

# Fluid Phase Equilibria

## Modeling phase equilibria in mixtures of mono- and dicarboxylic acids with hydrocarbons --Manuscript Draft--

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<b>Abstract:</b>	<p>In this work, a group contribution equation of state that specifically takes into account association effects (GCA-EOS) is extended to model mono- and di-carboxylic acids and their mixtures with alkanes, alkenes, and cycloalkanes. Given the predominant effect of association on the behavior of these mixtures, the acid monomer fractions in the liquid and vapor phases are set as a restriction in the parameterization of the model. The parameters are correlated with a databank comprising 1800 experimental points on phase equilibria and infinite dilution activity coefficients data, which encompass a temperature and pressure range of 236-524 K and 0.001-60 bar, respectively. The new set of GCA-EOS parameters allows a good prediction of vapor-liquid, liquid-liquid, and solid-liquid equilibrium conditions, as well as infinite dilution activity coefficients of binary and ternary mixtures containing monocarboxylic acids and hydrocarbons. We also show that this parameterization allows a qualitative and in some cases quantitative prediction of pure dicarboxylic acids and its mixtures with other acids and hydrocarbons.</p>
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Dear Luis, Mariana, and Pedro,

Please find enclosed the manuscript "Modeling phase equilibria in mixtures of mono- and dicarboxylic acids with hydrocarbons" by Francisco A. Sanchez, Alfonsina E. Andreatta and Selva Pereda, submitted for publication to the EQUIFASE 2022 special issue of Fluid Phase Equilibria.

We apologize for the delay in submitting the manuscript, which was intended to be submitted prior to March 15th. However, due to unforeseen circumstances, we experienced a delay in completing the manuscript. We appreciate your understanding and hope that this submission will be acceptable for review.

Thank you for your consideration.

Best regards,

Francisco

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## Modeling phase equilibria in mixtures of mono- and di-carboxylic acids with hydrocarbons

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### Abstract

In this work, a group contribution equation of state that specifically takes into account association effects (GCA-EOS) is extended to model mono- and di-carboxylic acids and their mixtures with alkanes, alkenes, and cycloalkanes. Given the predominant effect of association on the behavior of these mixtures, the acid monomer fractions in the liquid and vapor phases are set as a restriction in the parameterization of the model. The parameters are correlated with a databank comprising 1800 experimental points on phase equilibria and infinite dilution activity coefficients data, which encompass a temperature and pressure range of 236-524 K and 0.001-60 bar, respectively. The new set of GCA-EOS parameters allows a good prediction of vapor-liquid, liquid-liquid, and solid-liquid equilibrium conditions, as well as infinite dilution activity coefficients of binary and ternary mixtures containing monocarboxylic acids and hydrocarbons. We also show that this parameterization allows a qualitative and in some cases quantitative prediction of pure dicarboxylic acids and its mixtures with other acids and hydrocarbons.

**Keywords:** carboxylic acid; dicarboxylic acids; hydrocarbons; association; hydrogen bonding; GCA-EOS; group contribution

## 1. Introduction

Carboxylic acids are present in a wide range of industrial processes, including the production of nylon, biodegradable plastics, soaps and detergents, and pharmaceuticals. They have applications as corrosion inhibitors, food preservatives, surfactants and metal finishing compounds [1,2]. Low molecular weight carboxylic acids appear in a variety of industrial waste streams, from which they must be recovered, preventing pollution and generating a profit [3]. On the other hand, high molecular weight carboxylic acids (i.e. fatty acids) derived from fats and oils, are raw materials in the production of coverings, surfactants, plastics, and cleaning products [4].

Dicarboxylic acids are also compounds of industrial importance. Azelaic acid, for example, is a raw material used in the manufacture of added value products, such as plasticizers, polyurethanes, polyamides lubricants, nylon, capacitors, skin drugs among others [5]. The versatile properties of dicarboxylic acids make them important ingredients in the production of various commodities and specialty chemicals [6]. Moreover, the increased interest in biomass processing enhances the role of dicarboxylic acids, such as succinic or adipic, and other polyfunctional acids such as levulinic and lactic acids, as building blocks for the chemical industry of the future [7–9].

Knowledge of the phase behavior of organic acid mixtures is required to design and operate efficiently the separation units involved in their processing. In particular, crystallization and extractive crystallization processes are applied for separating mixtures containing dicarboxylic and fatty acids [10,11]. Therefore, not only knowledge on fluid phase equilibrium but also on solid-fluid equilibrium (SLE) is needed. Furthermore, the knowledge of the phase equilibria and thermodynamic properties is mandatory for reacting systems containing carboxylic acids such as esterifications, which are reversible reactions, in conventional reactors as well as reactive distillation [12].

The strength of hydrogen bonds in carboxylic acids causes that short chain carboxylic acids substantially deviate from ideal gas behavior, even at very low pressure, due to the formation of dimers even in the vapor phase. It is worth highlighting that theoretical and experimental evidences show that association does not go beyond the formation of dimers, mainly because steric hindrance, which prevents the conformation of higher oligomers [13].

Various approaches have been used in the literature to model carboxylic acids. Table 1 summarizes a literature review of articles modeling carboxylic acids, either pure or in mixtures with hydrocarbon. The firsts apply the classical activity coefficient models [2,14–28] or classical cubic equations of state (EOS) [29,30]. However, when dealing with vapor-liquid equilibria (VLE) of carboxylic acids, such models fail describing the vapor phase due to the dimerization of low molecular weight acids, which reduces almost to half the compressibility factor of pure carboxylic acid.

In this regard, advanced EOSs that take explicitly into account the hydrogen bonding formation offer a clear advantage over classical models. Most of these models belong to either the chemical theory [13,18,20,31–33] or statistical association fluid theory (SAFT) [34] family [29,35–50], which is derived from the thermodynamic perturbation theory of Wertheim [51]. Within these studies, several authors [39,40,42,47] discuss the best association scheme for carboxylic acids, modeling these mixtures with the 1A scheme (one single association site, able to cross- and self-associate), 2B scheme (one negative and one positive association sites), and even more complex approaches mixing both schemes [37]. In general, the conclusion is that the 1A association scheme offers the best performance taking into account precision and simplicity [52]. Nonetheless, there are more recent theoretical works that refine the Wertheim TPT in order to include the specific effect of molecular dimerization [39,53] in more realistic association schemes, which distinguish electronegative and positive association sites. These studies improve the model capabilities at expenses of the simplicity of solving monomer fraction for the 1A scheme. The literature review depicts that only few articles assess the modeling of the family of carboxylic acids thoroughly. As Table 1 shows, most contributions deal with a specific binary system, four of them model the normal carboxylic acid homologous family [41,42,49,50] but only the pure compound properties (vapor pressure and density). Up to our knowledge, Nguyen-Hyun and Mai [42] are the only authors that research a comprehensive database. They first model vapor pressure and density of carboxylic acids from acetic acid up to  $nC_{20}$  using the modified GC-PCP-SAFT, renamed as mg-SAFT, which is a homosegmented GC model. The authors model acetic acid molecularly, as is usually done in GC approach with the first members of any series, and by GC the rest of the members.

The aim of this work is to develop a thermodynamic model able to predict the phase behavior of mixtures containing a variety of organic acids in the context of biomass

valorization and processing, under a wide range of conditions and for different phase equilibrium types. In this sense, a group contribution (GC) approach model allows predicting phase behavior of systems for which experimental information is scarce or even not available, such as complex molecules derived from bioresources. For this purpose, the Group Contribution with Association EOS (GCA-EOS) [54] is extended to fluid-fluid and solid-fluid equilibria in mixtures containing monocarboxylic acids with alkanes, alkenes and cycloalkanes. Moreover, we evaluate the capabilities of the model to predict the phase behavior of dicarboxylic acids in both pure and binary mixtures with paraffins from the same regressed parameters. It worth noting that we follow a complete GC-approach; that is, without the introduction of new parameters or special groups for these molecules.

**Table 1.** Summary of thermodynamic modeling of carboxylic acid mixtures.

Thermodynamic model	Source	Model association	Systems
<i>Activity coefficient (<math>G^E</math>)</i>			
<b>Margules / van Laar</b>	Gao et al. [14]	no	VLE methanol + ethanoic and propanoic acids
<b>Wilson</b>	Giles & Wilson [21]	chemical theory dimerization in vapor phase	VLE propanoic + butanoic acids
	Malijevska et al. [23]	no	SLE acetic-propanoic
	Malijevska et al. [24]	chemical theory dimerization in vapor phase	VLE ethanoic + cyclohexane
	Yang et al. [25]	chemical theory (Hayden-O'Connell fug. coef. [55]) in vapor phase	VLE ethanoic + cyclohexane
	Wang et al. [26]	no	SLE fatty acids
	Gao et al. [14]	no	VLE methanol + ethanoic and propanoic acids
<b>modified Wilson</b>	Clifford et al. [2]	chemical theory dimerization in both phases	VLE propionic, butyric, valeric
	Malijevska et al. [24]	chemical theory dimerization in vapor phase	VLE ethanoic + cyclohexane
<b>Redlich-Kister</b>	Malijevska et al. [27]	no	SLE ethanoic + cyclohexane
	Malijevska et al. [24]	chemical theory dimerization in vapor phase	VLE ethanoic + cyclohexane
	Giles & Wilson [21]	chemical theory dimerization in vapor phase	VLE propanoic + butanoic acids
<b>NRTL</b>	Yang et al. [25]	chemical theory (Hayden-O'Connell fug. coef. [55]) in vapor phase	VLE ethanoic + cyclohexane
	Wang et al. [26]	no	SLE fatty acids
	Sewnarain et al. [28]	chemical theory (Hayden-O'Connell fug. coef. [55]) in vapor phase	VLE acid + acid (propanoic-hexanoic)
	Miyamoto et al. [15–17]	chemical theory dimerization in vapor phase	VLE acid + acid, + HC
<b>UNIQUAC</b>	Yang et al. [25]	chemical theory (Hayden-O'Connell fug. coef. [55]) in vapor phase	VLE ethanoic + cyclohexane
<b>UNIQUAC associated solution</b>	Nagata et al. [18]	chemical theory dimerization	VLE of formic-propanoic acids + HCs and its chlorides.
<b>UNIQUAC-A</b>	Fu & Sandler [35]	Wertheim association in liquid phase + chemical theory (Hayden-O'Connell fug. coef. [55]) in vapor phase	VLE ethanoic & propanoic acids with HC, ethanol, water in binary and ternary mixtures
	Plesnar et al. [19]		VLE acetic acid + octane
<b>UNIFAC</b>	Plesnar et al. [19]	chemical theory (Hayden-O'Connell fug. coef. [55]) in vapor phase	VLE acetic acid + octane
<b>A-UNIFAC</b>	Fu et al. [43]	Wertheim association in liquid phase + chemical theory (Hayden-O'Connell fug. coef. [55]) in vapor phase	VLE acetic/valeric acids + HC, and water + acetic/propanoic acid
	Ferreira et al. [44]		VLE acetic-pentanoic acids + <i>n</i> -alkanes, alcohols, esters and water.
<b>DISCUAQ</b>	González et al. [20]	Quasichemical theory	VLE, SLE and $h^E$ of carboxylic acids + HC
<i>Equations of state</i>			
<b>PHCT</b>	Grenzheuser & Gmehling [31]	Chemical theory	VP, $\Delta_{\text{vap}}h$ , and sat. volumes of C <sub>1</sub> -C <sub>7</sub> acids. VLE of carboxylic acid + paraffins and other systems.
<b>Anderko-Yu</b>	Anderko [32]	Chemical theory	VP, $\Delta_{\text{vap}}h$ , and $v^L$ of acetic acid.



<b>Twu-Cunningham</b>	Twu et al. [33]	Chemical theory	VP, $\Delta_{\text{vap}}h$ and $Z^V$ of acetic acid.
<b>PR + WS-NRTL</b>	Valtz et al. [29]	No	VP of hexanoic acid, + VLE with cyclohexane.
<b>PRSV + WS-NRTL</b>	Navarro-Espinosa [30]	No	VLE of acetic acid + methanol or ethanol
<b>MH</b>	Nan et al. [56]	Chemical theory	VLE & $h^E$ of acids + HCs and + acids
<b>NRHB</b>	Tsvintzelis et al. [53]	Veytsman's statistics + specific dimerization contribution	pure acid properties (VP, $\Delta h_{\text{vap}}$ and $Z^V$ ); binary VLE & $h^E$ acids + HC, acids + acids
<b>PHSC-AS</b>	Lee and Kim [45]	Wertheim TPT, 1A	VP of acetic and hexanoic acid, and LLE with $nC_{10}$ and water.
<b>GCA</b>	Ferreira et al. [46]	Wertheim TPT, 1A	VLE and $Z^V$ of organic acids (acetic-octanoic) + HCs, and other organics.
<b>CPA</b>	Derawi et al. [47]	Wertheim TPT, 1A vs 2B	VP and density of formic, acetic and propanoic acids, VLE with HCs, and LLE with $nC_{10}$ . Evaluate different association schemes.
	Muro-Suñé [48]	Wertheim TPT, 1A	LLE of acetic acid with HCs + other systems.
<b>GC-SAFT-VR</b>	dos Ramos et al. [49]	Wertheim TPT, 4B	VP of butanoic-eicosanoic acids; VLE acid + acid.
<b>SAFT-<math>\gamma</math></b>	Lymperiadis et al. [50]	Wertheim TPT, 3B	VP and liquid density of $C_3$ - $C_{16}$ carboxylic acids. VLE petanoic + $nC_7$
<b>SAFT-<math>\gamma</math>-Mie</b>	Dufal et al. [36]	Wertheim TPT, 5B	VP and liquid density of $C_4$ - $C_{12}$ carboxylic acids. VLE petanoic + $nC_7$
	Sadeqzadeh et al. [37]	Wertheim TPT, 5B	VP, liquid density, $\Delta_{\text{vap}}h$ of $C_4$ - $C_{10}$ carboxylic acids. VLE acid + n-alkane, acetone, water, ternary LLE water+acetone+butanoic acid
<b>PC-SAFT</b>	Yushu et al. [38]	Wertheim TPT, 2B	VLE water + acetic acid, propionic, or acrylic acid.
	Janeček et al. [39]	Wertheim TPT + dimerization term	VLE formic, acetic, and propanoic, with water and short chain alcohols.
<b>sPC-SAFT</b>	Ribeiro et al. [40]	Wertheim TPT. 1A and 2B schemes	Study of several acetic acid pure-compound properties (VP, saturated density, $\Delta_{\text{vap}}h$ , $c_p$ , etc.), VLE + water, ethanol, $nC_6$ .
<b>PCP-SAFT</b>	Valtz et al. [29]	Wertheim TPT, 1A	VLE hexanoic acid + cyclohexane
	Albers et al. [41]	Wertheim TPT, B2	VP and liquid density, $C_1$ - $C_{14}$ acids. Parameters from correlations and ab initio. VLE, LLE $nC_9$ y $nC_{12}$ + acetic acid.
<b>mg-SAFT</b>	Nguyen-Hyun & Mai [42]	Wertheim TPT. 1A and 2B schemes	VLE + LLE of carboxylic acids + HCs, and other organics.
<b>Theoretical works</b>			
<b>Molecular dynamics</b>	Vahid & Elliot [57]	SPEADM molecular simulation and TPT modeling from theoretical parameters	VP of carboxylic acids and VLE with water
<b>Ab-initio</b>	Vawdrey et al. [58]	B3LYP (ab initio)	Prediction of dimerization constants

$c_p$ : heat capacity;  $h^E$ : excess enthalpy;  $\Delta_{\text{vap}}h$ : vaporization enthalpy; HC: hydrocarbons; LLE: liquid-liquid equilibria; SLE: solid-liquid equilibria; TPT: thermodynamic perturbation theory; VP: vapor pressure; VLE: vapor-liquid equilibria;  $Z^V$ : vapor phase compressibility factor.

