

Solutions of alkyl methanoates and alkanes: Simultaneous modeling of phase equilibria and mixing properties. Estimation of behavior by UNIFAC with recalculation of parameters



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ABSTRACT

Isobaric vapor–liquid equilibria at $p = 101.32$ kPa (*iso-p* VLE) and the mixing properties, h^E and v^E , are determined for a set of twelve binary solutions: $\text{HCOOC}_u\text{H}_{2u+1}(1)+\text{C}_n\text{H}_{2n+2}(2)$ with $u = (1-4)$ and $n = (7-9)$. The (*iso-p* VLE) present deviations from the ideal behavior, which augment as u diminishes and n increases. Systems with [$u = 2, 3$, $n = 7$] and [$u = 4$, $n = 7, 8$] present a minimum-boiling azeotrope. The non-ideality is also reflected in high endothermic values, $h^E > 0$, and expansive effects, $v^E > 0$, for all the binaries, which increase regularly with n . However, for a same hydrocarbon, the properties diminish with increasing u . This, in turn, causes the dipolar effect of the methanoates to decrease, with the resulting reduction in mixing effects. As a result, other interpretations on the behavioral structural model of these systems are established. Modeling of the experimental quantities is carried out using the authors' model with good results, and comparisons are made with an adapted version of the NRTL model. Energetic properties of the solutions are predicted with the UNIFAC group contribution model, but the values obtained are not as good. Hence, parameters corresponding to the specific interaction HCOO/CH_2 are recalculated using a wider database, resulting in slightly better values. COSMO-RS methodology is also employed to assess the energetic effects of the mixing process. Apart from some exceptions, also mentioned here, the method gives an acceptable estimation of the behavior of these systems.

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1. Introduction

Some peculiar characteristics of alkyl methanoates give rise to unusual aspects of their behavior in solution that distinguish them from other esters [1]. Experimental data on macroscopic properties directly related to the net effects of the intermolecular interactions are required to enable their interpretation and modeling. The value of these esters in industrial sectors resides in their application as solvents or as a reagent in the production of formamide for use as propellants, or refrigerants, etc. In spite of the scientific and technical interest in methanoates, there is only limited information in the literature about solutions of these compounds with aliphatic hydrocarbons, the best known solvents. Previous works have reported experimental data of isobaric vapor–liquid equilibria [2–7] (*iso-p* VLE) and several mixing properties [3–10] (v^E , h^E) at different temperatures for some of the binaries selected, empirically defined by: $\{\text{HCOOC}_u\text{H}_{2u+1}(1)+\text{C}_n\text{H}_{2n+2}(2)$

$u = [1-4]$ $n = [7-9]\}$. In other words, considering the matrix composed of 24 systems, recent studies were focused on the saturated hydrocarbons: pentane [7], hexane [5] and decane [6], leaving the 12 systems corresponding to heptane, octane and nonane, for a later study, which are now included in this work. According to NIST information, in the ThermoLit database, only partial information is available (VLE, [2–4]; v^E , [8]; h^E , [9–13]; c_p^E , [11]) for some of the binaries we propose to study here. However, the database of the aforementioned matrix is still incomplete, and does not include VLE data for binaries of butyl methanoates with C7–C9 or methyl methanoates with C8 and C9. The contribution of this work is, therefore, to present the original experimental data of *iso-p* VLE for these systems, and to provide values for the remaining seven, to verify previously published results and those of other mixing properties, v^E and h^E , for the twelve systems, in an attempt to accurately establish the behavior of these solutions. It is also of value for our research to repeat some measurements, especially to confirm the presence of the azeotrope of the binary methyl methanoate + heptane, which was calculated [3] at an extreme ester composition (>0.99).

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Nomenclature

| | |
|--|---|
| B_{ii} | Second virial coefficients for pure component i |
| B_{ij} | Cross second virial coefficients for mixture i – j |
| c_i | Weighting coefficients for property i , Eq. (11) |
| c_p^E | Excess thermal capacity ($\text{J mol}^{-1} \text{K}^{-1}$) |
| GA | Genetic algorithm |
| G_{ij} | Parameters of NRTL model, Eq. (12) |
| g^E | Excess molar Gibbs function (J mol^{-1}) |
| g_{ij}^E | Coefficients Eqs. (8–10) |
| h^E | Excess molar enthalpy (J mol^{-1}) |
| h_{ij} | Coefficients of Eq. (1) for excess enthalpies |
| k_v | Parameter of Eq. (3) |
| k_h | Parameter of Eq. (5) |
| k_g | Parameter used for active fraction in the Gibbs function, Eq. (7) |
| N | Number of experimental points |
| OF | Objective function |
| p | Pressure (kPa) |
| p_i^0 | Vapor pressure of component i , (kPa) |
| q_k | Surface parameter of molecule k |
| R | Gas constant ($\text{J mol}^{-1} \text{K}^{-1}$) |
| r_k | Volume parameter of molecule k |
| s^E | Excess molar entropy ($\text{J mol}^{-1} \text{K}^{-1}$) |
| $s(y)$ | Standard deviation of a property y |
| T | Temperature (K) |
| v^E | Excess molar volume ($\text{m}^3 \text{mol}^{-1}$) |
| v_{ij} | Coefficients of Eq. (1) for excess volumes |
| x_i | Molar fraction in the liquid phase for component i |
| y_i | Molar fraction in the vapor phase for component i |
| y^E | Excess generic property |
| z_i | Active fraction of component i |
| Greek letters | |
| α | Non-random parameter of NRTL model, Eq. (15) |
| α_i | Isobaric thermal expansion coefficient of component i , K^{-1} |
| δ | Differences between isobaric thermal expansion coefficients |
| ρ | Density, kg m^{-3} |
| φ | Fugacity coefficient |
| $\Delta g_{ij1}, \Delta g_{ij2}, \Delta g_{ij3}$ | Coefficients for NRTL model given by Eq. (13) |
| γ_i | Activity coefficient of component i |
| τ_{ij} | Coefficients of NRTL equation |

To verify the broad capacity of the model used previously by the authors [5–7], all the thermodynamic quantities y^E were correlated as a function of two variables $y^E = \xi(x, T)$, using an appropriate

algorithm and a multivariate optimization method. Data correlation using the NRTL equation [14] is used to validate and compare the results obtained with the proposed model. Finally, the UNIFAC method [15] was applied, since in previous works [5–7] we have verified that the specific interaction HCOO/CH₂ produces values that become more distant from real values as the chain length of the saturated hydrocarbon increases. The database created with the 24 systems of the subset alkyl methanoates + alkanes can be used to recalculate the values for this interaction to improve theoretical predictions.

2. Experimental

2.1. Chemicals

Table 1 shows the specifications of all the chemicals used. All of them were of the highest commercial purity and were supplied by Sigma–Aldrich. They were degasified by ultrasound and stored in the dark over a 3 Å (Fluka) molecular sieve to remove traces of moisture. Before use, the purity of the products was checked again by gas chromatography with a HP-6890N equipped with FID, showing values coherent to the manufacturers', see Table 1. The quality of the products was also certified before use with the measurements of three properties (normal boiling point T_b^0 , density ρ , and refractive index n_D) which are compiled in Table 2; a comparison with published data reveals slight differences which are within the acceptable intervals of experimental uncertainty.

2.2. Apparatus and procedures

An Abbe refractometer by Zuzi-320 was used to measure the n_D at (298.15 ± 0.02) K. The temperature was kept constant by using a Heto-CB7 circulating water bath. Densities of pure compounds and solutions were measured ($\rho \pm 0.02$) kg m^{-3} by a DMA-60/602 vibrating tube densimeter, from Anton-Paar. The four working temperatures were obtained by passing a water current from a Polyscience 1166D thermostatic bath into the measuring cell, verifying the stability of the temperature ($T \pm 0.01$) K with a sensor connected to a DT-100 Anton Paar system, calibrated previously (ITS-90). The densimeter was calibrated with bidistilled water, degasified and purified in our laboratory (with a conductance lower than 1 μS) and nonane, following our standard practice [5–9]. Solutions were prepared by weighing and the average uncertainty of the compositions was ($x \pm 0.0002$). Excess volumes obtained from the densities showed an uncertainty of ($v^E \pm 2$) $\times 10^{-9} \text{m}^3 \text{mol}^{-1}$.

