
ALEXANDRU BARHALA*, DANA DRAGOESCU, MARIANA TEODORESCU
“Ilie Murgulescu” Institute of Physical Chemistry, 202, Splaiul Independentei, 060021, Bucharest, Romania

The data available in the literature and our recent data on vapour-liquid equilibrium (VLE), excess Gibbs energy, \( G^e \), and excess enthalpy, \( H^e \), for the homologous series of cyclopentanone + chloroalkane mixtures are examined in terms of the predictive group contribution models DISQUAC and UNIFAC. In our treatment, we present also how the structural effects and different types of molecular interactions are reflected by the thermodynamic excess properties of the mentioned series mixtures.

Keywords: vapour-liquid equilibria, cyclopentanone + chloroalkanes, thermodynamic excess properties, DISQUAC, UNIFAC group contribution models

The experimental vapour-liquid equilibria data (VLE) provide valuable information for the separation processes design based on phase composition differences from chemical, pharmaceutical, food and petrochemical industry, transport equipment design (pipes and reservoirs), mapping, monitoring and evaluation of gaseous and liquid chemical compounds behaviour in environment, for the prevention and diminution of ecological hazards, phase separation processes design and destruction of environmental pollutants and waste materials recycling.

On the other hand, these data are absolutely necessary for the development of new predictive methods of thermodynamic properties and testing of relevant theories of liquids.

The main possibility to obtain thermodynamic data for pure compounds and for their mixtures is to carry out experimental measurements, but these are very expensive and time consuming. Regardless of a huge number of experimental data available in the literature [1], there are still missing data concerning systems of practical and theoretical interest.

Other possibility of obtaining equilibrium data and associated thermophysical properties is the development of molecular models for prediction. In present, for the quantitative description of the behaviour of complex systems at phase equilibrium, in chemical engineering the use of semiempirical thermodynamic models still prevails [2].

The thermodynamic models represent the efficient instruments for materials designing and processing and are useful for prediction and correlation of volumetric properties and phase equilibria of fluid mixtures [3]. These operations are much facilitated especially by the availability of process simulators (for example, ASPEN Plus, ChemCAD, etc.), which are equipped with a variety of thermodynamic models and parameters databases that allow the calculation of thermophysical and thermodynamic properties of pure substances (vapour pressures, densities, etc.) and of real mixtures (phase equilibria, excess properties).

One of the theoretical methods developed for the estimation of the mixtures properties from experimental data of pure compounds is the group contribution method. The method is based on the idea that the physical properties of a substance can be subdivided into contributions of groups of atoms which form the molecule. In this assumption, the molecular interactions in binary systems are regarded as specific interactions between functional-structural groups from each molecule, the molecule being in this way thought as a collection of attached groups and the properties of mixtures are expressed in terms of group parameters (structural and energetic). The advantage of this approach is that a large number of molecules can be build-on from a rather small number of functional groups, therefore existing the possibility of description of a great variety of multi-component nonelectrolyte systems. The group contribution methods lead to satisfactory results for a variety of pure compounds and mixtures containing small molecules typically encountered in petrochemical industry, but they are not sufficiently tested for classes of substances for which the reference experimental data are missing.

From the group contribution methods, the UNIFAC (Universal Functional Activity Coefficients) [4] and ASOG (Analytical Solution of Groups) [5] methods are those of the greatest practical interest due to the availability of a large number of interaction parameters (tabulated). The critical analysis of these methods in different versions (original and modified) is found in specific and general papers [6-8]. For example, for the modified UNIFAC model (Dortmund) [9] the interaction parameters are determined mainly from experimental VLE and excess Gibbs energies \( (G^e) \) data, but for this purpose infinite dilution coefficients \( (γ^n) \), excess enthalpies of mixtures \( (H^e) \), excess heat capacities \( (C_p) \), liquid-liquid equilibrium (ELL) and solubilities data can be also used. These parameters are periodically revised and published once the new experimental data are accumulated, the most complete database being Dortmund Data Bank [10]. The UNIFAC model was implemented in all commercial process simulators, but the chemical engineers are often confronted with the absence of the interaction binary parameters for the systems of interest.

The DISQUAC model [11, 12], based on an original version of group surface in classical chemical Guggenheim-Barker lattice theory [13], presents a special interest. Comparing with classical theory, the DISQUAC model eliminates the difficulties in the treatment of mixtures containing pairs of different polarities taking into consideration the dispersive contribution (DIS) (of

* email: abarhala@chimfiz.icf.ro; Tel.: 0728750394
disorder) for each contact of surfaces of group pairs, supplemented eventually by an electrostatic contribution (of order), treated quasichemical (QUAC). Taking into account that an essential characteristic of DISQUAC model is that these parameters vary regularly with structure for the first terms of homologous series, the parameters can be used afterwards in $G^E$ and $H^E$ estimation for systems containing the same types of interactions and for which experimental data do not exist. The parameters variation is regular and similar classes of compounds follow the same rule. Consequently, the proximity effects due to inter- and intra-molecular interactions are reflected in the variation of parameters with molecular structure.

