Excess molar volumes of the ternary mixtures chlorobenzene + n-hexane + linear aliphatic alkane (C_{11}–C_{12}) at 298.15 K

A. Touriño a, M. Hervello a, A. Gayola b, G. Marínob, M. Iglesias c, *

aLaboratorio de Propiedades Físicas, Centro de Apoyo Científico y Tecnológico a la Investigación (CACTI), Universidad de Vigo, 36200 Vigo, Spain
bCentro Tecnológico Repsol YPF S.A., Autovía A-5, km 18. 28931 Móstoles, Madrid, Spain
cDepartament d’Enginyeria Química, Escola Técnica Superior d’Enginyeria Química, Universitat Rovira i Virgili, Avinguda Països Catalans 26, Campus Sesceletades, 43007 Tarragona, Spain

Received 3 June 2004; accepted 15 March 2005
Available online 22 August 2005

Abstract

Densities of the ternary mixtures chlorobenzene + n-hexane + (n-undecane or n-dodecane) have been measured at 298.15 K and atmospheric pressure. The excess molar volumes were computed from the experimental data and were fitted to the Nagata equation. The partial excess molar volumes were calculated, an interpretation in terms of composition and molecular size being made. The molecular radius was derived and compared from different thermodynamic property and models. The Peng–Robinson and Soave–Redlich–Kwong equations of state were applied, in combination with different mixing rules for excess molar volume prediction. The accurate obtained results by means of cubic equations of state show the applicability of binary interaction parameters to estimate multicomponent excess molar volumes or any other properties by means of adequate thermodynamic derivations.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Excess molar volumes; Density; n-Alkane; Chlorobenzene; Equation of state; Mixing rule

1. Introduction

One of the main problems of the chemical industrial growth is the generation of hazardous waste. In fact, due to stricter environmental regulations, many industries have to carefully consider pollution prevention in order to minimize adverse environmental impact. Hazardous pollutants (HAP) and volatile organic compounds (VOCs) thermal emission control devices usually require large amounts of energy and non-thermal ones require additional maintenance. The former techniques use large capital investments in heat recovery options and the latter, replacement of costly consumables and energy to regenerate the adsorbent. These factors make the separation and destruction of volatile organic hazardous products (also defined as VOHAPs) from emissions an extremely energy-intensive task to perform. The VOHAPs include a very wide range of individual substances, such as hydrocarbons, halocarbons and oxygenates that evaporate easily from water into air at normal air temperatures and are commonly used in industry for processes, such as degreasing, thinning, and dissolving. Specifically, chlorobenzene, a well-known dangerous substance enclosed into the Clean Air Act, is used as a degreaser in the metal industry. In the last few years, new cleaning technologies proposed are a synergistic blend of general existing techniques strongly oriented for low concentration and nuisance odor VOHAPs emissions in air or liquid streams. These kind of technologies are used to convert hazardous wastes into non-hazardous or reusable products, converting VOHAPs into biomass and avoiding the inherent high costs of destruction. Certain volatile compounds in waste stream that are converted in a reactor merge with a recyclable scrubber fluid which are used to aid in the capture of additional volatile compounds. These chemicals act as emulsifiers, absorbents, adsorbents, and surfactants simultaneously, working in combination with the recyclable
scrubber fluid. This kind of technology takes advantage of hydrogen-bonding chemistry and its ability to minimize the volatility of low-molecular-weight chemicals. The main weakness of this procedure is the strong dependence on thermodynamics in order to optimize the composition of the separation fluid and to study the characteristics of waste compounds in liquid environment in order to minimize adverse impacts and pollution prevention. The knowledge of thermophysical properties is an important step for the complete process synthesis and design on this field. Continuing our research on thermodynamic properties of mixtures related to industrial processes [1–6], we present a new study of densities of the ternary mixtures chlorobenzene + n-hexane + (n-undecane or n-dodecane) at 298.15 K and atmospheric pressure. The fitting parameters of polynomial equations which represent the composition dependence of the corresponding excess molar volumes are gathered. The partial excess molar volumes were computed, an interpretation in terms of composition and molecular size being made. The molecular radius was derived and compared from different thermodynamic properties and models. The Peng–Robinson [7] and Soave–Redlich–Kwong [8] equations of state were also applied with different mixing rules to predict ternary excess molar volumes, an accurate estimation being obtained from the binary parameters of the enclosed mixtures [9,10]. The accurate ternary predictions show the applicability of binary interaction parameters to estimate multicomponent excess molar volumes or any other properties by means of adequate thermodynamic relations from cubic equations of state.