## 2. Thermodynamic model

The GCA-EOS [54] is an extension of the GC-EOS [59] to associating mixtures. The original GC-EOS is based on the generalized van der Waals partition function. Briefly, in the GCA-EOS there are three contributions to the Helmholtz residual energy:

$$A^R = A^{\text{fv}} + A^{\text{att}} + A^{\text{assoc}} \quad (1)$$

The repulsive or free volume contribution ( $A^{\text{fv}}$ ) is represented by the Mansoori-Leeland-Carnahan-Starling equation for hard spheres [60], which is characterized by the critical hard-sphere diameter ( $d_c$ ) of each pure compound; and a reference temperature, usually the experimental critical temperature ( $T_c$ ). The attractive contribution ( $A^{\text{att}}$ ) is based on the van der Waals equation, combined with the local composition principle based on a group contribution approach. This term is characterized by the number of surface segments of each group ( $q_i$ ), and the surface energy ( $g_{ii}$ ), which is temperature dependent. Furthermore, each binary group interaction is characterized by one interaction parameter ( $k_{ij}$ ), which may be also temperature dependent; and two binary damping constant factors ( $\alpha_{ij} \neq \alpha_{ji}$ ). Detailed expressions for  $A^{\text{fv}}$  and  $A^{\text{att}}$  are given elsewhere [59]. Finally, the association ( $A^{\text{assoc}}$ ) term is a GC version of the SAFT equation developed by Chapman et al. [34]:

$$\frac{A^{\text{assoc}}}{RT} = \sum_{i=1}^{NGA} n_i^* \left[ \sum_{k=1}^{M_i} \left( \ln X_{ki} - \frac{X_{ki}}{2} \right) + \frac{M_i}{2} \right] \quad (2)$$

where  $NGA$  represents the number of associating functional groups,  $n_i^*$  is the total number of moles of associating group  $i$ ,  $X_{ki}$  the fraction of group  $i$  non-bonded through site  $k$ , and  $M_i$  the number of associating sites in group  $i$ . The total number of moles of associating group  $i$  is calculated from the number  $\nu_{ij}^*$  of associating groups  $i$  present in molecule  $j$  and the total amount of moles ( $n_j$ ) of species  $j$ :

$$n_i^* = \sum_{j=1}^{NC} \nu_{ij}^* n_j \quad (3)$$

where  $NC$  is the number of components. The fraction of groups  $i$  non-bonded through site  $k$  is determined by the expression [34]:

$$X_{ki} = \left( 1 + \sum_{j=1}^{NGA} \sum_{l=1}^{M_j} \frac{n_j^* X_{lj} \Delta_{lj,ki}}{V} \right)^{-1} \quad (4)$$

where  $V$  is the total volume. This summation includes all associating groups,  $NGA$ , and sites  $M_j$ . Moreover,  $X_{ki}$  depends on the association strength  $\Delta_{ki,lj}$ :

$$\Delta_{ki,lj} = \kappa_{ki,lj} \left[ \exp\left(\frac{\varepsilon_{ki,lj}}{RT}\right) - 1 \right] \quad (5)$$

The association strength between site  $k$  of group  $i$  and site  $l$  of group  $j$  is a function of the temperature ( $T$ ) and the association parameters  $\kappa$  and  $\varepsilon$ , which represent the volume and energy of association, respectively. In this work, we follow the approach proposed by Michelsen and Hendriks [61] to calculate the association contribution to pressure and chemical potential. Details of GCA-EOS derivatives are elsewhere [59,62].

In order to model solid-liquid equilibria (SLE), we assume pure solid phase precipitation; therefore, the fugacity of the pure solid solute can be calculated from the fugacity of the solute in the fluid phase [63] as follows:

$$\ln f^S(T, P) = \ln f^L(T, P) - \frac{\Delta_{\text{fus}} h}{RT_t} \left( \frac{T_t}{T} - 1 \right) + \frac{\langle \Delta_{\text{fus}} c_P \rangle}{R} \left( \frac{T_t}{T} - 1 - \ln \frac{T_t}{T} \right) - \frac{\Delta_{\text{fus}} v (P - P_t)}{RT} \quad (6)$$

where  $f^S$  and  $f^L$  are the fugacity of the solute as pure solid and liquid, respectively;  $P_t$  and  $T_t$  are the triple-point pressure and temperature of the solute, respectively; and  $\Delta_{\text{fus}} h$ ,  $\langle \Delta_{\text{fus}} c_P \rangle$ , and  $\Delta_{\text{fus}} v$  are the enthalpy, mean heat capacity, and volume change of fusion.

In practice, when the triple point data is not available, the  $T_t$  is replaced by the normal melting point temperature,  $T_m$ . Moreover, in this work, all SLE calculations are carried out at atmospheric pressure; hence, we disregard the last term that involves  $\Delta_{\text{fus}} v$ . Additionally,  $\langle \Delta_{\text{fus}} c_P \rangle$  is usually neglected when the temperature is close to the melting point, as is the case of paraffins and monocarboxylic acids treated in this work. On the other hand, most of dicarboxylic acids exhibit higher  $T_m$  than the rest of the components, which in principle would make it necessary to take their  $\langle \Delta_{\text{fus}} c_P \rangle$  into account in order to perform a detailed modeling. However, the effect of the uncertainty present in the  $\Delta_{\text{fus}} h$  and  $T_m$  of these substances is larger than the effect of including the  $\langle \Delta_{\text{fus}} c_P \rangle$

contribution. Therefore, we have neglected the contribution of the  $\langle \Delta_{\text{fus}} c_p \rangle$  for the calculation of all the solids in this work. Table 2 reports the pure compound melting temperatures and heats of fusion required for the SLE calculations. The scatter in dicarboxylic acids properties deserves special attention because they exhibit a high melting temperature. In this regard, we have collected all sources available up to our knowledge of experimental  $\Delta_{\text{fus}}h$  and  $T_m$  of dicarboxylic acids from literature, and provide an average value. On the other hand, some dicarboxylic acids exhibit one or more solid-solid transitions [64–66]; nonetheless, the reported values of  $\Delta_{\text{trs}}h$  are generally about 1-2 kJ/mol, which is in the order of the standard deviation usually found in  $\Delta_{\text{fus}}h$ , according to the data collected in this work (see Table 2). Also, the reported values  $T_{\text{tr}}$  may differ between 5 and 30 K [64,66]. Hence, in this work we also disregard solid-solid transitions of dicarboxylic acids except for suberic acid, whose  $\Delta_{\text{trs}}h$  is of the order of 9 kJ/mol, about one third of its  $\Delta_{\text{fus}}h$ . The final expression relating solid and liquid fugacities used in this work is

$$\ln f^S(T,P) = \ln f^L(T,P) - \frac{\Delta_{\text{fus}}h}{RT_m} \left( \frac{T_m}{T} - 1 \right) \quad (7a)$$

and for suberic acid below its solid-solid transition temperature:

$$\ln f^S(T,P) = \ln f^L(T,P) - \frac{\Delta_{\text{fus}}h}{RT_m} \left( \frac{T_m}{T} - 1 \right) - \frac{\Delta_{\text{trs}}h}{RT_{\text{trs}}} \left( \frac{T_{\text{trs}}}{T} - 1 \right) \quad (T < T_{\text{trs}}) \quad (7b)$$

**Table 2.** Pure compound heats of fusion and melting temperatures for solid-fluid equilibrium calculations.

	$\Delta_{\text{fus}}h$ (kJ/mol)	$T_m$ (K)	$\Delta_{\text{trs}}h$ (J/mol)	$T_{\text{trs}}$ (K)	Source
cyclohexane	2.675	279.7	-	-	[27,67]
acetic acid	11.73	289.8	-	-	[67]
propionic acid	10.66	252.6	-	-	[23]
octanoic acid	21.38	289.9	-	-	[4]
lauric acid	36.65	317.0	-	-	[4]
myristic acid	45.10	327.4	-	-	[4]
stearic acid	61.21	342.8	-	-	[67]
malonic acid	23.1	407.5	-	-	[68]
succinic acid	32.4±1.3	457.1±1.4	-	-	[64,65,69,70]
glutaric acid	20.9±1.8	369.1±2.5	-	-	[26,64–66,69–72]
2,2-dimethylsuccinic acid	38.1±0.8	412.0±1.4	-	-	[71,72]
2,3-dimethylsuccinic acid	16.9±0.8	392.5±0.1	-	-	[71,72]

3-methylglutaric acid	29.8±2.1	357.7±1.5	-	-	[69,71,72]
adipic acid	35.8±1.7	424.7±2.1	-	-	[26,64,65,69–71,73–75]
pimelic acid	27.7±2.8	376.5±4.0	-	-	[64–66,70,71,74]
suberic acid	29.6±1.7	414.4±0.9	8.9±0.2	405.4±1.7	[64,65,72,74,76]
azelaic acid	36.2±2.0	379.1±2.0	-	-	[5,64,65,70,74]
sebacic acid	43.8±4.1	405.4±1.1	-	-	[64,65,70,74–76]

### 2.1. Model parameterization

In a previous work, Ferreira et al. [46] achieved a good correlation and prediction of vapor-liquid equilibria (VLE) of mixtures comprising carboxylic acids with the GCA-EOS. However, we found a disagreement between the model prediction of pure carboxylic acid monomer fractions and data inferred from experimental *PVT* properties. On the other hand, in this work we also model liquid-liquid equilibria (LLE) data and challenge the model to predict the behavior of dicarboxylic acids.

For this task, we propose new GCA-EOS parameters for the organic acid functional groups. In order to model all the carboxylic acid family, we define molecularly the two first members of the homologous family, formic and acetic acid (HCOOH and CH<sub>3</sub>COOH, respectively) and the carboxylic acid group (CH<sub>*n*</sub>COOH, *n* = 0, 1, 2) for assembling the remaining organic acids. On the other hand, it is important to highlight that the parameters used to describe hydrocarbons are those reported by Skjold-Jørgensen [77] for normal alkanes, by Pusch and Schmelzer [78] for alkenes, and by Soria and coworkers [62,79] for branched and cycloalkanes.

Briefly, we first determine the GCA-EOS association parameters based on *PVT* properties of acetic acid, which are later used to describe the association strength of any carboxylic acid group. Secondly, we fit the attractive parameters (surface energy and binary interaction parameters) to phase equilibrium data of pure acids and binary mixtures with hydrocarbons. On one hand, this is done stepwise for formic and acetic acids, since they are built with a single group. Conversely, the correlation of pure and binary VLE for acids defined by group contribution (propionic and above) is performed simultaneously. At this stage, the free-volume parameters, (*d<sub>c</sub>*) are fixed to the value obtained from the critical constrains, i.e.,  $(\partial P/\partial V)_{T,n} = (\partial^2 P/\partial V^2)_{T,n} = 0$ , for all carboxylic acids except formic acid, since it decomposes at room temperature [80]; and thus, it is not

possible to set  $d_c$  using the critical constraints. Alternatively, we use the correlation proposed by Pereda et al. [81] to evaluate this parameter for formic acid:

$$\log d_c = 0.4152 + 0.4128 \log(0.04 v_{298K}[\text{cm}^3/\text{mol}]) \quad (8)$$

where  $v_{298K}$  is the saturated liquid molar volume of the compound at 298 K [67]. Finally, we challenge the model predictive capacity against phase equilibrium data not included in the parameterization procedure. At this step, we relax the restriction of the critical constraints for the  $d_c$  of carboxylic acids defined by GC; and, instead, it is fixed to a value that matches the experimental normal boiling point. Details of this procedure can be found in previous works [77,82].

As mentioned before, the vapor phase behavior of carboxylic acids deviates substantially from the ideal gas behavior, even at very low pressures. It is well known that this strong non-ideality is caused by the formation of dimers [13]. In this work, dimerization is represented by a double hydrogen bond association scheme (1A) of the carboxylic acid functional group, as proposed by Huang and Radosz [52]. Considering the major influence of association on the system non-ideality, it is important to ensure that the model portrays the experimental fraction of monomers for each carboxylic acid as close as possible. In a previous work, Soria et al. [83] determine the association parameters of the alcohol functional group using information on the fraction of non-associated molecules, derived from spectroscopic data of saturated liquid alcohols. This approach allows defining a single set of association parameters for the alcohol group, regardless of the alcohol, and modeling the non-associated fraction of  $n$ -alcohols up to 1-octanol (higher alcohol for which spectroscopic data was available). Unfortunately, up to our knowledge, this type of data is not available for carboxylic acids. In this context, the association of organic acids in the vapor phase provides an alternative source of information to estimate the monomer fractions, not only in the vapor but also in the liquid phase. We use experimental data on vapor-phase compressibility factors and the derived association constants of acetic acid reported by Miyamoto et al. [84] to define the GCA-EOS association parameters of the carboxylic acid group. According to Wolbach and Sandler [85] the association strength ( $\Delta$ ) is related to the association constant ( $K_{eq}$ ) by the following equation:

$$\Delta = 2RTK_{\text{eq}}/1 \text{ atm} \quad (9)$$

We set a pair of association parameters ( $\kappa$  and  $\varepsilon$ ) by solving Eqs. (5) and (9) for the  $K_{\text{eq}}$  values reported by Miyamoto et al. [84]. Thereafter, we use these association parameters to calculate the monomer fractions in the saturated liquid phase, by solving Eq. (4) with molar volume data of saturated liquid acetic acid from literature [86]. This first set of association parameters does not reproduce exactly the monomer fractions in the saturated liquid phases because the liquid molar volume predicted by the GCA-EOS depends also on the free-volume and attractive contributions, as well as on the association term. Therefore, we fit the association parameters by an iterative procedure [83] using, in the subsequent steps, the model prediction of the molar volume.

The parameterization procedure for the rest of the carboxylic acids is easier because of the group contribution approach of the GCA-EOS. The association parameters  $\kappa$  and  $\varepsilon$  determined for acetic acid are used, thereafter, to represent dimerization strength of all organic acids, including formic acid.