DISQUAC model has been successfully applied for the evaluation of thermodynamic properties of mixtures from different classes of organic substances [14-23].

In the last years, many studies on thermodynamic properties of mixtures containing halogenated hydrocarbons have been done, due to their practical importance as solvents, foaming agents, refrigeration fluids and air-conditioning systems with special impact on environment protection. In addition, from theoretical point of view, these mixtures have a great importance in testing of group contribution models, due to the variety of the molecules involved and the disponibility of thermodynamic data.

Concerning this thematical area, our research group have undertaken a systematic study regarding the thermodynamic properties of mixtures containing linear ketones [24-29] and cyclic ketones + chloroalkanes: cyclopentanone + 1-chloroalkanes (1-chlorobutane), + (α,ω)-dichloroalkanes (1,2-dichloroethane, 1,3-dichloropropane, + 1,4-dichlorobutane), + polychloroalkanes (trichloromethane, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane) [30-32].

The new and original thermodynamic data, obtained for the studied systems, permit the testing of vapour-liquid equilibria data and the excess thermodynamic properties prediction by application of UNIFAC and DISQUAC models.

Consequently, the aim of this work is to present the capability of DISQUAC and modified UNIFAC (Dortmund) methods to predict the vapour-liquid equilibria and excess thermodynamic properties in the binary systems of cycloketones + chloroalkane systems, in the view of extension of this group contribution models.

**Experimental part**

**Equipment and procedures**

The measurements of vapour-liquid equilibria for pure compounds and binary mixtures of cyclopentanone with chloroalkanes, mentioned above, have been carried out by using an isothermometer – static method – (majority of listed systems) and an ebulliometer – dynamic method – (cyclopentanone + 1,1,2,2-tetrachloroethane system), both realized in our laboratory. Working procedures and performances of the apparatuses have been described in previous papers [24, 26, 28, 33, 34]. In static method, the total vapour pressure is measured as a function of global composition of the system charged and degassed into the equilibrium cell. Experimental VLE data have been correlated with classical models of nonelectrolyte solutions (Redlich-Kister, Wilson, NRTL), nonideality of the vapour phase being corrected by second virial coefficients.

VLE data and excess thermodynamic properties prediction by DISQUAC and UNIFAC models

**DISQUAC model**

This model, in acceptance of the quasichemical theory, describes the properties of organic mixtures in terms of surfaces interactions, each molecule being characterized by geometrical and interaction parameters. The calculation of these parameters was presented in extent in other papers [11, 15, 17]. The equations for $G^E$ and $H^E$ calculation are the same as those previously used, and for a better understanding of model application, we remind here shortly some of its features.

In the DISQUAC model formulation, the interaction terms resulted from the excess thermodynamic properties, contain a dispersive term (dis) and a quasichemical term (quac) that are calculated independently and then simply added:

$$G^E_{\text{comb}} = G^E_{\text{int}} + G^E_{\text{dis}} + G^E_{\text{quac}}$$

$$H^E_{\text{dis}} + H^E_{\text{quac}}$$

(1)

where, for a binary system $G^E_{\text{comb}} = x_1 \ln \frac{\phi_1}{x_1} + x_2 \ln \frac{\phi_2}{x_2}$ is the Flory-Huggins combinatorial term in which

$$\phi_i = \frac{r_i x_i}{r_1 x_1 + r_2 x_2}$$

is the volume fraction of component 1; in general, $\phi$ = volume fraction, $x_\text{c}$ = mole fraction, and $r$ = relative molecular volume of component $i$ ($i = 1, 2$):

The terms $G^E_{\text{int}}$, $H^E_{\text{dis}}$ are given by Kehiaian [11]:

$$G^E_{\text{int}} = (q_1 x_1 + q_2 x_2) z_{\text{dis}}$$

$$H^E_{\text{dis}} = (q_1 x_1 + q_2 x_2) z_{\text{dis}}$$

$$g_{\text{dis}}^{x_1 x_2} = \sum_{n} \frac{(\alpha_{x_1} - \alpha_{x_2})^2 (\alpha_{x_1} - \alpha_{x_2})^2}{2}$$

$$h_{\text{dis}}^{x_1 x_2} = \sum_{n} (\alpha_{x_1} - \alpha_{x_2}) (\alpha_{x_1} - \alpha_{x_2})$$

(6)

where:

$q_{\text{dis}}^{x_1 x_2}$, $h_{\text{dis}}^{x_1 x_2}$ are the dispersive interchange parameters, of Gibbs energy and enthalpy, respectively of (st) contact; $\alpha_x$ is molecular surface fraction of s group on a molecule of type $i$; $q_{\text{dis}}^{x_1 x_2}$ is the relative area of the i type molecule, $\alpha_{x_i} = q_{x_i} / q$, and $z = q_{x_1} x_1 + q_{x_2} x_2$ is the surface fraction of component $i$ in mixture ($i = 1, 2$).