The h^E of the set $\{\text{HCOOC}_u\text{H}_{2u+1}(1) + \text{C}_n\text{H}_{2n+2}(2)\}$ with $u = [1-4]$ and $n = [7-9]$ were measured at three temperatures (291, 298 and 318) K using a Calvet type calorimeter, MS80D from Setaram. To carry out measurements at 291.15 K the room was conditioned to obtain an ambient temperature of $t_{\text{amb}} < 16^\circ\text{C}$, since the calorimetric system achieves thermal control by heating alone. The

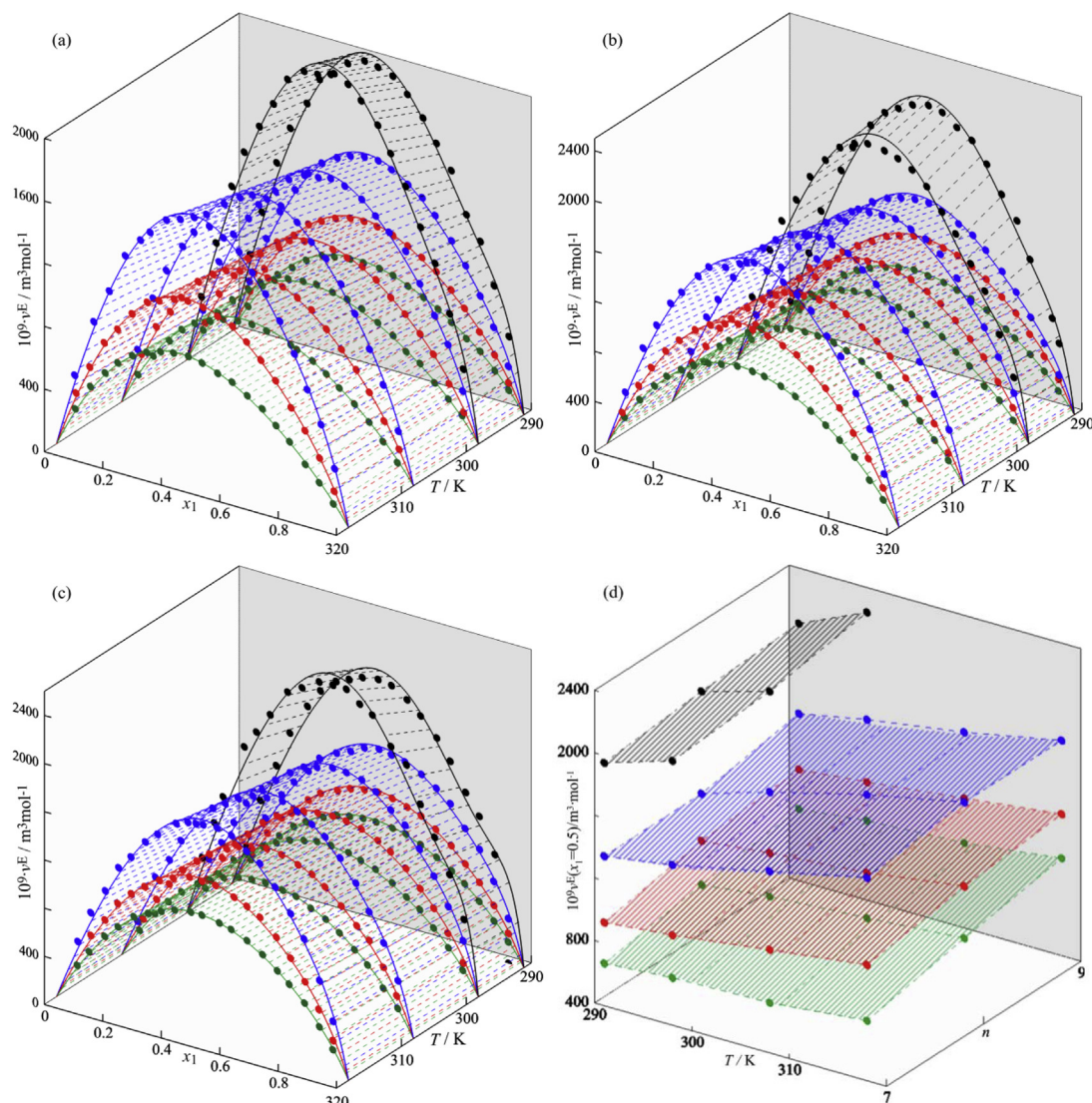
Table 1
Description of the materials used.

| Compound | Supplier | Purity w/w | Analytical method | Physical pretreatment |
|-------------------|----------|------------|--------------------|-------------------------------------|
| Methyl methanoate | Aldrich | >0.99 | GC | Degassed and molecular sieve 0.3 nm |
| Ethyl methanoate | Aldrich | >0.97 | GC | Degassed and molecular sieve 0.3 nm |
| Propyl methanoate | Aldrich | >0.97 | GC | Degassed and molecular sieve 0.3 nm |
| Butyl methanoate | Aldrich | >0.97 | GC | Degassed and molecular sieve 0.3 nm |
| Heptane | Aldrich | >0.99 | GC | Degassed and molecular sieve 0.3 nm |
| Octane | Aldrich | >0.99 | GC | Degassed and molecular sieve 0.3 nm |
| Nonane | Aldrich | >0.99 | GC | Degassed and molecular sieve 0.3 nm |
| Water | – | – | Conductivity meter | Double distillation |

GC, gas chromatography.

Table 2Experimental thermophysical properties^a of pure compounds. Densities and refractive indices were measured at atmospheric pressure.

| Compound | CAS-registry number | T_b^0 (K) | | ρ (kg m ⁻³) (T=298.15 K) | | $10^{3\alpha}$ (K ⁻¹) | | n_D (T=298.15 K) | |
|-------------------|---------------------|-------------|--|---|--|-----------------------------------|----------------------|--------------------|---------------------|
| | | Exp. | Lit. | Exp. | Lit. | Exp. | Lit. | Exp. | Lit. |
| Methyl methanoate | 107-31-3 | 304.70 | 304.65 ^a 304.90 ^b | 966.10 | 966.40 ^b 966.54 ^d | 1.52E-3 | 1.61E-3 ^c | 1.3415 | 1.3415 ^b |
| Ethyl methanoate | 109-94-4 | 327.33 | 327.30 ^a 327.46 ^b | 914.70 | 915.30 ^b 915.16 ^d | 1.47E-3 | 1.48E-3 ^c | 1.3580 | 1.3575 ^b |
| Propyl methanoate | 110-74-7 | 353.92 | 354.00 ^a 353.97 ^b | 899.83 | 899.60 ^b 899.08 ^d | 1.33E-3 | 1.30E-3 ^c | 1.3750 | 1.3750 ^b |
| Butyl methanoate | 592-84-7 | 380.13 | 379.75 ^a 379.25 ^b | 888.33 | 886.90 ^b 888.66 ^d | 1.22E-3 | 1.15E-3 ^c | 1.3872 | 1.3874 ^b |
| Heptane | 142-82-5 | 371.56 | 371.58 ^a 371.57 ^b | 679.66 | 679.49 ^b 679.48 ^e | 1.28E-3 | 1.24E-3 ^c | 1.3852 | 1.3851 ^b |
| Octane | 111-65-9 | 398.83 | 398.82 ^{a,b} 398.83 ^c | 698.52 | 698.62 ^b 698.60 ^e | 1.18E-3 | 1.15E-3 ^c | 1.3952 | 1.3951 ^b |
| Nonane | 111-84-2 | 423.94 | 423.95 ^a 423.97 ^b | 713.85 | 713.75 ^b 713.85 ^e | 1.11E-3 | 1.09E-3 ^c | 1.4031 | 1.4031 ^b |

^a Uncertainties u are: $u(T) = \pm 0.02$ K, $u(n_D) = \pm 0.0002$, and $u(\rho) = \pm 0.02$ kg m⁻³.^b Ref. [16].^c Ref. [17].^d Ref. [6].^e Ref. [18].**Fig. 1.** Experimental (x_1, T, v^E) data and surfaces constructed using Eqs. (1)–(3) for binaries: $\text{HCOO}(\text{CH}_2)_{u-1}\text{CH}_3(1) + \text{C}_n\text{H}_{2n+2}(2)$ [$u = (1-4)$, $n = (7-9)$]. (a) for $n = 7$, (b) for $n = 8$, (c) for $n = 9$. (d) Virtual surfaces generated by $[n, T, v^E(\text{at } x_1 = 0.5)]$. Labels: (●) $u = 1$, (●) $u = 2$, (●) $u = 3$, (●) $u = 4$.

apparatus was calibrated at each temperature producing a thermal effect with a power source in the laboratory cell, analogous to the mixing process, at several wattages lower than 100 mW, in an attempt to measure the reproducibility of the apparatus. To minimize the differences between the selected temperature and the real temperature of the calorimetric block, a fine-tuning on the controller of the thermopile of the apparatus was used as described previously [7]. The software Setsoft© was used to obtain the thermograms of each of the tests carried out at different compositions ($x \pm 0.0003$) and/or temperatures ($T \pm 0.005$) K. The calibration carried out was compared with measurements obtained for the binary propanol+benzene at 298.15 and 318.15 K [19], estimating a mean error lower than ($h^E \pm 1\%$) J mol⁻¹. There are no data in the literature for systems at 291 K, so data obtained by extrapolating values obtained for the binary cyclohexane+hexane at 298.15 K [20], and at 288.15 and 318 K [21] were used as a reference; in this case, the uncertainties of the h^E measurements were slightly higher than 1%, and for the compositions corresponded to ($x \pm 0.0003$).

The *iso-p* VLE characteristic values and the boiling points for pure compounds were obtained with the same ebullometer that was used by our group in previous works [22,23]. To achieve conditions of $p = (101.32 \pm 0.02)$ kPa, a DH-PPC2 pressure controller/calibrator was used operating with vacuum and N₂-atmosphere. The two phases (liquid and vapor) recirculate in a small capacity still, ~60 cm³, until stability of temperature ($T \pm 0.02$) K and pressure. The temperature was measured using a Comark-6800 digital thermometer, using Pt-100 probes and previously calibrated according to ITS-90. Samples of the phases were analyzed by densimetry and the compositions determined by a regressive method using a mathematical expression obtained previously for the binary studied, as follows:

$$0 = \rho - (x_1\rho_1 + x_2\rho_2) - x_1x_2(a_0 + a_1x_1 + a_2x_1^2) \quad (1)$$

The a_i parameters are obtained by applying a least-squares method to the experimental data $\rho = \rho(x_1)$ at $T = 298.15$ K of the

binary considered. In Eq. (1), ρ_i are the densities of the pure i -compounds and ρ the densities of the solution of the sample (in the vapor or liquid phase). In this way, the uncertainty in the compositions obtained by regression was estimated as ($x, y \pm 0.002$).