Finally, the remaining acids are assembled with the carboxylic acid groups ( $\text{CH}_2\text{COOH}$ ,  $\text{CHCOOH}$  or  $\text{CCOOH}$ ), which are described with the same set of attractive parameters and differs only in their size. In this case, the parameterization involves the simultaneous fitting of the new pure group parameters and its binary interaction parameters with the paraffin groups ( $\text{CH}_3$ ,  $\text{CH}_2$ ,  $\text{CHCH}_3$ ) needed to assemble de alkyl chains. For this purpose, we use pure monocarboxylic acids vapor pressure data and binary data with selected hydrocarbons. In the next section, the reader can find details about the specific data fitted in each case. Up to our knowledge, the experimental data available for branched carboxylic acids is rather scarce. Thus, the groups  $\text{CH}_2\text{COOH}$ ,  $\text{CHCOOH}$  and  $\text{CCOOH}$ , share all the parameters, except for the segment surface area ( $q$ ), which is calculated straight forwards from Bondi's rules [87]. This approach is analogous to the UNIFAC method for the "main group" and "subgroup" approach; and it has been applied successfully to represent the phase equilibria of secondary alcohols, eters, and esters in a variety of systems [82,88].

### 3. Results and discussion

This section reports the results obtained in the calculation of pure and binary phase equilibrium properties with the GCA-EOS. We first discuss the correlation and prediction of monocarboxylic acids. Afterwards, we challenge the model with dicarboxylic acids pure and binary phase equilibria, following a completely predictive approach.

#### 3.1. Phase equilibria of monocarboxylic acid

Pure-group parameters of acetic acid were fitted from experimental pure-vapor pressure data, while binary interaction parameters were fitted correlating simultaneously VLE and LLE data with hydrocarbons [17,19,89,90]. This ensures a balance between the model performance on both kinds of phase equilibrium. On the other hand, experimental data of pure propionic acid vapor pressure were used for the  $\text{CH}_2\text{COOH}$  functional group [91–95], together with VLE data of propionic acid + *n*-heptane [17], and butyric acid + *n*-octane [96]. VLE data and activity coefficients were applied to determine the binary interaction parameters with the alkene [17,97] and cycloalkane [98] groups, as shown in the next section. Tables 3 and 4 show, respectively, the pure-group energy and binary interaction parameters derived from the parameterization process, while Table 5 reports the energy and volume of association that quantify dimerization of carboxylic acids. As can be seen in Table 3, the pure group surface energy for acetic ( $\text{CH}_3\text{COOH}$ ) and carboxylic group ( $\text{CH}_n\text{COOH}$ ) are rather similar, like their binary interaction parameters with aliphatic groups, which is a sign of a robust parameterization. Table 3 also shows that the surface energy parameter for formic acid is higher, which is expected because the formic acid does not include a paraffinic carbon, in contrast with the other acid groups. This allowed us to assume that the values of  $\alpha_{ij}$  for formic and  $\text{C}_3+$  acids are equal to the values obtained from acetic acid + paraffins, thereby reducing the number of adjustable binary parameters. This is particularly advantageous in case of formic acid + paraffins, since the only experimental data are the azeotropic points summarized by Horsley [99].



**Table 3.** GCA-EOS pure-group parameters for the residual term: group surface area ( $q$ ), reference temperature ( $T^*$ ) and surface energy ( $g$ ).

Group $i$	$q_i$	$T_i^*/\text{K}$	$g_{ii}^*/(\text{atm cm}^6 \text{ mol}^{-2})$	$g_{ii}^{\prime}$	$g_{ii}^{\prime\prime}$	Source
CH <sub>3</sub>	0.848	600	316910	-0.9274	0.0	[77]
CH <sub>2</sub>	0.540	600	356080	-0.8755	0.0	[77]
CH <sub>3</sub> CH	1.076	600	303749	-0.8760	0.0	[62]
(B)CH <sub>3</sub>	0.848	600	282715	-0.63930	0.0	[62]
(B)CH <sub>2</sub>	0.540	600	294524	-0.82330	0.0	[62]
CH <sub>2</sub> =CH	1.176	600	337980	-0.6764	0.0	[78]
CH=CH	0.867	600	403590	-0.7631	0.0	[78]
cyCH <sub>2</sub> <sup>a</sup>	0.560 <sup>C5</sup> /0.540 <sup>C6</sup>	600	466550	-0.6062	0.0	[79]
HCOOH	1.532	588	606438	-0.01548	0.0	this work
CH <sub>3</sub> COOH	2.072	591.9	517649	-0.1751	-0.0344	this work
CH <sub>2</sub> COOH	1.764					
CHCOOH	1.452	591.9	526489	-0.100	-0.050	this work
CCOOH	1.224					

<sup>a</sup>cyCH<sub>2</sub> group surface area ( $q$ ) depends on the ring number of carbons [79]. The values reported here are only for the cycloalkanes included in the databank (cyclopentane and cyclohexane).

**Table 4.** GCA-EOS binary interaction parameters for the residual contribution.

Group $i$	Group $j$	$k_{ij}^*$	$k_{ij}^{\prime}$	$a_{ij}$	$a_{ji}$	Source
HCOOH	CH <sub>3</sub>	0.8146	0	0	3.9	Azeotropic data of FA+nC <sub>5</sub> ,
	CH <sub>2</sub>	0.9667	0	0	6.5	FA+nC <sub>8</sub> [99]
	CH <sub>n</sub> COOH ( $n = 0-3$ )	0.9964	0	0	0	VLE FA+AA [16]
CH <sub>3</sub> COOH	CH <sub>3</sub>	0.8892	-0.0350	0	3.9	VLE AA with nC <sub>6</sub> and nC <sub>8</sub> , LLE
	CH <sub>2</sub>	0.9351	-0.0350	0	6.5	AA+nC <sub>10</sub> [17,19,89,90]
	cyCH <sub>2</sub>	0.890	-0.0627	0	0	VLE AA + cC <sub>6</sub> [17,27]
	CH <sub>2</sub> =CH	0.9684	0	0	0	VLE AA + 1-hexene [17]
	CH <sub>n</sub> COOH ( $n = 0-2$ )	1	0	0	0	uncorrelated parameters <sup>a</sup>
CH <sub>n</sub> COOH ( $n = 0-2$ )	CH <sub>3</sub> /(B)CH <sub>3</sub> <sup>a</sup>	0.9211	-0.0350	0	3.9	PV PA [91-95], VLE PA + nC <sub>7</sub>
	CH <sub>2</sub> /(B)CH <sub>2</sub> /CHCH <sub>3</sub> <sup>a</sup>	0.9213	-0.0310	0	6.5	and BA + nC <sub>8</sub> [17,96]
	CH <sub>2</sub> =CH/CH=CH <sup>a</sup>	0.980	0	0	0	VLE PA+1-hexene, $\gamma^\infty$ of alkanes in SA [17,97]
	cyCH <sub>2</sub>	0.925	-0.0100	0	0	VLE PA+cyclohexane [98]

Compounds references: formic acid (FA), acetic acid (AA), propionic acid (PA), butanoic acid (BA), stearic acid (SA).

Data references: pure compound vapor pressure (PV), vapor-liquid equilibria (VLE), liquid-liquid equilibria (LLE) and infinite dilution activity coefficient ( $\gamma^\infty$ ).

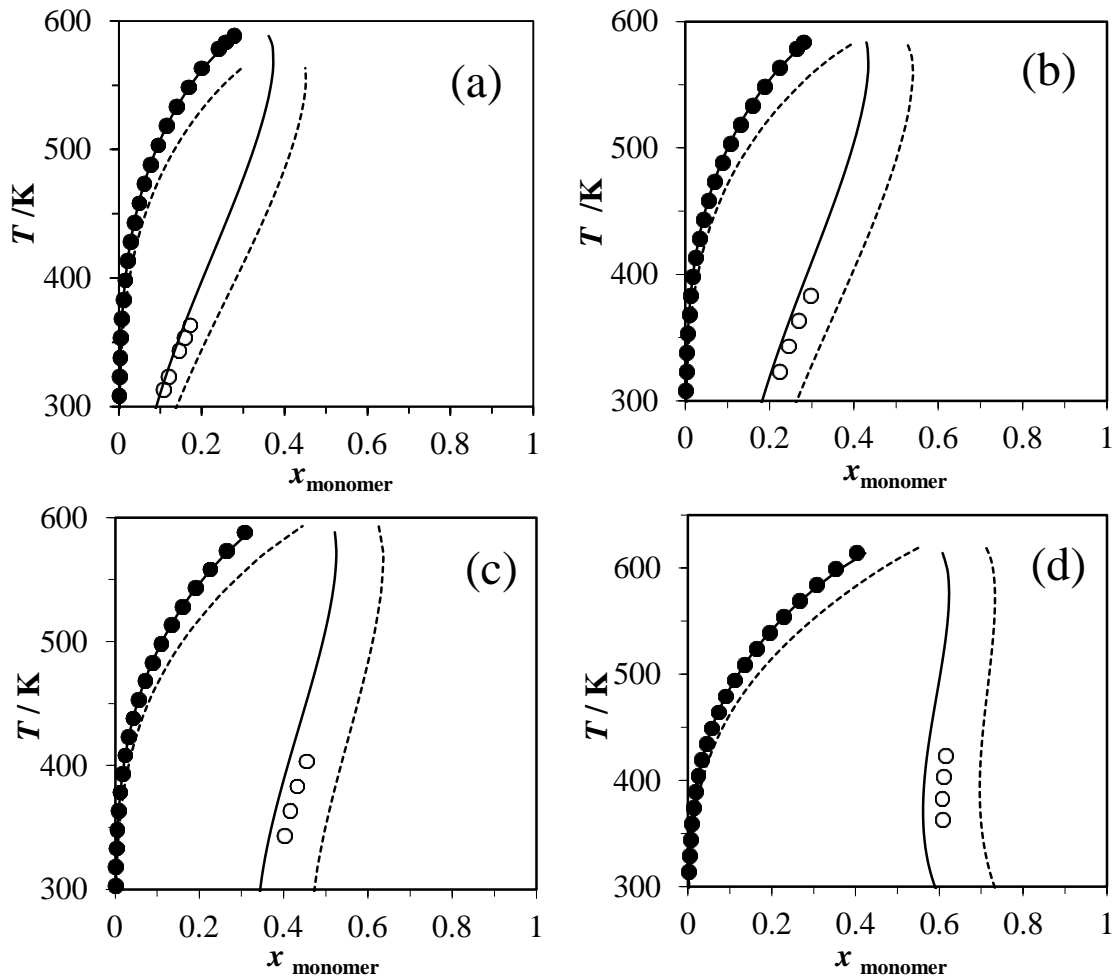
<sup>a</sup> Extrapolated values based on physical similarity, as suggested by Skjold-Jørgensen [77].

**Table 5.** GCA-EOS self-association parameters of carboxylic acids

Association group	$\varepsilon/R$ (K)	$\kappa$ (cm <sup>3</sup> mol <sup>-1</sup> )	Source
COOH	6517.1	0.0238	PVT of acetic acid [84]

Fig. 1 shows the fraction of monomers of low molecular weight carboxylic acids in saturated liquid and vapor phases, up to temperatures near their critical points. The empty symbols represent the monomer fractions derived from the experimental vapor com-

compressibility factors measured by Miyamoto et al. [84]. The filled symbols correspond to the monomer fraction in the saturated liquid phase, obtained by solving Eq. (4) with the same values of association parameters needed to represent the vapor phase, and with data on saturated liquid densities from the literature [86]. At this point, it is worth recalling that we model the carboxylic acids with the same association strength regardless of its hydrocarbon chain. In fact, the solid lines in Fig. 1a represent the GCA-EoS correlation of acetic acid monomer fractions, and Figs. 1b, 1c and 1d are the predictions for that of propionic, butyric, and valeric acids, respectively. The dashed lines are the monomer fractions predicted by the GCA-EoS with the previous association parameters for carboxylic acids [46].



**Figure 1.** Monomer molar fractions of monocarboxylic acids in the saturated vapor (○) and liquid (●) phases, derived from experimental data on compressibility factors [84]: (a) acetic acid; (b) propionic acid; (c) butyric acid; (d) valeric acid. Dashed lines: GCA-EoS predictions based on previous parameterization [46]. Solid lines: GCA-EoS correlation (a) and predictions (b, c, d) based on this work parameterization

Table 6 shows the degree of correlation and prediction achieved in the calculation of vapor pressures of monocarboxylic acids. The values of the hard-sphere diameters of these compounds are reported. As it was already mentioned, in this work, the  $d_c$  value of acetic acid is calculated from the critical constraints. On the other hand, for the other carboxylic acids that are modeled by group contribution, the  $d_c$  value is fixed to match a given point of the vapor pressure curve [59]. Nonetheless, the GCA-EOS predicts with good accuracy their critical temperature and pressure (see Table 6), with average error of 1.2% and 3.2%, respectively. In this regard, all linear, monocarboxylic acids, from propanoic and above, are very well predicted. On the other hand, the largest errors appear for branched acids, isobutyric and 2-ethylhexanoic acid; nonetheless, still these results are reasonable accurate for a GC prediction. Table 6 also includes the prediction of neovaleric acid  $T_c$ , which is not available in the open literature. Last, the largest error in  $T_c$  corresponds to formic acid; nonetheless, it should be taken into account that this compound is unstable and decomposes before reaching the critically state; hence, its critical coordinates are subject to a large uncertainty.

**Table 6.** GCA-EOS correlation\* and prediction of mono- and di-carboxylic acids vapor pressures.

Compound	$T_c$ (K)	$d_c$ <sup>a</sup> (cm/mol <sup>1/3</sup> )	AARD%		$\Delta T_r$ <sup>b</sup>	AARD (P)% <sup>c</sup>	Reference
			$T_c$	$P_c$			
formic acid*	588.0	3.0896 <sup>d</sup>	7.5	-	0.51-0.77	0.3	[80,93]
acetic acid*	591.9	3.6545 <sup>e</sup>	0.2	0.5	0.51-0.90	1.5	[95,100,101]
propionic acid*	600.8	4.0300 <sup>e</sup>	0.4	2.6	0.50-0.73	1.5	[91–95]
isobutyric acid	605.0	4.4152	2.2	1.4	0.49-0.74	1.4	[80,94,95]
butyric acid	615.7	4.4276	0.6	3.2	0.45-0.80	1.5	[91,93–95,102,103]
neovaleric acid	603.7 <sup>f</sup>	4.6800	-	-	0.57-0.78	2.3	[104]
isovaleric acid	629.0	4.7648	1.7	0.3	0.58-0.74	1.4	[80,94]
valeric acid	639.2	4.7610	1.1	0.2	0.58-0.90	3.5	[80,93–95]
hexanoic acid	659.0	5.0551	1.2	1.1	0.51-0.81	2.6	[91,93–95,105]
heptanoic acid	677.3	5.3365	1.5	5.9	0.51-0.73	3.5	[94,105,106]
2-ethylhexanoic acid	674.6	5.6594	2.2	10	0.59-0.76	1.8	[107,108]
octanoic acid	694.3	5.5927	1.6	1.6	0.52-0.73	4.2	[95,105]
nonanoic acid	710.7	5.8504	1.7	0.3	0.52-0.74	3.1	[95,105]
decanoic acid	725.5	6.0822	1.8	2.9	0.53-0.66	3.7	[95,105]
lauric acid	743	6.5198	0.5	3.5	0.51-0.77	8.1	[105,109–111]
myristic acid	763	6.9098	0.2	6.9	0.49-0.79	9.1	[105,109–112]
palmitic acid	785	7.2845	0.1	3.8	0.47-0.80	10	[105,109–112]
stearic acid	803	7.6350	0.4	4.2	0.49-0.81	8.4	[110,111]

<sup>a</sup> Unless noticed,  $d_c$  values are calculated from a from a saturation point [77].