For a binary system, $G^E_{\text{dis}}$ and $H^E_{\text{dis}}$ have been presented in other work [11].

$$G^E_{\text{quac}} = x_1 \mu_{\text{int}}^{x_1 x_2} + x_2 \mu_{\text{int}}^{x_2 x_1}$$

$$\mu_{\text{int}}^{x_1 x_2} = z_{\text{quac}} \sum_{i} \frac{\alpha_{x_i}}{X_i} \ln (X_i / x_i)$$

(8)

$$H^E_{\text{quac}} = \left( \frac{1}{2} \right) (q_1 x_1 + q_2 x_2) \sum_{n} X_{x_1} X_{x_2} \left( (\xi_{x_1} X_{x_1} + \xi_{x_2} X_{x_2} \right) h_{\text{quac}}^{x_1 x_2}$$

(9)

$$\eta_{\text{quac}} = \exp \left[ - \frac{g_{\text{quac}}^{x_1 x_2}}{z_{\text{quac}}} \right]$$

(10)

where $g_{\text{quac}}^{x_1 x_2}$ and $h_{\text{quac}}^{x_1 x_2}$ are the quasichemical interchange parameters of Gibbs energy and enthalpy, respectively of the contact (st), and $z$ is the “coordination number". The quantities $X_i$, $q_i X_i$ are obtained by solving the system of $\lambda$ equations ($\lambda$ is the number of contact surfaces):

$$X_{x_i} \left( x_i + \sum_{i} X_i \eta_{x_i} \right) = \alpha_{x_i}$$

(11)
The temperature dependence of dispersive or quasichemical parameters was expressed through one equation with 2 constants as it follows:

\[
\frac{g_n(T)}{RT} = C_{n,1} + C_{n,2} \left( \frac{T}{T_0} \right)
\]

\[
\frac{h_n(T)}{RT} = C_{n,3} \left( \frac{T}{T_0} \right)
\]

\[
C_{n,0} = \frac{g_n(T_0)}{RT_0} \quad \text{and} \quad C_{n,2} = \frac{h_n(T_0)}{RT_0}
\]

where \( T_0 = 298.15 \, \text{K} \), while \( C_{n,1} \) and \( C_{n,2} \) are named interchanged energetic parameters/coefficients.

For the coordination number \( z \), it was chosen like "reference value" \( z = 4 \) [15].

Each contact \((st)\) is thus characterized by two dispersive interchange parameters and two quasichemical interchange parameters (for Gibbs energy and for enthalpy). Therefore, for determination of the thermodynamic properties of a mixture, the following parameters \( r_k \), \( q_k \), \( a_k \), \( C_{diff} \), \( C_{dd} \), \( C_{q} \), \( C_{ad} \), \( C_{cd} \), \( C_{k} \), \( C_{kd} \) where \( k \) is the component of mixture, and \( (st) \) is the type of contact, are necessary.

In the frame of DISQUAC model, the mixtures of linear/cyclic ketones with chloroalkanes are regarded as possessing four types of surfaces: (I) type a, aliphatic (CH\(_3\), CH\(_2\), CH, C), which are assumed to exert the same force field), (II) type c, cyclic (c-CH\(_2\)), (III) type d, chloro (Cl) and (IV) type k, carbonyl (CO). The four types of surfaces a, c, d and k generate six pairs of contacts: ac, ad, ak, cd, ck and kd.

The cycloketone + chloroalkane mixtures are generally described by the help of the following interchange coefficients:

\[
C_{ac,1}^{dd}, C_{ac,1}^{dc}, C_{ac,1}^{cd}, C_{ad,1}^{dd}, C_{ad,1}^{dc}, C_{ak,1}^{dd}, C_{ak,1}^{dc}, C_{ac,2}^{dd},
\]

and

\[
C_{ad,2}^{dd}, C_{cd,2}^{dc}, C_{ck,2}^{dd}, C_{cd,1}^{dc}, C_{cd,1}^{dd}, C_{cd,2}^{dc}, C_{cd,2}^{dd}, C_{ck,2}^{dc}, C_{cd,1}^{dd},
\]

Assessment of geometrical parameters

The total relative molecular volume, \( r_i \), the total surfaces, \( q_i \), and the molecular surface fractions, \( \alpha_i \), for the compounds presented in mixtures are usually calculated adiabatically on the basis of the group volumes and surfaces recommended by Bondi [35], arbitrarily taking the volume and surface of methane as unity [11]. The geometrical parameters of the groups appearing in the studied mixtures have been estimated previously [15, 16, 36, 37] and cumulated in paper [38]. The geometrical parameters used in this paper are presented in tables 1 and 2.