2. Experimental

The substances employed were purchased from Merck (Lichrosolv quality). The started minimum purity of all reagents was 0.99 mass fraction. The purity of the reagents was checked by gas chromatography. Chemicals were dried over molecular sieves (type 4a or 3a, 1/16 in., Aldrich cat. No. 20.860-4 or 20.858-2, respectively) and ultrasonic treatment for degassing them. The densities of reagents was 0.99 mass fraction. The purity of the reagents (Lichrosolv quality). The started minimum purity of all compounds is 0.99 mass fraction. The purity of the reagents.

Millipore quality water (resistivity, 18.2 MΩ·cm) and ambient air. All solutions were made by weight, using a Mettler At-261 Delta Range balance with a precision of ±10−4 g, covering the whole composition range of the ternary mixtures. The uncertainty in the molar fraction calculation was estimated better than 10−4. The accuracy in the calculation of excess molar volumes was determined as being better than 10−3 cm³·mol⁻¹. The densities of pure compounds are compared with literature values in Table 1 [11].

3. Data procedure

3.1. Correlation of derived properties

The excess molar volumes for the ternary mixtures were computed by applying the following equation:

\[
V^E = \sum_{i=1}^{n} x_i M_i \left( \rho_{i} - \rho_{i}^{-1} \right)
\]

(1)

where \( \rho \) and \( \rho_i \) denote the density of the mixture and pure compounds, respectively. The computed values using these equations are shown in Table 2, with the experimental data. The excess molar volumes were fitted to a Redlich–Kister [12] type expression for every binary mixture, according to the equation:

\[
V^E_{ij} = x_i x_j \sum_{p=0}^{m} A_p (x_i - x_j)^p
\]

(2)

where \( A_p \) are the fitting parameters obtained by the unweighted least squares method, and \( m \) is the degree of the polynomial expansion, optimized by means of the \( F \)-test due to Bevington [13]. The parameters of the binary contributions were gathered in previous works [9,10].

The excess molar volumes of mixing of the ternary mixture were fitted by the equations

\[
V^E_{123} = V^E_{12} + V^E_{13} + V^E_{23} + A_{123}
\]

(3)

where \( V^E_{ij} \) is the binary contribution expressed for every binary mixture by Eq. (2) and have been correlated to Eqs. (3) and (4), and \( A_{123} \) is the ternary contribution to the derived property by means of the equation of Nagata and Tamura [14]:

\[
A_{123} = x_{1} x_{2} x_{3} RT \left( B_0 - B_1 x_{1} - B_2 x_{2} - B_3 x_{1}^2 - B_4 x_{2}^2 - B_5 x_{1} x_{2} - B_6 x_{1}^3 - B_7 x_{2}^3 - B_8 x_{1} x_{2}^3 \right)
\]

(4)

where \( x_i \) is the molar fraction, \( R \) is the universal constant for gases, and \( T \) is the temperature in Kelvin. The fitting parameters and their mean square root deviations corresponding to Eqs. (3) and (4) are enclosed in Table 3. The