<sup>b</sup>  $T_r$  = reduced temperature (lower limit corresponds to a vapor pressure of 0.01 bar)

<sup>c</sup>  $AARD(P) = \frac{1}{NP} \sum_i \left| 1 - \frac{P_{calc,i}^v}{P_{exp,i}^v} \right|$ ;  $NP$  = number of experimental data points.

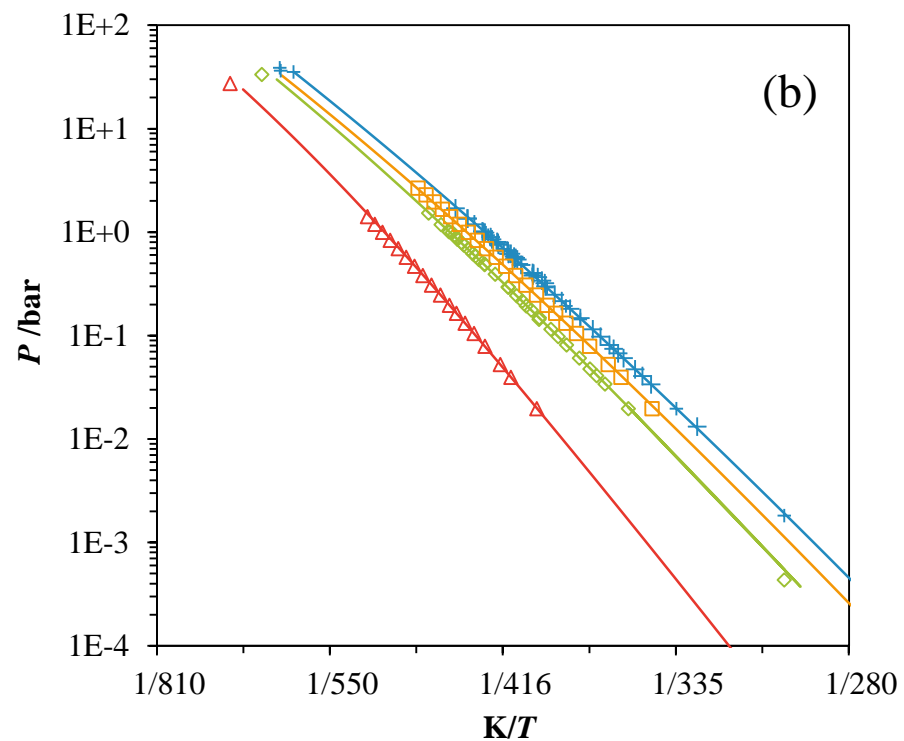
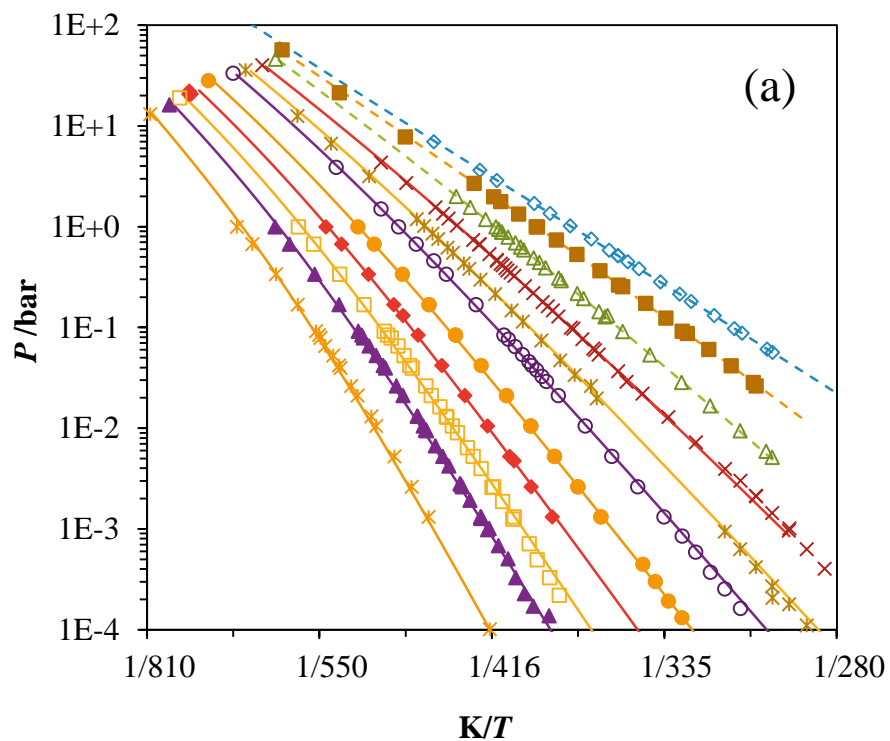
<sup>d</sup> Calculated with Pereda et al. correlation [81] (Eq. 8).

<sup>e</sup> Calculated from the critical constraints, i.e.,  $(\partial P/\partial V)_{T,n} = (\partial^2 P/\partial V^2)_{T,n} = 0$ .

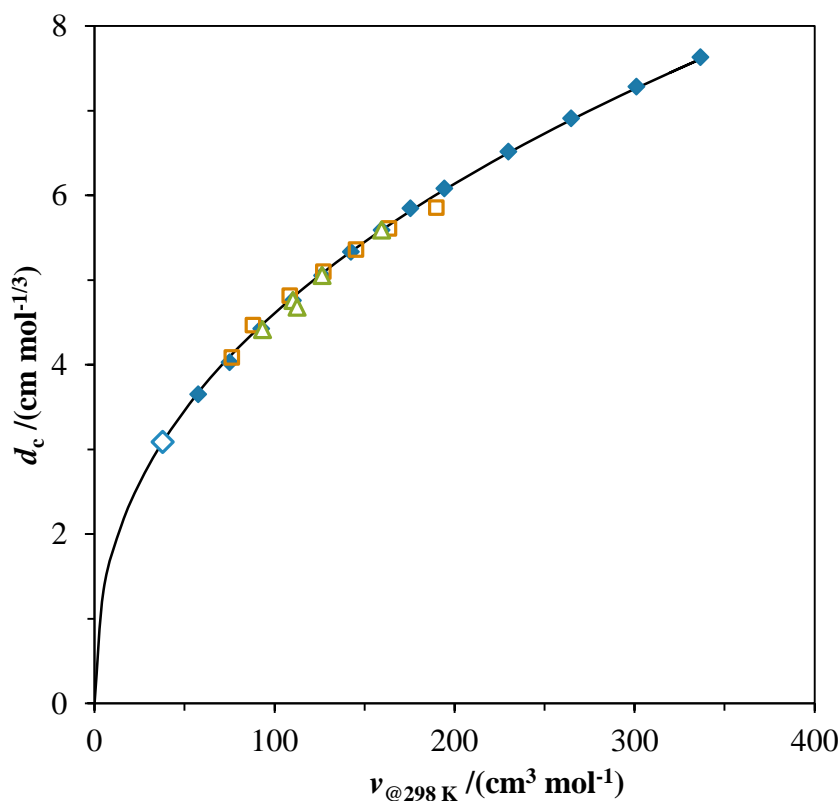
<sup>f</sup> Not available in the open literature, predicted using the GCA-EOS.

Fig. 2 illustrates the GCA-EOS correlation and prediction of the vapor pressures of monocarboxylic up to the critical point. We arbitrarily set this lower bound based on our experience regarding the precision of pure-compound vapor pressure data. Specifically, Fig. 2a shows the vapor pressure of the normal monocarboxylic acids' homologue series up to 18 carbon atoms, and their correlation and prediction with the GCA-EOS. An accurate representation of the vapor pressure is obtained for low to high molecular weight acids. Fatty acids showed higher deviations; however, a 10% relative deviation can be considered a good result, considering their low vapor pressure. On the other hand, Fig. 2b depicts the GCA-EOS prediction of branched monocarboxylic acids. The precision achieved is comparable to the that obtained for linear carboxylic acids, as shown also in Table 6, proving that the assumption that  $\text{CH}_2\text{COOH}$ ,  $\text{CHCOOH}$ , and  $\text{CCOOH}$  groups only differs in the number of surface segments is robust.

Additionally, a further measure of the robustness of the parameterization consists on analyzing the trend of the repulsive contribution parameter,  $d_c$ , since it is evaluated from vapor-pressure data for most of the carboxylic acids treated in this work. Figure 3 depicts the trend of  $d_c$  of the acids listed in Table 6 against their liquid molar volume calculated from the DIPPR correlation [86] at 298 K. However, for fatty acids, the triple point liquid density is shown instead due to their high melting temperature. As can be seen, the  $d_c$  depicts a smooth relation with the molar volume, independently of the nature of the acid, even for dicarboxylic acids, which are discussed in the subsequent section. Figure 3 shows that there is a physical trend of the  $d_c$  of carboxylic acids and the liquid density. Furthermore, the  $d_c$  values obtained by fitting a vapor pressure datapoint follows closely the correlation developed by Pereda et al. [81]. This result encouraged us to apply Eq. 8 to evaluate the  $d_c$  of compounds such as formic acid, or other acids for which experimental vapor pressure is not available.



**Figure 2.** (a) Vapor pressures of linear monocarboxylic acids. Symbols: ( $\diamond$ ) formic, ( $\blacksquare$ ) acetic, ( $\triangle$ ) propionic, ( $\times$ ) butyric, ( $\circ$ ) hexanoic, ( $\bullet$ ) octanoic, ( $\blacklozenge$ ) decanoic, ( $\square$ ) lauric, ( $\blacktriangle$ ) myristic, and ( $*$ ) stearic acids. (b) Vapor pressures of branched acids: (+) isobutyric, ( $\square$ ) neovaleric, ( $\diamond$ ) isovaleric, and ( $\triangle$ ) 2-ethylhexanoic acids. Lines: GCA-EOS correlation (dashed) and prediction (solid). For detailed references to experimental data, please see Table 6.



**Figure 3.** GCA-EOS critical diameters ( $d_c$ ) as a function of the liquid molar volume at 298 K [86]. Symbols: carboxylic acids treated in this work: (◆) linear carboxylic acids, (△) branched carboxylic acids, (□) dicarboxylic acids, and (◇) calculated value [81] for formic acid. Solid line:  $d_c$  calculated with the correlation proposed by Pereda et al. [81].

Regarding the binary experimental data, about 13% of the collected data was used for the parameterization procedure, and Table 7 lists the accuracy of the GCA-EOS correlation for each data set. In average, the GCA-EOS correlations show a deviation of about 3.4% and 1.9% in bubble pressure and vapor composition, respectively; and 6% in infinite dilution activity coefficient data, which is the typical experimental error of these type of data.

In a second stage, we challenge the model predictive capacity against experimental phase equilibrium data of binary systems not included in the parameterization procedure. In overall, the GCA-EOS depicts good accuracy in predictive calculations, as shown in Table 8, except for some infinite dilution activity coefficients of hydrocarbons in carboxylic acids. The average deviations for VLE data are 3.3% and 2.1% in bubble pressure and vapor composition, respectively, which are similar to the accuracy achieved in the correlated data (see Table 7). The binary systems of isobutyric acid with *n*-heptane and with cyclohexane [116] show the larger deviations, about 7% in bubble

pressure, which is a good result considering that branched acids are completely predicted by GCA-EOS. On the other hand, the model average deviation in infinite dilution activity coefficient is about 11%, being the largest deviation for palmitic acid 17-20%, while myristic and stearic acids activity coefficients are below 10% in average. Last, the average error for the predicted SLE data is about 9%, which is also a good result taking into account that it is a complete prediction and that the modeling of a solid phase precipitation also involves a number of uncertain assumptions.

**Table 7.** GCA-EOS correlation of VLE and infinite dilution activity coefficients of binary mixtures containing monocarboxylic acids.

Compounds		$T/K$	$P/\text{bar}$	AARD%		No. exp points	Reference
1	2		$P$	$y_2$			
<b>Vapor-liquid equilibria (VLE)</b>							
<i>Acid + alkanes &amp; alkenes</i>							
acetic acid	<i>n</i> -hexane	313	0.1-0.4	5.2	3.5	9	[17]
	<i>n</i> -octane	323-399	0.07-1.01	4.4	4.5	73	[19,113,114]
	<i>n</i> -decane	389-391	1.01	4.0	0.74	11	[115]
	1-hexene	313	0.1-0.45	5.6	4.0	9	[17]
propionic acid	cyclohexane	313-386	0.09-1.01	2.1	6.4	44	[17,24,25]
	<i>n</i> -hexane	313	0.04-0.37	2.1	0.4	9	[17]
	1-hexene	313	0.04-0.40	2.3	0.3	9	[17]
<i>n</i> -butyric acid	cyclohexane	298, 318	0.5-0.3	2.8	-	36	[98]
	<i>n</i> -octane	398-438	1.01	1.4	-	20	[96]
<i>Acid + acid</i>							
formic acid	acetic acid	343-391	20-101	1.2	2.2	23	[16]
<b>Infinite dilution activity coefficient of paraffins in acids (<math>\gamma^\infty</math>)</b>							
		$T/K$	$P/\text{bar}$	AARD( $\gamma_2^\infty$ )%			
Stearic acid	1-pentene	354-384	1.01	7.2		3	[97]
	1-hexene	354-384	1.01	5.1		3	[97]
	1-heptene	354-384	1.01	4.9		3	[97]
	1-octene	354-384	1.01	6.9		3	[97]