**DISQUAC interchange parameters**

The general procedure for the interaction parameters estimation has been explained in detail in other works [11, 15, 17, 38].

**DISQUAC interchange parameters for the CO/Cl contact** for entire class of binary mixtures of linear ketones with 1-chloroalkanes, \( \alpha,\omega \)-dichloroalkanes and several pyc chloroalkanes have been recently published [38]. The determined \( C_{diff}^{dd} \) and \( C_{diff}^{dc} \) coefficients \((n=1, 2)\) follow quite simple rules: (a) the \( C_{diff}^{dd} \) and \( C_{diff}^{dc} \) coefficients for the 1-chloroalkane + ketone \( [\text{CH}_3(\text{CH}_2)_u\text{CO}(\text{CH}_2)_v\text{CH}_3] \) mixtures, vary regularly with the \( u+v \) size of the hydrocarbon chain of a ketone; (b) for the small molecules of \( \alpha,\omega \)-dichloroalkanes, where the proximity effects are great, the \( C_{diff}^{dd} \) coefficients vary with the length of the aliphatic chain \( m \) between the chlorine groups \((\text{for } m \leq 10 \text{ the } C_{diff}^{dd} \text{ coefficients are independent of the nature of ketone)}\).

For the mixtures of cyclic ketones + chloroalkanes similar rules are expected; this aspect pursues to be evidenced when, sufficient experimental data will exist, for entire class of mixtures.

In our calculations use has been made of dispersive and quasichemical parameters for the contacts ac, ad, ak, cd, ck and kd, which are known from thermodynamic properties of the mixtures: cycloalkanes + n-alkanes [39], chloroalkanes + n-alkanes [16], chloroalkanes + cycloalkanes [15], cyclic ketones + cycloalkanes [16], linear ketones + chloroalkanes [38], determined by us. In the DISQUAC predictions of this work, for the contact kd we considered cyclopentanone like 3-pentanone, meaning

| Table 1 | TOTAL RELATIVE MOLECULAR VOLUME \( r_i \), TOTAL SURFACE \( q_i \), AND MOLECULAR SURFACE FRACTIONS \( \alpha_{ai} \) (CH\(_3\), CH\(_2\), C, GROUPS) AND \( \alpha_{di} \) (CO GROUP) FOR CHLOROALKANES, CALCULATED FROM GROUP INCREMENTS |
|---|---|---|---|---|
| Chloroalkane | \( r_i \) | \( q_i \) | \( \alpha_{ai} \) | \( \alpha_{di} \) |
| 1-chlorobutane | 3.2699 | 2.7483 | 0.7742 | 0.2258 |
| 1,2-dichloroethane | 2.5526 | 2.1724 | 0.4286 | 0.5714 |
| 1,3-dichloropropane | 3.1501 | 2.6379 | 0.5294 | 0.4706 |
| 1,4-dichlorobutane | 3.7477 | 3.1035 | 0.6000 | 0.4000 |
| chloroform | 2.5409 | 2.2828 | 0.1752 | 0.8248 |
| 1,1,1-trichloroethane | 3.1378 | 2.6138 | 0.2797 | 0.7203 |
| 1,1,2,2-tetrachloroethane | 3.6519 | 2.9035 | 0.1354 | 0.8646 |

| Table 2 | TOTAL RELATIVE MOLECULAR VOLUME \( r_i \), TOTAL SURFACE \( q_i \), AND MOLECULAR SURFACE FRACTIONS \( \alpha_{ci} \) (c-CH\(_2\) GROUPS) AND \( \alpha_{ki} \) (CO GROUPS) FOR CYCLOPENTANONE, CALCULATED FROM GROUP INCREMENTS |
|---|---|---|---|
| Cycloketone | \( r_i \) | \( q_i \) | \( \alpha_{ci} \) | \( \alpha_{ki} \) |
| cyclopentanone | 3.0292 | 2.4368 | 0.2264 | 0.7736 |
the linear ketone with the same carbon atoms as cyclopentanone. Using these coefficients, we predicted the data of VLE, $G^E$ and $H^E$ that are presented in table 5. According to some authors [15], the VLE prediction performances by using this model, are comparable only with those realized with modified UNIFAC model.