Table 1 Experimental and literature data for pure liquids at 298.15 K

<table>
<thead>
<tr>
<th>Component</th>
<th>( M_w ) (g·mol⁻¹)</th>
<th>( \rho ) (g·cm⁻³)</th>
<th>Experimental</th>
<th>Literature*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorobenzene</td>
<td>112.560</td>
<td>1.1008</td>
<td>1.1011</td>
<td></td>
</tr>
<tr>
<td>n-Hexane</td>
<td>86.177</td>
<td>0.6551</td>
<td>0.65484</td>
<td></td>
</tr>
<tr>
<td>n-Undecane</td>
<td>156.311</td>
<td>0.7365</td>
<td>0.7365</td>
<td></td>
</tr>
<tr>
<td>n-Dodecane</td>
<td>170.337</td>
<td>0.7451</td>
<td>0.74518</td>
<td></td>
</tr>
</tbody>
</table>

mean square root deviations presented were computed using Eq. (5), where \( z \) is the value of the property, and \( n_{\text{DAT}} \) is the number of experimental data:

\[
\sigma = \left( \frac{1}{n_{\text{DAT}}} \sum_{i=1}^{n_{\text{DAT}}} \left( V_i^E - V_i^{\text{pred}} \right)^2 \right)^{1/2}.
\] (5)

Fig. 1a and b shows curves of constant excess molar volume by application of Eq. (3) for the ternary mixtures chlorobenzene+n-hexane+(n-Undecane or n-Dodecane). For both systems, excess molar volumes are found to be negative, except at low molar fraction of n-hexane. This zone presents a slight expansive trend, showing a maximum at equimolar composition of the binary chlorobenzene+(n-Undecane or n-Dodecane) [10]. These two molecules show a steric hindrance effect between the phenyl group and the large aliphatic chain that impede the molecular packing. The n-hexane shows a high capability to be enclosed into (n-Undecane or n-Dodecane) and chlorobenzene molecules by its low molar weight, this trend being slighter for n-hexane dilution. In Fig. 1c and d,
the ternary contributions (Eq. (4)) to the excess molar volumes are shown, which are positive for the two ternary mixtures, except at low chlorobenzene composition, where negative values are shown. The ternary contribution to the excess molar volume means about 30% of the derived value at the same composition range. In open literature, no values were found, as far as we know, for the excess molar volume of these ternary mixtures.

3.2. Partial excess molar volumes

Partial molar quantities are important in the study of the dependence of an extensive property on phase composition at constant pressure and temperature, because they show its trend with molar fraction variation. They should be applied to any extensive property of a single-phase system such as volume, Gibbs energy or any other.

In what is referred to an excess property, the partial excess molar volume of a component in a binary mixture can be determined from excess molar volume data taking into account the Redlich–Kister expression to fit the excess values. The expression for the partial excess molar volume should be written as:

\[ \bar{\nu}_i^E = (1 - x_i)^2 \sum_{p=0}^{m} A_p (2x_1 - 1)^p + x_i \sum_{p=1}^{m} (-2)^{p-1} p A_p (2x_1 - 1)^{p-1} \]

where the symbols keep the meaning explained above. From Eq. (6), the corresponding limiting partial excess molar volumes should be determined by considering \( x_i \) null for each case, such limiting values being dependent

---

Fig. 1. Constant value lines of ternary excess molar volume (cm\(^3\) mol\(^{-1}\)) for (a) chlorobenzene+\(n\)-hexane+\(n\)-undecane, (b) chlorobenzene+\(n\)-hexane+\(n\)-dodecane and ternary contribution to the excess molar volume for (c) chlorobenzene+\(n\)-hexane+\(n\)-undecane and (d) chlorobenzene+\(n\)-hexane+\(n\)-dodecane at 298.15 K.
only on these correlation parameters. Fig. 2 shows the
trends of partial excess molar volumes with the corre-
sponding molar fraction for the binary mixtures chlor-
obenzene+undecane and chlorobenzene+dodecane. In Table 4, the
values of limiting partial excess molar volumes at 298.15 K
for the binary mixtures are enclosed. The partial excess
molar volumes for the binary mixtures (n-hexane+n-
undecane, n-hexane+n-dodecane and chlorobenzene+n-
hexane) were reported in earlier papers [9,10]. In these
figures, a similar behaviour in two binary mixtures can be
observed, showing a continuous expansion trend caused by
the chlorobenzene for decreasing aliphatic hydrocarbon
mole fractions.

3.3. Estimation of derived properties

In the last few years, interest in equations of state for the
prediction of thermodynamic properties (excess molar
volumes, partial excess and partial molar volumes, phase
equilibria, excess molar enthalpies, etc.) has increased. This
fact is due to its simplicity as a model, low data require-
ments and versatility in operation conditions. A consider-
able number of equations of state are available in the
literature, most of them being adequate to obtain acceptable
results by simple rules if the parameters are obtained from
the encosed binary mixtures in the multicomponent system.
In this case, the Peng–Robinson (PR) [7] and Soave–
Redlich–Kwong (SRK) [8] equations were tested in
combination with mixing rules of one or two parameters
in the copressure and cavolume factors. For a binary
mixture, at constant $P$ and $T$, the excess molar volume is
expressed as follows:

$$V^E = \Delta V = V_m - \sum_{i=1}^{n} x_i V_i = \sum_{i=1}^{n} x_i (\bar{V}_i - V_i)$$ (7)

where $\bar{V}_i$ is the partial molar volume defined by:

$$\bar{V}_i = - \left( \frac{\partial P}{\partial n_i} \right)_{T,V,n} \left( \frac{\partial P}{\partial V_m} \right)_{T,n}$$ (8)

where the differential quantities and the molar volume are
computed from the corresponding equation of state and the
partial derivatives depend on the applied mixing rule. A
general expression for the equations of state is

$$P = \frac{RT}{V-b} - \frac{a}{(V+\delta_1 b)(V+\delta_2 b)}$$ (9)

which represents the SRK equation when $\delta_1 = 1$, $\delta_2 = 0$, and
the PR equation when $\delta_1 = 1 + \sqrt{2}$, $\delta_2 = 1 - \sqrt{2}$. Four
different combining rules were incorporated into these
equations. General equations for the applied mixing rules
can be expressed as follows:

$$a = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j (1 - k_{ij} - l_{ij} X) (a_{ij})^{1/2}$$ (10)

$$b = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j (1 - m_{ij}) \left( \frac{b_i + b_j}{2} \right)$$ (11)

where $k_{ij}$, $l_{ij}$ and $m_{ij}$ are fitting parameters to be calculated for
each binary mixture, being $l_{ij} = m_{ij} = 0$ for the first mixing rule
(R1), $l_{ij} = 0$ for the second (R2), and $k_{ij}$, $l_{ij}$, $m_{ij} \neq 0$ and $X = T$
for the third (R3), and $k_{ij}$, $l_{ij}$, $m_{ij} \neq 0$ and $X = (x_i - x_j)$ for the
last one (R4). In every case $k_{ij} = k_{ji}$, $l_{ij} = l_{ji}$ and
$m_{ij} = m_{ji}$.

For every pure substance and the PR and SRK equations,
the repulsion-covolume factor, $b_i$, is kept constant at its
critical point values and can be expressed as follows:

$$b_i = K_i \frac{RT_{ci}}{P_{ci}}$$ (12)

where $T_{ci}$ and $P_{ci}$ are the critical temperature and pressure of
the component $i$ in the mixture, and $K_i$ is a constant, whose

<table>
<thead>
<tr>
<th>Compound</th>
<th>$P_c$ (atm)</th>
<th>$T_c$ (K)</th>
<th>$Z_a$</th>
<th>$\omega$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorobenzene</td>
<td>44.61</td>
<td>632.40</td>
<td>0.265</td>
<td>0.2490</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>23.73</td>
<td>507.43</td>
<td>0.264</td>
<td>0.3047</td>
</tr>
<tr>
<td>n-Undecane</td>
<td>19.40</td>
<td>638.76</td>
<td>0.243</td>
<td>0.5362</td>
</tr>
<tr>
<td>n-Dodecane</td>
<td>18.00</td>
<td>658.20</td>
<td>0.238</td>
<td>0.5752</td>
</tr>
</tbody>
</table>

$^a$ [15].

Table 4
Partial excess molar volumes at infinite dilution of the binary mixtures encosed into the studied ternary mixtures at 298.15 K

<table>
<thead>
<tr>
<th></th>
<th>$\bar{V}_i^{E}$ (cm$^3$ mol$^{-1}$)</th>
<th>$\bar{V}_i^{E}$ (cm$^3$ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorobenzene</td>
<td>1.002</td>
<td>0.900</td>
</tr>
<tr>
<td>(1)+n-undecane (2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>0.879</td>
<td>0.990</td>
</tr>
<tr>
<td>(1)+n-dodecane (2)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 6  
Computed binary interaction parameters using different mixing rules on the Peng–Robinson and Soave–Redlich–Kwong equations of state and ternary prediction results, expressed through the root mean square deviations $\sigma$.

<table>
<thead>
<tr>
<th></th>
<th>Soave–Redlich–Kwong</th>
<th>Peng–Robinson</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R1</td>
<td>R2</td>
</tr>
<tr>
<td>$n$-Hexane+</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$n$-Undecane</td>
<td>$k_{ij} = 0.033413$ (0.0645)</td>
<td>$k_{ij} = 0.012548$</td>
</tr>
<tr>
<td>$m_{ij} = -0.026541$ (0.0112)</td>
<td>$l_{ij} = -0.000177$</td>
<td>$l_{ij} = 0.033376$</td>
</tr>
<tr>
<td>$n$-Hexane+</td>
<td>$k_{ij} = 0.035609$ (0.0576)</td>
<td>$k_{ij} = 0.020143$</td>
</tr>
<tr>
<td>$n$-Dodecane</td>
<td>$m_{ij} = -0.038469$ (0.0208)</td>
<td>$l_{ij} = -0.002413$</td>
</tr>
<tr>
<td>Chlorobenzene+</td>
<td>$k_{ij} = 0.019789$ (0.0106)</td>
<td>$k_{ij} = 0.017018$</td>
</tr>
<tr>
<td>$n$-Hexane</td>
<td>$m_{ij} = -0.026688$ (0.0104)</td>
<td>$l_{ij} = -0.002744$</td>
</tr>
<tr>
<td>Chlorobenzene+</td>
<td>$k_{ij} = -0.094049$ (0.0097)</td>
<td>$k_{ij} = -0.085826$</td>
</tr>
<tr>
<td>$n$-Undecane</td>
<td>$m_{ij} = -0.089134$ (0.0080)</td>
<td>$l_{ij} = -0.000163$</td>
</tr>
<tr>
<td>Chlorobenzene+</td>
<td>$k_{ij} = -0.122575$ (0.0271)</td>
<td>$k_{ij} = -0.094833$</td>
</tr>
<tr>
<td>$n$-Dodecane</td>
<td>$m_{ij} = -0.111286$ (0.0068)</td>
<td>$l_{ij} = -0.002970$</td>
</tr>
<tr>
<td>Chlorobenzene+</td>
<td>$m_{ij} = -0.111286$ (0.0063)</td>
<td>$m_{ij} = -0.101326$ (0.0063)</td>
</tr>
<tr>
<td>$n$-Hexane+</td>
<td>$m_{ij} = 0.14441$ (0.10154)</td>
<td>$m_{ij} = 0.09977$ (0.09977)</td>
</tr>
<tr>
<td>Chlorobenzene+</td>
<td>$m_{ij} = 0.14441$ (0.10154)</td>
<td>$m_{ij} = 0.09977$ (0.09977)</td>
</tr>
</tbody>
</table>
value should be 0.08664 for SRK [8] and 0.0778 for PR [7]. The attraction–cohesion parameter, \( a_i \), contains a generalized function of temperature:

\[
\alpha_i = K_2 \frac{R^2 T_i^3}{P_{ci}} \alpha_i
\]

where

\[
\alpha_i = \left[ 1 + m_i \left( 1 - T_i^{1/2} \right) \right]^2
\]

and

\[
m_i = K_3 + K_4 \omega_i - K_5 \omega_i^2
\]

In these equations, \( \omega_i \) stands for the acentric factor, and \( K_i \) is constant with values \( K_2 = 0.42748, K_3 = 0.480, K_4 = 1.574 \) and \( K_5 = 0.176 \) for SRK [8] and \( K_2 = 0.45724, K_3 = 0.37464, K_4 = 1.54226 \) and \( K_5 = 0.26992 \) for PR [7]. For pure substances, \( T_{ci}, P_{ci}, \omega_i \) and \( Z_i \) values [15] are enclosed in Table 5. For calculating the binary interaction parameters for each mixing rule, the objective function represented by Eq. (16) was minimized.

\[
OF = \frac{\sum_{i=1}^{n} \left( \alpha_{i,exp} - \alpha_{i,pred} \right)^2}{\alpha_{i,exp}}
\]

A Marquardt [16] algorithm was applied to calculate the parameters, in combination with a Newton–Raphson method to solve the equation. From the fitting binary parameters, the excess molar volume of a higher order multicomponent system can be easily estimated, by applying the same mixing rules, extended for multicomponent cases, and so it was done, obtaining predictions for the ternary excess molar volumes that were compared with the set of experimental data.

In Table 6, the binary coefficients from Eqs. (10) and (11) are listed, together with root mean square deviations \( \sigma \) from the experimental data (in brackets). For the binary systems, similar \( \sigma \) values were obtained for all mixing rules, except for R1 mixing rule, where the poorest results are obtained. Mixing rule R4 shows the best results. Both equations of state offer good agreement with the binary excess molar volume data. In the system with \( n \)-undecane, the \( \sigma \) values for the calculated ternary contributions are essentially the same for all four mixing rules and both equations of state tested. For the other system, the best results for the ternary excess volumes were provided by the R4 mixing rule in both equations. The accuracy in the representation of measured data varies when changing the mixing rule, while both equations of state perform equally when using the same mixing rule.

### 3.4. Estimation of molecular radius of liquids

The molecular radius is one of the molecular parameters which reflects their structural characteristics. Liquids in mixing environment behave in a different way than individually due to the fact that the interaction between molecules is different attending to the composition of the mixture and temperature conditions. The molecular radius is not only related to the number and kind of atoms but also to the nature and internal organization building functional groups. It is an important parameter in the different theories of liquids [17–21] and its utility for the estimation of properties of liquids has been proved earlier [22–25]. Acoustic, optical and vibrational techniques are powerful tools for physicochemical studies of liquids. Ultrasonic velocity, density or refractive index are useful to estimate the molecular radius in pure liquids and mixtures. In fact, different methods [26–30] enclosing different approximations to the model of closely packed molecules with face-centered cubic structures have been used in the open literature. As far as we know, the methods commented above have not been analyzed for multicomponent mixtures in order to provide an idea about the dependence of the molecular radius on temperature, composition and functionality of molecules. In this item, an attempt is made in order to estimate the variation of the molecular radius as functional alkane length and composition in the studied ternary mixtures. The values of the refractive index for mixtures were taken from a previously published paper [31]. The availability of alternative procedures by different properties is desirable, as well as to test comparatively the accuracy for different systems. We applied in this work the Gladstone equation (refraction and volumetric dependence) and the close-packed face-centered cubic structure (CP-

![Fig. 3. Molecular radii for (■) Gladstone equation and (+) close packed face-centered cubic equation (CP-FCC) in chlorobenzene+\( n \)-hexane+(a) \( n \)-undecane or (b) \( n \)-dodecane at 298.15 K.](image-url)
FCC) model (solely volumetric dependence) (Eqs. (17) and (18), respectively) to estimate the molecular radius:

\[
 r = \left[ \frac{3}{4\pi N} \left( \frac{n_B^3 - 1}{n_B^3 + 2} + \frac{M_W}{\rho} \right) \right]^{1/3} \tag{17}
\]

\[
 r = \frac{1}{2} \left[ \frac{\sqrt{2M_W}}{\rho N} \right]^{1/3} \tag{18}
\]

In Fig. 3a and b, the molecular radii for both ternary mixtures are shown versus \( z = \prod_{i=1}^{N} x_i \), where \( x_i \) is the molar fraction of the mixture. Both models predict similar results but the decreasing size series are the following: Gladstone equation: \( r_{n\text{-dodecane}}>r_{n\text{-undecane}}>r_{\text{chlorobenzene}}>r_{n\text{-hexane}} \) and CP-FCC equation: \( r_{n\text{-dodecane}}>r_{n\text{-undecane}}>r_{n\text{-hexane}} \). These methods compute slight differences in what is referred to radii of \( n\text{-hexane} \) and chlorobenzene. At any case, their similar size attending to these results are in line with the effect of \( n\text{-hexane} \) in chlorobenzene+\( n\text{-alkane} \). The molecular radii show a progressive decrease towards the binary chlorobenzene+\( n\text{-hexane} \) at both mixtures. In these figures, as obviously the method CP-FCC shows, the higher values at any composition should be observed, because this method is based upon the assumption that there is no free space among molecules.

4. Results and conclusions

In this work, the densities of the mixtures chlorobenzene+\( n\text{-hexane} \)\( +(n\text{-undecane or } n\text{-dodecane}) \) have been measured at 298.15 K, the excess molar volumes being calculated. These data were correlated by polynomial expressions which fitted the data well. Not surprisingly, the systems exhibited a strong contractive tendency attending to the solvent (\( n\text{-undecane or } n\text{-dodecane} \)) composition, but with a weakening effect as the aliphatic chain increases. No values for the ternary mixtures were found in the open literature as far as we know. It is well known that when non-polar compounds are mixed, slight variations in the intermolecular interactions take place. The new specific dispersive interactions that appear could be suitably measured by volumetric techniques. Usually, these kind of mixtures show a moderate non-ideal behaviour, which is severely conditioned by the difference in molecular volume among the components in mixture. In this case, the steric hindrance is the most important factor in mixing thermodynamics due to the globular structure and polarity in the halogenated compound and the quasi-linear chain of \( n\text{-alkanes} \). Disruption of polar interaction among chlorobenzene molecules deals progressively from negative to positive values through the aliphatic homologous series of \( n\text{-alkanes} \) when molecular weight is increased, but this trend is conditioned by \( n\text{-hexane} \). In the mixture chlorobenzene+\( n\text{-hexane} \)\( +(n\text{-undecane or } n\text{-dodecane}) \), the tendency in excess property could be explained according to the steric hindrance between the phenyl group and the long aliphatic chain (\( n\text{-undecane or } n\text{-dodecane} \)), the molecular packing made difficult by induction and polar interaction. In the binary chlorobenzene+\( n\text{-undecane or } n\text{-dodecane} \), local maxima could be observed at equimolar composition. The results gather the strong interaction of chlorobenzene and short chains of inert alkanes due to similar size and the need for knowledge about thermodynamics on cosolvents to awaken these interactions in multicomponent separation by liquid entrainers. The mixing rules applied on cubic equations of state can be used to any higher order multicomponent mixture, requiring only binary parameters and affording a simple calculation procedure. Due to these reasons, the equation of state approach is seen to be a powerful instrument for predicting excess molar volumes.

References

[11] TRC Thermodynamic Tables (Thermodynamic Research Center, Texas A&M University: College Station, TX, 1994).