**Table 8.** GCA-EOS predictions of vapor-liquid equilibria in binary mixtures containing monocarboxylic acids.

Compounds		$T/K$	$P/\text{bar}$	AARD%		No. exp points	Source of experimental data
1	2			$P$	$y_2$		
<i>Carboxylic acid + paraffin</i>							
acetic acid	<i>n</i> -butane	423-523	2.4-59	9.8	14	33	[117]
	<i>n</i> -hexane	342-391	1.01	1.3	5.2	13	[118]
	<i>n</i> -heptane	293-313	0.05-0.15	1.9	2.9	66	[119,120]
		298, 318	0.02-0.15	5.0	-	30	[121]
propanoic acid	cyclohexane	298, 318	0.01-0.3	3.1	-	38	[121]
	<i>n</i> -heptane	323	0.02-0.2	3.6	1.66	20	[122]
		298, 318	0.02-0.15	3.9	-	32	[98]
isobutyric acid	<i>n</i> -octane	392-414	1-1.01	3.3	3.7	27	[123]
	<i>n</i> -heptane	298, 318	0.003-0.15	6.0	-	30	[116]
		<i>n</i> -octane	397-427	1.01	3.2	-	19
neovaleric acid	cyclohexane	298, 318	0.01-0.3	8.2	-	28	[116]
	<i>n</i> -heptane	298, 318	$10^{-3}$ -0.15	3.8	-	31	[116]
	<i>n</i> -valeric acid	<i>n</i> -heptane	323-373	0.01-0.5	3.0	0.54	35
<i>n</i> -hexanoic acid	cyclohexane	413-484	0.1-16	3.4	0.14	33	[29]
<i>Binary mixture of carboxylic acids</i>							
formic acid	acetic acid	317-391	0.27-1.01	2.1	2.0	62	[16,125–129]
	propionic acid	373-414	1.01	2.0	2.5	42	[16,130–132]
	<i>n</i> -butyric acid	373-437	1.01	5.4	2.5	5	[130]
	<i>n</i> -valeric acid	323-373	0.01-1	12	1.7	35	[133]
acetic acid	propionic acid	391-413	1.01	2.4	3.2	34	[132,134]
	<i>n</i> -butyric acid	391-437	1.01	2.5	1.1	6	[2]
propionic	<i>n</i> -butyric acid	361-413	0.1-0.96	1.1	0.87	39	[21,28]
	<i>n</i> -valeric acid	370-413	0.01-0.98	2.6	3.0	48	[2]
isobutyric	<i>n</i> -butyric acid	372-383	0.14	5.8	2.0	10	[28]
	<i>n</i> -valeric acid	382-413	0.1-0.64	2.9	1.5	48	[2]
<i>n</i> -butyric acid	isovaleric acid	383-393	0.14	7.1	2.3	9	[28]
	<i>n</i> -hexanoic acid	383-411	0.14	4.9	4.6	8	[28]
<i>n</i> -hexanoic acid	<i>n</i> -octanoic acid	389-449	0.03-0.13	4.9	3.5	29	[135,136]
<i>n</i> -octanoic acid	<i>n</i> -decanoic acid	415-434	0.03-0.13	3.7	2.4	9	[135]
<i>n</i> -decanoic acid	lauric acid	475-499	0.13	5.0	3.4	14	[135]
lauric acid	myristic acid	481-503	0.07	1.5	1.3	13	[135]
myristic acid	palmitic acid	503- 524	0.07	3.5	4.6	12	[135]



**Table 8b.** GCA-EOS predictions of infinite dilution activity coefficients in binary mixtures containing monocarboxylic acids

Compounds		$T/K$	$P/\text{bar}$	AARD( $\gamma_\infty$ )%		No. exp points	Source of experimental data
1	2			1	2		
<i>Acid + paraffin</i>							
decanoic acid	<i>n</i> -hexane	314-353	1.01	12		5	[137]
	<i>n</i> -heptane	314-353	1.01	12		5	[137]
	isooctane	314-353	1.01	17		4	[137]
	1-hexene	314-353	1.01	11		4	[137]
lauric acid	cyclohexane	314-353	1.01	1.9		6	[137]
	<i>n</i> -hexane	329-358	1.01	13		4	[137]
	<i>n</i> -heptane	329-358	1.01	13		6	[137]
	isooctane	329-358	1.01	16		6	[137]
	1-hexene	329-358	1.01	13		3	[137]
myristic acid	cyclohexane	329-358	1.01	1.6		5	[137]
	<i>n</i> -hexane	338-358	1.01	8.5		3	[137]
	<i>n</i> -heptane	338-358	1.01	9.2		5	[137]
	isooctane	338-358	1.01	11		3	[137]
palmitic acid	1-hexene	338-358	1.01	9.2		4	[137]
	cyclohexane	338-358	1.01	7.7		5	[137]
	<i>n</i> -hexane	348-395	1.01	17		10	[137–139]
	<i>n</i> -heptane	340-395	1.01	17		10	[137–139]
stearic acid	isooctane	340-374	1.01	20		6	[137–139]
	1-hexene	340-395	1.01	18		10	[137–139]
	cyclohexane	340-395	1.01	6.0		10	[137–139]
	<i>n</i> -pentane	384-354	1.01	9.5		3	[97]
stearic acid	<i>n</i> -hexane	384-354	1.01	4.8		3	[97]
	<i>n</i> -heptane	384-354	1.01	7.9		3	[97]
	<i>n</i> -octane	384-354	1.01	9.3		3	[97]

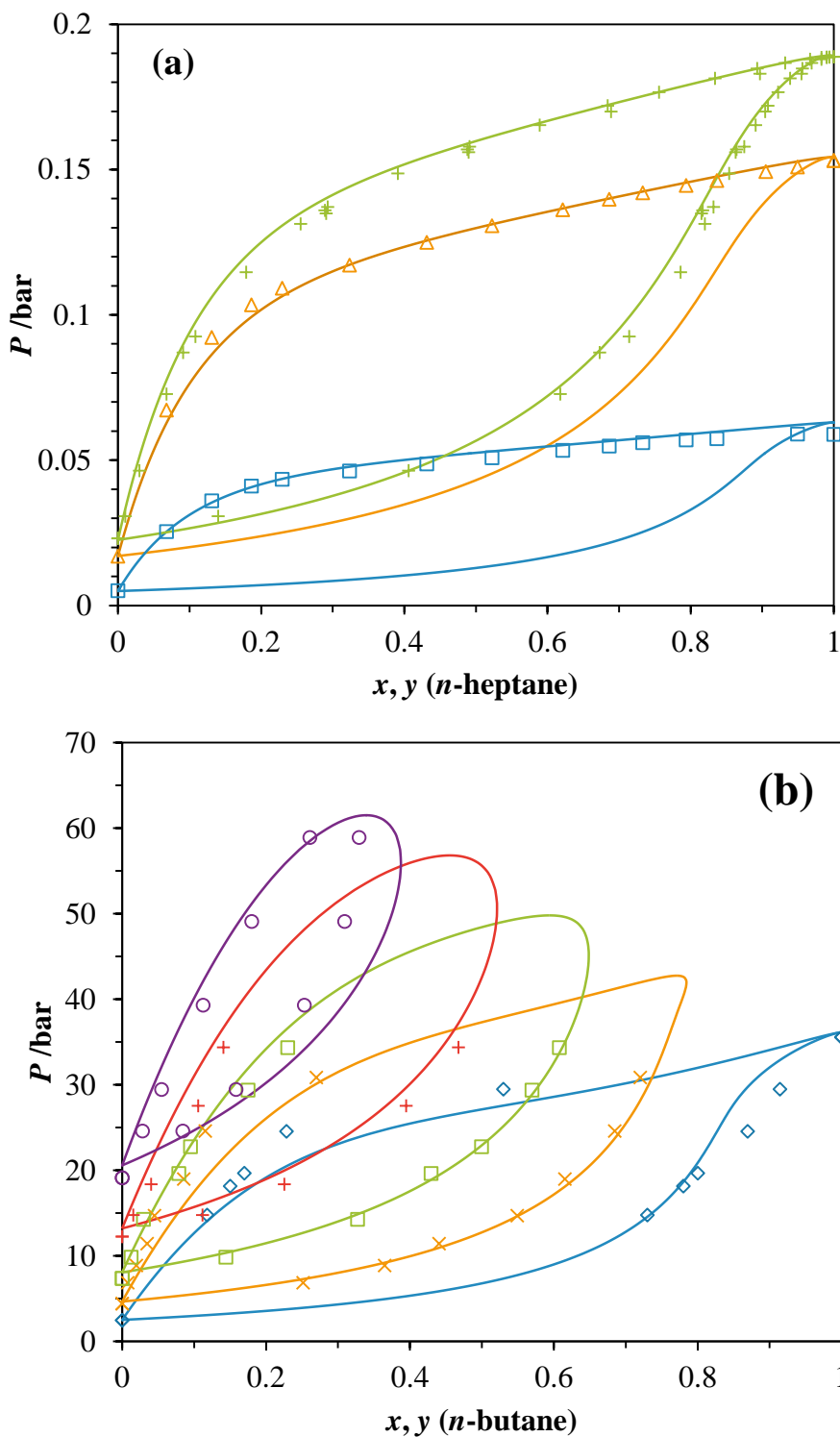
**Table 8c.** GCA-EOS predictions of solid-liquid equilibria in binary mixtures containing monocarboxylic acids

Compounds		$T/K$	$P/\text{bar}$	AARD( $x$ )%		No. exp points	Source of experimental data
1	2			1	2		
<i>Acid + paraffin</i>							
acetic acid	<i>n</i> -heptane	244-288	1.01	14		15	[140]
acetic acid	cyclopentane	252-286i	1.01	11	-	15	[140]
	cyclohexane	272-289	1.01	22	0.45	18	[27]
<i>Acid + acid</i>							
acetic acid	propionic acid	235-290	1.01	3.8	0.55	23	[23]
myristic acid	caprylic acid	286-328	1.01	2.3	5.8	9	[4]
lauric acid	myristic acid	308-328	1.01	2.4	3.9	13	[4]

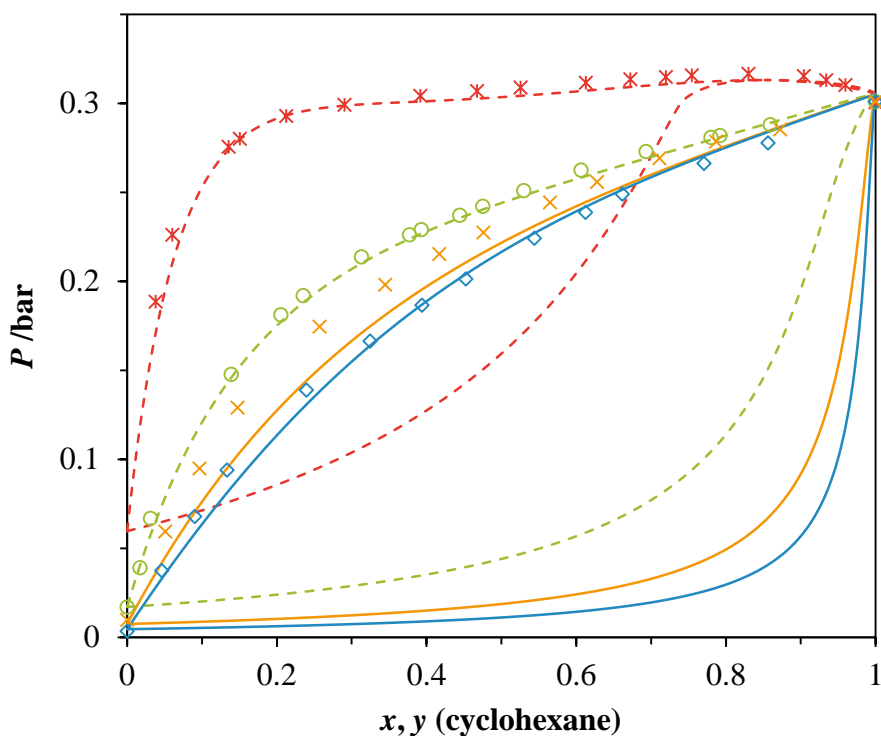
Figures 4 to 6 illustrate VLE behavior for selected binary systems and GCA-EOS correlations (dashed lines) and predictions (solid lines). Fig. 4 depict GCA-EOS predictions for the binary systems *n*-heptane with propionic acid and *n*-butane + acetic acid from

298 up to 523 K. These results show that the model is able to predict the effect of temperature on the phase behavior in wide range of conditions. Figure 5 shows the GCA-EOS correlation of the binary mixture cyclohexane + acetic and propionic acid [98,121], and prediction of the binary mixtures cyclohexane with isobutyric and neovaleric acid [116]. In this case, the quality of the predictions shows the robustness of the GC approach of the model, even for branched carboxylic acids. Last, same strength can also be observed with binary systems of formic acids and *n*-alkane homologues. Fig. 6 depicts the correlation of two equilibrium points: azeotropic composition of the systems formic acid + *n*-pentane and formic acid + *n*-octane [99], which allows fitting the binary interaction parameters of formic acid – CH<sub>3</sub>/CH<sub>2</sub>. As can be seen, based on the first two, the model is able to qualitatively predict the azeotropic composition of the binary systems of formic acid with *n*-hexane and *n*-heptane. From this figure, it is worth noting that the GCA-EOS predicts high immiscibility between formic acid and *n*-alkanes, which still requires experimental confirmation.

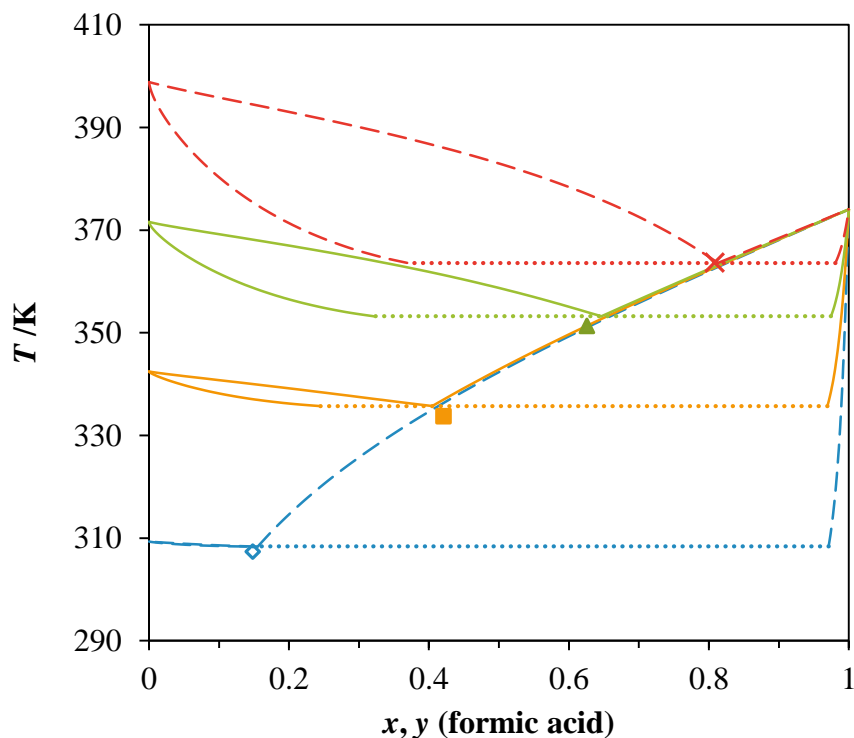
Regarding SLE calculations, the GCA-EOS shows a good predictive capacity for almost all mixtures of carboxylic acid and *n*-alkanes assessed in this work. Fig. 7.a depicts the GCA-EOS accuracy to predict SLE of binary mixtures of acetic acid + propionic acid [23] and acetic acid + *n*-heptane [140]. On the other hand, Fig. 7,b presents the GCA correlation and prediction of SLE of the acetic acid + cyclopentane and cyclohexane binaries, respectively.