**UNIFAC model**

The modified UNIFAC model (Dortmund) [9] differs from the original UNIFAC [5] by one combinatorial term and the temperature dependence of group interaction parameters:

$$
\psi_{mn} = \exp\left[\frac{a_{nm} + b_{nm} T + c_{nm} T^2}{T}\right]
$$

UNIFAC model, as a model based on group contribution method, does not distinguish between interaction parameters of linear or cyclic ketone groups. This situation appears because either systems that contain cycloketones have not been introduced in the model database, or they were not tested yet. For this reason, we considered also, for this model, the studied cyclic ketone as a linear ketone with the same C atoms (cyclopentanone like 3-pentanone).

For the investigated mixtures, geometrical parameters: of volume, $R_k$, and of area surface, $Q_k$, and interaction parameters of groups: $a_{nm}$, $b_{nm}$, and $c_{nm}$, where $k$, $n$ and $m$ denote the different structural groups of the investigated mixtures, were taken from the version 1993 of modified UNIFAC (Do [9]) (tables 3 and 4).

The UNIFAC calculations have been made by using the package software PHEQ (Phase Equilibria database and calculation program) elaborated in [40].

**Results and discussions**

In table 5, the comparison between experimental data and those obtained by DISQUAC and modified UNIFAC are presented, for VLE, equimolar excess Gibbs energy, $G^E_{0.5}$ and equimolar excess enthalpy, $H^E_{0.5}$, at the systems of cyclopentanone + chloroalkanes studied in this work. For the sake of clarity, the table includes also, the standard deviations of pressure defined as $\sigma(P) = \left(\sum_{i=1}^{N} (P_{\text{exp}} - P_{\text{cal}})^2 / N\right)^{1/2}$, $N$ being the number of experimental points.

For phase equilibria (VLE), the vapour pressure predictions of these mixtures are generally, well represented by both models. The $P-T-x-y$ diagrams for the systems of cyclopentanone with various chloroalkanes are presented in figures 1, 3, 5, 7, 9, 11.

Although UNIFAC model use a small number of parameters, what makes it more attractive, the results of prediction for $G^E$ and $H^E$ obtained with DISQUAC model are clearly better (it does not ignore the important steric and proximity effects). In the case of 1-chlorobutane + cyclopentanone, the predictions for $G^E$ with both models are almost identic (fig. 2). If in $G^E$ prediction by DISQUAC model, the modality of considering cyclic ketone as a linear ketone with the same number of carbon number (cyclization effect being neglected) gave good results, the $G^E$ prediction by UNIFAC model conducted to unsatisfactory results (figs. 6, 10, 13), sometimes different as sign (for the systems 1,2-dichloroethane, 1,4-dichlorobutane and 1,1,1-trichloroethane + cyclopentanone (figs. 4, 8, 12).

### Table 3

<table>
<thead>
<tr>
<th>Main group</th>
<th>Sub-group</th>
<th>$R_k$</th>
<th>$Q_k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 “CH₂”</td>
<td>CH₃</td>
<td>0.6325</td>
<td>1.0608</td>
</tr>
<tr>
<td>1 “CH₃”</td>
<td></td>
<td></td>
<td>0.7081</td>
</tr>
<tr>
<td>1 “CH₄”</td>
<td></td>
<td></td>
<td>0.3554</td>
</tr>
<tr>
<td>9 “CH₂CO”</td>
<td>CH₂CO</td>
<td>1.7048</td>
<td>1.5542</td>
</tr>
<tr>
<td>21 “CCI”</td>
<td>CH₂Cl</td>
<td>0.9919</td>
<td>1.3654</td>
</tr>
<tr>
<td>22 “CC₂”</td>
<td>CHCl₂</td>
<td>1.8000</td>
<td>2.1473</td>
</tr>
<tr>
<td>23 “CC₃”</td>
<td>CCl₃</td>
<td>2.6500</td>
<td>2.3778</td>
</tr>
<tr>
<td>42 “c-CH₂”</td>
<td>c-CH₂</td>
<td>0.7136</td>
<td>0.8635</td>
</tr>
</tbody>
</table>

