applied this model to organic liquid mixtures, with good results. An alternative model developed by Shereshefsky (1967) calculates the energy change in the surface layer due to interchange between one mol of solute and solvent. The author considered that the mixture ST obeys the law of additivity, surface layer is in equilibrium with the bulk phase, and components have approximately the same surface area. This model was applied to seventeen polar and non-polar binary mixtures, and good results were obtained. According to the author, the deviation between model correla-

tion and experimental data was within experimental uncertainty.

Comparing Eberhart's (1966) with Shereshefsky's (1967) model, one may realize that after rearrangement the models are equivalent.

C. Wang-Fu (WF)

The Wang-Fu (Fu *et al.*, 1986) model is based on the Hildebrand-Scott equation, modified to non-ideal mixtures by using the local composition concept proposed by Wilson (1964). The authors evaluated 251 binary mixtures and obtained deviations of approximately 0.46%. Li *et al.* (2000) used the Wang-Fu model in their study, but without the temperature dependence presented in the original work. Then, the f_{ij} parameters were considered constants.

D. Excess ST and Relich-Kister (RK)

The dependence of mixture ST on composition may be represented by the excess ST. Some expressions may be found in the literature correlating the excess properties to the composition. Redlich and Kister (1948) proposed a polynomial equation, and this expression is used in this work in the same way of Bezerra *et al.* (2010).

E. LWW model

Li *et al.* (2000) proposed a model based on Wilson's (1964) model to describe the excess Gibbs energy and presented simplifying assumptions to reduce the model to two parameters per binary mixture.

F. Jouyban-Acree (JA₁ and JA₂)

Jouyban *et al.* (2004) studied binary and ternary mixtures used in pharmaceutical formulations. They proposed a general composition-additive equation for mixture ST, employing volumetric, weight or molar fraction as composition and three adjustable parameters. Following Bezerra *et al.* (2010), volumetric fraction was chosen for the composition and two versions of the model were used, with one (JA1) and two (JA2) adjustable parameters. The authors tested this model in the correlation of aqueous solutions ST, with deviations from experimental data of 1.39%. This equation is usually known as the Jouyban-Acree model.

G. WSD model

Winterfeld *et al.* (1978) extended Kirkwood and Buff's (1949) model to multicomponent mixtures and applied it to polar and non-polar binary systems. The regression of binary hydrocarbon mixture parameters allowed for the description of experimental data with deviations that were below 3%. Negligible vapor phase density and liquid volume additivity were applied.

H. Development of the proposed model (VC₁ and VC₂)

Based on a previous work by our group (Bezerra *et al.*, 2010), the volumetric fraction version of the simplified Jouyban *et al.* (2004) model was used along with an analogy to the relationship between the Sprow and Prausnitz and Hildebrand-Scott models (Poling *et al.*, 2001) in order to generate a new predictive mixture ST model by discarding the excess term in Eq. 1:

$$\ln(\sigma) = \sum_i \phi_i \ln(\sigma_i) - \frac{1}{2} \sum_j \phi_j \left(\sum_k \phi_k \ln \left(\frac{\sigma_k}{\sigma_j} \right) \right)^2 + \ln \sigma^E \quad (1)$$

The first term in the previous equation is the ideal solution term, the last one is the non-ideality term, while the other is a correction due to differences in the pure components ST. It is worthwhile to recall that the $-1/2$ coefficient in Eq. 1 was derived empirically in a direct analogy with the relation between the Sprow and Prausnitz and Hildebrand–Scott models. This model proved to be the most accurate among the predictive models studied in our previous work. However, preliminary studies pointed out that the coefficient $-1/2$ was effective in improving the performance of the proposed model when comparing it with the predictive Jouyban-Acree model, but led to values of $\ln \sigma^E$ that were not easily described by simple excess functions. In order to solve this inadequacy for correlative models, a simple and effective change was proposed: the coefficient $-1/2$ turns into 1, and then the final model is:

$$\ln(\sigma) = \sum_i \phi_i \ln(\sigma_i) + \sum_j \phi_j \left(\sum_k \phi_k \ln \left(\frac{\sigma_k}{\sigma_j} \right) \right)^2 + \ln \sigma^E \quad (2)$$

Aiming at keeping an analogy with the Jouyban-Acree model, the non-ideality term for the one-parameter version (VC₁) is presented in Eq. 3 and for the two parameters (VC₂) is presented in Eq. 4.

$$\ln \sigma^E = \phi_1 \phi_2 A \text{ for VC}_1 \quad (3)$$

$$\ln \sigma^E = \phi_1 \phi_2 [A + (\phi_1 - \phi_2)] B \text{ for VC}_2 \quad (4)$$

These non-ideality terms should not be confused with the reference Redlich-Kister model presented in the next section.