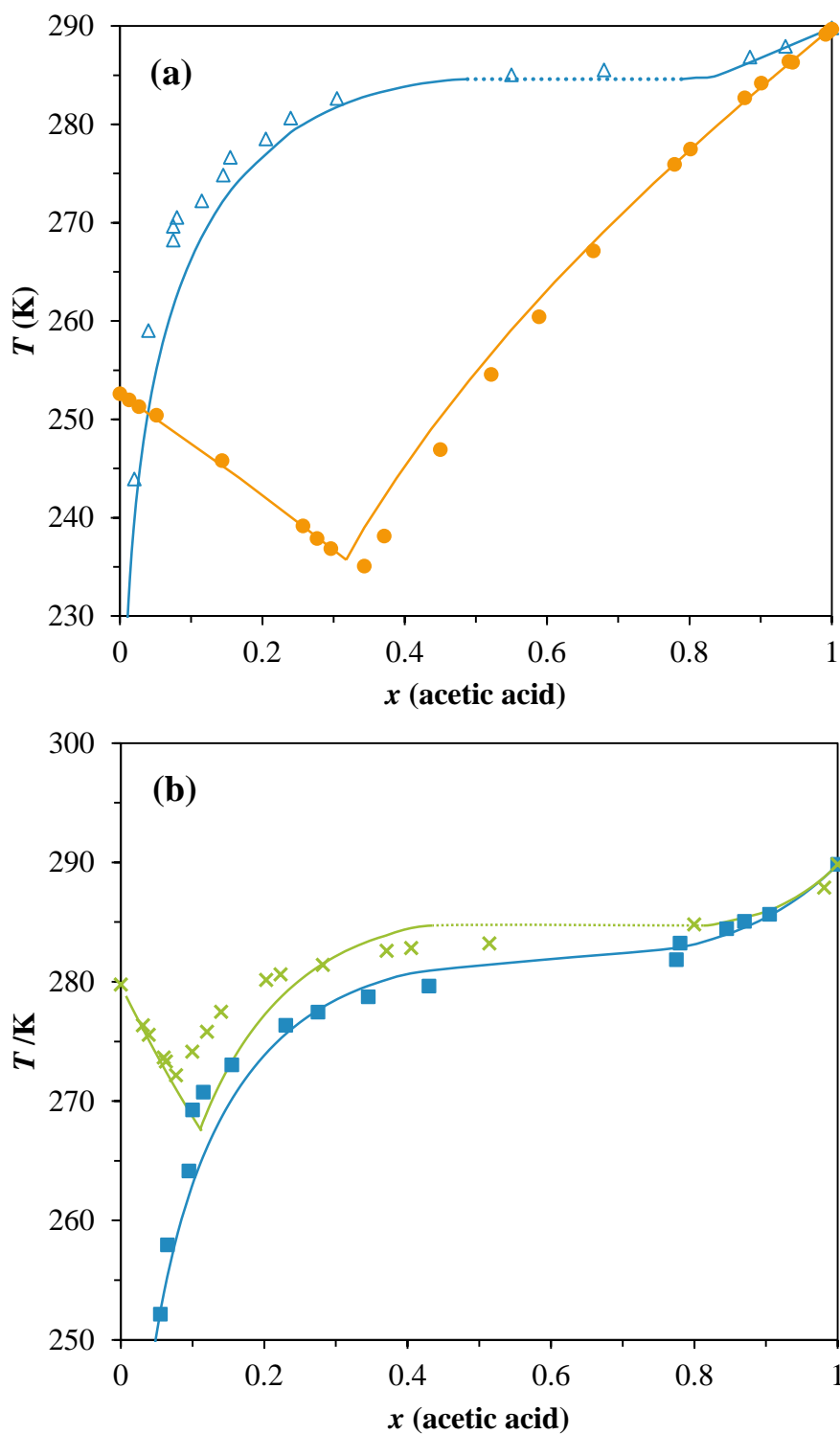
**Figure 4.** Vapor-liquid equilibria of *n*-alkanes + carboxylic acids. **(a)** *n*-heptane (1) + propionic acid (2). GCA-EoS predictions (solid lines) and experimental data [98,122] at 298.15(□), 318.15(△) and 323.15(●) K. **(b)** of *n*-butane + acetic acid at (◇) 423 K, (×) 448 K, (□) 473 K, (+) 498 K, and (○) 523 K [117].



**Figure 5.** Vapor-liquid equilibria of cyclohexane (1) + carboxylic acids at 318 K. Symbols: experimental data [98,116,121] of (\*) acetic, (O) propionic, (×) isobutyric, and (◇) neovaleric acid. Dashed and solid lines: correlation and prediction, respectively.

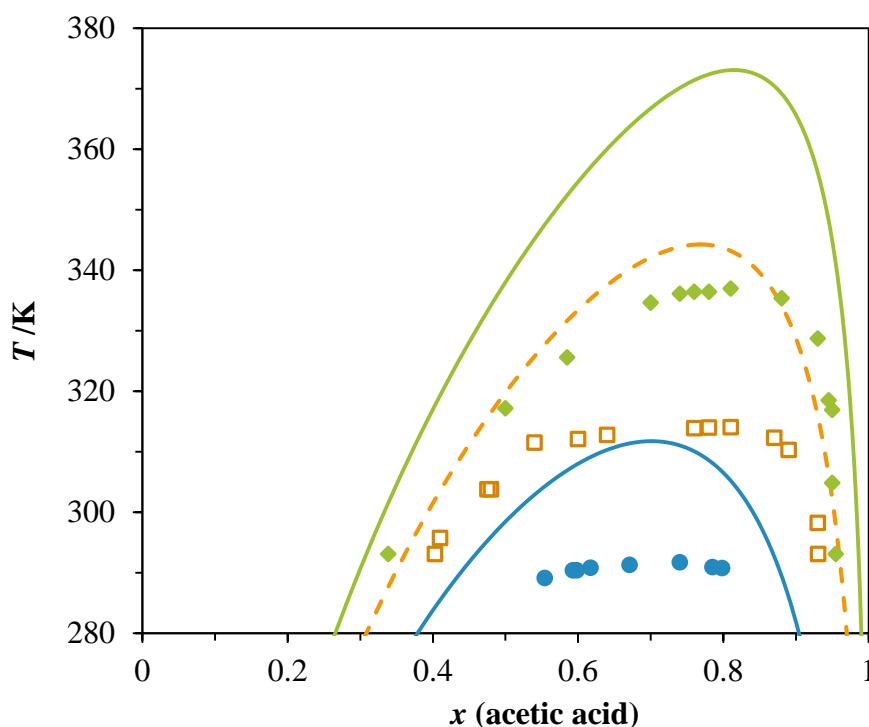


**Figure 6.** Vapor-liquid equilibria of formic acid + *n*-alkanes at atmospheric pressure. Symbols: azeotropic data from Ref. [99] for (◇) *n*-pentane, (■) *n*-hexane, (▲) *n*-heptane, and (×) *n*-octane. Dashed and solid lines: correlation and prediction, respectively. Dotted line: predicted VLLE condition.



**Figure 7.** Solid-liquid equilibria of carboxylic acids binary systems at atmospheric pressure. (a) (●) of the acetic acid (1) + propionic acid [23], and (△) acetic acid (1) + *n*-heptane [140]. (b) acetic acid + (○) cyclopentane [140] and (×) cyclohexane [27]. Lines: GCA-EOS predictions.

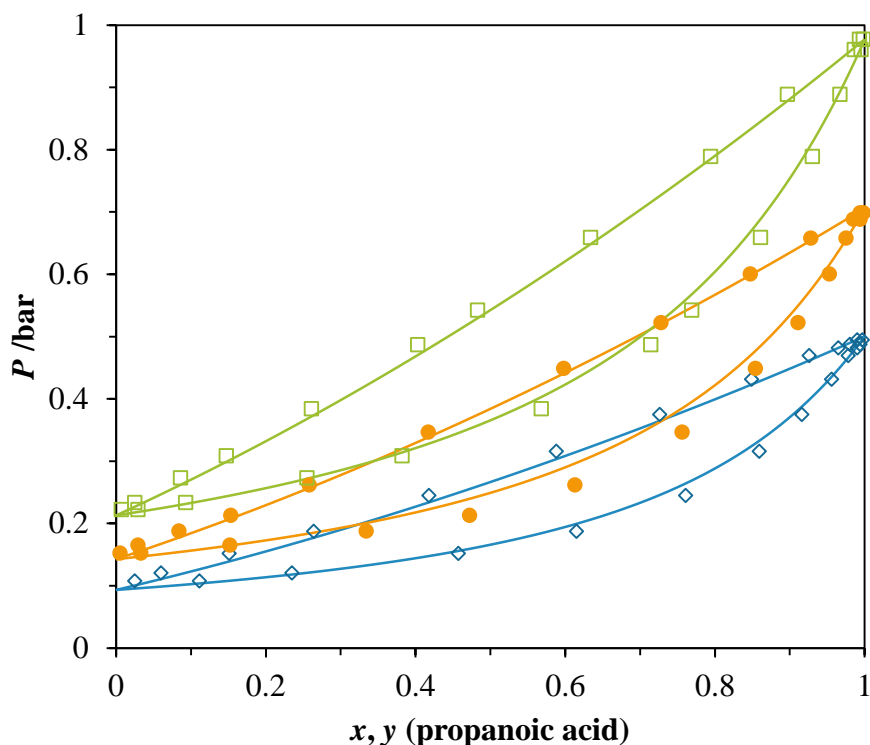
Regarding liquid-liquid equilibrium (LLE), the only data available in the literature up to our knowledge for mixtures of carboxylic acids with hydrocarbons are those reported by Zieborak and Olszewski [89], and Richard et al. [90], for acetic acid with *n*-alkanes (*n*-octane, *n*-decane and *n*-dodecane). As shown in Fig. 8, the GCA-EOS is able to predict qualitatively the low temperature asymmetric liquid immiscibility; however, important deviations are shown in the prediction of the upper critical end-point temperatures (UCEP). It is worth highlighting that the GCA-EOS, as any model based on mean-field theory, does not describe the non-analytical behavior of critical points. In this regard, the model follows well the LLE at temperatures 20 K below the UCEP, as seen in Fig. 8.



**Figure 8.** Liquid-liquid equilibria of acetic acid + *n*-alkanes. Symbols: experimental data of (●) *n*-octane, (□) *n*-decane, and (◆) *n*-dodecane [89,90]. Dashed and solid lines: GCA-EOS correlation and prediction, respectively.

On the other hand, it is always a challenge for group contribution models to predict a near-ideal phase behavior when the system contains functional groups with high non-ideal interactions. This is the case of mixtures comprising carboxylic acids, where the polar and associating carboxylic acid groups ( $\text{CH}_2\text{COOH}$ ,  $\text{CHCOOH}$ ) interact with the non-polar methyl groups ( $\text{CH}_2$ ,  $\text{CH}_3$ ). In this regard, the GCA-EOS equation is able to predict the near-ideal VLE and SLE behavior with high accuracy. For instance, Fig. 9

and 14 show the ideal VLE behavior of the binary mixture propionic acid + valeric acid and the also ideal SLE behavior of the binary mixtures of myristic acid with caprylic and lauric acids, respectively.



**Figure 9.** Vapor-liquid of propionic acid (1) + valeric acid (2) binary system. GCA-EoS predictions (solid lines) and experimental data [2] at ( $\diamond$ ) 393.15, ( $\bullet$ ) 403.15 and ( $\square$ ) 413.15 K.

Finally, there are few ternary phase equilibrium data available in the literature of systems comprising carboxylic acids. Table 9 compares GCA-EoS predictions with the isothermal vapor liquid equilibrium data of 3 ternary systems reported by Miyamoto et al. [15]. Good results were obtained, with absolute deviations in phase compositions of the order of 7%.

**Table 9.** GCA-EoS predictions of vapor liquid equilibria in ternary systems.

Compounds			NP	T/K	P/kPa	AARD(%) in liquid(L) and vapor(V) phase compositions			
1	2	3				$x_1$	$x_2$	$x_3$	
HCOOH	CH <sub>3</sub> COOH	C <sub>2</sub> H <sub>5</sub> COOH	6	343	0.16-0.29	L	3.0	4.6	4.0
						V	6.5	5.8	7.7
CH <sub>3</sub> COOH	C <sub>2</sub> H <sub>5</sub> COOH	<i>n</i> -C <sub>3</sub> H <sub>7</sub> COOH	6	358	0.10-0.22	L	9.0	1.6	10
						V	4.4	2.1	8.4
<i>n</i> -C <sub>6</sub> H <sub>14</sub>	CH <sub>3</sub> COOH	C <sub>2</sub> H <sub>5</sub> COOH	6	323	0.31-0.49	L	16	8.3	17
						V	1.4	5.2	13

Experimental data from reference [15].

### 3.2. Phase equilibria prediction of dicarboxylic acids

In this section we show the results of applying the GC principle to the prediction of dicarboxylic acids. This is a difficult task because of the interaction of both carboxylic groups within the molecule, what hinders applying a GC approach. Furthermore, dicarboxylic acids are solid at room temperature, and also exhibit low vapor pressure. Some of them even decompose before boiling [70,141], what encumbers measuring their vaporization properties. Hence, it is worth investigating how a conscious parameterization of a GC model from monocarboxylic acids performs dicarboxylic acids. It is worth recalling that the definition of the acid group that we propose promotes a group as electroneutral as possible, in order to ensure that the group behaves equally in different contexts [142]. In this regard, succinic acid is assembled with just two  $\text{CH}_2\text{COOH}$  groups, without any paraffinic group involved. On the other hand, malonic acid is modeled with one  $\text{CH}_2\text{COOH}$  and one  $\text{CCOOH}$ . Note that the quaternary carbon in the  $\text{CCOOH}$  group has no interaction area; therefore,  $q_{\text{CCOOH}}$  equals that of a conventional  $\text{COOH}$  group of UNIFAC and previous GCA EOS works. Regarding the free-volume contribution, we obtain most of  $d_c$  parameters from one vapor-liquid saturation temperature [143] as for monocarboxylic acids. There are two exceptions: 1) malonic and succinic acids, for which sublimation pressure was used [144] with the help of Eq. (7); and 2) all branched dicarboxylic acids, for which the same  $d_c$  as their linear counterpart was employed. Despite this, the  $d_c$  of dicarboxylic acids obtained here follow well the trend shown in Figure 3.