3. Experimental results and correlation

3.1. Mixing properties. Interpretation of results

The values (x, T, ρ, v^E) of twelve solutions {HCOO(CH₂)_{u-1}CH₃(1) + C_nH_{2n+2}(2) [$u = (1-4), n = (7-9)$]} in the temperature interval (291–318) K and at atmospheric pressure, are shown in Table S1 (Supporting information, SI) and are plotted on a graph in Fig. 1. The solutions present expansive effects with a quasi-symmetric distribution of coordinates (x_1, v^E). The values obtained acceptably coincide with ones published previously [2–8], although the v^E for the methyl methanoate+heptane system ($u = 1, n = 7$), are slightly higher, see Fig. S1 (SI). From Fig. 1d, which compiles the $v^E = [(x_1 = 0.5), T, n]$ of all the solutions studied, some observations can be made about the volumetric behavior of these binaries. For the same composition, v^E diminishes significantly as the number of hydrocarbons in the alkanolic radical of the methanoate, u , increases. By contrast, v^E increases both with temperature T and with the hydrocarbon chain-length n . If we consider the net effects, the variation in the alkanolic chain of the ester has a greater influence on the final volume of the solution than the corresponding increase in saturated hydrocarbon chain length expressed by $(\partial v^E / \partial u)_{n, T, x} > (\partial v^E / \partial n)_{u, T, x}$. The dipolar effect of the –HCOO group in the final mixture diminishes owing to the presence of the hydrocarbon which, in its accommodation, makes the distance between the dipoles increase.

Mathematical modeling of (x, v^E, T) data was done using a polynomial equation [7,23] which, for a generic excess quantity y^E is:

Table 3
Coefficients of Eqs. (1)–(3), obtained in the correlation of (x, T, v^E) with $y_{ij} = v_{ij}$, and (x, T, h^E) with $y_{ij} = h_{ij}$, and standard deviations s .

| | Methyl methanoate(1) + | | | Ethyl methanoate(1) + | | | Propyl methanoate(1) + | | | Butyl methanoate(1) + | | |
|----------------|------------------------|-----------|-----------|-----------------------|-----------|-----------|------------------------|-----------|-----------|-----------------------|-----------|-----------|
| | Heptane(2) | Octane(2) | Nonane(2) | Heptane(2) | Octane(2) | Nonane(2) | Heptane(2) | Octane(2) | Nonane(2) | Heptane(2) | Octane(2) | Nonane(2) |
| k_{i0}^{j-i} | 2.372 | 2.631 | 2.891 | 1.821 | 2.019 | 2.219 | 1.506 | 1.670 | 1.835 | 1.282 | 1.422 | 1.563 |
| δ | -2.43E-4 | -3.42E-4 | -4.14E-4 | -1.93E-4 | -2.92E-4 | -3.64E-4 | -5.27E-5 | -1.51E-4 | -2.24E-4 | 6.50E-5 | -3.38E-5 | -1.06E-4 |
| v_{00} | 9.367E4 | -8.161E3 | -5.123E4 | 4.260E7 | 1.850E7 | -1.818E7 | 2.536E7 | 1.893E7 | 1.606E7 | 1.775E7 | 1.379E6 | 1.064E7 |
| v_{01} | -1.605E3 | 1.196E4 | -4.499E4 | -2.937E5 | -1.365E5 | 1.067E5 | -1.733E5 | -1.298E5 | -1.132E5 | -1.186E5 | -1.330E4 | -7.500E4 |
| v_{02} | 6.836E1 | 2.806E1 | 2.271E2 | 5.434E2 | 2.903E2 | -1.106E2 | 3.200E2 | 2.490E2 | 2.276E2 | 2.145E2 | 4.767E1 | 1.524E2 |
| v_{10} | 8.449E4 | 3.838E4 | 3.827E5 | -1.219E8 | -1.651E8 | 8.540E7 | -7.051E7 | -1.801E7 | -1.842E7 | -5.044E7 | -3.502E7 | -1.427E6 |
| v_{11} | -8.508E4 | 9.553E4 | 4.633E4 | 8.137E5 | 1.090E6 | -5.486E5 | 4.648E5 | 1.181E5 | 1.323E5 | 3.273E5 | 2.364E5 | 1.528E4 |
| v_{12} | 1.607E2 | -4.677E2 | -3.251E2 | -1.417E3 | -1.865E3 | 8.068E2 | -7.987E2 | -2.309E2 | -2.781E2 | -5.505E2 | -4.212E2 | -6.126E1 |
| v_{20} | 4.114E4 | -1.393E4 | -1.963E4 | 6.974E7 | 1.094E8 | -7.624E7 | 4.788E7 | 1.423E7 | -1.346E7 | 4.988E7 | 5.524E7 | -3.881E6 |
| v_{21} | 1.111E5 | -1.243E5 | -9.514E3 | -4.622E5 | -7.209E5 | 4.969E5 | -3.109E5 | -8.897E4 | 7.920E4 | -3.184E5 | -3.681E5 | 2.161E4 |
| v_{22} | -2.926E2 | 5.209E2 | 1.500E2 | 8.016E2 | 1.230E3 | -7.621E2 | 5.231E2 | 1.599E2 | -8.943E1 | 5.178E2 | 6.245E2 | -1.434E1 |
| $s(v^E)$ | 48 | 73 | 75 | 28 | 33 | 33 | 13 | 18 | 21 | 11 | 10 | 11 |
| k_{i0}^{j-i} | 2.366 | 1.737 | 2.366 | 1.697 | 1.881 | 2.066 | 1.426 | 1.581 | 2.599 | 1.228 | 1.362 | 1.496 |
| δ | -2.43E-4 | -2.24E-4 | -3.42E-4 | -1.93E-4 | -2.92E-4 | -3.64E-4 | -5.27E-5 | -1.51E-4 | -4.14E-4 | 6.50E-5 | -3.38E-5 | -1.06E-4 |
| h_{00} | 2.073E5 | -3.060E8 | 8.256E3 | -7.609E7 | -1.154E7 | -2.606E8 | -4.193E7 | -7.180E7 | 8.306E5 | -7.888E7 | -1.353E8 | -1.035E8 |
| h_{01} | 6.485E4 | 1.997E6 | -4.573E3 | 5.224E5 | 5.095E4 | 1.712E6 | 2.726E5 | 4.792E5 | 8.288E4 | 5.112E5 | 8.848E5 | 6.774E5 |
| h_{02} | -1.585E2 | -3.220E3 | 8.579E1 | -8.584E2 | 1.035E0 | -2.762E3 | -4.135E2 | -7.675E2 | -2.151E2 | -8.051E2 | -1.420E3 | -1.079E3 |
| h_{10} | 3.211E4 | 6.492E8 | 1.041E5 | 3.511E8 | 9.072E7 | 7.124E8 | 1.458E8 | 9.438E7 | -3.864E5 | 2.231E8 | 1.806E8 | 2.923E8 |
| h_{11} | -2.434E5 | -4.235E6 | 7.571E4 | -2.358E6 | -4.944E5 | -4.673E6 | -9.400E5 | -6.353E5 | -2.296E5 | -1.441E6 | -1.177E6 | -1.908E6 |
| h_{12} | 7.172E2 | 6.861E3 | -3.861E2 | 3.916E3 | 5.821E2 | 7.593E3 | 1.484E3 | 1.035E3 | 6.419E2 | 2.306E3 | 1.895E3 | 3.083E3 |
| h_{20} | -1.287E5 | -4.138E8 | -1.394E5 | -2.762E8 | -2.419E8 | -5.910E8 | -1.457E8 | -8.112E7 | -5.357E4 | -2.236E8 | -8.926E7 | -2.503E8 |
| h_{21} | 1.676E5 | 2.699E6 | -9.386E4 | 1.836E6 | 1.507E6 | 3.864E6 | 9.403E5 | 5.335E5 | 1.249E5 | 1.448E6 | 5.887E5 | 1.632E6 |
| h_{22} | -4.995E2 | -4.382E3 | 4.016E2 | -3.030E3 | -2.303E3 | -6.274E3 | -1.501E3 | -8.600E2 | -3.257E2 | -2.335E3 | -9.639E2 | -2.644E3 |
| $s(h^E)$ | 37 | 8 | 36 | 18 | 39 | 13 | 12 | 14 | 49 | 9 | 16 | 20 |

$$y^E = z_1 z_2 \sum_{i=0}^m \left(\frac{y_{i0}}{T} + y_{i1} + y_{i2} T \right) z_i^i \quad (1)$$

where z_i is the so-called active fraction of component i , represented by:

$$z_1 = \frac{x_1}{(x_1 + k^{2-1} x_2)} \text{ and } z_2 = 1 - z_1 \quad (2)$$

for compounds 1 and 2, respectively. The values of the parameter k^{2-1} depend on the property studied. Hence, the quotient of the molar volumes v_i^0 of the pure compounds [7] corresponds to the value assigned in the correlation of excess volumes, in this case referenced as k_v^{2-1} . Although the quality of fit of the data is moderately dependent on the value assigned to this parameter, we decided to establish this value, taking into account these considerations.

$$k_v^{2-1} = \frac{v_2^0}{v_1^0} \exp[\delta(T - T_0)] = k_{v,0}^{2-1} \exp[\delta(T - T_0)] \quad (3)$$

where $\delta = \alpha_2 - \alpha_1$, is the difference between the thermal expansion coefficients of the two pure species and T_0 a reference temperature, of 298.15 K for this work. For the case of volumes, the parameters y_{ij} of the model are called v_{ij} and are obtained by a least-squares

regression procedure. The results are recorded in Table 3 together with the standard deviations of the fits calculated as:

$$s(y^E) = \left[\sum_{i=1}^N \frac{(y_{i,\text{exp}}^E - y_{i,\text{cal}}^E)^2}{N} \right]^{0.5} \quad (4)$$

The values of $s(y^E)$ and the representation of the surfaces $v^E = v^E(x, T)$ in Fig. 1 show fits of acceptable quality, validating the use of the proposed model. The highest values of the statistical parameter correspond to the binaries of methyl methanoate + alkane, mainly due to the fact that the k_v^{2-1} values are very distant from optimum values in the correlative procedure. Nonetheless, for the set of three binaries containing that methanoate, the mean error is less than 5%.

The experimental (x, h^E, T) values measured for the twelve systems $\{\text{HCOO}(\text{CH}_2)_{u-1}\text{CH}_3(1) + \text{C}_n\text{H}_{2n+2}(2) [u = (1-4), n = (7-9)]\}$ at temperatures of (291, 298 and 318) K, are shown in Table S2 (SI), except for the ones published previously. Fig. 2 shows the endothermic effects, $h^E > 0$, for all the solutions. The function $h^E = h^E(u, n)$ at constant T and x monotonically decreases in relation to u and increases in relation to n , analogous to the v^E , obeying $(\partial h^E / \partial u)_{n,T,x} > (\partial h^E / \partial n)_{u,T,x}$. The most noteworthy aspects of the

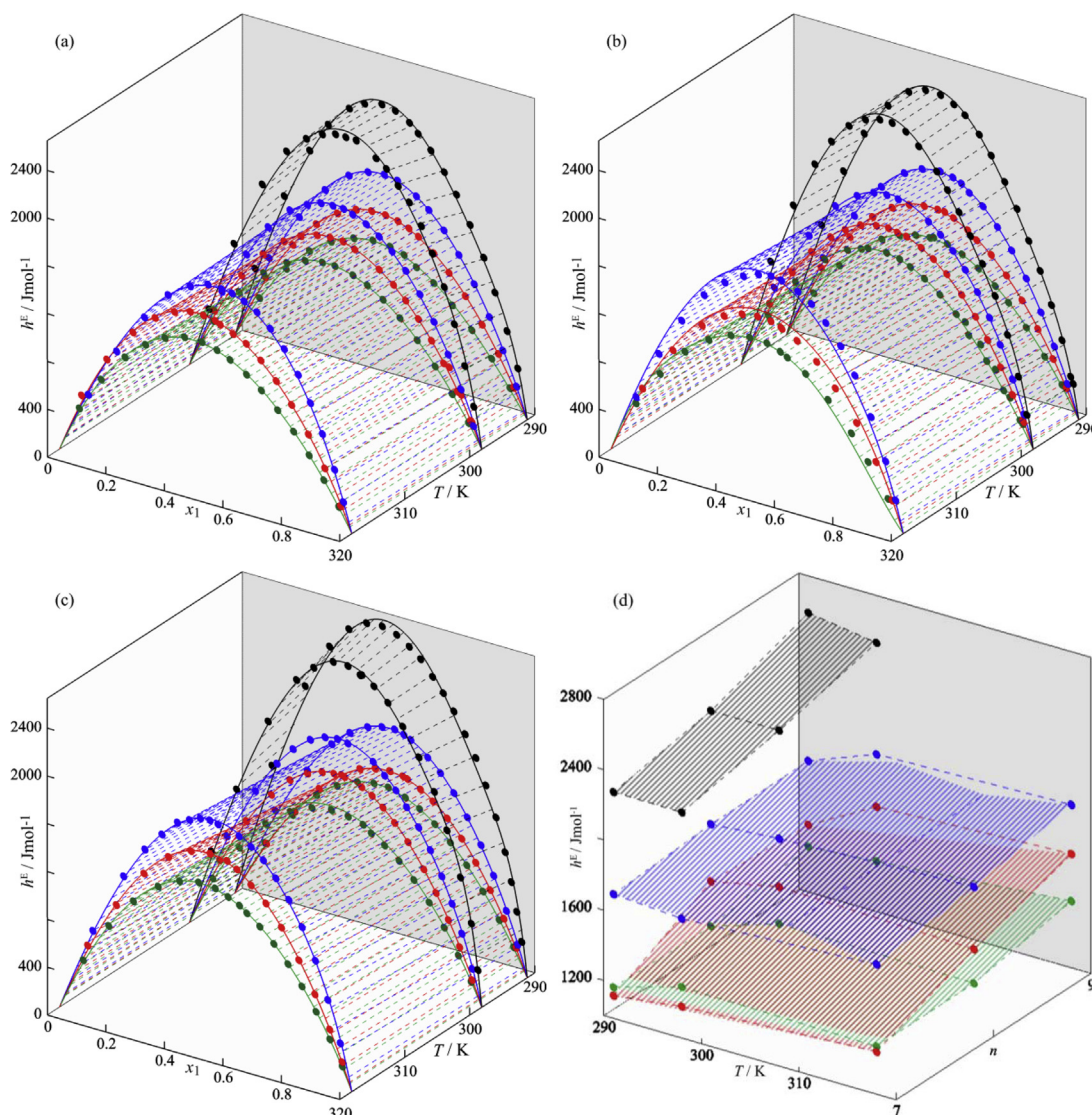


Fig. 2. Experimental (x_1, T, h^E) data and surfaces constructed using Eqs. (1) (2) and (5) for binaries: $\text{HCOO}(\text{CH}_2)_{u-1}\text{CH}_3(1) + \text{C}_n\text{H}_{2n+2}(2) [u = (1-4), n = (7-9)]$. (a) for $n=7$, (b) for $n=8$, (c) for $n=9$. (d) Virtual surfaces generated by $[n, T, h^E]$ (at $x_1=0.5$). Labels: (●) $u=1$, (●) $u=2$, (●) $u=3$, (●) $u=4$.

effect of temperature on the mixing enthalpy are reflected in the thermal slope. The gradient is $(\partial h^E/\partial T)_{n,u,p,x} < 0$ for the three binaries with methyl methanoate, and this coefficient is quantitatively higher as n increases. When $u=2$ (ethyl methanoate), in the thermal range (291–298) K, the gradient is found to increase with hydrocarbon chain length. In this interval, the binary ethyl methanoate+heptane presents a coefficient $(\partial h^E/\partial T)_{n,u,p,x} < 0$ that changes direction, with $(\partial h^E/\partial T)_{n,u,p,x} > 0$, in the interval (298–318) K, producing a minimum. This effect has already been studied for mixtures of saturated hydrocarbons and ethanoates in a previous work [22] and was found to be caused by configurational changes in the spatial arrangement of the ester. The other binaries present energetic effects of the mixing process that increase regularly with temperature.

Data correlation of $h^E = h^E(x, T)$ was carried out using expressions (1) and (2), suitably modifying the concept of k^{i-j} . Assuming that the energetic interactions depend on the contact surfaces of the

molecules, this parameter is calculated as a quotient of the molecular surfaces, and is nominated as k_h^{2-1} , by:

$$\begin{aligned} k_h^{2-1} &= \frac{q_2}{q_1} \left(\frac{v_2^0 r_1}{v_1^0 r_2} \right)^{2/3} \exp \left[\frac{2\delta(T - T_0)}{3} \right] \\ &= k_q^{2-1} \left(\frac{k_{v,0}^{2-1}}{k_r^{2-1}} \right)^{2/3} \exp \left[\frac{2\delta(T - T_0)}{3} \right] \\ &= k_{h,0}^{2-1} \exp \left[\frac{2\delta(T - T_0)}{3} \right] \end{aligned} \quad (5)$$

where q_i and r_i correspond, respectively, to normalized parameters of surface and volume, calculated from the group coefficients published by Hansen et al. [26]. Values of the coefficients $y_{ij} = h_{ij}$ and of the $s(h^E)$, Eq. (4), resulting from the correlation are compiled in Table 3. The quality of fit is acceptable for all solutions at the different working temperatures, see the enthalpic surfaces shown in Fig. 2.

The mixing effects observed for the different solutions are justified within the context of a structural model proposed in

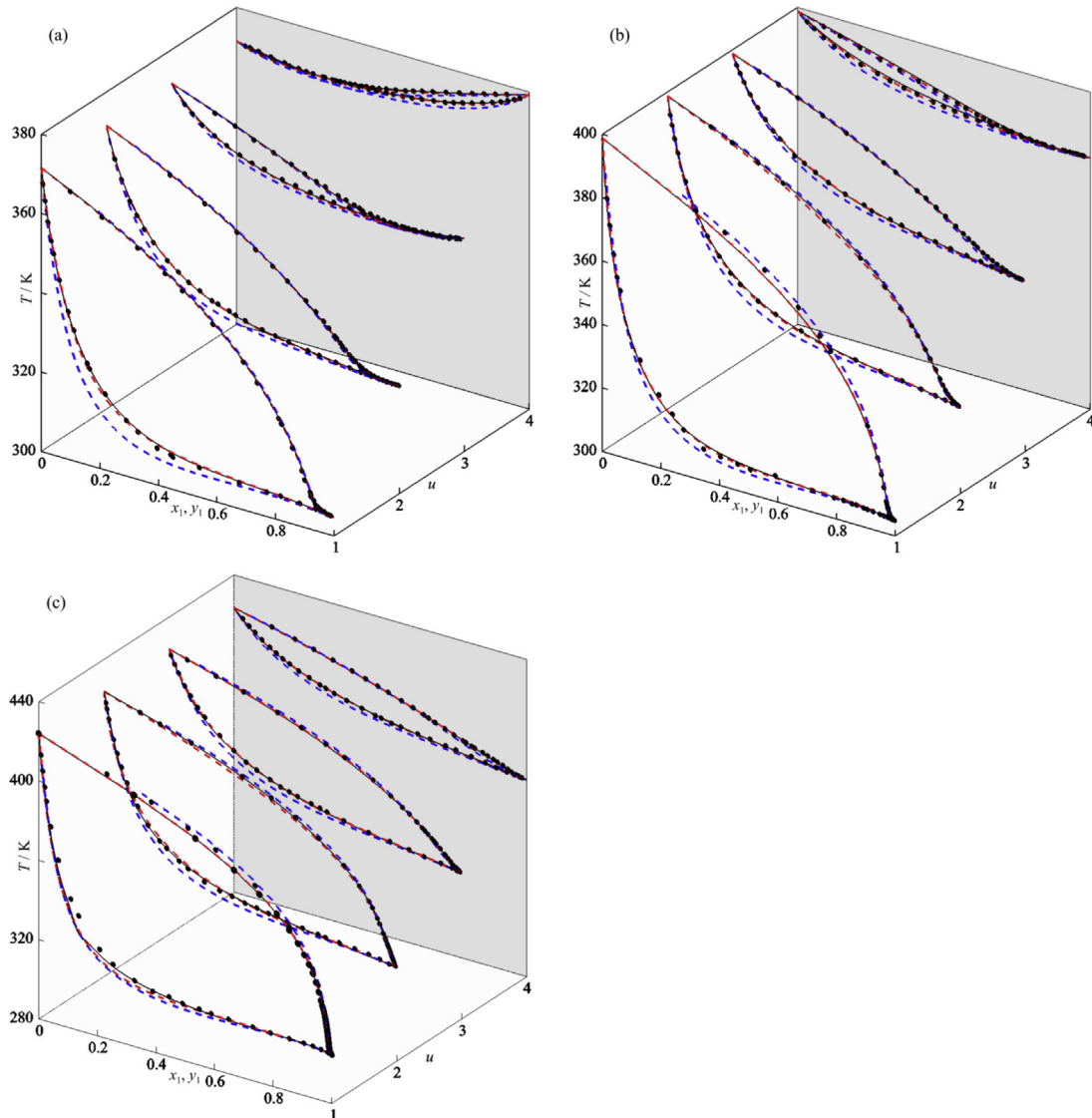


Fig. 3. 3D-Representation of iso-101.32 kPa VLE data: (u, T, x, y) (●), for the binaries: $\text{HCOO}(\text{CH}_2)_{u-1}\text{CH}_3(1) + \text{C}_n\text{H}_{2n+2}(2)$ [$u=(1-4)$, $n=(7-9)$]. Lines indicate the results obtained using different theoretical expressions: proposed model (—) Eqs. (7)–(10), NRTL model [14] (- - - -), and UNIFAC [15] (- - - -).

previous works [27]. It is necessary to take into account the specific interactions of methanoates, since in a pure state these molecules present dipole–dipole interactions caused by the electronegativity of the oxygen atoms, which are polar molecules. However, they also present apolar interactions that acquire more importance as the alkyl radical increases in size. Moreover, in the case of methanoates, mutual interactions are presented by the hydrogen bonds (H-bond) [28], between the labile hydrogen of methanoate and the oxygen of the carboxyl group. As the hydrocarbon molecules invade the core of the methanoate the dipole–dipole and the H-bond forces are weakened. All this affects the final net energetic effect, which increases with alkane chain length. By contrast, as u increases, the polarity of the methanoates is reduced (weaker dipole–dipole interactions) and its capacity for interaction by Van der Waals is increased, diminishing the endothermic mixing effects. We consider that all these explanations justify the results obtained for v^E and h^E .

3.2. Vapor–liquid equilibria

VLE (T,x,y) data measured for the systems {HCOO(CH₂) _{$u-1$} CH₃(1) + C _{n} H_{2 $n+2$} (2) [$u=(1-4)$, $n=(7-9)$]} at $p=101.32$ kPa are compiled in Table S3 (SI). The solutions with methyl methanoate present large differences between the dew points and bubble points, see Fig. 3, typical of solutions with a pronounced deviation from ideal behavior. This phenomenon increases with the number of carbons in the alkane chain n , and decreases with the chain length of the methanoate, u . The experimental data obtained here are in accordance with other previous studies, Fig. S2 (SI). Four binaries (corresponding to: $u=2-4$, $n=7$; and $u=4$, $n=8$) present minimum-boiling azeotropes, whose coordinates are shown in Table 4, together with values published in the literature [2–4,29]. The comparison between both sets of data (experimental and published) reveals a high degree of coincidence, with the exception of the binary methyl methanoate + heptane. In a previous work [3], an azeotrope was reported to appear at concentrations close to unity, which was not found experimentally in this actual work. Moreover, as mentioned, the theoretical

estimates do not predict the presence of this singular point either, so its existence cannot be rigorously verified. The activity coefficients, γ_i , in Table S3 (SI) are calculated according to the expression:

$$\gamma_i = \frac{y_i p \phi_i}{x_i p_i^0} = \frac{y_i p}{x_i p_i^0} \exp \left[\frac{(B_{ii} - v_i^0)(p - p_i^0) + 2p \delta_{ij} y_{j \neq i}}{RT} \right] \quad (6)$$

where p_i^0 is the vapor pressure of component i at the equilibrium temperature, calculated by Antoine's equation using the coefficients published previously [5,25]. The second virial coefficients B_{ii} of the pure compounds and mixtures (B_{12}) were estimated using the method proposed by Tsonopoulos [30]. These are used to calculate the function $\delta_{12} = 2B_{12} - B_{11} - B_{22}$, while the molar volumes v_i^0 of the pure compounds, are calculated with Rackett's equation [31]. Table S3 (SI) compiles the values calculated for the adimensional Gibbs function: $g^E/RT = \sum_{i=1}^2 x_i \ln \gamma_i$. The γ_1 values are quantitatively high, presenting positive deviations from ideal values, owing to the methanoate/alkane interactions. This behavior is to be expected and also reflects the high endothermic nature, $h^E > 0$, of the solutions. Fig. 3 shows the experimental values (u , x_1 , γ_1 , g^E/RT) for the different solutions. More specifically, the behavior of $g^E/RT = \phi(u)$, with $\partial \phi(u)/\partial u < 0$, is similar to that of other excess properties.

In works of this kind is important to check the quality of phase equilibrium data due to the impact they have on thermodynamic-mathematical modeling. Therefore, several tests were used to verify the thermodynamic consistency of the VLE data, two of the methods proposed by Van Ness: the point-to-point test [32] with the modifications proposed by Fredenslund et al. [33], and the direct test [34]. The procedure suggested by Wisniak was also used [35]. The results obtained by the different methods are compiled in Table S4 (SI). All systems verify the restriction established by Fredenslund et al., the method proposed by Wisniak, when $D_{\max} < 5$, is not satisfied in two binaries. Finally, the direct method based on a simple model for the activity coefficients is not satisfied for systems containing methyl methanoate, possibly due to the more complex behavior of this compound in the binary.

Table 4
Azeotropic coordinates (T_{az} , x_{az}) found in the binaries xalkyl methanoate+(1-x) alkane at $p=101.32$ kPa using different methods.

| | Heptane | | | Octane | | |
|-------------------|----------------|---|---|----------------|---|--------|
| | Exp. | Cal. | Lit. | Exp. | Cal. | Lit. |
| Methyl methanoate | zeotropic | | (304.69; 0.992) ^d | zeotropic | | |
| Ethyl methanoate | (327.3; 0.988) | (327.2; 0.991) ^b (327.2; 0.990) ^c (327.1; 0.961) ^e (327.2; 0.990) ^g | – | zeotropic | | |
| Propyl methanoate | (352.2; 0.763) | (352.1; 0.780) ^b (351.7; 0.781) ^c (351.4; 0.759) ^e (352.2; 0.785) ^g (352.6; 0.806) ^h | (351.4; 0.736) ^a (352.2; 0.786) ^a (352.2; 0.736) ^f | zeotropic | | |
| Butyl methanoate | (368.8; 0.297) | (368.7; 0.316) ^b (368.7; 0.305) ^c (367.8; 0.352) ^e (368.7; 0.334) ^g (369.2; 0.325) ^h | (>367.2, <0.3457) ^a | (379.1; 0.872) | (379.2; 0.901) ^b (379.0; 0.891) ^c (378.5; 0.839) ^e (378.9; 0.890) ^g (379.1; 0.948) ^h | – – |

^a Azeotropic data [29].

^b Calculated by our model, Eqs. (7)–(10).

^c Calculated by NRTL [14].

^d Ref. [3].

^e Estimated by UNIFAC [15].

^f Ref. [2].

^g Estimated by UNIFAC (new parameters).

^h Estimated by COSMO-RS [37].

Table 5

Coefficients of the model defined by Eqs. (7)–(10) and those of NRTL model, obtained in the simultaneous correlation of different properties (*iso*-101.32 kPa VLE + h^E + c_p^E) of the binaries generically represented by $\{HCOO(CH_2)_u-1CH_3(1)+C_nH_{2n+2}(2) [u=(1-4), n=(7-9)]\}$, and standard deviations *s* for each of the properties.

| | Proposed model, Eqs. (7)–(10) | | | NRTL model | | |
|----------|------------------------------------|--------------|--------------|------------------|------------------|----------|
| | <i>i</i> = 0 | <i>i</i> = 1 | <i>i</i> = 2 | Δg_{12j} | Δg_{21j} | <i>j</i> |
| | Methyl methanoate(1)+ heptane(2) | | | | | |
| g_{11} | -2.323E3 | 3.627E4 | -3.409E3 | 1.069E3 | 3.294E2 | 1 |
| g_{12} | 8.398E-1 | 2.640 | -4.100 | -3.123E4 | -5.119E3 | 2 |
| g_{13} | -9.239E-1 | 1.893 | -1.524 | -1.819E2 | -6.202E1 | 3 |
| g_{14} | 4.026E6 | -2.189E7 | 1.572E7 | 2.490E-1 | 1.397E-1 | 4 |
| g_{15} | 1.629E-1 | -5.906E-1 | 4.621E-1 | | | |
| k_{g0} | 1.835 | | 0.022 | 0.023 | 0.357 | α |
| <i>B</i> | -3.72E-3 | | 0.054 | 0.066 | | |
| k_{h0} | 2.366 | | 39 | 25 | | |
| δ | -2.43E-4 | | | | | |
| | Methyl methanoate (1) + octane(2) | | | | | |
| g_{11} | 6.423E4 | 9.898E2 | -1.186E5 | 1.008E3 | 5.825E1 | 1 |
| g_{12} | 1.059E1 | 4.702 | 2.349E1 | -2.645E4 | -9.234E2 | 2 |
| g_{13} | -6.118 | 8.117E-1 | -6.667 | -1.763E2 | -1.071E1 | 3 |
| g_{14} | -1.350E7 | -1.583E7 | -2.217E6 | 2.862E-1 | 2.345E-2 | 4 |
| g_{15} | 6.887E-1 | -2.183E-1 | 9.608E-1 | | | |
| k_{g0} | 1.568 | | 0.033 | 0.016 | -0.625 | α |
| <i>B</i> | -1.56E-2 | | 0.190 | 0.198 | | |
| k_{h0} | 2.366 | | 43 | 32 | | |
| δ | -3.42E-4 | | | | | |
| | Methyl methanoate (1) + nonane(2) | | | | | |
| g_{11} | -8.651E4 | 4.995E4 | -7.142E4 | 9.159E1 | 3.985E1 | 1 |
| g_{12} | 9.764 | 5.092 | -2.738 | 2.701E5 | -2.541E5 | 2 |
| g_{13} | -2.077 | 2.722 | -1.018 | -6.435E1 | 2.850E1 | 3 |
| g_{14} | 6.220E6 | -3.271E7 | 2.593E7 | 2.212 | -1.995 | 4 |
| g_{15} | 3.804E-1 | -8.979E-1 | 5.703E-1 | | | |
| k_{g0} | 0.816 | | 0.017 | 0.031 | 2.8E-5 | α |
| <i>B</i> | 9.38E-3 | | 0.073 | 0.191 | | |
| k_{h0} | 2.599 | | 61 | 112 | | |
| δ | -4.14E-4 | | | | | |
| | Ethyl methanoate (1) + heptane(2) | | | | | |
| g_{11} | -2.297E4 | 2.758E3 | -5.583E4 | 1.374E2 | -4.327E2 | 1 |
| g_{12} | -5.008E-1 | -9.183E-1 | 1.067 | -6.429E3 | 1.268E4 | 2 |
| g_{13} | 8.857E-1 | 7.613E-1 | 1.205 | -1.822E1 | 7.357E1 | 3 |
| g_{14} | 4.624E6 | -2.829E6 | 6.162E6 | -4.731E-2 | -8.698E-2 | 4 |
| g_{15} | -9.395E-2 | -1.419E-1 | -1.092E-1 | | | |
| k_{g0} | 2.292 | | 0.010 | 0.014 | -0.078 | α |
| <i>B</i> | -6.04E-3 | | 0.027 | 0.081 | | |
| k_{h0} | 1.697 | | 20 | 25 | | |
| δ | -1.93E-4 | | | | | |
| | Ethyl methanoate (1) + octane(2) | | | | | |
| g_{11} | 1.471E5 | -7.985E4 | 2.596E5 | -2.740E2 | 5.702E2 | 1 |
| g_{12} | -1.441 | 5.999 | 8.445E-1 | 5.121E3 | -1.347E4 | 2 |
| g_{13} | -3.595 | -1.004 | -7.691 | 5.148E1 | -1.018E2 | 3 |
| g_{14} | -1.350E7 | 3.769E6 | -2.866E7 | -1.218E-1 | 1.882E-1 | 4 |
| g_{15} | 3.210E-1 | 2.907E-1 | 7.358E-1 | | | |
| k_{g0} | 3.413 | | 0.008 | 0.013 | -0.410 | α |
| <i>B</i> | -9.31E-3 | | 0.049 | 0.169 | | |
| k_{h0} | 1.881 | | 44 | 43 | | |
| δ | -2.92E-4 | | | | | |
| | Ethyl methanoate (1) + nonane(2) | | | | | |
| g_{11} | 9.851E4 | 7.314E4 | 5.416E4 | -4.595E2 | 3.538E2 | 1 |
| g_{12} | 1.486E1 | -3.677 | -9.930 | 1.151E4 | -1.016E4 | 2 |
| g_{13} | -7.737 | -1.713 | 2.096 | 7.883E1 | -5.931E1 | 3 |
| g_{14} | -2.463E7 | -4.834E6 | 4.918E6 | -1.058E-1 | 7.077E-2 | 4 |
| g_{15} | 8.075E-1 | 2.608E-1 | -2.915E-1 | | | |
| k_{g0} | 1.980 | | 0.020 | 0.031 | -0.201 | α |
| <i>B</i> | 3.93E-4 | | 0.077 | 0.275 | | |
| k_{h0} | 2.066 | | 23 | 39 | | |
| δ | -3.64E-4 | | | | | |
| | Propyl methanoate (1) + heptane(2) | | | | | |
| g_{11} | -2.969E4 | -2.146E4 | 2.371E5 | 2.235E1 | 1.463E2 | 1 |
| g_{12} | -2.474 | -1.649E1 | 1.232E1 | -5.603E2 | -3.724E3 | 2 |
| g_{13} | 1.962 | 6.289 | -1.205E1 | -3.636 | -2.557E1 | 3 |
| g_{14} | 6.398E6 | 1.770E7 | -3.544E7 | 2.535E-3 | 4.187E-2 | 4 |
| g_{15} | -2.335E-1 | -7.105E-1 | 1.364 | | | |
| k_{g0} | 4.081 | | 0.003 | 0.005 | -0.798 | α |

Table 5 (Continued)

| | Proposed model, Eqs. (7)–(10) | | | NRTL model | | | |
|----------|---------------------------------|-----------|-----------|------------------------------------|------------------|-----------|----------|
| | $i=0$ | $i=1$ | $i=2$ | Δg_{12j} | Δg_{21j} | j | |
| | Methyl methanoate(1)+heptane(2) | | | | | | |
| B | -1.59E-2 | | 0.112 | $\leftarrow s(\gamma) \rightarrow$ | 0.121 | | |
| k_{h0} | 2.366E0 | | 65 | $\leftarrow s(h^E) \rightarrow$ | 35 | | |
| δ | 5.96E-1 | | 0.03 | $\leftarrow s(c_p^E) \rightarrow$ | 0.05 | | |
| | Propyl methanoate (1)+octane(2) | | | | | | |
| g_{i1} | 9.193E3 | -4.318E4 | 7.260E4 | | 3.266E2 | -1.096E2 | 1 |
| g_{i2} | 1.197E1 | 1.059E1 | 8.726E-1 | | -1.121E4 | 4.160E3 | 2 |
| g_{i3} | -4.086 | -2.229 | -2.460 | | -5.270E1 | 1.747E1 | 3 |
| g_{i4} | -1.250E7 | -7.975E6 | -8.009E6 | | 3.641E-2 | -8.620E-3 | 4 |
| g_{i5} | 4.329E-1 | 2.545E-1 | 2.539E-1 | | | | |
| k_{g0} | 2.207 | | 0.015 | $\leftarrow s(g^E) \rightarrow$ | 0.012 | -0.295 | α |
| B | -2.06E-3 | | 0.037 | $\leftarrow s(\gamma) \rightarrow$ | 0.057 | | |
| k_{h0} | 1.581 | | 17 | $\leftarrow s(h^E) \rightarrow$ | 24 | | |
| δ | -1.51E-4 | | | | | | |
| | Propyl methanoate (1)+nonane(2) | | | | | | |
| g_{i1} | 1.950E5 | -1.516E5 | 1.654E5 | | 1.015E5 | -1.285E5 | 1 |
| g_{i2} | 1.578E1 | 6.284 | -1.964E1 | | -8.138E1 | -1.653E2 | 2 |
| g_{i3} | -1.106E1 | 2.071 | 1.586 | | 1.393 | -8.795E-1 | 3 |
| g_{i4} | -3.626E7 | 9.433E6 | 3.195E6 | | | | 4 |
| g_{i5} | 1.164 | -0.146 | 0.045 | | | | |
| k_{g0} | 1.614 | | 1.564E-2 | $\leftarrow s(g^E) \rightarrow$ | 2.627E-2 | 1.339E-4 | α |
| B | 3.99E-3 | | 0.045 | $\leftarrow s(\gamma) \rightarrow$ | 0.114 | | |
| k_{h0} | 1.737 | | 21 | $\leftarrow s(h^E) \rightarrow$ | 19 | | |
| δ | -2.24E-4 | | | | | | |
| | Butyl methanoate (1)+heptane(2) | | | | | | |
| g_{i1} | 5.995E4 | -1.262E4 | 2.307E5 | | 9.786E3 | -1.184E4 | 1 |
| g_{i2} | -3.316E-1 | 8.729E-1 | -3.452 | | 2.323E1 | -1.773E1 | 2 |
| g_{i3} | -1.504 | -3.918E-1 | -6.004 | | 3.754E-2 | -8.867E-2 | 3 |
| g_{i4} | -5.702E6 | 1.180E6 | -2.058E7 | | | | 4 |
| g_{i5} | 1.349E-1 | 9.235E-2 | 6.298E-1 | | | | |
| k_{g0} | 0.552 | | 6.511E-3 | $\leftarrow s(g^E) \rightarrow$ | 6.799E-3 | -7.727E-2 | α |
| B | 1.28E-2 | | 0.029 | $\leftarrow s(\gamma) \rightarrow$ | 0.033 | | |
| k_{h0} | 1.228 | | 10 | $\leftarrow s(h^E) \rightarrow$ | 11 | | |
| δ | 6.50E-5 | | | | | | |
| | Butyl methanoate (1)+octane(2) | | | | | | |
| g_{i1} | 6.086E4 | 8.428E4 | -9.221E4 | | 9.906E2 | -4.791E2 | 1 |
| g_{i2} | 6.929 | 1.697 | 9.455 | | -2.907E4 | 1.475E4 | 2 |
| g_{i3} | -3.999 | -3.780 | 2.448E-1 | | -1.688E2 | 8.096E1 | 3 |
| g_{i4} | -1.317E7 | -9.749E6 | -1.328E6 | | 2.300E-1 | -1.037E-1 | 4 |
| g_{i5} | 4.108E-1 | 4.689E-1 | -6.506E-2 | | | | |
| k_{g0} | 0.327 | | 0.014 | $\leftarrow s(g^E) \rightarrow$ | 0.010 | -0.349 | α |
| B | 1.61E-2 | | 0.040 | $\leftarrow s(\gamma) \rightarrow$ | 0.047 | | |
| k_{h0} | 1.362 | | 18 | $\leftarrow s(h^E) \rightarrow$ | 17 | | |
| δ | -3.38E-5 | | | | | | |
| | Butyl methanoate (1)+nonane(2) | | | | | | |
| g_{i1} | 9.009E4 | -1.360E4 | -4.996E4 | | 6.976E1 | 4.265E1 | 1 |
| g_{i2} | 3.978 | -1.631E0 | 7.729E-1 | | -2.705E3 | -7.134E2 | 2 |
| g_{i3} | -3.958 | 5.898E-1 | 1.632 | | -1.062E1 | -7.911 | 3 |
| g_{i4} | -1.290E7 | 2.871E6 | 4.174E6 | | -2.538E-4 | 1.803E-2 | 4 |
| g_{i5} | 4.055E-1 | -2.871E-2 | -2.007E-1 | | | | |
| k_{g0} | 1.822 | | 0.014 | $\leftarrow s(g^E) \rightarrow$ | 0.016 | -1.301 | α |
| B | 1.28E-3 | | 0.026 | $\leftarrow s(\gamma) \rightarrow$ | 0.052 | | |
| k_{h0} | 1.496 | | 21 | $\leftarrow s(h^E) \rightarrow$ | 22 | | |
| δ | -1.06E-4 | | | | | | |

4. Modeling of properties of alkyl methanoate + alkanes solutions

4.1. Equations and correlation procedures

The VLE (T, x, y) data of the systems chosen are modeled using Eq. (1), rewritten now for Gibbs function as:

$$g^E = z_1 z_2 \sum_{i=0}^m g_i(p, T) z_1^i \quad (7)$$

where m is the degree of the polynomial to be established by the investigator, in which the g_i coefficients are given by the following equation,

$$g_i(p, T) = g_{i1} + g_{i2} p^2 + g_{i3} p T + \frac{g_{i4}}{T} + g_{i5} T^2 \quad (8)$$

z_i is obtained from a similar expression to Eq. (2). The physical significance of parameter k^{i-j} in the correlation of values of g^E and the calculation procedure cannot be established in the same way as for other properties, Eqs. (3) and (5). Nonetheless, we assume that these can be formulated in a similar way to previous equations, in

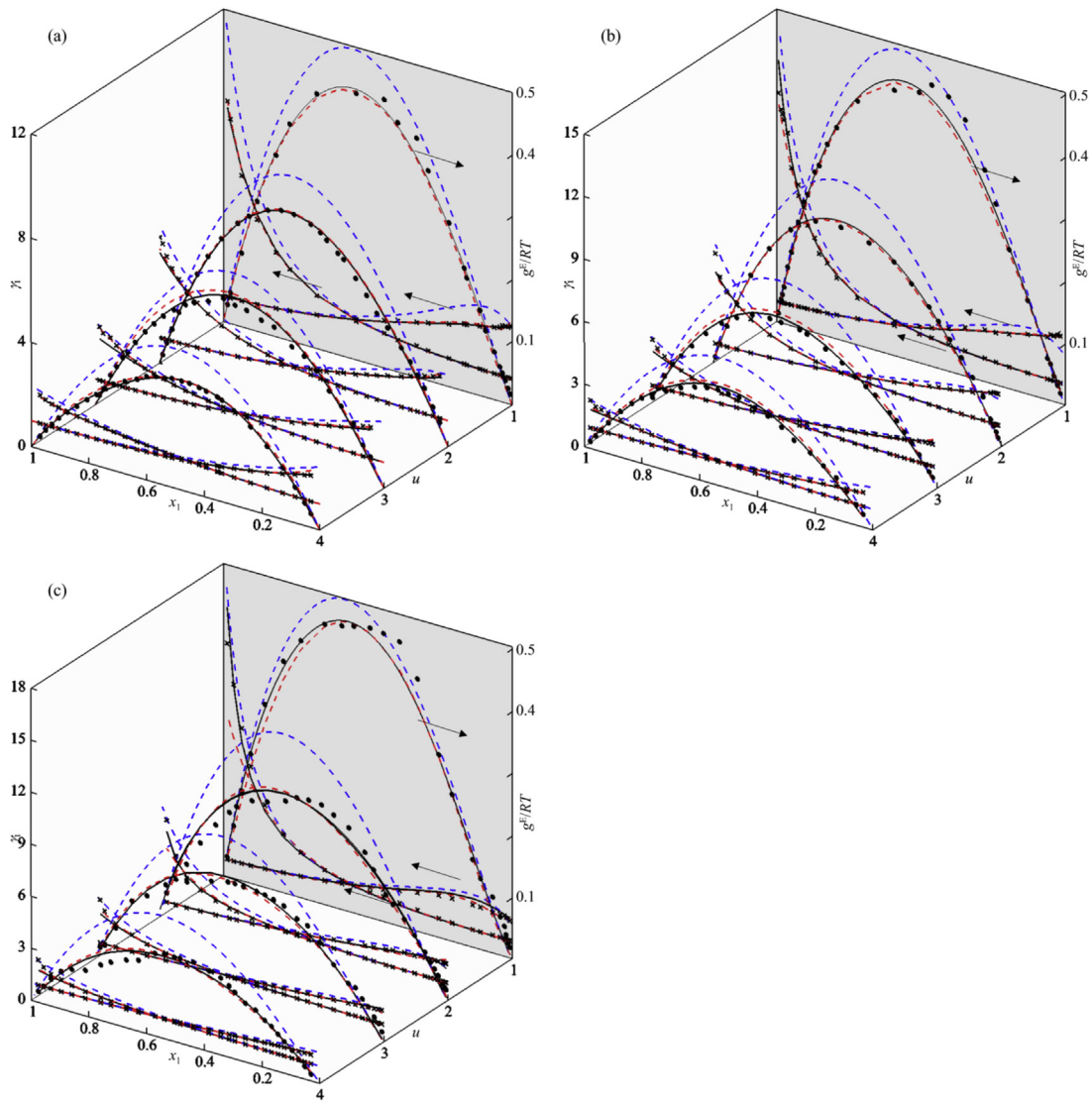


Fig. 4. 3D-Representation of iso-101.32 kPa VLE data: $(u, x, g^E/RT)$ (●) and (u, x, γ_i) (×), for the binaries: $\text{HCOO}(\text{CH}_2)_{u-1}\text{CH}_3(1) + \text{C}_n\text{H}_{2n+2}(2)$ [$u=(1-4)$, $n=(7-9)$]. Lines indicate the results obtained using different theoretical expressions: proposed model (—) Eqs. (7)–(10), NRTL model [14] (- - - -), and UNIFAC [15] (- - - -).

other words as: $k_g^{2-1} = k_{g,0}^{2-1} \exp[\phi(T)]$, making $\phi(T)$ adopt a simple form such as: $B(T - T_0)$. The values for $k_{g,0}^{2-1}$ and B of each system are obtained as additional parameters in the correlation, considering a reference temperature of $T_0 = 298.15$ K.

The procedure followed involves a simultaneous correlation of the different properties of each system. Hence, starting with the definition of g^E , mathematical expressions for the enthalpies and heat capacities can be obtained as first and second derivatives, respectively, of Eq. (7).

$$h^E = g^E - T \left(\frac{\partial g^E}{\partial T} \right)_{x,p} = z_1 z_2 \sum_{i=0}^m h_i \left(g_{i1} + g_{i2} p^2 + \frac{2g_{i4}}{T} - g_{i5} T^2 \right) z_i^i \quad (9)$$

$$c_p^E = \left(\frac{\partial h^E}{\partial T} \right)_{x,p} = z_1 z_2 \sum_{i=0}^m c_i \left(-\frac{2g_{i4}}{T^2} - 2g_{i5} T \right) z_i^i \quad (10)$$

The values corresponding to the entropy can be estimated from Eqs. (7) and (9): $Ts^E = g^E - h^E$. Data were only found in the literature for the binary of propyl methanoate + heptane [11] of $c_p^E = c_p^E(x)$ at $T = 298.15$ K, and were used to correlate the properties of this system. In this case, when Eq. (10) is used the corresponding

Table 6
UNIFAC parameters for the interaction HCOO/CH₂. Original parameters [15] and those calculated in this work.

| | CH ₂ | HCOO (this work) | HCOO (Ref. [15]) |
|------------------|----------------------|-----------------------|------------------|
| CH ₂ | 0 | $a = 459.7$ | $a = 508.4$ |
| | 0 | $b = -0.653$ | $b = -0.6215$ |
| | 0 | $c = -1.52\text{E-}4$ | $c = 0$ |
| HOOC (this work) | $a = 502.9$ | 0 | 0 |
| | $b = -1.869$ | 0 | 0 |
| | $c = 1.57\text{E-}3$ | 0 | 0 |
| HOOC (Ref. [15]) | $a = 238.5$ | 0 | 0 |
| | $b = -0.5358$ | 0 | 0 |
| | $c = 0$ | 0 | 0 |

parameter k_c^{2-1} is also determined in order to fit the c_p^E corresponding to the active fraction z_i of this property according to Eq. (2), although only at 298.15 K.

Then, using all information available the correlation of their corresponding properties, for each binary, is carried out using a genetic algorithm [24] and a multiobjective optimization procedure to minimize the objective function OF defined as:

$$OF = \sum_{i=1}^2 c_{VLE} s(\gamma_i) + c_h s(h^E) + c_c s(c_p^E) \quad (11)$$

where $s(y^E)$ is the standard deviation (Eq. (4)) of the generic property y^E , the c_i are weighting coefficients, used to minimize to OF for the different results that constitute the *Pareto front*. The optimum values obtained for each case are recorded in Table 5, which also shows the $s(y^E)$ of the different properties, corroborating the quality of fits. The model reproduces well the diagrams (T, x, y), Fig. 3, also giving good representations of the h^E , of the function $h^E = h^E(T)$, and of c_p^E , see Figs. S3–S5. The model established now also acceptably reproduces the azeotropic points, especially the temperatures, and with slight differences in the values of the compositions, <5%, see Table 4.

The same fitting procedure was used with the NRTL model [14].

$$g^E = x_1 x_2 RT \left[\frac{\tau_{12} G_{12}}{x_1 G_{12} + x_2} + \frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} \right] \quad (12)$$

being $G_{ij} = \exp(-\alpha \tau_{ij})$ and α an adjustable parameter in the correlation procedure. The dependence of τ_{ij} on temperature can be tackled in two ways, although here we adopted the following expression:

$$\tau_{ij} = \Delta g_{ij1} + \frac{\Delta g_{ij2}}{T} + \Delta g_{ij3} \ln(T) + \Delta g_{ij4} T \quad (13)$$

proposed by Aspen Tec. Inc.© [36] that has already been used in previous works [18]. For correlation of h^E and c_p^E the expressions derived from Eq. (12) are used,

$$h^E = R x_1 x_2 \left[\frac{\tau'_{12} G_{12}}{x_1 G_{12} + x_2} + \frac{x_2 \tau_{12} G'_{12}}{(x_2 + x_1 G_{12})^2} + \frac{\tau'_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{x_1 \tau_{21} G'_{21}}{(x_1 + x_2 G_{21})^2} \right] \quad (14)$$

$$\text{Being now : } \tau'_{ij} = \frac{-\Delta g_{ij2}}{T^2} + \frac{\Delta g_{ij3}}{T} + \Delta g_{ij4} \text{ and } G'_{ij} = -\alpha G_{ij} \tau'_{ij} \quad (15)$$

and for c_p^E :

$$c_p^E = -x_1 x_2 RT \left[2 \frac{\partial}{\partial T} \left(\frac{G_{12} \tau_{12}}{G_{12} x_1 + x_2} + \frac{G_{21} \tau_{21}}{G_{21} x_2 + x_1} \right) + T \frac{\partial^2}{\partial T^2} \left(\frac{G_{12} \tau_{12}}{G_{12} x_1 + x_2} + \frac{G_{21} \tau_{21}}{G_{21} x_2 + x_1} \right) \right] \quad (16)$$

Parameters of the NRTL model, Δg_{ijk} and α , are obtained using the same procedure as that indicated previously for the proposed model. The numerical values are shown in Table 5 with the standard deviations of each fit. Fig. 4 shows the curves obtained with NRTL model for γ_i and g^E , giving acceptable representations in all cases. In summary, the overall evaluation of the correlation process with these two models is acceptable in both cases, although the NRTL model does not reproduce the change in h^E slope observed in some of the systems. As shown in Table 4, the estimation of azeotropes with this model is acceptable.

4.2. Prediction of properties

Predictions were made for the *iso-p* VLE and the h^E of the systems chosen using the UNIFAC group contribution method with the original published parameters [15], see Table 6, corresponding to the specific interaction HCOO/CH₂. The VLE curves estimated are shown in Figs. 3 and 4, where some discrepancies can be observed, with values of g^E/RT higher than those calculated experimentally; while predictions of h^E and c_p^E are shown in Figs. S3–S6 (SI). Estimates of h^E , and specifically of c_p^E , are not good, presenting overall standard deviations, respectively, of $\bar{s}(h^E) = 113 \text{ J mol}^{-1}$ and $\bar{s}(c_p^E) = 0.6 \text{ J mol}^{-1} \text{ K}^{-1}$. Prediction of the azeotropes is not acceptable either, and the differences increase with increasing chain length of the compounds studied, a frequent observation with this method. Hence, considering the experimental database generated with this and previous works [2–7], the parameters of the above interaction were recalculated. A GA implemented in MATLAB®, was used minimizing an objective function similar to that of Eq. (11). Table 6 shows the new coefficients and those of the original work [15].

The new set of values noticeably improves the estimates of all systems used in the database, especially h^E and c_p^E , for which the global standard deviation is reduced to 83 J mol^{-1} and $0.2 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively. Estimation of the azeotropic points also improves, as shown in Table 4. Parallel to this, the properties of the binaries studied here were calculated using the COSMO-RS methodology, in order to obtain some additional information about the structural behavior of the solutions. The method gives acceptable predictions for the different properties, even for h^E , although it does not obey changes in temperature. It also gives acceptable predictions (from both qualitative and quantitative perspectives) of the presence of azeotropes in the binaries of [$u=2, n=7$]; [$u=3, n=7$]; and [$u=4, n=7,8$], but does not estimate the presence of the singular point for the methyl methanoate+heptane system, nor, in this case, for the binary ethyl methanoate+heptane. On the negative side, for systems containing methyl methanoate, the method predicts the existence of a region of immiscibility with formation of vapor–liquid–liquid equilibria (VLLE), confirmed by estimations of g^E values much higher than experimental ones.

5. Conclusions

Experimental information provided in this paper completes the matrix composed of 24 systems alkyl (methyl to butyl) methanoates+alkanes (pentane to decane), completing the one

presented in previous works [5–7]. Several conclusions can be drawn from these studies, some specific for the solutions containing methanoates, and others which are not. The energetic effects (endothermic) and volumetric (expansive) state show that in addition to the classical interactions due to Van der Waals forces and dipolar attractions, it is convenient to also consider those due to associative effects by hydrogen bonds, which are more pronounced in the methyl methanoate solutions, with values of $\gamma_i^\infty > 20$. This is also reflected in the high entropic values such as those shown in the estimates of Figs. S3–S6. The influence of temperature on the different interactions is not regular since

variation in this parameter does not affect interactions equally. The multiproperty correlation and the usefulness of the proposed model in all works of this series can be emphasized, since the procedure was modified by appropriately adapting it to each case, even including treatment of LLE data [7]. To perform the modeling a multiobjective optimization procedure and a powerful computer-mathematical tool, such as a GA, were used. Application of the NRTL model to contrast the usefulness of our model has limited value because it does not represent well the LLE and it has no pressure terms to represent the volumetric properties. The UNIFAC model has the same limitations, but being a predictive and non-correlative method produces estimates that deviate from the actual values, when the chain-length of compounds increases. These differences are also apparent when thermodynamic properties are obtained by derivation, and increase with the order. Finally, when the database created with the 24 systems was used, the parameters corresponding to the specific interaction HCOO/CH_2 were recalculated now giving better results.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.fluid.2015.05.031>.

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