### Table 4

<table>
<thead>
<tr>
<th>n</th>
<th>m</th>
<th>$a_{nm}$ (K)</th>
<th>$b_{nm}$</th>
<th>$c_{nm}$ (K$^{-1}$)</th>
<th>$a_{nm}$ (K)</th>
<th>$b_{nm}$</th>
<th>$c_{nm}$ (K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9</td>
<td>433.60</td>
<td>0.1473</td>
<td>0.0</td>
<td>199.00</td>
<td>-0.8709</td>
<td>0.0</td>
</tr>
<tr>
<td>1</td>
<td>21</td>
<td>401.00</td>
<td>-0.7277</td>
<td>0.0</td>
<td>-65.685</td>
<td>0.07409</td>
<td>0.0</td>
</tr>
<tr>
<td>1</td>
<td>22</td>
<td>-233.66</td>
<td>1.2561</td>
<td>0.0</td>
<td>311.55</td>
<td>-1.1856</td>
<td>0.0</td>
</tr>
<tr>
<td>1</td>
<td>23</td>
<td>-653.74</td>
<td>4.5311</td>
<td>-0.008735</td>
<td>1302.6</td>
<td>-8.4270</td>
<td>0.01442</td>
</tr>
<tr>
<td>1</td>
<td>42</td>
<td>-680.95</td>
<td>4.0194</td>
<td>-0.006878</td>
<td>1020.8</td>
<td>-6.0746</td>
<td>0.01015</td>
</tr>
<tr>
<td>9</td>
<td>21</td>
<td>-99.976</td>
<td>0.0</td>
<td>0.0</td>
<td>55.270</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>9</td>
<td>22</td>
<td>-18.695</td>
<td>-0.5261</td>
<td>0.0</td>
<td>-219.94</td>
<td>1.0749</td>
<td>0.0</td>
</tr>
<tr>
<td>9</td>
<td>23</td>
<td>810.17</td>
<td>-3.2209</td>
<td>0.002144</td>
<td>48.64</td>
<td>-0.7950</td>
<td>0.003713</td>
</tr>
<tr>
<td>9</td>
<td>42</td>
<td>156.53</td>
<td>-0.7135</td>
<td>0.0</td>
<td>498.92</td>
<td>-0.04400</td>
<td>0.0</td>
</tr>
<tr>
<td>21</td>
<td>22</td>
<td>70.790</td>
<td>0.0</td>
<td>0.0</td>
<td>-66.210</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>21</td>
<td>23</td>
<td>592.40</td>
<td>-4.2459</td>
<td>0.006905</td>
<td>603.29</td>
<td>-3.9770</td>
<td>0.006248</td>
</tr>
<tr>
<td>21</td>
<td>42</td>
<td>-65.685</td>
<td>0.07409</td>
<td>0.0</td>
<td>401.00</td>
<td>-0.7277</td>
<td>0.0</td>
</tr>
<tr>
<td>22</td>
<td>23</td>
<td>187.43</td>
<td>-3.4460</td>
<td>0.006718</td>
<td>1468.9</td>
<td>-5.0000</td>
<td>0.003701</td>
</tr>
<tr>
<td>22</td>
<td>42</td>
<td>34.133</td>
<td>-0.3925</td>
<td>0.0</td>
<td>193.77</td>
<td>0.03179</td>
<td>0.0</td>
</tr>
<tr>
<td>23</td>
<td>23</td>
<td>42.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>
Table 5
EXCESS GIBBS ENERGY, $G^e$ EXCESS ENTHALPY, $H^e$ AT EQUIMOLAR COMPOSITION AND STANDARD DEVIATIONS IN PRESSURE OBTAINED FOR THE CYCLOPENTANONE + CHLOROALKANE MIXTURES, AT DIFFERENT TEMPERATURES, BY DISQUAC AND UNIFAC MODELS