Table 10 and Figure 10 show the prediction of the critical temperature, pressure, and vapor pressure data, when available. As can be seen, the  $T_c$  of all dicarboxylic acids are very well predicted according the data of Nikitin et al. [145]. Surprisingly, the best prediction was obtained for succinic acid for both,  $T_c$  and  $P_c$ , which exhibits a maximum  $T_c$  within the homologue's series up to  $\text{C}_{10}$ . On the other hand, the model predicts with larger errors the critical pressure of glutaric and longer acids, for what we can assume that the model predicts only qualitatively these  $P_c$ . Last, the predicted vapor pressures also present larger deviations from experimental data; nonetheless, we should take into account that the data provided by Stull [143] are a compilation of different sources available, and that dicarboxylic acids are unstable at high temperatures [145]. Moreover, the sublimation pressure of azelaic and pimelic acids are acceptably well predicted. This



implies that the sublimation enthalpy of these compounds is acceptable for being a prediction.

**Table 10.** GCA-EOS prediction of dicarboxylic acids vapor pressures

Compound	$T_c$ (K)	$d_c$ <sup>a</sup> (cm/mol <sup>1/3</sup> )	AARD%		$\Delta T_r$ <sup>b</sup>	AARD ( $P$ )% <sup>c</sup>	Reference
			$T_c$	$P_c$			
malonic acid	833 <sup>d</sup>	4.087	-	-	-	-	this work
succinic acid	851	4.470	0.2	0.5	-	-	[145]
glutaric acid	840	4.816	0.7	23	0.52-0.69	13	[143,145,146]
2,2-dimethylsuccinic acid	794 <sup>d</sup>	5.1 <sup>e</sup>	-	-	-	-	this work
2,3-dimethylsuccinic acid	778 <sup>d</sup>	5.1 <sup>e</sup>	-	-	-	-	this work
3-methylglutaric acid	823 <sup>d</sup>	5.1 <sup>e</sup>	-	-	-	-	this work
adipic acid	841	5.100	1.1	17	0.51-0.73	14	[143,145]
pimelic acid	842	5.360	1.0	21	0.52-0.73	12	[143,145]
suberic acid	844	5.610	1.1	18	0.53-0.73	6	[143,145]
azelaic acid	844	5.855	0.9	14	0.53-0.75	11	[143,145]
sebacic acid	845	6.095	0.9	11	0.54-0.74	14	[143,145]

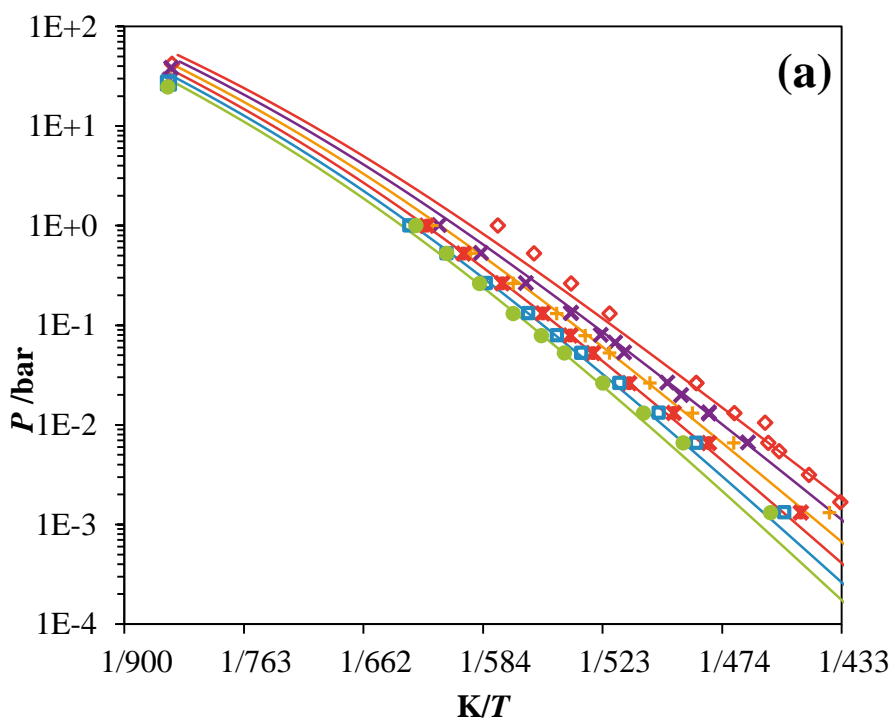
<sup>a</sup> Unless noticed,  $d_c$  values are calculated from a from a saturation point [77].

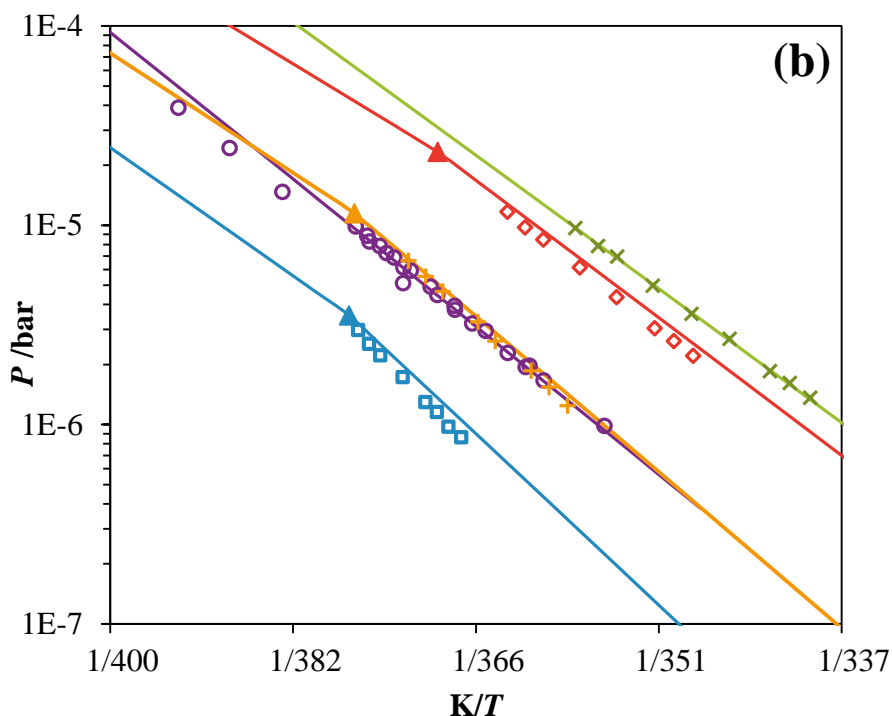
<sup>b</sup>  $T_r$  = reduced temperature (lower limit corresponds to a vapor pressure of 0.001 bar)

<sup>c</sup>  $AARD(P) = \frac{1}{NP} \sum_i \left| 1 - \frac{P_{calc,i}^v}{P_{exp,i}^v} \right|$ ;  $NP$  = number of experimental data points.

<sup>d</sup> Not available in the open literature, predicted using the GCA-EOS.

<sup>e</sup> Same as the linear isomer



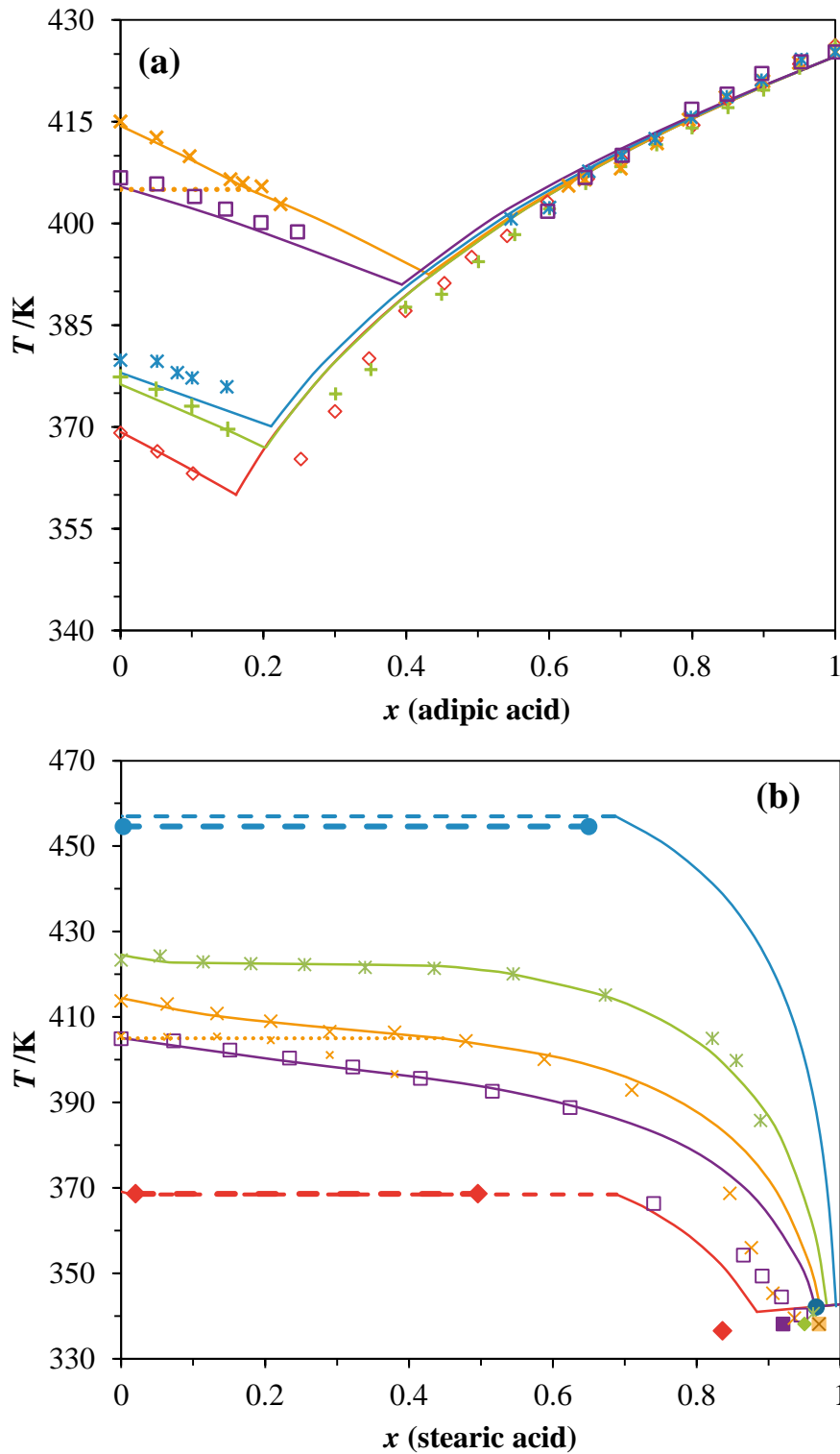


**Figure 10.** Vapor pressure of selected dicarboxylic acids. **(a)** Vapor pressure of ( $\diamond$ ) glutaric, ( $\square$ ) adipic, (+) pimelic, ( $*$ ) suberic, ( $\square$ ) azelaic, and ( $\bullet$ ) sebacid acids [143,145,146] **(b)** Sublimation pressures of ( $\times$ ) malonic, ( $\circ$ ) succinic, ( $\diamond$ ) glutaric, (+) pimelic, and ( $\square$ ) azelaic [144,147,148] acids. Symbols experimental data; lines: GCA EOS predictions. Solid triangles: predicted triple point.

Table 11 lists the equilibrium prediction results of binary systems with dicarboxylic acids. Here it is clear that the predictions of these systems show larger deviations than for monocarboxylic systems, with an average error of 10%. Nonetheless, most of the errors are also accompanied by the uncertainty in their melting properties listed in Table 2. Figure 11a shows binary dicarboxylic acid SLE, for which the GCA EOS represent them well because it captures the ideal solution of these compounds. On the other hand, Figure 11b depicts the SLE of stearic + some dicarboxylic acids, which are non-ideal mixtures. The model follows qualitatively the presence of the eutectic point. Furthermore, the model also predicts qualitatively the miscibility gap of stearic + succinic and glutaric acids reported by Berchiesi et al. [149].

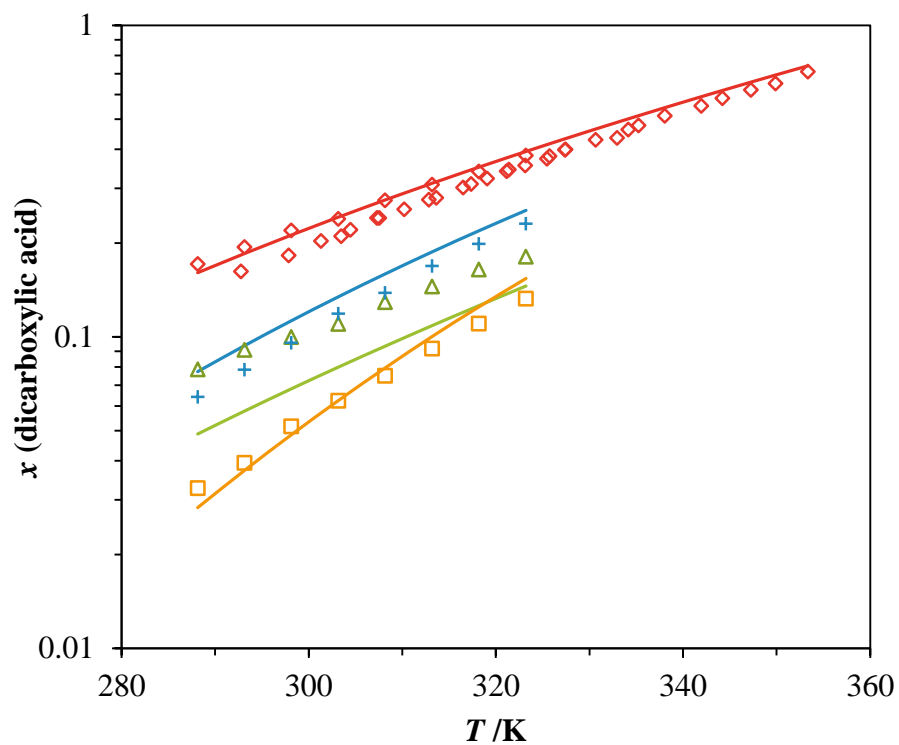
**Table 11.** Solid-liquid equilibria prediction of systems involving dicarboxylic acids.