III. METHODOLOGY

In a previous work, Bezerra *et al.* (2010) studied ST of thirty-six binary hydrocarbon mixtures, compiling a data bank involving paraffinic (P), naphthenic (N), and aromatic (A) molecules. Classes of compounds are Paraffinic/Paraffinic (P/P), Paraffinic/Naphthenic (P/N), Naphthenic/Naphthenic (N/N), Naphthenic/Aromatic (N/A), Aromatic/Aromatic (A/A), and Paraffinic/ Aromatic (P/A). In the present work we have expanded this data bank, and the added systems are presented in Table 1. Additional information about the classes is presented in Table 2.

In order to evaluate the accuracy of the models in representing experimental data, root-mean square-deviations (RMSD) were obtained between calculated and experimental ST. The parameters for the correlative models were regressed using a least-squares procedure.

A. Reference Model: Redlich-Kister (RK)

The RK model was used as a reference, in the same way presented by Bezerra *et al.* (2010), and then its RMSD is used to estimate experimental uncertainties.

B. F-Test

The experimental uncertainties and/or the number of experimental repetitions for the majority of the data

used in this work were not available. Then, a rigorous statistical evaluation was not possible in order to compare modeling deviations with experimental uncertainties. For this reason, in this study, some considerations were made aiming at performing an F-test (Montgomery and Runger, 2003). From the few references providing the number of experimental repetitions, the limits found were four and fifteen repetitions for each experimental point. The following hypotheses were used:

- The number of repetitions was considered the same for all data, being adopted the limit of fifteen;
- The pure (random) error of the experimental data was considered equal to the deviation error of the RK model;
- A 95% confidence level was used;
- The test statistics was rewritten in order to relate it to the RMSD of a given model and to that of the RK model, given by:

Table 1. Evaluated mixtures with their respective references and compound classes

| No. | P | WSD | Class |
|-----------------|------------------------|------------------------|-------|
| 37 ^a | <i>n</i> -pentane | <i>n</i> -heptane | P/P |
| 38 ^b | <i>n</i> -hexane | <i>n</i> -heptane | P/P |
| 39 ^b | <i>n</i> -hexane | <i>n</i> -octane | P/P |
| 40 ^c | <i>n</i> -decane | <i>n</i> -dodecane | P/P |
| 41 ^d | <i>n</i> -nonane | JP-10 | P/N |
| 42 ^d | <i>n</i> -dodecane | JP-10 | P/N |
| 43 ^d | <i>n</i> -tridecane | JP-10 | P/N |
| 44 ^e | <i>n</i> -pentane | Cyclohexane | P/N |
| 45 ^f | Cyclohexane | <i>n</i> -hexane | P/N |
| 46 ^g | Cyclohexane | <i>n</i> -heptane | P/N |
| 47 ^h | Cyclohexane | 2,2,4-trimethylpentane | P/N |
| 48 ⁱ | Cyclohexane | methylcyclohexane | N/N |
| 49 ^g | Benzene | Cyclohexane | N/A |
| 50 ^j | Cyclohexane | Toluene | N/A |
| 51 ⁱ | Cyclohexane | Tetralin | N/A |
| 52 ⁱ | Methylcyclohexane | Tetralin | N/A |
| 53 ^k | Benzene | Toluene | A/A |
| 54 ^l | Benzene | 1,3,5-trimethylbenzene | A/A |
| 55 ^m | Benzene | diphenylmethane | A/A |
| 56 ⁿ | Benzene | bis(4-cumyl)-methane | A/A |
| 57 ⁿ | <i>o</i> -xylene | bis(4-cumyl)-methane | A/A |
| 58 ⁿ | <i>m</i> -xylene | bis(4-cumyl)-methane | A/A |
| 59 ⁿ | <i>p</i> -xylene | bis(4-cumyl)-methane | A/A |
| 60 ⁿ | Cumene | bis(4-cumyl)-methane | A/A |
| 61 ^o | 1,2,4-trimethylbenzene | diphenylmethane | A/A |
| 62 ⁿ | Tetralin | bis(4-cumyl)-methane | A/A |
| 63 ⁱ | Benzene | tetralin | A/A |
| 64 ^e | Pentane | benzene | P/A |
| 65 ^e | Pentane | toluene | P/A |
| 66 ^e | Pentane | <i>m</i> -xylene | P/A |
| 67 ^e | pentane | <i>p</i> -xylene | P/A |
| 68 ^p | benzene | <i>n</i> -hexane | P/A |
| 69 ^g | benzene | <i>n</i> -heptane | P/A |
| 70 ^q | benzene | 2,2,4 trimethylpentane | P/A |
| 71 ^r | toluene | <i>n</i> -octane | P/A |