<table>
<thead>
<tr>
<th>Chloroalkane</th>
<th>T(K)</th>
<th>N</th>
<th>Experimental</th>
<th>DISQUAC</th>
<th>UNIFAC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$G^e_{0.5}$</td>
<td>$H^e_{0.5}$</td>
<td>$\sigma(P)$</td>
</tr>
<tr>
<td>1-chlorobutane</td>
<td>298.15</td>
<td>13</td>
<td>201$^{32}$</td>
<td>-</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>308.15</td>
<td>13</td>
<td>189$^{32}$</td>
<td>87$^{32}$</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>318.15</td>
<td>13</td>
<td>209$^{32}$</td>
<td>-</td>
<td>0.20</td>
</tr>
<tr>
<td>1,2-dichloroethane</td>
<td>298.15</td>
<td>12</td>
<td>-360$^{30}$</td>
<td>-</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>303.15</td>
<td>12</td>
<td>-332$^{30}$</td>
<td>-</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>305.15</td>
<td></td>
<td>-</td>
<td>-4$^{50}$</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>308.15</td>
<td>12</td>
<td>-370$^{30}$</td>
<td>-</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>313.15</td>
<td>12</td>
<td>-327$^{30}$</td>
<td>-</td>
<td>0.03</td>
</tr>
<tr>
<td>1,3-dichloropropane</td>
<td>298.15</td>
<td>13</td>
<td>-327$^{32}$</td>
<td>-</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>308.15</td>
<td>14</td>
<td>-216$^{32}$</td>
<td>-2693$^{32}$</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>318.15</td>
<td>14</td>
<td>-169$^{32}$</td>
<td>-</td>
<td>0.07</td>
</tr>
<tr>
<td>1,4-dichlorobutane</td>
<td>298.15</td>
<td>17</td>
<td>-105$^{32}$</td>
<td>-</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>308.15</td>
<td>17</td>
<td>19$^{32}$</td>
<td>-2122$^{32}$</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>318.15</td>
<td>17</td>
<td>29$^{32}$</td>
<td>-</td>
<td>0.04</td>
</tr>
<tr>
<td>chloroform</td>
<td>298.15</td>
<td>13</td>
<td>-831$^{**}$</td>
<td>-2366$^{41}$</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>308.15</td>
<td>13</td>
<td>-829$^{**}$</td>
<td>-</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td>318.15</td>
<td>13</td>
<td>-790$^{**}$</td>
<td>-</td>
<td>0.12</td>
</tr>
<tr>
<td>1,1,1-trichloroethane</td>
<td>298.15</td>
<td>13</td>
<td>60$^{30}$</td>
<td>-</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>303.15</td>
<td>13</td>
<td>87$^{30}$</td>
<td>-</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>305.15</td>
<td></td>
<td>20$^{30}$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>308.15</td>
<td>13</td>
<td>58$^{30}$</td>
<td>-</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>313.15</td>
<td>13</td>
<td>71$^{30}$</td>
<td>-</td>
<td>0.04</td>
</tr>
<tr>
<td>1,1,2,2-tetrachloroethane</td>
<td>308.15</td>
<td>-</td>
<td>-2836$^{32}$</td>
<td>-1057</td>
<td>-2091</td>
</tr>
<tr>
<td></td>
<td>318.15</td>
<td></td>
<td>-2797$^{42}$</td>
<td>-1023</td>
<td>-2115</td>
</tr>
<tr>
<td></td>
<td>343.15</td>
<td>18</td>
<td>-966$^{31}$</td>
<td>-1007</td>
<td>-2169</td>
</tr>
<tr>
<td></td>
<td>353.15</td>
<td>18</td>
<td>-956$^{31}$</td>
<td>-1016</td>
<td>-2188</td>
</tr>
<tr>
<td></td>
<td>363.15</td>
<td>18</td>
<td>-893$^{31}$</td>
<td>-1016</td>
<td>-2207</td>
</tr>
</tbody>
</table>

** Our own unpublished data

Fig. 1. Isothermal VLE for the system 1-chlorobutane + cyclopentanone. Curves, calculated values with UNIFAC; solid symbols, experimental values [32]

Fig. 2. Molar excess Gibbs energy for the 1-chlorobutane + cyclopentanone system at 308.15 K. Curves, calculated values with DQ (-----) and UNIFAC (-----.) models; solid symbols, experimental values [32]
Fig. 3. Isothermal VLE for the 1,2-dichloroethane + cyclopentanone system. Curves, calculated values with DISQUAC; full symbols, experimental values [30]

Fig. 4. Molar excess Gibbs energy for the 1,2-dichloroethane + cyclopentanone system at 303.15 K. Curves, calculated values with DQ (-----) and UNIFAC (-----) models; solid symbols, experimental values [30]

Fig. 5. Isothermal VLE for 1,3-dichloropropane + cyclopentanone system. Curves, calculated values with DISQUAC; solid symbols, experimental values [32]

Fig. 6. Molar excess Gibbs energy for the 1,3-dichloropropane + cyclopentanone system at 318.15 K. Curves, calculated values with DQ (-----) and UNIFAC (-----) models; solid symbols, experimental values [32]

Fig. 7. Isothermal VLE for the 1,4-dichlorobutane + cyclopentanone system. Curves, calculated values with DISQUAC; solid symbols, experimental values [32]

Fig. 8. Molar excess Gibbs energy for the 1,4-dichlorobutane + cyclopentanone system at 308.15 K. Curves, calculated values with DQ (-----) and UNIFAC (-----) models; solid symbols, experimental values [32]
In figure 14 the $H^E$ prediction, for the 1,1,2,2-tetrachloroethane + cyclopentanone system at 308.15 K by both models, is presented in comparison with experimental calorimetric data.

The poorer performance of $G^E$ and $H^E$ predictions by UNIFAC can be explained by the fact that this model does not consider proximity effects. Maybe an improvement of prediction could be achieved by definition of a new structural group “c-CH$_2$CO”, in the frame of this model.

It was observed that in the cyclopentanone + chloroalkane systems the increasing of inductive effect of chloroalkane molecules could be the reason for the experimental values. However, the agreement between the calculated and experimental values for the systems under study is better than in the case of n-pentane, due to the fact that this model does not consider proximity effects.
CI atoms leads to stronger specific interactions between unlike molecules. A similar situation was also noted in the case of linear ketone mixtures [38], or of n-alkyl alkanoates + chloroalkanes [17].

Negative or high negative G\textsubscript{E} and H\textsubscript{E} values and the well defined minima of their composition dependence (around molar fraction 0.5) indicate the fact that in these mixtures specific interactions take place with complex formation between the two components, due to the H-bonds.

These negative excess Gibbs energies determined from experimental VLE data and those estimated negative excess enthalpies can be explained by the fact that acidic H atoms of the H-CCl, HC-Cl, H\textsubscript{2}C-Cl, form strong hydrogen bonds with the c-C=O group.

These properties are similar with those observed previously [24, 25], in mixtures of 3-pentanone + 1,2-dichloroethane, + 1,3-dichloropropane, + chloroform, + 1,1,2,2-tetrachloroethane, i.e. mixtures of linear ketone with the same C atoms number like cyclopentanone.

Though the UNIFAC model has a large applicability in different thermodynamic properties prediction, nevertheless DISQUAC model represents one alternative model, which can be used when other models failed or they do not predict these properties with sufficient accuracy.

**Conclusions**

It was tested the capacity of prediction and thermodynamic modelling of vapour-liquid equilibrium (VLE) and excess quantities (G\textsubscript{E} and H\textsubscript{E}) data for selected mixtures of cyclopentanone + chloroalkane.

The studied systems have a different thermodynamic behaviour: while the 1-chlorobutane, 1,1,2,2-tetrachloroethane + cyclopentanone mixtures show a real behaviour, with positive deviations from Raoult law, the 1,2-dichloroethane, 1,3-dichloropropane, chloroform and 1,1,2,2-tetrachloroethane + cyclopentanone mixtures present negative deviations, the 1,4-dichlorobutane + cyclopentanone mixture being practically ideal.

This behaviour is also evidenced by excess Gibbs molar energy, G\textsubscript{E}, calculated from isothermal VLE data. It has small positive values (10 - 30 J mol\textsuperscript{-1}) for the quasi ideal 1,4-dichloroethane + cyclopentanone system, positive larger values (50 - 80 J mol\textsuperscript{-1}) for the 1,1,1-trichloroethane + cyclopentanone system, and (200 J mol\textsuperscript{-1}) for the 1-chlorobutane + cyclopentanone system, moderate negative values (-170 - -370 J mol\textsuperscript{-1}) for the 1,2-dichloroethane or 1,3-dichloropropane + cyclopentanone systems, and much more negative (-800 - -900 J mol\textsuperscript{-1}) for the chloroform and 1,1,2,2-tetrachloroethane + cyclopentanone systems.

For the vapour-liquid equilibrium (VLE), the vapour pressures predictions of these mixtures are well represented by both DISQUAC and UNIFAC models. For G\textsubscript{E} and H\textsubscript{E}, the best results were obtained with DISQUAC model. Excepting the case of the 1-chlorobutane + cyclopentanone system where the predictions for the G\textsubscript{E} with the two models are almost identical, for the other systems, the prediction with UNIFAC model, gave unsatisfying results.

For the DISQUAC model, an improvement of quantitative description of thermodynamic behaviour of these types of systems (cycloketones + chloroalkanes) is expected to be obtained after the determination of generalized parameters, specific for the cyclocarbonil / chlorine interaction (c-C=O/Cl) which will be made once the new experimental data are collected.

The authors express their thanks to Dr. H.V. Kehiaian (ITODYS, Université Paris, VII, France), for the initiation of the research program concerning VLE and DISQUAC correlation in ketone + chloroalkane mixtures, for the fruitful comments and discussions. Also, we address thanks to Prof. Dr. D. Geanã for the permission to use the PHEQ package programs for UNIFAC modeling, for his assistance in calculations, and for constructive discussions.

**References**

5. Kojima K., Tochigi K., Prediction of vapor-liquid equilibria by the ASOG method, Kodansha Ltd. Tokyo, 1979
10. *** The Dortmund Data Bank (DDB), DDBST (Software and Separation Technology) GmbH (Oldenburg), Germany, Version 2006
22. Batiu I., Fluid Phase Equilib., 227, 2005, p. 113
41. TAMRES M., SEARLES S., J R., J. A.C.S., 81, 1959, p.2100

Manuscript received: 7.08.2007