Impact of critical point restriction on the calculation of surface tension of organic acids using group contribution models

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Impacto de la restricción del punto crítico en el cálculo de la tensión superficial de ácidos orgánicos utilizando modelos de contribución grupal

impacte de la restricció del punt crític en el càlcul de la tensió superficial dels àcids orgànics utilitzant models de contribució de grup

ABSTRACT

This manuscript reports the calculation of surface tension of organic acids using new group contribution models. These models were obtained from the Jasper equation and the van der Waals principle of corresponding states. A special analysis was performed to determine the impact of incorporating the critical point restriction on the performance of tested group contribution models. This restriction was incorporated via a penalty term on the objective function used in the group contribution determination, and using the reduced temperature as the input model variable. A total of 885 experimental surface tension data points for 78 organic acids (including aliphatic, aromatic, dicarboxylic, and polyfunctional acids) were used to compare the performance of these group contribution models. The results showed that tested models calculated the surface tension of polyfunctional and aliphatic organic acids with modeling errors lower than 5%. However, the calculation of surface tension of aromatic and dicarboxylic acids was challenging for all tested models. The incorporation of critical point restriction of surface tension as a penalty term in the data processing stage did not improve the performance of tested group contribution models. Group contribution models that used the reduced temperature as an input variable showed the best performance for the calculation of the surface tension of these organic compounds.

Keywords: Surface Tension, Organic Acids, Fatty Acids, Group Contribution

RESUMEN

Este manuscrito informa el cálculo de la tensión superficial de los ácidos orgánicos utilizando nuevos modelos de contribución de grupo. Estos modelos se obtuvieron a partir de la ecuación de Jasper y el principio de estados correspondientes de van der Waals. Se realizó un análisis especial para determinar el impacto de incorporar la restricción del punto crítico en el desempeño de los modelos de contribución de grupo. Esta restricción se incorporó mediante un término de penalización sobre la función objetivo utilizada en la determinación de la contribución del grupo, y utilizando la temperatura reducida como variable de entrada del modelo. Se utilizó un total de 885 puntos de datos de tensión superficial experimental para 78 ácidos orgánicos (incluidos ácidos alifáticos, aromáticos, dicarboxílicos y polifuncionales) para comparar el rendimiento de estos modelos de contribución de grupo. Los resultados mostraron que los modelos probados calcularon la tensión superficial de ácidos orgánicos polifuncionales y alifáticos con errores de modelado inferiores al 5%. Sin embargo, el cálculo de la tensión superficial de los ácidos aromáticos y dicarboxílicos fue un desafío para todos los modelos probados. La incorporación de la restricción del punto crítico de la tensión superficial como término de penalización en la etapa de procesamiento de datos no mejoró el desempeño de los modelos de contribución de grupo. Los modelos de contribución de grupo que utilizaron la temperatura reducida como variable de entrada mostraron el mejor rendimiento para el cálculo de la tensión superficial de estos compuestos orgánicos.

Paraules clau: Tensión Superficial, Ácidos Orgánicos, Ácidos Grasos, Contribución de Grupo

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RESUM:

Aquest manuscrit informa del càlcul de la tensió superficial dels àcids orgànics mitjançant nous models de contribució de grup. Aquests models es van obtenir a partir de l'equació de Jasper i el principi de van der Waals dels estats corresponents. Es va realitzar una anàlisi especial per determinar l'impacte de la incorporació de la restricció del punt crític en el rendiment dels models de contribució de grup provats. Aquesta restricció es va incorporar mitjançant un terme de penalització sobre la funció objectiu utilitzada en la determinació de la contribució del grup i utilitzant la temperatura reduïda com a variable del model d'entrada. Es van utilitzar un total de 885 punts de dades experimentals de tensió superficial per a 78 àcids orgànics (inclosos àcids alifàtics, aromàtics, dicarboxílics i polifuncionals) per comparar el rendiment d'aquests models de contribució grupal. Els resultats van mostrar que els models provats calculaven la tensió superficial dels àcids orgànics polifuncionals i alifàtics amb errors de modelatge inferiors al 5%. Tanmateix, el càlcul de la tensió superficial dels àcids aromàtics i dicarboxílics va ser un repte per a tots els models provats. La incorporació de la restricció del punt crític de la tensió superficial com a terme de penalització en l'etapa de processament de dades no va millorar el rendiment dels models de contribució de grup provats. Els models de contribució grupal que utilitzaven la temperatura reduïda com a variable d'entrada van mostrar el millor rendiment per al càlcul de la tensió superficial d'aquests compostos orgànics.

Paraules clau: Tensió superficial, àcids orgànics, àcids grassos, contribució grupal

1. INTRODUCTION

Organic acids are present in different natural substances obtained from fruits (Enomoto et al., 2018), vegetables and seafood (Lund, 2013; Batt and Patel, 2014). The experimental determination and modeling of the thermodynamic properties of this family of chemical compounds are essential for the design and simulation of process units involved in the production of several commercial products, such as edible oils (Díaz-Tovar et al., 2011), fatty acids (Batt and Patel, 2014), biodiesel and fuel additives (Ceriani et al., 2015; Pérez-Cisneros et al., 2016; Di Nicola et al., 2016), food additives (Ng and Koh, 2016), detergents (Gotoh, 2017), disinfectants (Batt and Patel, 2014) and other organic compounds (Lu et al., 2019). Particularly, the surface tension is a relevant thermodynamic property of organic acids that is required in the process engineering of absorption, distillation, purification, extraction and (liquid-liquid) dispersion units (Díaz-Tovar et al., 2011).

Several models have been reported for the correlation and prediction of the surface tension of pure components using different databases such as DETHERM and DIPPR (Mulero et al., 2016; Pierantozzi et al., 2021; Cachadiña et al., 2022; Mulero et al., 2022). The available thermodynamic models for the calculation of surface tension are based on different approaches and theories such as corresponding states (Zhang et al., 2018; Cachadiña and Mulero, 2020), group contributions (Cunico et al., 2013; Naef and Acree, 2018), quantitative structure-property relationships (Knotts et al., 2001) and artificial intelligence methods such as artificial neural networks (Faúndez et al., 2020). For instance, Knotts et al. (2001) proposed a quantitative structure-property relationship model for the calculation of surface tension using a set of organic compounds from the DIPPR database. This model obtained an absolute average deviation of 3.2% for estimating this thermodynamic property of the tested compounds. Di Nicola and Moglie (2011) introduced two models using the principle of corresponding states for the correlation and prediction of surface tension of different compounds. The first model employed the acentric factor and dipole moment in combination with the critical temperature and pressure of the pure component. The second model excluded the dipole moment where an absolute average deviation of < 2% was achieved. Gharagheizi et al. (2012) reported a corresponding state model to estimate the surface tension of pure compounds from 75 chemical families including aromatic carboxylic, dicarboxylic, aliphatic and polyfunctional acids. This model used the temperature, critical properties and boiling temperature of each compound as input variables. Surface tension was estimated with an absolute mean relative deviation of 18%. Another surface tension model based on the corresponding state principle was applied by Di Nicola et al. (2016). The critical density, Boltzmann's constant, Avogadro's number and radius of gyration of the molecule were used as the input variables in this model. The prediction capabilities of this model were tested via the estimation of the surface tension of different organic acids (e.g., valeric acid, lauric acid, palmitic acid, stearic acid, oleic acid, benzoic acid, o-toluic acid, m-toluic acid). Recently, Cachadiña and Mulero (2020) introduced a new corresponding states model for the calculation of the surface tension of organic acids as a function of temperature using dimensionless reduced coordinates. This model required the critical temperature and a value of the surface tension at a low reference temperature. This model included three parameters that were obtained from the processing of surface tension data of 17 organic acids. The results indicated that this approach was more accurate than other models reported in the literature, and it was also proposed as a prediction tool to calculate this thermodynamic property. Yang et al. (2020) applied an approach similar to that reported by Cachadiña and Mulero (2020). This model utilized the maximum and minimum temperatures with the corresponding values of surface tension of 29 carboxylic acids selected from the DIPPR commercial database. The results showed an absolute average deviation of 5% for the carboxylic acids. Herein, it is convenient to indicate that the models based on the principle of corresponding states explicitly contain the condition of the surface tension at the critical temperature, which is equal to zero. The incorporation of this restriction usually favors the prediction of surface tension over

the entire range of the gas-liquid interface. Finally, Pierantozzi et al. (2021) calculated the surface tension of 98 organic acids with a neural network model. The independent variables of this model were the reduced temperature, the normal boiling temperature and the acentric factor. An absolute deviation of 1.33% with a maximum deviation of 14.3% was obtained for the calculation of this property by using a hidden layer with 41 neurons.

Sattari and Bakare (2018) discussed some challenges in the calculation of surface tension using different thermodynamic models. They highlighted the limitations of corresponding-states models to predict the surface tension of alcohols, acids and halogenated compounds. Some models may require input data (e.g., detailed molecular properties or experimental data of surface tension at triple point temperature) that are not be available for some compounds thus limiting their application in process simulators, as well as their precision owing to the increment of model uncertainty generated by the estimation of missing parameters (Díaz-Tovar et al., 2011). In this direction, the models based on group contributions offer several advantages for the calculation of different thermodynamic properties of both organic and inorganic compounds (Gani, 2019). This type of thermodynamic models is an interesting alternative to predict the process engineering properties of organic acids and can be easily incorporated into available process simulators.

This manuscript describes the assessment and comparison of first-order group contribution models for the surface tension calculation of organic acids, based on their molecular structures. A detailed statistical analysis of the performance of these group contribution models was performed to identify the best alternative for the calculation of this property. In particular, the impact of incorporating the theoretical restriction for this property at the critical point in the parameter estimation procedure of the group contribution models was analyzed and discussed. The model performance was also studied by considering different subfamilies of tested organic acids. Therefore, this manuscript provides new findings for the prediction of this relevant property of these organic compounds using this type of predictive thermodynamic models.

2. DESCRIPTION OF GROUP CONTRIBUTION MODELS USED FOR THE CALCULATION OF SURFACE TENSION OF ORGANIC ACIDS

A set of group contribution models was proposed for the calculation of the surface tension (σ, mN/m) of organic acids. Four models were based on the empirical correlation proposed by Jasper (1972), which is defined as

$$\sigma = A - BT \tag{1}$$

where T is the temperature, A and B are the model parameters defined for each compound.

The model parameters (i.e., A and B) were calculated using the group contribution approach where different functionalities were utilized

GC1 model:

$$A = \sqrt{\left(\sum_{i=1}^{N} f_i a_{GC1,i}\right)^2} \tag{2}$$

$$B = \sqrt{\left(\sum_{j=1}^{N} f_i b_{GC1,i}\right)^2} \tag{3}$$

GC2 model:

$$A = \sqrt{\left(\sum_{i=1}^{N} f_i a_{GC2,i}\right)^2} \tag{4}$$

$$B = \sqrt{\left(\left(\sum_{j=1}^{N} f_i b_{GC2,i} + \left(\sum_{j=1}^{N} f_i b_{GC2,i}\right)^2\right)^2\right)} \tag{5}$$

where f_i is the frequency of functional group i from the organic acid molecule, a_i and b_i are the corresponding contributions of this functional group to the surface tension value, respectively. The group contributions of GC1 and GC2 models were determined with a non-linear regression of the surface tension experimental database via the minimization of the next objective function

$$\epsilon = \sum_{i=1}^{n_\sigma} \left(\frac{\sigma_i^{exp} - \sigma_i^{cal}}{\sigma_i^{exp}}\right)^2 \tag{6}$$

where n_σ is the number of experimental values contained in the database, σ^{exp} and σ^{cal} are the experimental and calculated values of surface tension of tested organic acids, respectively.

Alternatively, the theoretical restriction of σ at the critical point (i.e., $\sigma(T_c) = 0$) was incorporated as a penalty term to determine the group contributions for the calculation of A and B parameters. This implied that the non-linear regression of the experimental σ database was done via the minimization of the next objective function

$$\epsilon_{T_c} = \sum_{i=1}^{n_\sigma} \left(\frac{\sigma_i^{exp} - \sigma_i^{cal}}{\sigma_i^{exp}}\right)^2 + \sum_{i=1}^{n_{T_c}} \left(\frac{T_{c,i}^{exp} - T_{c,i}^{cal}}{T_{c,i}^{exp}}\right)^2 \tag{7}$$

where T_c^{cal} was obtained from the group contribution model via the next relationship

$$T_c^{cal} = \frac{A}{B} \tag{8}$$

and T_c^{exp} is the experimental value of critical temperature of tested organic acid. Therefore, this parameter estimation problem was resolved to determine the group contributions of GC1(T_c) using Eqs. (1), (2) and (3), and GC2(T_c) using Eqs. (1), (4) and (5), respectively. To avoid the uncertainty caused by T_c calculation of

the organic acids with missing experimental values of their critical points, Eq. (7) considered only the available experimental values of critical temperature of 24 organic acids (n_{Tc}) included in the database. It is also convenient to remark that preliminary calculations showed that a better model performance was obtained using T given in °C instead of K. Therefore, this temperature unit was used for all the models reported in this manuscript.

Alternatively, Eq. (2) was modified to consider the reduced temperature (T_r) in the calculation of σ

$$\sigma = \left(1 - \frac{T}{T_c}\right) C \qquad (9)$$

where the C parameter was defined as
GC1(T_r) model

$$C = \sqrt{\left(\sum_{i=1}^{N} f_i c_{GC1,i}\right)^2} \qquad (10)$$

GC2(T_r) model

$$C = \sqrt{\left(\sum_{j=1}^{N} f_i c_{GC2,i} + \left(\sum_{j=1}^{N} f_i c_{GC2,i}\right)^2\right)^2} \qquad (11)$$

For these models, the parameter estimation was performed via the global minimization of objective function given by Eq. (6) without any restriction.

Finally, the GC-CSP model was defined using the van der Waals principle of corresponding states

$$\sigma = \sigma_0 \left(1 - \frac{T}{T_c}\right)^n \qquad (12)$$

where $n = 1.24$ and σ_0 are the model parameters. In particular, σ_0 was calculated via group contributions (d_i) using the next expression

$$\sigma_0 = \sum_{i=1}^{N} f_i d_i \qquad (13)$$

In this case, the model parameter estimation was also performed via the minimization of Eq. (6) without applying any restriction. Tc experimental values were obtained for tested compounds if available; otherwise, they were calculated using the group contribution model of Joback and Reid (1987) that is already implemented in the Aspen Plus ® simulator.

The group contribution parameters of these surface tension models were determined using a combined optimization strategy from the Simulated Annealing and Quasi-Newton methods included in the Optimization Toolbox of the MATLAB® software to globally minimize the objective functions given by Eqs. (6) and (7). These parameter estimation problems were resolved 1000 times with different random initial values of group contributions (i.e., optimization variables) with the aim of performing an exhaustive exploration of the search space for all the model parameters and these results were utilized to identify their best values. This strategy was applied to identify the global solution due to the presence of several local minima in the objective function. Note that the determination of the group contribution parameters is an unbounded optimization problem. Simulated Annealing is recognized as a reliable numerical method to resolve this type of global optimization problems.

The surface tension database used to determine the group contribution parameters contained 885 experimental points for 78 organic acids. The experimental data covered surface tension values up to 54.68 mN/m at -35.1 - 426.95 °C (i.e., T_r from 0.3 to 0.95), which were collected from different sources (Wohlfarth and Wohlfarth, 1997; Wohlfarth, 2008; Wohlfarth, 2016). Table 1 summarizes the characteristics of surface tension database that was used in this study. 18 functional groups were defined to obtain the molecular structure of tested organic acids and to predict their surface tension, see Table 2, where nonaromatic and aromatic ring groups were differentiated. 80% of database was randomly selected for the determination of group contribution parameters, while the remaining 20% was employed to evaluate the predictive capacity of tested models.

All these models with the best group contribution parameters were compared and analyzed using the percentage deviation (PD_i), absolute average deviation (AAD), root mean square error ($RMSE$) and standard deviation (SD) as statistical metrics

$$PD_i = \left(\frac{\sigma_i^{exp} - \sigma_i^{cal}}{\sigma_i^{exp}}\right) \cdot 100\% \qquad (14)$$

$$AAD = \frac{1}{n_\sigma} \sum_{i=1}^{n_\sigma} |PD_i| \qquad (15)$$

$$RMSE = \sqrt{\frac{1}{n_\sigma} \sum_{i=1}^{n_\sigma} (\sigma^{exp} - \sigma^{cal})^2} \qquad (16)$$

$$SD = \sqrt{\frac{1}{n_\sigma - 1} \sum (|PD_i| - \overline{|PD_i|}} \qquad (17)$$

3. RESULTS AND DISCUSSION

Figure 1 and Table 2 show the performance of tested group contribution models for the correlation and prediction of surface tension of organic acids, while Table 3 contains the corresponding group contribution parameters. Overall, these models showed $RMSE$ and AAD values from 1.98 to 2.81 and from 3.00 to 5.08%, respectively, with $R^2 > 0.98$. These group contribution models followed the next trend based on these metrics: GC2(T_r) < GC1(T_r) < GC1(T_c) < GC1 < GC2 < GC-CSP < GC2(T_c). The largest deviations between the model estimations and the experimental values of surface tension data occurred for GC1, GC1(T_c) and GC2 models. It was found that GC2(T_r) model presented the best performance to calculate the surface tension of these organic compounds with the lowest PD values (i.e., 1.32E-03 – 65.55 %). On the other hand, the results also indicated that the incorporation of critical
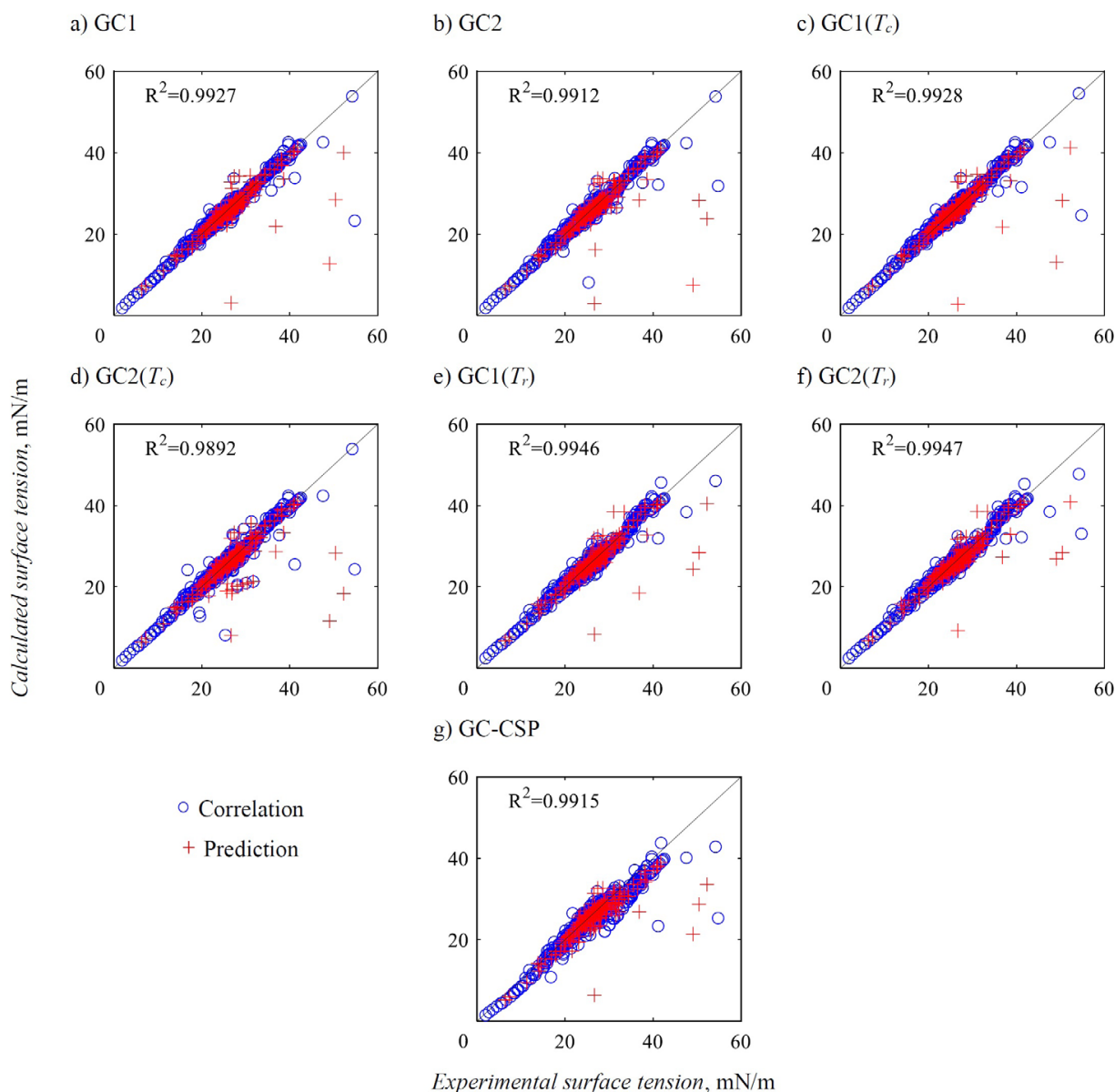
a) GC1 — $R^2=0.9927$

b) GC2 — $R^2=0.9912$

c) GC1(T_c) — $R^2=0.9928$

d) GC2(T_c) — $R^2=0.9892$

e) GC1(T_r) — $R^2=0.9946$

f) GC2(T_r) — $R^2=0.9947$

g) GC-CSP — $R^2=0.9915$

○ Correlation

+ Prediction

Calculated surface tension, mN/m

Experimental surface tension, mN/m

Figure 1. *Performance of tested group contribution models for the calculation of surface tension of organic acids.*

point restriction in the objective function did not improve the performance of GC1 and GC2 models. In particular, the performance of GC2 model was slightly deteriorated by the utilization of this constraint during the group contribution determination where PD values of GC2(Tc) ranged from 2.65E-03 to 76.40 %. GC1 and GC1(Tc) models showed a comparable performance without a statistically significant difference (i.e., p-level > 0.05) with PD values of 6.03E-03 - 88.46 % and 4.80E-03 - 89.62 %, respectively. The worst group contribution model corresponded to GC2(Tc) with PD values of 2.65E-03 - 76.40 %. In addition, the model based on the principle of corresponding states (GC-CSP) was outperformed by other models, see Figure 1 and Table 2. Herein, it is necessary to recall that the surface tension calculation with GC1(T_r), GC2(T_r) and GC-CSP required the critical temperature of organic acid as input variable, which could be considered as a disadvantage for compounds with limited experimental

information. As indicated, this critical property was predicted using the method of Joback and Reid (1987) for several organic acids included in the database. Therefore, the Tc estimation could be a source of uncertainty in the surface tension prediction of several organic acids using these models. An additional analysis of GC1(T_r), GC2(T_r), and GC-CSP performance was conducted to verify the impact of this uncertainty source, and the results are presented in Table 4. For example, AAD and $RMSE$ values of GC-CSP model were 0.27% and 1.01 for organic acids with available experimental Tc values and 1.79% and 4.95 for those compounds where their Tc was calculated with Joback and Reid model. These findings confirmed that Tc estimation increased the errors for the surface tension calculation. In addition, the model performance was compared using the Tc predictions from the Constantinou and Gani (1994) group contribution model (also implemented in the

Table 1. *Description of the experimental database used for the group contribution models to calculate the surface tension of organic acids.*

				T, °C		σ, mN/m		
No.	Compound	CAS	N	Min	Max	Min	Max	T_c, °C
1	Formic acid	64-18-6	57	0	100.45	29	40.38	277.03
2	Acetic acid	64-19-7	134	10	280	2.71	29.3	319.52
3	Propionic acid	79-09-4	87	-35.1	300	1.91	32.4	329.41
4	Butyric Acid	107-92-6	86	0	163.35	14	29.2	350.81
5	Valeric acid	109-52-4	35	-20	207.85	11	30.79	366.55
6	Hexanoic acid	142-62-1	31	-20	132.3	17.16	31.2	389.80
7	Heptanoic acid	111-14-8	20	0	75.2	23.94	29.84	405.80
8	Octanoic acid	124-07-2	32	16.1	151.2	18.3	29.2	420.80
9	Nonanoic acid	112-05-0	11	20	180	16.7	29.7	438.79
10	Decanoic acid	334-48-5	20	20	151.2	19.2	29.17	448.78
11	Undecanoic acid	112-37-8	3	20	75	26.05	30.64	454.85
12	Lauric acid	143-07-7	31	44.4	141	20.8	28.71	469.85
13	Tridecanoic acid	638-53-9	2	70	75	27.19	27.36	473.44
14	Myristic acid	544-63-8	31	54.25	149.3	21	28.8	489.85
15	Pentadecanoic acid	1002-84-2	4	70	75	27.4	28.61	503.85
16	Palmitic acid	57-10-3	22	65	149.3	22.1	28.6	511.85
17	Heptadecanoic acid	506-12-7	7	66.9	141	22.5	29.26	518.85
18	Oleic acid	112-80-1	18	20	180	21.6	32.8	511.21
19	Stearic acid	57-11-4	16	70	150	22.7	28.96	529.85
20	Arachidic Acid	506-30-9	5	75.25	95	27.6	29.29	546.85
21	Acrylic acid	79-10-7	2	13	30	28.1	29.62	342.22
22	Isobutyric acid	79-31-2	42	-20	150	13.8	28.83	331.81
23	Isovaleric acid	503-74-2	26	0	175	12.6	27.33	355.81
24	2-Ethylhexanoic acid	149-57-5	1	20	20	27.8	27.8	401.45
25	Cyclopropanecarboxylic acid	1759-53-1	5	20	85.9	27.64	34.29	398.63
26	Levulinic acid	123-76-2	29	20	115	32.9	42.53	464.47
27	Benzoic acid	65-85-0	5	122.3	170	27	31.29	481.85
28	o-Toluic acid	118-90-1	6	140	200	25.7	31.7	489.85
29	4-Methylvaleric acid	646-07-1	17	15	132.3	17.16	27	389.50
30	Cyclobutanecarboxylic acid	3721-95-7	7	20	86.9	26.81	33.43	408.86
31	Vinylacetic acid	625-38-7	6	14.3	87.3	22.23	29.46	376.73
32	Brassidic acid	506-33-2	2	20	30	27.28	27.4	543.20
33	Docosanoic acid	112-85-6	7	30	95	27.61	37.61	640.44
34	2-Cyclopentyl valeric acid	5732-83-2	11	0	195.3	18.9	34.3	525.67
35	2-Ethylbutyric acid	88-09-5	2	-15	20	26.2	50.43	381.06
36	2-Nonenoic acid	3760-11-0	4	20	180	19.6	32.1	472.36
37	2,2,3-Trimethylcyclopent-3-ene-1-acetic acid	25435-53-4	10	20	200	19.62	35.12	470.51
38	2-Butyloctanoic acid	27610-92-0	1	70	70	25.48	25.48	526.93
39	2-Ethyldecanoic acid	2874-76-2	1	70	70	25.73	25.73	526.93
40	4-Methylundecanoic acid	20496-87-1	1	70	70	27.04	27.04	526.93
41	2-Propyldecanoic acid	60948-96-1	1	70	70	25.21	25.21	548.55
42	2-Butyldecanoic acid	52304-09-3	1	70	70	25.35	25.35	570.52
43	2-Butyldodecanoic acid	25354-95-4	1	70	70	26.4	26.4	481.33
44	2-Propyltetradecanoic acid	53705-91-2	1	70	70	26.1	26.1	489.30
45	2-Butyltetradecanoic acid	22890-20-6	1	70	70	26.55	26.55	496.74
46	2-Ethylhexadecanoic acid	54240-85-6	1	70	70	27.97	27.97	496.74
47	2-Octyldecanoic acid	619-39-6	1	70	70	26.15	26.15	662.96
48	2-Propylhexadecanoic acid	56256-90-7	1	70	70	27.28	27.28	687.47
49	Terephthalic acid	100-21-0	1	427	427	26.67	26.67	533.26
50	Fumaric acid	110-17-8	1	300	300	16.77	16.77	500.72
51	Diglycolic acid	110-99-6	1	148	148	52.26	52.26	546.67
52	Isophthalic acid	121-91-5	1	346	346	49.08	49.08	733.95
53	Pyruvic acid	127-17-3	1	13.6	13.6	47.56	47.56	358.74
54	DL-Tartaric acid	133-37-9	1	206	206	54.78	54.78	555.71
55	Acetoxyacetic acid	13831-30-6	1	90.65	90.65	54.2	54.2	420.68
56	Linolenic acid	463-40-1	1	-11.1	-11.1	36.18	36.18	515.17
57	Isocrotonic acid	503-64-0	1	15.5	15.5	27.46	27.46	370.35
58	Methoxyacetic acid	625-45-6	1	7.85	7.85	41.82	41.82	418.20
59	Malic acid	6915-15-7	1	130	130	26.66	26.66	508.03
60	Dodecanedioic acid	693-23-2	1	128	128	28.24	28.24	551.02
61	Salicylic acid	69-72-7	1	158	158	30.73	30.73	466.00

62	Glycolic acid	79-14-1	1	79.5	79.5	36.82	36.82	341.74
63	Phthalic acid	88-99-3	1	191	191	26.85	26.85	526.65
64	Pyromellitic acid	89-05-4	1	280.85	280.85	25.35	25.35	620.14
65	Itaconic acid	97-65-4	1	165.6	165.6	41.15	41.15	542.26
66	Ricinoleic acid	141-22-0	1	16	16	35.81	35.81	572.16
67	3,3-Dimethylacrylic acid	541-47-9	5	85	177	19.4	27.9	400.83
68	Nonadecanoic acid	646-30-0	2	70	75	28.63	29.57	535.97
69	2-Ethyldodecanoic acid	2874-75-1	1	70	70	26.36	26.36	570.52
70	2-Hexyloctanoic acid	60948-91-6	1	70	70	25.81	25.81	570.52
71	2-Methyltridecanoic acid	24323-31-7	1	70	70	27.54	27.54	570.52
72	2-Hexyldecanoic Acid	25354-97-6	1	70	70	26.45	26.45	481.81
73	alpha-Eleostearic acid	506-23-0	2	20	20	31.04	33.42	686.35
74	beta-Eleostearic acid	544-73-0	2	20	20	31.04	33.42	686.35
75	Elaidic Acid	112-79-8	1	20	20	26.56	26.56	510.19
76	Erucic Acid	112-86-7	1	20	20	28.56	28.56	553.79
77	2-Methylbutyric acid	116-53-0	1	-80.15	-80.15	38.62	38.62	368.75
78	m-Toluic acid	99-04-7	6	140	200	25.7	31.7	497.85

Table 2. *Performance of tested group contribution models for the calculation of the surface tension of organic acids.*

STATISTICAL METRICS

Model	RMSE	AAD ± SD, %	|PD| min, %	|PD| max, %
GC1	2.30	3.00 ± 5.48	6.08E-03	88.46
GC2	2.54	3.33 ± 6.18	2.55E-04	88.94
GC1(T_c)	2.29	3.05 ± 5.47	4.80E-03	89.62
GC2(T_c)	2.81	3.79 ± 7.02	2.65E-03	76.40
GC1(T_r)	1.99	3.80 ± 4.92	8.47E-03	68.77
GC2(T_r)	1.98	3.84 ± 4.71	1.32E-03	65.55
GC-CSP	2.60	5.08 ± 6.23	4.04E-04	76.09

Table 3. *Group contribution parameters for the calculation of surface tension of organic acids..*

| Group	GC1		GC2		GC1(T_c)		GC2(T_c)		GC1(T_r)	GC2(T_r)	GC-CSP
	a_{GC1}	b_{GC1}	a_{GC1}	b_{GC2}	a_{GC1}	b_{GC1}	a_{GC1}	b_{GC2}	c_{GC1}	c_{GC2}	d_i
	Non-ring groups										
(CHOOH)	39.424	0.102	40.172	-1.104	40.167	0.116	40.172	-1.103	82.411	8.592	38.409
(-COOH)	14.008	0.025	13.987	0.016	14.928	0.029	13.982	-2.30E-04	-28.353	3.533	16.799
(-CH3)	13.983	0.065	14.005	0.067	13.059	0.061	14.002	0.083	-22.019	3.097	12.229
(-CH2-)	0.333	-0.001	0.316	-0.002	0.322	-0.002	0.316	-0.002	0.100	-0.010	0.289
(=CH-)	0.687	-0.004	0.594	0.001	0.776	-0.003	0.593	0.008	-1.001	0.073	-0.021
(>C=)	-8.046	-0.071	4.071	-0.007	-7.836	-0.076	4.069	-0.014	11.560	-2.417	-9.697
(=CH2)	13.506	0.022	15.583	-1.112	14.483	0.052	15.583	-1.105	-23.937	3.222	12.489
(>CH-)	-15.392	-0.071	-15.562	-0.072	-14.604	-0.071	-15.565	-0.089	119.087	-3.344	-14.495
-O-	13.629	-0.063	13.612	-1.141	13.653	-0.073	13.611	-1.138	-26.696	1.635	15.490
-OH	13.043	0.045	19.259	0.047	11.974	0.042	19.263	0.061	-15.093	3.991	20.163
>C=O	16.082	0.020	15.911	0.017	16.121	0.024	15.906	0.015	-19.951	1.279	13.069
	Non-aromatic ring groups										
(=CH-)	-14.692	-2.859	-18.687	0.334	-11.661	2.350	-18.685	0.329	75.453	-3.665	-31.306
(-CH2-)	-1.354	-0.009	-1.651	-0.002	-0.890	-0.001	-1.650	0.003	5.774	-0.325	-0.999
(>CH-)	25.166	0.096	25.949	0.069	22.603	0.068	25.944	0.068	-44.917	4.463	19.266
(>C<)	-17.442	-0.331	-22.859	0.077	-14.266	-2.049	-22.856	0.063	32.449	-3.250	18.952
(>C=)	-11.148	2.971	-2.196	-1.778	-13.367	-0.492	-2.201	-1.789	81.722	-3.026	-27.160
	Aromatic ring groups										
(-CH=)	4.863	0.008	10.291	-0.184	4.176	0.005	10.291	-0.181	10.614	1.296	7.863
(>C=)	3.276	0.018	-21.157	-0.174	5.335	0.024	-21.157	-0.159	38.733	-2.194	-8.960
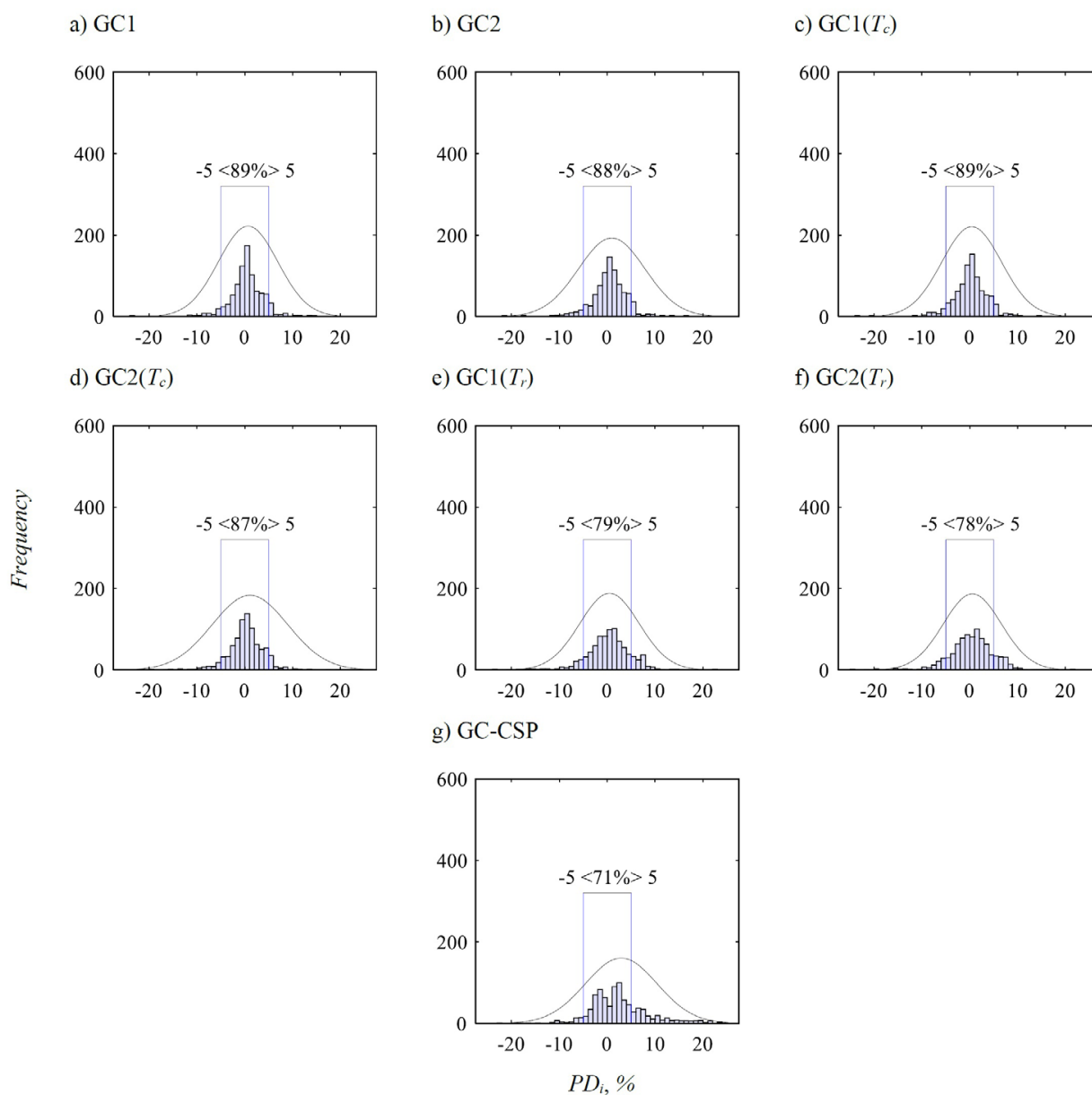
Figure 2. *Histogram of PD values of tested group contribution models for the calculation of surface tension of organic acids.*

Table 4. *Impact of critical temperature source on the performance of group contribution models for the calculation of surface tension of organic acids.*

Model	AAD, %	RMSE
GC-CSP with experimental Tc	0.27	1.01
GC-CSP with Tc calculated with Joback-Reid model	1.79	4.95
GC-CSP with Tc calculated with Constantinou-Gani model	2.16	5.42
GC1(T_r) with experimental Tc	0.22	1.04
GC1(T_r) with Tc calculated with Joback-Reid model	0.89	3.55
GC1(T_r) with Tc calculated with Constantinou-Gani model	1.05	3.98
GC2(T_r) with experimental Tc	0.23	1.07
GC2(T_r) with Tc calculated with Joback-Reid model	0.81	3.53
GC2(T_r) with Tc calculated with Constantinou-Gani model	1.02	4.08

a) GC1 b) GC2 c) GC1(T_c)

d) GC2(T_c) e) GC1(T_r) f) GC2(T_r)

g) GC-CSP

○ Correlation

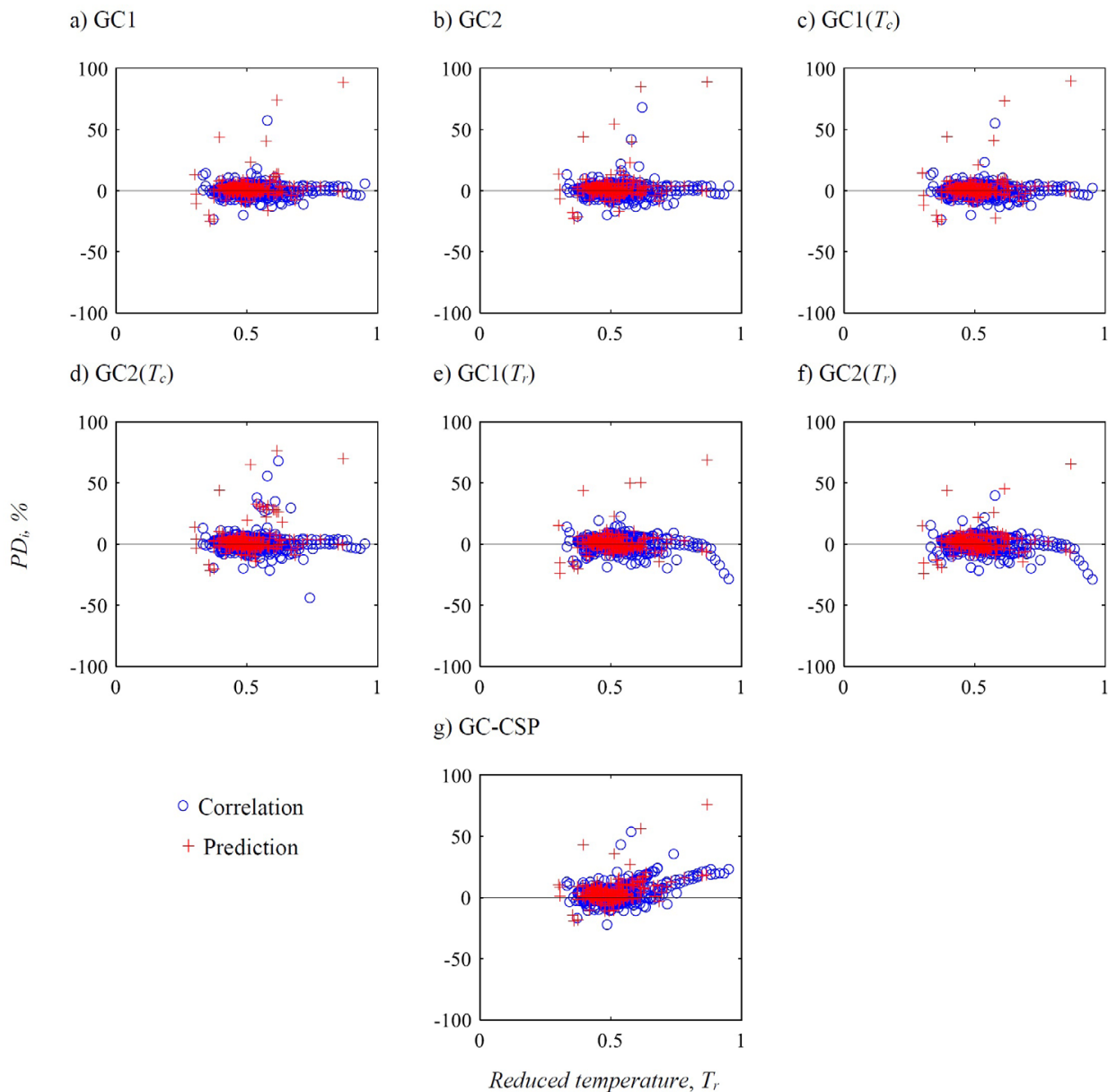+ Prediction

PD$_i$, %

Reduced temperature, T$_r$

Figure 3. *PD values of tested group contribution models for the surface tension calculation of organic acids as a function of reduced temperature (T$_r$).*

Aspen Plus ® simulator). In this case, the GC-CSP model exhibited *AAD* and *RMSE* values of 2.16% and 5.42, respectively. These calculations proved that the source of *Tc* estimation could affect the surface tension prediction using *Tc*-based models such as those derived from the theory of corresponding states. Similar results were obtained for GC1(T_r) and GC2(T_r) models, which depended on T_r, see Table 4.

On the other hand, GC1, GC1(T_c), GC2 and GC2(T_c) models showed a distribution of modeling errors similar to a normal distribution where 87 − 89 % of the surface tension data was calculated with *PD* values of ±5%, see Figure 2. GC1(T_r) and GC2(T_r) group contribution models calculated 79 and 78% of the surface tension data, respectively, with a *PD* value of ±5%. It was also confirmed that the GC-CSP model displayed the worst performance, with 71% of the surface tension calculations having *PD* of ±5%. The

performance of tested surface tension models with respect to the reduced temperature ($T_r = T/Tc$) is shown in Figure 3. The modeling errors varied depending on the T_r region. The surface tension database contained a significant amount of experimental data at 0.30 < Tr < 0.75 where *PD* values ranged from 2.55E-04 to 84.76% for these group contribution models. It was also confirmed that the highest errors for the calculation of surface tension were obtained by all the models near to the critical point (i.e., $T_r \rightarrow 1$) particularly for those group contribution models where *Tc* was an input variable. For T_r > 0.75, the models followed the next trend in terms of *AAD* for the surface tension calculation: GC-CSP > GC2(T_r) > GC1(T_r) > GC1 > GC2 > GC1(Tc) > GC2(Tc). However, it was clear that GC-CSP was outperformed by the other group contribution models at all *Tr* values, see Figures 1 − 3.

Table 5. *Performance of group contribution models for the calculation of surface tension of different organic acid families.*

Family	Statistical metrics	Group contribution models						
		GC1	GC2	GC1(T$_c$)	GC2(T$_c$)	GC1(T$_r$)	GC2(T$_r$)	GC-CSP
N-aliphatic acids	±1% PD_i	32.19	31.57	31.26	31.57	22.24	20.53	14.46
	±5% PD_i	87.56	87.71	87.09	86.94	73.09	73.87	75.12
	±10% PD_i	98.76	98.76	98.76	98.76	96.58	97.05	88.80
	$AAD \pm DE$	2.51 ± 2.33	2.56 ± 2.33	2.57 ± 2.35	2.59 ± 2.37	3.49 ± 3.33	3.52 ± 3.28	4.27±4.57
	PD_i min	0.02	2.55E-04	4.80E-03	2.65E-03	8.47E-03	1.32E-03	4.04E-04
	PD_i max	20.05	19.96	20.00	19.97	28.46	28.89	24.23
Other aliphatic acids	±1% PD_i	43.89	25.00	37.78	28.89	20.56	18.33	5.00
	±5% PD_i	83.89	82.22	86.67	78.33	83.89	82.78	55.56
	±10% PD_i	94.44	93.89	95.56	91.67	93.89	95.00	85.00
	$AAD \pm DE$	2.98 ± 5.03	3.49 ± 5.03	3.01 ± 5.01	3.90 ± 5.84	3.70 ± 4.81	3.56 ± 4.54	5.79±5.46
	PD_i min	0.01	3.44E-03	5.19E-03	6.30E-03	3.65E-02	0.02	1.12E-01
	PD_i max	43.56	43.91	44.00	43.99	43.70	43.77	43.13
Polyfunctional acids	±1% PD_i	15.79	15.79	18.42	15.79	2.63	2.63	2.63
	±5% PD_i	78.95	78.95	78.95	81.58	76.32	71.05	31.58
	±10% PD_i	84.21	86.84	86.84	89.47	84.21	81.58	84.21
	$AAD \pm DE$	5.98 ± 11.47	5.90 ± 11.16	5.87 ± 11.04	6.16 ± 13.52	5.95 ± 9.07	6.26 ± 8.48	8.71±10.22
	PD_i min	0.16	1.67E-02	0.05	0.51	0.98	0.96	2.25E-01
	PD_i max	57.43	54.51	55.10	64.97	49.79	39.72	53.81
Aromatic acids	±1% PD_i	28.57	0.00	14.29	0.00	4.76	0.00	9.52
	±5% PD_i	66.67	19.05	57.14	0.00	61.90	19.05	28.57
	±10% PD_i	66.67	61.90	85.71	0.00	90.48	90.48	42.86
	$AAD \pm DE$	11.87 ± 23.77	19.60 ± 27.00	12.07 ± 23.73	32.20 ± 17.56	9.03 ± 17.13	10.89 ± 15.27	13.82±18.26
	PD_i min	0.13	1.89	0.11	13.82	0.60	2.74	0.41
	PD_i max	88.46	88.94	89.62	76.40	68.77	65.55	76.09
Dicarboxylic acids	±1% PD_i	0.00	0.00	33.33	0.00	0.00	33.33	0.00
	±5% PD_i	33.33	33.33	33.33	33.33	33.33	33.33	0.00
	±10% PD_i	66.67	33.33	66.67	33.33	66.67	66.67	33.33
	$AAD \pm DE$	8.25 ± 8.44	11.47 ± 9.84	9.83 ± 11.90	28.22 ± 22.36	11.00 ± 10.77	10.30 ± 10.67	28.59±19.17
	PD_i min	1.91	2.34	0.76	2.63	1.25	0.74	6.90
	PD_i max	17.84	21.89	23.30	0.00	22.56	21.80	43.27
Overall	±1% PD_i	33.67	28.70	31.64	29.49	20.56	18.87	11.86
	±5% PD_i	85.76	84.41	85.76	82.71	75.03	74.12	67.91
	±10% PD_i	96.38	96.16	97.18	94.35	95.25	95.71	86.55
	$AAD \pm DE$	3.00 ± 5.48	3.33 ± 6.18	3.05 ± 5.47	3.79 ± 7.02	3.80 ± 4.92	3.84 ± 4.71	5.08±6.23
	PD_i min	0.01	2.55E-04	4.80E-03	2.65E-03	8.47E-03	1.32E-03	4.04E-04
	PD_i max	88.47	88.94	89.62	76.40	68.77	65.55	76.09

Table 5 shows a modeling error analysis of surface tension considering the 5 subfamilies of tested organic acids: a) 21 N-aliphatic acids, b) 37 other aliphatic acids, c) 10 polyfunctional acids, d) 7 aromatic acids and e) 3 dicarboxylic acids. *PD* values for the calculation of surface tension ranged from 2.55E-04 to 28.89, 3.44E-03 to 44.00, 1.67E-02 to 64.97, 0.11 to 89.62 and 0.74 to 43.27 % for N-aliphatic, other aliphatic, polyfunctional, aromatic and dicarboxylic acids, respectively. In general, these group contribution models showed the following trend (based on *AAD*) to calculate the surface tension of organic acid families:

GC1: N-aliphatic < other aliphatic < polyfunctional < dicarboxylic < aromatic

GC1(*Tc*): N-aliphatic < other aliphatic < polyfunctional < dicarboxylic < aromatic

GC1(*T$_r$*): N-aliphatic < other aliphatic < polyfunctional < aromatic < dicarboxylic

GC2: N-aliphatic < other aliphatic < polyfunctional < dicarboxylic < aromatic

GC2(*Tc*): N-aliphatic < other aliphatic < polyfunctional < dicarboxylic < aromatic

GC2(*T$_r$*): N-aliphatic < other aliphatic < polyfunctional < dicarboxylic < aromatic

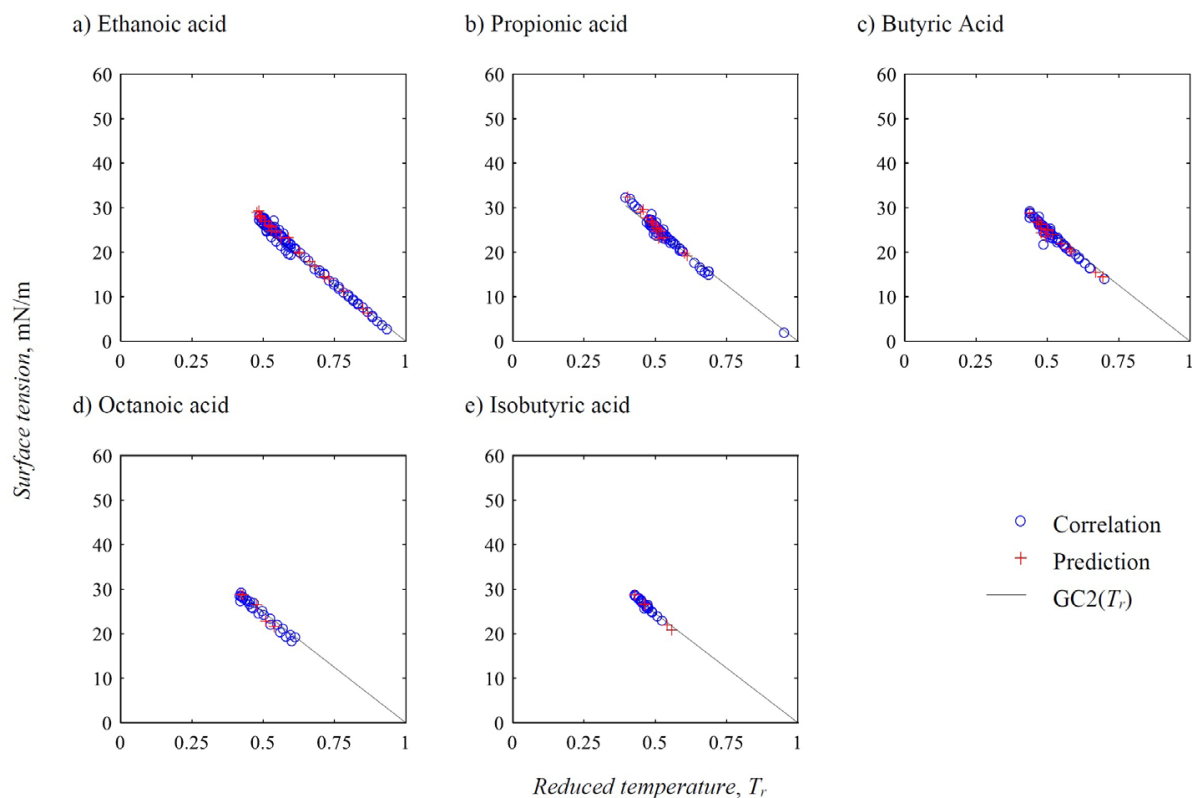GC-CSP: N-aliphatic < other aliphatic < polyfunctional < aromatic < dicarboxylic

Figure 4. *Experimental and calculated surface tension of organic acids using GC2(T_r) model. a) Ethanoic acid, b) Propionic acid, c) Butyric Acid, d) Octanoic acid and e) Isobutyric acid.*

The surface tension of N-aliphatic and other aliphatic organic acids was calculated with the lowest modeling error where more than 82% of the data were obtained with *PD* values of ±5% using GC1 and GC2. Their counterparts, that is $GC(Tc)$ and $GC(T_r)$, showed a similar performance, while an acceptable performance to calculate the surface tension of N-aliphatic acids was obtained by GC-CSP model, but it provided estimations with more uncertainty for the family of other aliphatic acids, see Table 5. The calculation of surface tension of aromatic and dicarboxylic acids achieved the highest *PD* values (e.g., up to 89.6% for the p-benzenedicarboxylic acid) for all tested group contribution models. In general, $GC1(Tc)$ outperformed other group contribution models with ±10% *PD* values for 97% of its surface tension calculations, while GC-CSP was the worst to calculate this thermodynamic property, with 87% of its calculations corresponding to *PD* values of ±10%.

Finally, it was analyzed the estimation of *Tc* using the group contribution parameters (i.e., *A* and *B*) of the GC1, GC2, GC1(*Tc*) and GC2(*Tc*) models that were obtained from the Jasper equation, see Eq. (1). This analysis was performed to assess the thermodynamic consistency of these models to satisfy the critical point condition. Organic acids with available *Tc* experimental values were included in this analysis. It was found that these models estimated the values of *Tc* with errors from 0.11 and up to 2200 % where GC2 model had the worst performance in estimating

the *Tc* of tested organic acids. GC1(*Tc*) model was the best for the *Tc* prediction using *A* and *B* parameters.

Based on these results, the $GC2(T_r)$ model was identified as the best group contribution model to predict the surface tension of organic acids where Figure 4 exemplifies its performance for selected organic acids.

4. CONCLUSIONS.

This study reports the performance of group contribution models in the calculation and prediction of the surface tension of organic acids. Special emphasis has been placed on analyzing the incorporation of the critical point restriction in the calculation of the surface tension of these compounds. This restriction was incorporated as a penalty term in the objective function utilized for the group contribution determination and also via the reduced temperature as input variable of these models. The results showed that the incorporation of the reduced temperature in the group contribution model allowed for better surface tension estimations for this family of organic compounds. It was also found that the performance of these models was sensitive to the source of critical temperature of the organic acid, and the experimental values improved the calculation of its surface tension. The set of tested group contribution models was able to correctly calculate the surface tension of N-aliphatic organic acids obtaining modeling errors

lower than 5%. However, all the models failed to calculate the surface tension of dicarboxylic and aromatic organic acids, which showed the highest deviations for this thermodynamic property. The prediction of surface tension of dicarboxylic and aromatic organic acids was challenging and, consequently, future studies should focus on the development of second or third-order group contribution models to handle the modeling of this thermodynamic property of these organic compounds.

REFERENCES.

1. Batt C.A., Patel P. Encyclopedia of Food Microbiology. Academic Press (2014).
2. Cachadiña I., Hernández A., Mulero A. Surface tension of esters. Temperature dependence of the influence parameter in density gradient theory with Peng-Robinson equation of state. Case Studies in Thermal Engineering 36 (2022) 102193.
3. Cachadiña I., Mulero A. A New corresponding-states model for the correlation and prediction of the surface tension of organic acids. Industrial and Engineering Chemistry Research 59 (2020) 8496-8505
4. Ceriani R., Gonçalves C.B., Coutinho J.A.P. Prediction of Viscosities of Fatty Compounds and Biodiesel by Group Contribution. Energy and Fuels 25 (2015) 3712–3717.
5. Constantinou L., Gani R. New group contribution method for estimating properties of pure compounds. AIChE Journal 40 (1994) 1697–1710.
6. Cunico L. P., Hukkerikar A.S., Ceriani R., Sarup B., Gani R. Molecular structure-based methods of property prediction in application to lipids: A review and refinement. Fluid Phase Equilibria 357 (2013) 2–18.
7. Di Nicola G., Coccia G., Pierantozzi M. A new equation for the surface tension of carboxylic acids. Fluid Phase Equilibria 417 (2016) 229–236.
8. Di Nicola G., Moglie M. A generalized equation for the surface tension of refrigerants. International Journal of Refrigeration 34 (2011) 1098-1108.
9. Díaz-Tovar C.A., Gani R., Sarup B. Lipid technology: Property prediction and process design/analysis in the edible oil and biodiesel industries. Fluid Phase Equilibria 302 (2011) 284–293.
10. Enomoto H., Sato K., Miyamoto K., Ohtsuka A., Yamane H. Distribution Analysis of Anthocyanins, Sugars, and Organic Acids in Strawberry Fruits Using Matrix-Assisted Laser Desorption/Ionization-Imaging Mass Spectrometry. Journal of Agricultural and Food Chemistry 66 (2018) 4958–4965.
11. Faúndez C.A., Campusano R.A., Valderrama J.O. Misleading results on the use of artificial neural networks for correlating and predicting properties of fluids. A case on the solubility of refrigerant R-32 in ionic liquids. Journal of Molecular Liquids 298 (2020) 112009.
12. Gani R. Group contribution-based property estimation methods: advances and perspectives. Current Opinion in Chemical Engineering 23 (2019) 184-196.
13. Gharagheizi F., Eslamimanesh A., Sattari M., Mohammadi A.H., Richon D. Development of corresponding states model for estimation of the surface tension of chemical compounds. AIChE Journal 59 (2012) 613–621.
14. Gotoh K. The role of liquid penetration in detergency of long-chain fatty acid. Journal of Surfactants and Detergents 8 (2005) 305–310.
15. Jasper J.J. The surface tension of pure liquid compounds. Journal of Physical and Chemical Reference Data 1 (1972) 841-1010.
16. Joback K., Reid R. Estimation of pure-component properties from group-contributions. Chemical Engineering Communications 57 (1987) 233–243.
17. Knotts T.A., Wilding W.V., Oscarson J.L., Rowley R.L. Use of the DIPPR Database for Development of QSPR Correlations: Surface Tension. Journal of Chemical Engineering Data 46 (2001) 1007–1012.
18. Lu J., Lv Y., Qian X., Jiang Y., Wu M., Zhang W., Zhou J., Dong W., Xin F., Jiang M. Current advances in organic acid production from organic wastes by using microbial co-cultivation systems. Biofuels, Bioproducts and Biorefining 14 (2019) 481–492.
19. Lund E.K. Health benefits of seafood; Is it just the fatty acids? Food Chemistry 140 (2013) 413–420.
20. Mulero A., Cachadiña I., Sanjuán E.L. Recommended Correlations for the Surface Tension of Aliphatic, Carboxylic, and Polyfunctional Organic Acids. Journal of Physical and Chemical Reference Data 45 (2016) 033105.
21. Mulero A., Cachadiña I., Cardona L., Valderrama J.O. Pressure–Surface Tension–Temperature Equation of State for n-Alkanes. Industrial and Engineering Chemistry Research 61 (2022) 3457-3473.
22. Naef R., Acree W. Calculation of the Surface Tension of Ordinary Organic and Ionic Liquids by Means of a Generally Applicable Computer Algorithm Based on the Group-Additivity Method. Molecules 23 (2018) 1224.
23. Ng W.K., Koh C.B. The utilization and mode of action of organic acids in the feeds of cultured aquatic animals. Reviews in Aquaculture 9 (2016) 342–368.
24. Pérez-Cisneros E.S., Mena-Espino X., Rodríguez-López V., Sales-Cruz M., Viveros-García T., Lobo-Oehmichen R. An integrated reactive distillation process for biodiesel production. Computers & Chemical Engineering 91 (2016) 233–246.
25. Pierantozzi M., Mulero N., Cachadiña I. Surface Tension of Liquid Organic Acids: An Artificial Neural Network Model. Molecules 26 (2021) 1636.
26. Sattari M., Bakare B.F. A novel method for developing a corresponding states model for the prediction of liquid surface tension of gases. Fluid Phase Equilibria 465 (2018) 107-116.
27. Wohlfarth C., Wohlfarth B. Surface Tension of Pure Liquids and Binary Liquid Mixtures. Springer (1997).

28. Wohlfarth C. Surface Tension of Pure Liquids and Binary Liquid Mixtures, Supplement to Volume IV/16. Springer (2008).
29. Wohlfarth C. Surface Tension of Pure Liquids and Binary Liquid Mixtures: Supplement to Volume IV/24. Springer (2016).
30. Yang S., Tia, J., Jiang H. Corresponding state principle based correlation for the surface tension of carboxylic acids. Fluid Phase Equilibria 506 (2020) 112421.
31. Zhang C., Tian J., Zheng M., Yi H., Zhang L., Liu S. A new corresponding state-based correlation for the surface tension of organic fatty acids. Modern Physics Letters B 32 (2018) 1750361.