^a(Mohsen-Nia *et al.*, 2010); ^b(Pugachevich and Belyarov, 1970); ^c(Ramakrishnan *et al.*, 1976); ^d(Zhang *et al.*, 2011); ^e(Mahl *et al.*, 1972); ^f(Clever *et al.*, 1963); ^g(Herrmann, 1994); ^h(Evans and Clever, 1964); ⁱ(Kanade *et al.*, 1992); ^j(Segado *et al.*, 1991); ^k(Konobeev and Lyapin, 1970); ^l(Kovalenko and Trifonov, 1953); ^m(Koefoed and Villadsen, 1958); ⁿ(Toropov and Mat'yakubova, 1963); ^o(Pugachevich and Mukhtarov, 1979); ^p(Ridgway and Butler, 1967); ^q(Toropov and Kabanova, 1961); ^r(Ling and van Winkle, 1958). ^{b,c,e,f} (apud Wohlfarth and Wohlfarth, 1997).

Table 2. Minimum (T_{min}) and maximum (T_{max}) temperatures evaluated, sum of the number of temperatures of the systems (NT), and sum of the number of data points of the systems (NP) for each class

| Class | Systems | Tmin (K) | Tmax (K) | NT | NP |
|--------|---------|----------|----------|-----|------|
| P/P | 13 | 293.15 | 343.15 | 39 | 241 |
| P/N | 11 | 287.81 | 298.15 | 28 | 338 |
| N/N | 3 | 298.15 | 298.15 | 3 | 29 |
| N/A | 13 | 293.15 | 308.16 | 26 | 279 |
| A/A | 17 | 293.15 | 343.15 | 42 | 320 |
| P/A | 14 | 293.15 | 327.88 | 28 | 226 |
| Global | 71 | 287.81 | 343.15 | 166 | 1433 |

$$TF = (RMSD/RMSD_{RK}) / \sqrt{1 + F_0 v_n/v_d} \quad (5)$$

where v_n and v_d are the numerator and denominator degrees of freedom in the original F-test, subscript RK is relative to Redlich-Kister result, and F_0 is the reference F-test value for the confidence level and degrees of freedom used. In this way, for TF below 1 it is not possible to distinguish between the performances of the evaluated model and of the reference RK model. In this case, the evaluated model describes experimental data with deviations from these data that are within the experimental uncertainty.

IV. RESULTS

In this section, the performances of the correlative models are presented along with the F-test for the two-parameter correlative models.

A. Evaluation of models performance

The RMSD obtained by one- and two-parameter correlative models are presented in Tables 3 and 4, and the obtained parameters for VC₁ and VC₂ are presented in Table 5. Analyzing the performances of the one-parameter correlations, one can see that the deviations of JA₁ and VC₁ are very similar; the greater difference between the performances of these models was for paraffinic/paraffinic mixtures, for which class the difference between JA₁ and VC₁ deviations is 26% of that of RK, the reference model.

Table 3. RMSD for one-parameter models

| Class | P | WSD | ES | JA ₁ | VC ₁ |
|--------|-------|-------|-------|-----------------|-----------------|
| P/P | 0.124 | 0.116 | 0.124 | 0.120 | 0.105 |
| P/N | 0.119 | 0.118 | 0.109 | 0.112 | 0.111 |
| N/N | 0.074 | 0.081 | 0.076 | 0.076 | 0.076 |
| N/A | 0.080 | 0.096 | 0.076 | 0.079 | 0.079 |
| A/A | 0.133 | 0.136 | 0.141 | 0.128 | 0.124 |
| P/A | 0.267 | 0.311 | 0.158 | 0.236 | 0.235 |
| Global | 0.143 | 0.154 | 0.122 | 0.134 | 0.130 |

Table 4. RMSD for two-parameter models and RK

| Class | WF | LWW | JA ₂ | VC ₂ | RK |
|--------|-------|-------|-----------------|-----------------|-------|
| P/P | 0.188 | 0.112 | 0.107 | 0.091 | 0.058 |
| P/N | 0.113 | 0.11 | 0.095 | 0.094 | 0.075 |
| N/N | 0.052 | 0.059 | 0.061 | 0.061 | 0.035 |
| N/A | 0.068 | 0.067 | 0.060 | 0.060 | 0.042 |
| A/A | 0.141 | 0.125 | 0.115 | 0.110 | 0.058 |
| P/A | 0.140 | 0.157 | 0.142 | 0.129 | 0.080 |
| Global | 0.128 | 0.113 | 0.103 | 0.097 | 0.061 |

Table 5. Parameters for VC₁ and VC₂^a

| No. | 10 ² A, Eq. 3 | 10 ² A, Eq. 4 | 10 ² B, Eq. 4 |
|-----|--------------------------|--------------------------|--------------------------|
| 1 | -2.55 | -2.18 | -5.1 |
| 2 | -16.64 | -16.64 | -0.1 |
| 3 | -4.41 | -4.59 | 2.0 |
| 4 | 0.38 | 0.24 | 3.1 |
| 5 | -14.28 | -14.14 | -1.6 |
| 6 | -29.74 | -30.21 | -2.2 |
| 7 | -34.46 | -34.26 | 0.8 |
| 8 | -30.80 | -34.25 | -13.4 |
| 9 | -3.17 | -3.28 | -3.3 |
| 10 | -11.57 | -11.60 | -0.7 |
| 11 | -9.61 | -9.64 | 2.1 |
| 12 | -19.04 | -19.04 | -1.3 |
| 13 | 1.95 | 1.95 | 0.2 |
| 14 | -12.51 | -12.40 | 1.3 |
| 15 | -8.31 | -8.26 | 0.5 |
| 16 | -13.07 | -13.10 | 2.0 |
| 17 | -18.78 | -18.72 | 2.1 |
| 18 | -13.66 | -13.55 | 1.9 |
| 19 | -14.39 | -14.36 | 2.0 |
| 20 | -12.79 | -12.78 | 0.5 |
| 21 | -13.84 | -13.68 | 2.4 |
| 22 | -12.57 | -12.25 | 1.9 |
| 23 | -10.82 | -10.47 | 3.3 |
| 24 | -12.40 | -12.35 | 3.4 |
| 25 | -2.97 | -2.92 | 0.6 |
| 26 | -2.23 | -2.28 | 1.9 |
| 27 | -36.54 | -36.27 | -2.5 |
| 28 | -25.08 | -25.27 | 2.2 |
| 29 | -35.25 | -35.08 | -0.9 |
| 30 | -23.23 | -23.15 | -3.1 |
| 31 | -31.20 | -31.41 | -3.2 |
| 32 | -36.44 | -35.76 | 8.6 |
| 33 | -18.94 | -19.18 | 11.9 |
| 34 | -10.21 | -9.97 | -4.1 |
| 35 | -36.46 | -36.50 | 13.3 |
| 36 | -33.36 | -32.92 | 6.8 |
| 37 | -14.40 | -14.03 | 7.2 |
| 38 | -1.89 | -1.87 | -0.4 |
| 39 | -6.14 | -6.09 | 0.5 |
| 40 | -1.64 | -1.64 | 0.0 |
| 41 | -24.22 | -24.20 | 1.3 |
| 42 | -12.16 | -12.06 | 10.1 |
| 43 | -13.72 | -13.72 | -0.4 |
| 44 | -25.69 | -25.52 | 3.7 |
| 45 | -11.72 | -11.45 | -3.5 |
| 46 | -8.06 | -8.08 | -1.7 |
| 47 | -13.71 | -14.02 | -4.5 |
| 48 | -1.60 | -1.65 | 6.5 |
| 49 | -12.73 | -12.74 | -0.6 |
| 50 | -10.00 | -10.08 | -6.1 |
| 51 | -30.52 | -30.20 | 3.8 |
| 52 | -33.24 | -33.10 | 2.0 |
| 53 | -0.51 | -0.51 | 0.0 |
| 54 | -2.62 | -2.45 | 2.2 |
| 55 | -16.90 | -16.64 | 3.6 |
| 56 | -8.76 | -8.33 | 2.0 |
| 57 | -1.59 | -2.05 | -3.6 |
| 58 | -8.17 | -8.04 | 0.9 |
| 59 | -4.38 | -5.00 | -4.2 |
| 60 | -3.53 | -3.92 | -3.0 |
| 61 | -17.04 | -16.52 | 3.4 |
| 62 | -0.81 | -0.61 | 1.9 |
| 63 | -16.49 | -16.56 | -1.2 |
| 64 | -84.23 | -83.22 | 30.6 |

| No. | 10^2 A, Eq. 3 | 10^2 A, Eq. 4 | 10^2 B, Eq. 4 |
|-----|-----------------|-----------------|-----------------|
| 65 | -81.28 | -78.99 | 21.6 |
| 66 | -68.19 | -67.12 | 13.4 |
| 67 | -48.28 | -48.54 | -3.9 |
| 68 | -36.29 | -36.33 | -13.2 |
| 69 | -32.50 | -32.81 | -15.3 |
| 70 | -50.80 | -50.83 | -1.2 |
| 71 | -13.50 | -13.45 | 2.3 |

^a For systems 1 to 36 see Bezerra *et al.* (2010).

The best overall performances were for ES and VC₁, with the difference between the RMSD of these models only 13% of that of RK. However, ES is much more sensitive to the obtained parameter than VC₁, what is undesirable, and also VC₁ is related to a predictive model with good performance (Bezerra *et al.*, 2010), while ES is not. Besides, VC₁ is a model linear in the parameters, and then no local minima in the parameter estimation are found. RMSD of P and WSD are greater than VC₁'s by 21% and 39% of RK's, respectively.

Analyzing the performances of the two-parameter correlations, one can see that the best overall performance was for VC₂. The difference between the RMSD of this model from the other models is 10%, 26%, and 51% of RK RMSD for JA₂, LWW, and WF, respectively. The highest relative difference between JA₂ and VC₂ is for the paraffinic/paraffinic class, with JA₂ RMSD greater than VC₂'s by 28% of the RK RMSD for this class.

These results show that the proposed models performs slightly better than usual references in the related literature, such as P, WSD, WF, and LWW models, although being models linear in the parameters, and then more interesting to used in parameter estimation.

Also, the very simple term added to the JA model slightly enhances the performance of the one- and two-parameter models, especially for the paraffinic/paraffinic class.

Comparing VC₂ and VC₁, the difference between these models deviations are from 23% to 133% those of RK, being the 133% for the paraffinic/aromatic class, 45% for the naphthenic/aromatic class, and 43% for the naphthenic/naphthenic class. Hence for these classes the second parameter is pronouncedly more effective, especially for the paraffinic/aromatic class.

Even the best model proposed here presents deviations about 60% higher than that of the reference model. This result motivated the performance of an F-test for some models, in order to find out if these deviations may be considered comparable to the experimental uncertainties.

B. F-Test for Two-Parameter Models

F-test results are presented in Table 6, where values lower than or equal to one are in bold face, i.e., systems for which the model described experimental data with deviations compatible to the experimental uncertainties. In an overall analysis, for the majority of systems studied the models led to a lack of adjustment that cannot be explained by experimental uncertainties. In this sense, even using two adjustable parameters in some models

there are still opportunities for improving these models. To perform a doubtless evaluation, experimental data should be provided with high accuracy and with the individual uncertainties and numbers of repetitions for each data point.

The overall comparison between VC₁ and VC₂ shows the importance of the extra parameter in VC₂. The first model represented experimental data with deviations within experimental uncertainties only for one system (number 20), while VC₂ achieved this goal for 11 systems. The average *TF* values of VC₁ are especially higher than those of VC₂ for paraffinic/paraffinic and paraffinic/aromatic classes.

The overall comparison between JA₂ and VC₂ is that VC₂ correlates data within experimental uncertainties for 11 systems, while JA₂ does for 9 systems, reinforcing the better performance of the proposed model.

Table 6. *TF* (Eq. 5) values for some models

| No. | VC ₁ | JA ₂ | VC ₂ |
|-----|-----------------|-----------------|-----------------|
| 1 | 2.3 | 2.0 | 1.5 |
| 2 | 1.2 | 1.6 | 1.2 |
| 3 | 1.4 | 1.5 | 1.3 |
| 4 | 1.7 | 1.3 | 1.3 |
| 5 | 1.1 | 1.0 | 1.0 |
| 6 | 1.5 | 2.6 | 1.5 |
| 7 | 2.5 | 5.3 | 2.5 |
| 8 | 2.0 | 1.4 | 1.8 |
| 9 | 50.9 | 10.4 | 10.4 |
| 37 | 1.7 | 1.5 | 1.4 |
| 38 | 1.9 | 1.8 | 1.8 |
| 39 | 1.5 | 1.1 | 1.1 |
| 40 | 2.3 | 2.4 | 2.4 |
| P/P | 5.5 | 2.6 | 2.2 |
| 10 | 1.2 | 1.1 | 1.2 |
| 11 | 1.1 | 1.0 | 1.0 |
| 12 | 1.1 | 1.1 | 1.1 |
| 13 | 1.8 | 0.9 | 0.9 |
| 41 | 1.3 | 1.3 | 1.3 |
| 42 | 2.4 | 1.7 | 1.7 |
| 43 | 1.2 | 1.2 | 1.2 |
| 44 | 1.5 | 1.1 | 1.1 |
| 45 | 1.9 | 1.7 | 1.5 |
| 46 | 1.1 | 1.1 | 1.0 |
| 47 | 1.6 | 0.4 | 0.4 |
| P/N | 1.5 | 1.1 | 1.1 |
| 14 | 1.5 | 1.3 | 1.3 |
| 15 | 1.6 | 1.6 | 1.6 |
| 48 | 2.5 | 1.8 | 1.8 |
| N/N | 1.9 | 1.6 | 1.6 |
| 16 | 2.1 | 1.8 | 1.8 |
| 17 | 2.8 | 2.1 | 2.1 |
| 18 | 2.5 | 1.2 | 1.2 |
| 19 | 1.7 | 1.2 | 1.3 |
| 20 | 1.0 | 1.0 | 1.0 |
| 21 | 1.4 | 1.2 | 1.2 |
| 22 | 2.5 | 2.3 | 2.3 |
| 23 | 2.0 | 1.1 | 1.1 |
| 24 | 1.9 | 1.1 | 1.1 |
| 49 | 1.2 | 1.2 | 1.2 |
| 50 | 2.0 | 1.2 | 1.1 |
| 51 | 1.5 | 1.0 | 1.0 |
| 52 | 2.0 | 1.8 | 1.8 |
| N/A | 1.9 | 1.4 | 1.4 |

| Table 6. continuation | | | |
|-----------------------|-----------------|-----------------|-----------------|
| No. | VC ₁ | JA ₂ | VC ₂ |
| 25 | 1.9 | 1.8 | 1.8 |
| 26 | 2.1 | 2.0 | 2.0 |
| 27 | 1.4 | 1.1 | 1.1 |
| 28 | 1.4 | 1.3 | 1.3 |
| 29 | 1.2 | 1.2 | 1.2 |
| 30 | 1.1 | 1.0 | 1.0 |
| 53 | 1.4 | 1.4 | 1.4 |
| 54 | 1.2 | 1.1 | 1.1 |
| 55 | 1.8 | 1.6 | 1.6 |
| 56 | 3.6 | 4.3 | 3.4 |
| 57 | 6.4 | 5.1 | 5.1 |
| 58 | 4.9 | 5.1 | 4.9 |
| 59 | 2.1 | 1.2 | 1.1 |
| 60 | 9.2 | 9.5 | 9.1 |
| 61 | 1.2 | 1.2 | 1.0 |
| 62 | 3.1 | 3.0 | 2.5 |
| 63 | 28.0 | 13.2 | 13.2 |
| A/A | 4.2 | 3.2 | 3.1 |
| 31 | 1.3 | 1.2 | 1.2 |
| 32 | 1.9 | 1.3 | 1.2 |
| 33 | 1.8 | 0.8 | 0.9 |
| 34 | 3.2 | 3.3 | 3.0 |
| 35 | 5.3 | 5.2 | 1.3 |
| 36 | 1.6 | 1.2 | 1.2 |
| 64 | 4.8 | 2.2 | 2.2 |
| 65 | 13.9 | 1.0 | 1.0 |
| 66 | 9.1 | 1.8 | 1.8 |
| 67 | 1.4 | 1.4 | 1.4 |
| 68 | 4.6 | 1.2 | 1.2 |
| 69 | 1.6 | 1.1 | 1.1 |
| 70 | 5.4 | 5.0 | 5.4 |
| 71 | 3.4 | 3.0 | 3.0 |
| P/A | 4.2 | 2.1 | 1.8 |
| Global | 3.5 | 2.2 | 2.0 |
| Pass ^a | 1 | 9 | 11 |

Note: bold numbers are visual guidelines to cases where models described experimental data within experimental uncertainty. ^a Pass means the number of systems for which the model is able to correlate experimental data within experimental uncertainty.

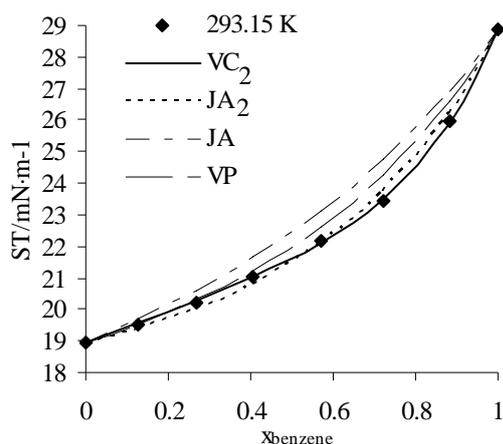


Fig. 2. Experimental data (Ridgway and Butler, 1967) and JA₂ and VC₂ correlations for mixture 35, along with the predictions of Jouyban-Acree (JA) and of the predictive version (VP) of our model (Bezerra *et al.*, 2010).

C. Graphical Evaluation

In order to graphically the comparison between some evaluated models, experimental data and model calcula-

tions are presented for a system with high chemical nature and shape asymmetry but the same number of carbons (mixture 35, n-hexane/benzene, presented at Fig. 2). This figure shows the performance of JA₂ and VC₂, and also of the corresponding predictive models JA and VP, respectively (Bezerra *et al.*, 2010).

VP performs better than JA, as explored in our earlier paper. But now the importance of the correlative models is shown: JA₂ and VC₂ perform much better than JA and VP, respectively. Also, the importance of the extra term in VC₂, in comparison to JA₂, is also shown: JA₂ underestimates ST of the mixture at low concentrations of benzene and overestimates it at high concentrations.

V. CONCLUSIONS

This work presents a new correlative model for mixture surface tension calculation, based on a predictive model recently presented by our group. One- and two-parameter versions were tested and compared to literature correlative models with the same number of parameters. The proposed models are linear in the parameters, and then parameter estimation cannot lead to local minima. The two-parameter version of the proposed models achieved the best overall performance.

A rigorous statistical analysis was not performed, since the number of repetitions or the experimental uncertainties were not available for most mixtures. Some assumptions were made in order to perform a feasible statistical evaluation, which identified that even for the best model there are still opportunities of improvement towards describing the mixture surface tension with deviations within the experimental uncertainties. The two-parameter model was able to achieve this goal for 11 out of 71 systems, while the one-parameter model achieved this goal for only one system, showing the need of the second parameter for high accuracy applications.

Also, the very simple term added to the Jouyban-Acree model slightly enhances the performance of the one- and two-parameter models, especially for the paraffinic/paraffinic class. The original Jouyban-Acree model presents three parameters, but in this study only the one- and two-parameter versions were evaluated.

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REFERENCES

- Bezerra, E.S., J.M.T. Santos and M.L.L. Paredes, "A new predictive model for liquid/air surface tension of mixtures: Hydrocarbon mixtures," *Fluid Phase Equilib.*, **288**, 55-62 (2010).
- Eberhart, J.G. "The surface tension of binary liquid mixtures," *J. Phys. Chem.*, **70**, 1183-1186 (1966).
- Evans Jr., H.B. and H.L. Clever, "Surface tensions of binary mixtures of isoctane with benzene, cyclohexane, and n-dodecane at 30°," *J. Phys. Chem.*, **68**, 3433-3435 (1964).

- Fu, J., B. Li and Z. Wang, "Estimation of fluid-fluid interfacial tensions of multicomponent mixtures," *Chem. Eng. Sci.*, **41**, 2673-2679 (1986).
- Hugill, J.A. and A.J. Van Welsenes, "Surface tension: a simple correlation for natural gas + condensate systems," *Fluid Phase Equilib.*, **29**, 383-390 (1986).
- Jouyban, A., A. Fathi-Azarbayjani and W. Acree Junior, "Surface tension calculation of mixed solvents with respect to solvent composition and temperature by using Jouyban-Acree model," *Chem. Pharm. Bull.*, **52**, 1219-1222 (2004).
- Kirkwood, J.G. and F.P. Buff, "The statistical mechanical theory of surface tension," *J. Chem. Phys.*, **17**, 338-343 (1949).
- Li, C., W. Wang, and Z. Wang, "A surface tension model for liquid mixtures based on the Wilson equation," *Fluid Phase Equilib.*, **175**, 185-196 (2000).
- MacLeod, D.B. "On a relation between surface tension and density," *Trans. Faraday Soc.*, **19**, 38-41 (1923).
- Montgomery, D.C. and G.C. Runger, *Estatística aplicada e probabilidade para engenheiros*, Ed. LTC, Rio de Janeiro (2003).
- Mohsen-Nia, M., H. Rasa and S.F. Naghibi, "Experimental and theoretical study of surface tension of n-pentane, n-heptane, and some of their mixtures at different temperatures," *J. Chem. Thermodyn.*, **42**, 110-113 (2010).
- Poling, B.E., R.C. Reid and J.M. Prausnitz, *The properties of gases and liquids*, McGraw-Hill, New York (2001).
- Ramírez-Verduzco, L.F., A. Romero-Martínez and A. A. Trejo, "Prediction of the surface tension, surface concentration, and the relative Gibbs adsorption isotherm of binary liquid systems," *Fluid Phase Equilib.*, **246**, 119-130 (2006).
- Redlich, O. and A.T. Kister, "Thermodynamics of nonelectrolyte solutions – x-y-t relations in a binary system," *Ind. Eng. Chem.*, **40**, 341-348 (1948).
- Riazi, M.R. and T.A. Al-Sahhaf, "Physical properties of n-alkanes and n-alkylhydrocarbons: application to petroleum mixtures," *Ind. Eng. Chem.*, **34**, 4145-4148 (1995).
- Ridgway, K. and P.A. Butler, "Physical properties of the ternary system benzene-cyclohexane-hexane," *J. Chem. Eng. Data*, **12**, 509-515 (1967).
- Shereshefsky, J.L. "A theory of surface tension of binary solutions: I. Binary liquid mixtures of organic compounds," *J. Colloid Interf. Sci.*, **24**, 317-322 (1967).
- Sudgen, S. "A relation between surface tension, density, and chemical composition," *J. Chem. Soc.*, **125**, 1177-1189 (1924).
- Tahery, R.; H. Modarress, and I. Satherley, "Surface tension prediction and thermodynamic analysis of the surface for binary solutions," *Chem. Eng. Sci.*, **60**, 4935-4952 (2005).
- Wilson, G.M. "Vapor-liquid equilibrium. XI. A new expression for the excess free energy of mixing," *J. Am. Chem. Soc.*, **86**, 127-130 (1964).
- Winterfeld, P.H., L.E. Scriven, and H.T. Davis, "An approximate theory of interfacial tensions of multicomponent systems: applications to binary liquid-vapor tensions," *AIChE J.*, **24**, 1010-1014 (1978).
- Wohlfarth, Ch. and B. Wohlfarth, *Surface Tension of Pure Liquids and Binary Liquid Mixtures*, Springer, Berlin (1997).
- Zhang, L., Y. Guo, J. Xiao, X. Gong and W. Fang, "Density, Refractive Index, Viscosity, and Surface Tension of Binary Mixtures of exo-Tetrahydrodicyclopentadiene with Some n-Alkanes from (293.15 to 313.15) K," *J. Chem. Eng. Data*, **56**, 4268-4273 (2011).

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