Compound		T /K	AARD(x)%		N	Reference
1	2		1	2		
malonic	acetic acid	288-323	29	-	8	[150]
succinic acid	acetic acid	288-335	17	-	26	[6,150,151]
	propionic acid	288-329	30	-	10	[152]
glutaric acid	acetic acid	288-323	8.6	-	38	[150,151,153]
	propionic acid	288-329	30	-	10	[152]
	adipic acid	363-426	0.26	6.7	19	[26]
	2,2-dimethylsuccinic acid	359-413	1.7	20	18	[72]
2,2-dimethylsuccinic acid	2,3-dimethylsuccinic acid	347-392	2.9	4.9	16	[72]
	3-methylglutaric acid	344-369	3.4	1.1	11	[72]
	pimelic acid	346-377	3.7	1.7	19	[71]
	3-methylglutaric acid	354-411	17	0.59	17	[71]
	pimelic acid	366-411	19	1.5	16	[71]
	suberic acid	389-414	14	3.2	16	[72]
	azelaic acid	367-413	18	5.8	16	[154]
2,3-dimethylsuccinic acid	sebacic acid	388-413	14	2.1	16	[154]
	pimelic acid	356-393	5.2	2.6	17	[71]
	suberic acid	375-414	3.6	4.4	19	[72]
	azelaic acid	361-414	4.4	5.1	15	[154]
3-methylglutaric acid	sebacic acid	377-407	3.3	1.7	16	[154]
	pimelic acid	344-377	1.5	3.7	15	[71]
	suberic acid	362-393	1.0	4.2	20	[72]
	azelaic acid	347-380	3.0	5.9	17	[154]
adipic acid	sebacic acid	354-407	2.5	6.3	19	[154]
	acetic acid	288-388	12	-	41	[150,151,155-157]
	propionic acid	290-330	53	-	10	[152]
	pimelic acid	369-425	6.5	1.8	18	[71]
	suberic acid	403-425	2.6	1.2	14	[74]
	azelaic acid	376-425	2.6	10	11	[74]
	sebacic acid	399-425	4.4	5.8	11	[74]
pimelic acid	stearic acid	340-425	13	-	13	[76]
	acetic acid	288-323	15	-	8	[150]
	suberic acid	371-415	3.3	3.1	13	[74]
	azelaic acid	363-376	2.5	4.1	13	[74]
suberic acid	sebacic acid	370-404	2.3	2.2	12	[74]
	acetic acid	288-323	8.3	-	8	[150]
	azelaic acid	374-411	4.0	10	12	[74]
	sebacic acid	394-412	1.7	1.2	12	[74]
	stearic acid	340-314	20	-	13	[76]
azelaic acid	acetic acid	288-323	8.6	-	8	[150]
	sebacic acid	376-405	3.5	7.9	11	[74]
sebacic acid	acetic acid	288-323	16	-	8	[150]
	stearic acid	340-405	23	-	13	[76]

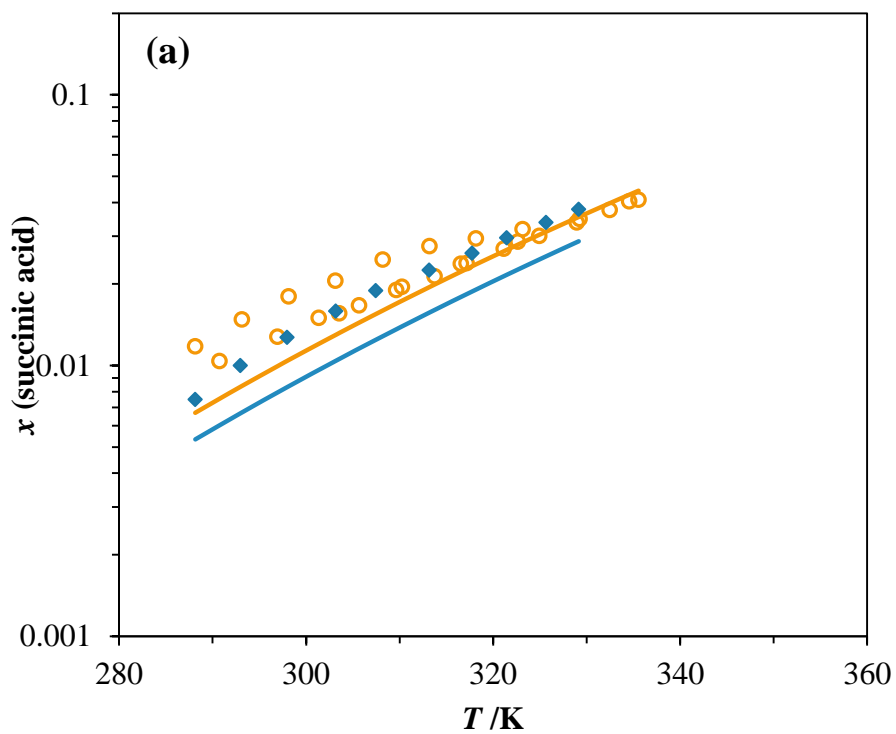


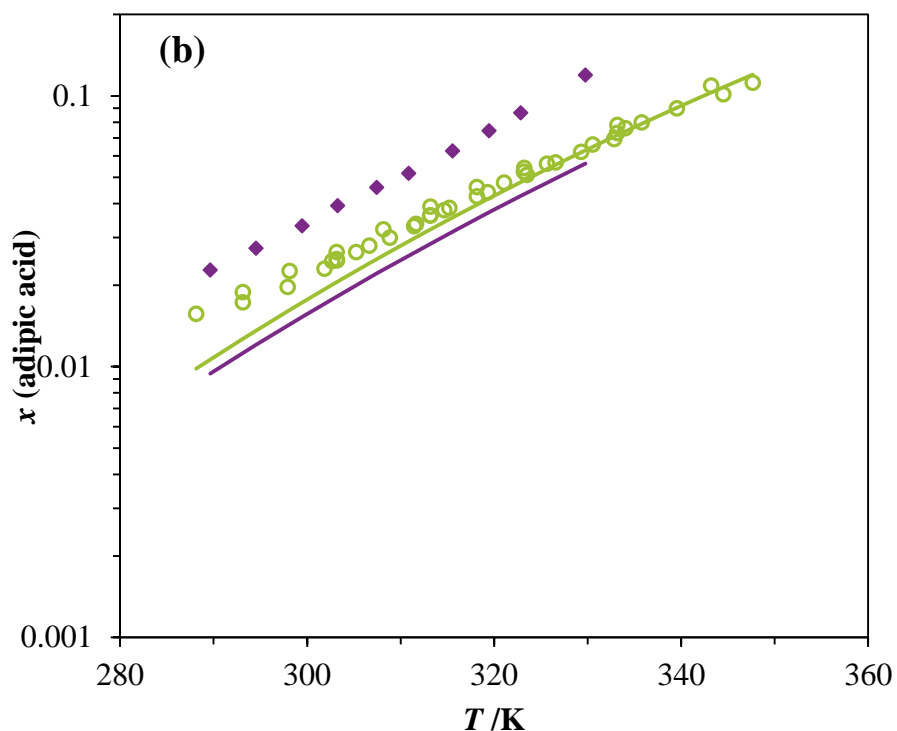
**Figure 11.** Solid-liquid equilibria of dicarboxylic acids. **(a)** adipic acid + ( $\diamond$ ) glutaric, (+) pimelic, ( $\times$ ) suberic, ( $*$ ) azelaic, and ( $\square$ ) sebaccic acids. **(b)** stearic acid + ( $\circ$ ) succinic, ( $\diamond$ ) glutaric, ( $*$ ) adipic, ( $\times$ ) suberic, and ( $\square$ ) sebaccic acids. Empty symbols: Ma et al. [76]; filled symbols: Berchiesi et al. [149]. Solid lines: GCA-EOS predictions. Dotted line and small symbols: suberic solid-solid transition. Dashed lines: solid-liquid equilibria.

Figure 12 depicts the solubility of selected dicarboxylic acids, from malonic to azelaic acids, in acetic acid. As can be seen, the model catches qualitatively the solubility of all acids, with an average error of 13%. On the other hand, the model performance falls abruptly for propionic acid as solvent, as shown in Table 11 and Figure 13. The GCA EOS predicts a slight decrease in the solubility of succinic acid when switching from acetic acid to propionic acid as solvent. This is because of the  $\text{CH}_3$  group present in propionic acid which subtly increases the activity coefficient of the solute. On the other hand, the experimental data of Yu et al. [6] and Luo et al. [151] for acetic acid, and Luo et al. [152] for propionic acid, suggest a constant activity coefficient for succinic acid in both solvents, as seen in Figure 13a. On the contrary, the data of Luo et al. [152] shows a much larger solubility of glutaric and adipic acids in propionic acid than in acetic acid [150,151,153,155–157], while the GCA EOS predict a similar trend as for succinic acid. Moreover, the miscibility gaps of stearic + succinic or glutaric acids in Figure 11b implies that, at some point, the activity coefficient should increase with the monocarboxylic acid alkyl chain, as the GCA EOS predicts. This suggests a possible non-additive behavior for these systems; nonetheless, to the best of our knowledge, there are no data between propionic and stearic acids. However, the model is able to predict the solubility of adipic acid in other solvent mixtures. For instance, Figure 14 depicts the solubility of adipic acid in mixtures of acetic and cyclohexane. Adipic acid is basically non-miscible with cyclohexane, and the model captures well the change in solubility as the solvent composition changes. Hence, although results for the solubility in propionic acid against the available data are rather poor, the overall performance of the model on dicarboxylic acids is good from a predictive point of view.

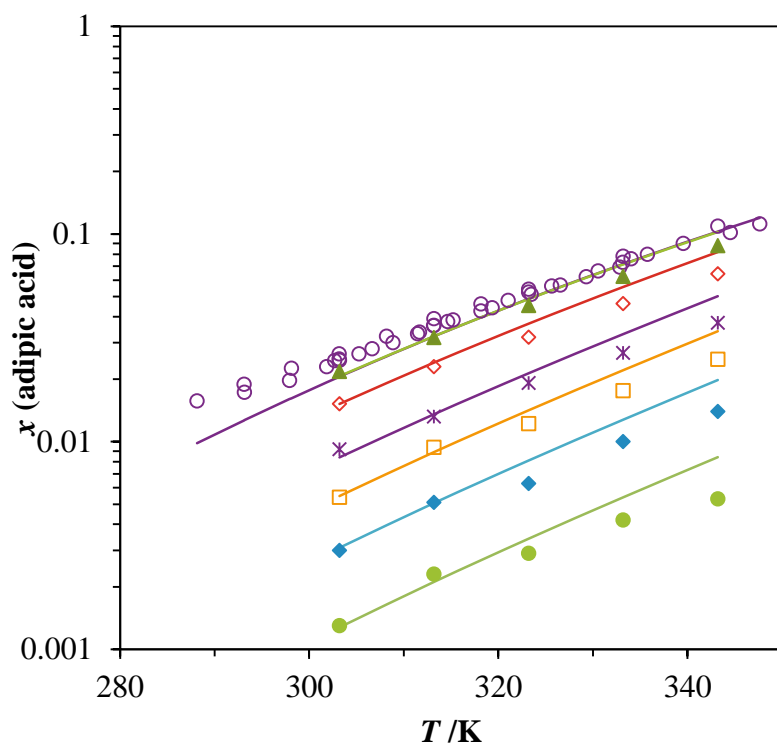


**Figure 12.** Solubility of selected dicarboxylic acids in acetic acids: ( $\Delta$ ) malonic, ( $\diamond$ ) glutaric, (+) pimelic and ( $\square$ ) azelaic acids. Symbols: experimental data [150,151,153]; lines: GCA EOS predictions.





**Figure 13.** Solubility of dicarboxylic acids in (○) acetic and (◆) propionic acids. (a) Succinic acid [6,150–152]. (b) Adipic acid [150–152,155–157]. Symbols: experimental data. Solid lines: GCA EOS predictions.



**Figure 14.** Solubility of adipic acid in acetic acid-cyclohexane mixtures. Symbols: (○) 100% (w), (▲) 80% (w), (◇) 60% (w), (\*) 40% (w), (□) 30% (w), (◆) 20% (w), and (●) 10% (w) of acetic acid [156]. Lines: GCA EOS predictions

## 4. Conclusions

In this work, we carry out a new parameterization of the GCA-EOS, with the aim of modeling the phase behavior of mixtures comprising mono- and di-carboxylic acids and hydrocarbons. For this purpose, three carboxylic acid groups were defined: the formic (HCOOH) and acetic (CH<sub>3</sub>COOH) acid, molecular groups needed to represent the first two members of the carboxylic acid family, and the aliphatic acid functional group (CH<sub>n</sub>COOH,  $n = 0, 1, 2$ ) to describe the acid function in the remaining aliphatic acids. Considering the predominant effect of association in the phase behavior of these mixtures, we show the importance of modeling the carboxylic acid monomer fractions in liquid and vapor phases, which we set as a constrain during the parameterization process. In this work, we show the robustness of the new parameterization of GCA-EOS with accurate predictions of vapor-liquid and solid-liquid equilibrium conditions, as well as infinite dilution activity coefficients of binary and ternary mixtures of monocarboxylic acids and hydrocarbons. Furthermore, we also challenge the model to predict phase behavior of pure dicarboxylic acids and its mixtures with paraffins. We show that the model is capable of predicting these systems with a good degree of precision without the need to include new interaction parameters, new specific functional groups, or second-order functional groups, as required by other models. These results encourage to extend the model to more challenging systems, like those present in the biomass processing industry in the context of value-added product search and processing.

### List of symbols

$A$	Helmholtz free energy
$AARD(Z)\%$	average absolute relative deviation in variable $Z$ : $\frac{100}{N} \sum_i^N \left  1 - \frac{Z_{\text{calc } i}}{Z_{\text{exp } i}} \right $
$ARD(Z)\%$	absolute relative deviation in $Z$ : $100 \times \left  1 - \frac{Z_{\text{calc}}}{Z_{\text{exp}}} \right $
$c_p$	molar heat capacity at constant pressure
$d_{ci}$	effective hard sphere diameter of component $i$ evaluated at $T_c$
$f_i$	fugacity of the pure compound $i$
$g_{ji}$	group energy per surface segment of group $j$
$h$	molar enthalpy
$K_{\text{eq}}$	equilibrium dimerization constant
LLE	liquid-liquid equilibria
$NC$	number of components in the mixture
$NG$	number of attractive groups in the mixture



$NGA$	number of associating groups in the mixture
$n_i$	number of moles of compound $i$ .
$n_j^*$	number of moles of associating group $j$ .
$P$	pressure
$q_j$	number of surface segments of group $j$
$R$	universal gas constant
$r_j$	number of volume segments of group $j$
SLE	solid-liquid equilibria
$T$	temperature
$T_{ci}$	critical temperature of component $i$
$V$	mixture total volume
$v$	molar volume
VLE	vapor-liquid equilibria
VP	vapor pressure
$X_{ki}$	non-bonded fraction of site $k$ in group $i$
$x_i$	molar composition in liquid phase of component $i$
$y_i$	molar composition in vapor phase of component $i$
$\Delta Z\%$	AARD% in variable $Z$

### *Greek symbols*

$\alpha_{ij}$	non-randomness parameter between groups $i$ and $j$
$\Delta_{ki,lj}$	association strength between site $k$ of group $i$ and site $l$ of group $j$
$\varepsilon_{ki,lj}$	energy of association between site $k$ of group $i$ and site $l$ of group $j$
$\kappa_{ki,lj}$	volume of association between site $k$ of group $i$ and site $l$ of group $j$
$\nu_{ij}^*$	number of associating groups $j$ in compound $i$
$\phi_i$	fugacity coefficient of compound $i$ .

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**Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: