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Vapour pressure and excess Gibbs energy of binary 1, 2-dichloroethane + cyclohexanone, chloroform + cyclopentanone and chloroform + cyclohexanone mixtures at temperatures from 298.15 to 318.15 K

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ABSTRACT

The vapour pressures of the binary systems 1,2-dichloroethane + cyclohexanone, chloroform + cyclopentanone and chloroform + cyclohexanone mixtures were measured at temperatures between 298.15 and 318.15 K. The vapour pressures vs. liquid phase composition data for three isotherms have been used to calculate the activity coefficients of the two components and the excess molar Gibbs energies, G^E , for these mixtures, using Barker's method. Redlich–Kister, Wilson, NRTL and UNIQUAC equations, taking into account the vapour phase imperfection in terms of the 2-nd virial coefficient, have represented the G^E values. No significant difference between G^E values obtained with these equations has been observed. Our data on vapour–liquid equilibria (VLE) and excess properties of the studied systems are examined in terms of the DISQUAC and modified UNIFAC (Dortmund) predictive group contributions models.

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1. Introduction

The design or optimization of separation processes requires new thermodynamic data regarding the behaviour of chemical systems. These data are very important also from a theoretical or fundamental viewpoint and the development of models which can predict this behaviour when experimental information is missing.

Due to their practical importance as solvents, foaming agents, refrigeration fluids and air conditioning systems, as well as because of their impact in the environment cleaning, in the last years, many studies have been made on thermodynamic properties of mixtures containing halogenated hydrocarbons.

Linear and cyclic ketones are molecules of high polarity; therefore they are expected to have strong specific interaction with chloroalkanes giving large deviations from ideal behaviour, most likely negative ones, depending not only on the solvent polarity, but also on the compounds nature and their molecular structure. In the open literature, there are only few data for systems of cyclic ketones with chloroalkanes and they are referring mostly to densities, excess volumes, excess enthalpies, relative permittivities, refractive indices and viscosities [1].

In previous papers, we have reported experimental VLE data for (cyclopentanone + 1,2-dichloroethane, +1,1,1-trichloroethane) [2], (1,1,2,2-tetrachloroethane + cyclopentanone and +cyclohexanone) [3] and (cyclopentanone + 1,3-dichloropropane, +1,4-dichlorobutane, +1-chlorobutane) [4]. The predictive ability of two group contribution models, DISQUAC and modified UNIFAC (Dortmund) for cyclopentanone + chloroalkane binary mixtures have been tested and presented extensively very recently [5].

Following up our research program on measuring the vapour–liquid equilibria (VLE) in mixtures of cyclic ketones with chloroalkanes, this contribution presents VLE measurements on 1,2-dichloroethane + cyclohexanone, chloroform + cyclopentanone and chloroform + cyclohexanone, for which no such experimental data are available [6,7].

The supplementary purpose of this work is the checking of the predictive capability (for the studied systems) of the above-mentioned two group contribution models.

To correlate the experimental VLE data, different G^E models were used: Redlich–Kister [8], Wilson [9], NRTL [10], UNIQUAC [11].

2. Experimental

2.1. Apparatus and procedure

The vapour pressure, P , measurements of pure compounds and binary mixtures were carried out by a static method, in which total

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Table 1Physical properties of pure compounds, vapour pressure P , second virial coefficients B_{aa} and liquid molar volumes V^0 for pure compounds at working temperatures

Compound	Properties							
	$n_D^{298.15\text{K}}$		$\rho^{298.15\text{K}}$ (kg/m ³)		Vapour pressure P (kPa)		V^0 (cm ³ mol ⁻¹)	$-B_{aa}$ (cm ³ mol ⁻¹)
	This work	Literature	This work	Literature	This work	Literature	This work	This work
Cyclopentanone	1.4347	1.4347 [16]	945.3	944 [17]	$T_1 = 298.15\text{ K}: 1.71$ $T_2 = 308.15\text{ K}: 2.80$ $T_3 = 318.15\text{ K}: 4.64$	1.53 [18] 2.65 [18] 4.40 [18]	87.12 87.86 88.83	6064 5121 4372
Cyclohexanone	1.4482	1.4480 [19]	943.0	942.5 [19]	$T_1 = 298.15\text{ K}: 0.64$ $T_2 = 308.15\text{ K}: 1.16$ $T_3 = 318.15\text{ K}: 1.92$	0.58 [20] 1.05 [20] 1.79 [20]	91.74 92.66 93.61	9810 8231 6982
1,2-Dichloroethane	1.4421	1.4421 [21]	1250.9	1245.67 [21]	$T_1 = 298.15\text{ K}: 10.81$ $T_2 = 308.15\text{ K}: 17.02$ $T_3 = 318.15\text{ K}: 25.77$	10.53 [22] 16.65 [22] 25.43 [22]	75.81 76.37 77.66	1678 1491 1337
Chloroform	1.4428	1.4430 [23]	1475.9	1479.84 [23]	$T_1 = 298.15\text{ K}: 26.45$ $T_2 = 308.15\text{ K}: 40.19$ $T_3 = 318.15\text{ K}: 58.68$	26.41 [20] 39.96 [20] 58.64 [20]	90.28 91.36 92.48	1242 1119 1016

pressure is measured as a function of the overall composition in the equilibrium cell. Use has been made of an isotenoscope based on Surovy's design [12]. The working procedure and the performance of the apparatus were described in a previous paper [13].

The equilibrium cell with a total volume of 80 cm³ is tightly connected with an Hg-filled U-tube as a null manometer surrounded by a thermostated jacket. The cell is equipped with other fitting-on thermostated mantle. The temperature of this mantle is the actually equilibrium temperature, T , while the temperature of the jacket of the null manometer is maintained (1–2 K) higher in order to prevent the partial condensation of the vapours in the upper part of the apparatus. The isotenoscope is joined via the null manometer to an external mercury manometer which make possible to measure accurately the pressure within the range of 0.1–100 kPa.

After thermostating the equilibrium cell at the required temperature, the difference of mercury levels in the null manometer is equalized with dry air and the pressure, P , is read at the external manometer. The manometric readings were performed with a Griffin and George Ltd. (London, UK) Type 4214 cathetometer to within ± 0.01 mm. The measured equilibrium pressures were reproducible to better than 20 Pa. In order to avoid the cell volume modifications the level of mercury in the null manometer was maintained always at the same position. In this way the volume of the vapour space in the cell was kept nearly constant (70 cm³).

Mixtures of known composition of about 10 cm³ were prepared by weighting, measured to within 10^{-7} kg, and thoroughly degassed in the equilibrium cell by alternate freezing, high vacuum pumping and thawing, as described by Ronc and Ratcliff [14] and Young et al. [15]. During the vapour pressure measurement the liquid in the equilibrium cell was stirred by means of a magnetic stirrer.

The equilibrium temperature, T , was measured with an accuracy of 0.1 K against IST-90 by means of a mercury thermometer calibrated at the Institute of Metrology Bucharest.

The experimental uncertainties are: ± 0.1 K, ± 0.02 kPa, and ± 0.001 for temperature, pressure and molar fraction, respectively.

2.2. Materials

All the substances used were commercial products from Aldrich of the first grade purity. The purity of substances, checked by gas chromatography, was not less than 99.8 mol %. Evidence of chemical purity is also provided by comparison of measured refractive indices, $n_D^{298.15\text{K}}$, densities, $\rho^{298.15\text{K}}$ and vapour pressures with the literature values, in Table 1.

The liquids were dried and stored over 4A molecular sieves and used without further purification.

3. Results, correlation of experimental data and discussions

The direct experimental values, x – P – T , the calculated vapour phase compositions, y , and the derived thermodynamic quantities (excess Gibbs energy, G^E), for the binary systems at temperatures 298.15, 308.15, and 318.15 K are presented in Table 2 and Figs. 1–6. In Figs. 1–3, the experimental VLE data are presented together with those calculated by correlation with a 4th order Redlich–Kister equation; a good agreement between the data is observed. These isotherms show that the studied systems exhibit negative deviations from Raoult's law.

The pure component vapour pressures agree fairly well with literature data in the range of our VLE measurements (Table 1).

The isothermal vapour–liquid equilibrium (VLE) data of the mixtures were correlated by Barker's method [24] using well-known expressions for G^E , Redlich–Kister, Wilson, NRTL and UNIQUAC.

Vapour phase imperfection was accounted for in terms of the 2-nd molar virial coefficient, estimated by the method of Tsonopoulos [25]. Liquid molar volumes were estimated by the Rackett equation [26]. The critical properties of substances were taken from

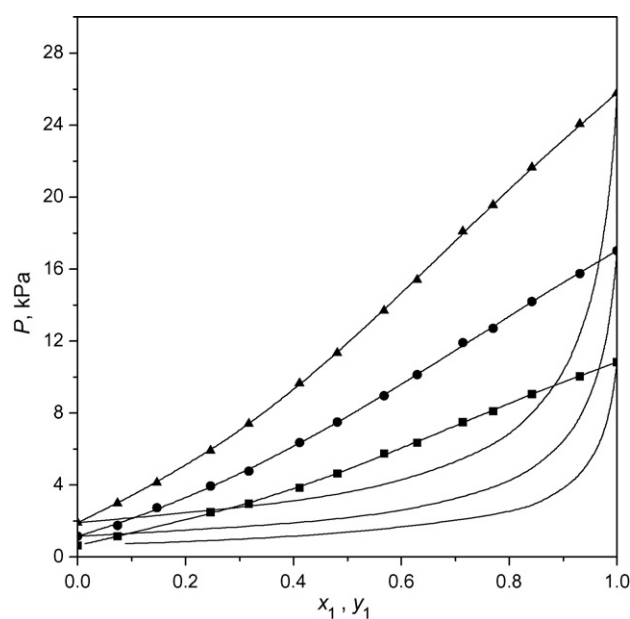


Fig. 1. Isothermal VLE for 1,2-dichloroethane (1) + cyclohexanone (2) system. The symbols represent experimental data at $T = [298.15$ (■), 308.15 (●), 318.15 (▲)] K and the curves are obtained from a 4th order Redlich–Kister equation.

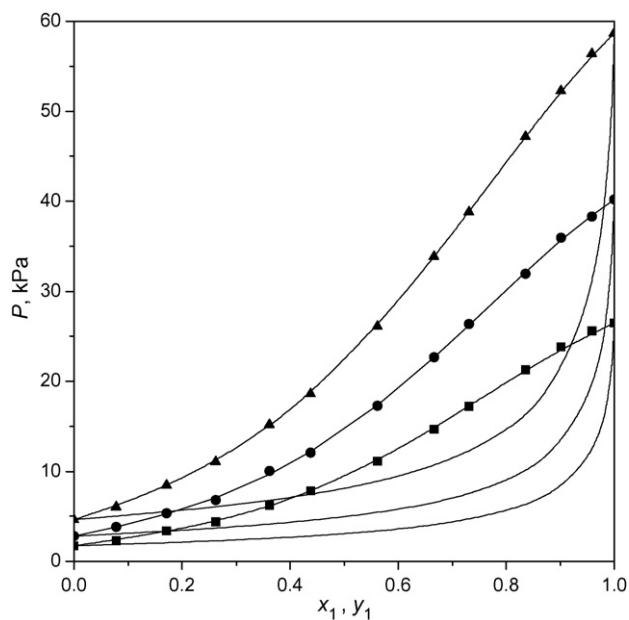


Fig. 2. Isothermal VLE for chloroform (1)+cyclopentanone (2) system. The symbols represent experimental data at $T=[298.15 (\blacksquare), 308.15 (\bullet), 318.15 (\blacktriangle)]$ K and the curves are obtained from a 4th order Redlich–Kister equation.

Ambrose's report [27]. In Table 1 are given the molar volumes, V^0 , and second virial coefficient, B_{aa} , of the pure compounds used in the data reduction.

In Table 2 the values of G^E were determined using a three parameters Redlich–Kister expression (1):

$$G^E(\text{J mol}^{-1}) = RTx_1x_2 \sum_{i=1}^3 A_i(x_1 - x_2)^{i-1} \quad (1)$$

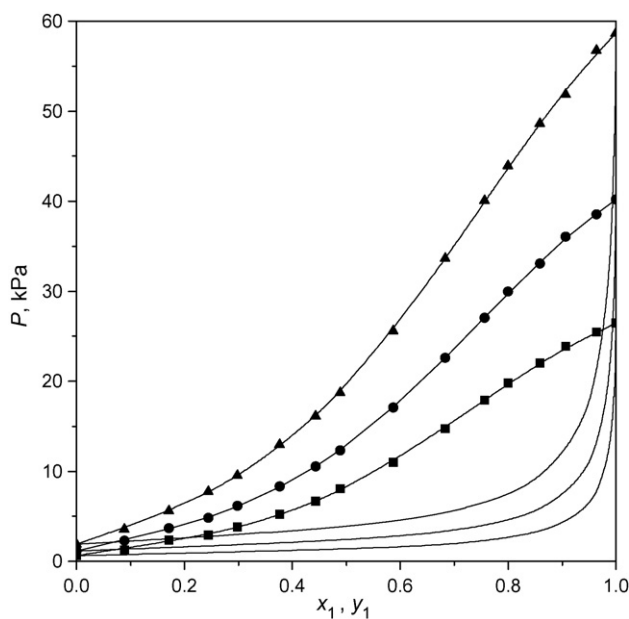


Fig. 3. Isothermal VLE for chloroform (1)+cyclohexanone (2) system. The symbols represent experimental data at $T=[298.15 (\blacksquare), 308.15 (\bullet), 318.15 (\blacktriangle)]$ K and the curves are obtained from a 4th order Redlich–Kister equation.

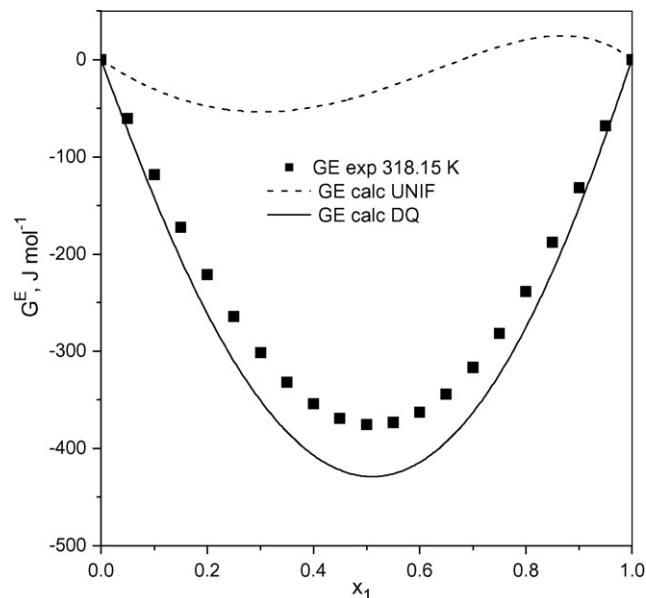


Fig. 4. Molar excess Gibbs energies for 1,2-dichloroethane (1)+cyclohexanone (2) mixture at $T=318.15$ K. Curves, calculated values with DQ (—) and UNIFAC (---) models; solid symbol, experimental values.

The parameters A_i were determined by regression through minimization of the objective function Q :

$$Q = \sum_j^N \left[\frac{P_{\text{calc},j} - P_{\text{exp},j}}{P_{\text{exp},j}} \right]^2 \quad (2)$$

For the mixtures under study, the values of standard deviation σ_p ($\sigma_p = \left[\sum_j^N (P_{\text{calc},j} - P_{\text{exp},j})^2 / (N - m) \right]^{1/2}$) where: N = number of experimental points; m = number of equation parameters), for all the equations used in correlation are between 0.05 and 0.88 kPa as can be seen in Table 3. The binary parameters A_{ij} , are $(k_{ij} - k_{ii})$ for

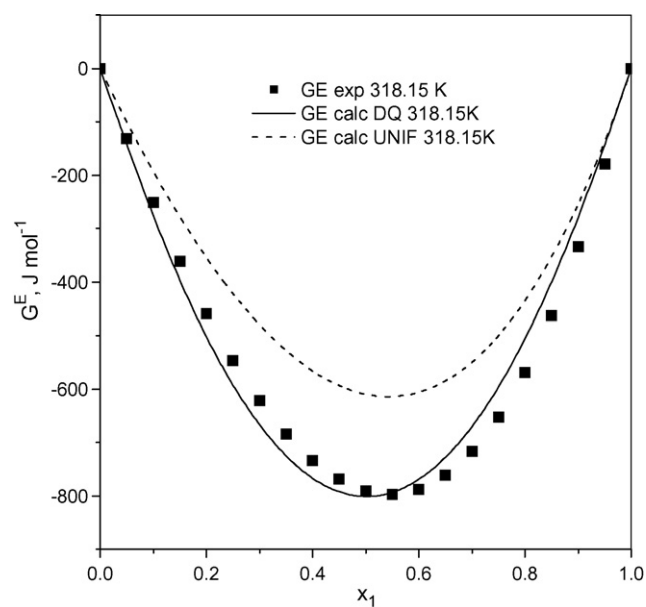


Fig. 5. Molar excess Gibbs energies for chloroform (1)+cyclopentanone (2) mixture at $T=318.15$ K. Curves, calculated values with DQ (—) and UNIFAC (---) models; solid symbol, experimental values.

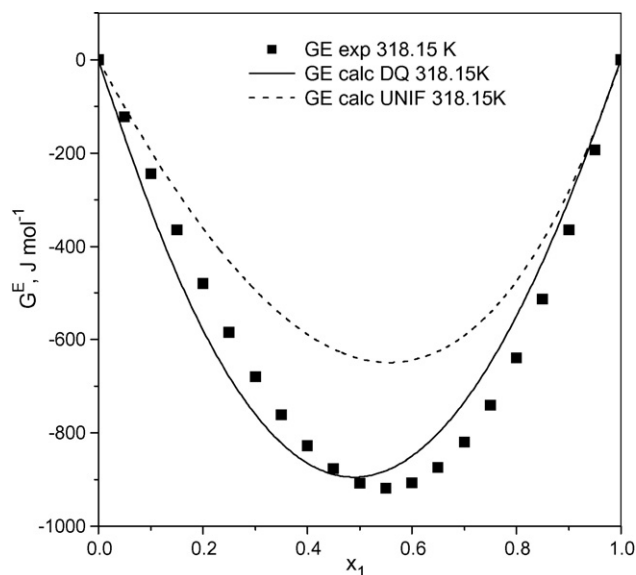


Fig. 6. Molar excess Gibbs energies for chloroform (1) + cyclohexanone (2) mixture at $T = 318.15$ K. Curves, calculated values with DQ (—) and UNIFAC (---) models; solid symbol, experimental values.

the Wilson equation ($g_{ij} - g_{ii}$) for the NRTL equation, and ($u_{ij} - u_{ii}$) for the UNIQUAC equation. In the case of chloroform + cycloketone, the correlation with the Wilson model failed probably due to some numerical problems in the fitting procedure.

The calculated excess Gibbs energy for mixtures is negative over the whole concentration range.

For 1,2-dichloroethane + cyclohexanone mixture it increases, in absolute value, with increasing temperature. This unexplainable behaviour is in contrast with that earlier observed by us for 1,2-dichloroethane + cyclopentanone [2]. A similar situation was encountered in the case of systems of cycloethers with chloroalkanes (tetrahydropyran + 1-chloropentane in comparison with the tetrahydrofuran + 1-chloropentane mixture) [28]. For mixtures of cyclopentanone and cyclohexanone with chloroform the absolute value of the excess Gibbs energy decreases with increasing temperature. In the case of chloroform + cyclohexanone, G^E is more negative than for chloroform + cyclopentanone, at the same temperature. A similar behaviour is found for systems of 1,1,2,2-tetrachlorethane with the same cyclic ketones [3].

From the variation of G^E with temperature it was possible to calculate the equimolar excess enthalpy, H^E , using the Gibbs–Helmholtz equation. Values obtained for chloroform + cyclopentanone, -1436 J mol^{-1} , and for chloroform + cyclohexanone, -1506 J mol^{-1} , at an average temperature of 308.15 K, agree reasonably with the calorimetric values at 298.15 K, which are: -2366 and -2583 J mol^{-1} , respectively [29].

For 1,2-dichloroethane + cyclohexanone the calculated value of H^E is 377 J mol^{-1} , while the calorimetric value at 303.15 K is -741 J mol^{-1} [30]. The difference of around 1000 J mol^{-1} is the same as in the case of systems with chloroform, although the sign is opposite. However, the calculated value of H^E for 1,2-dichloroethane + cyclohexanone is a bit unusual compared to the value for 1,2-dichloroethane + cyclopentanone system (-714 J mol^{-1}) [2], for which no calorimetric data are available.

The same aspect is met when H^E is calculated from the variation of G^E with temperature in the case of tetrahydrofuran and tetrahydropyran + 1-chloropentane mixtures [28] for which H^E values are -429 and 49 J mol^{-1} , respectively. In this case no calorimetric data are available, too.

Table 3

Parameters of the equations used to correlate VLE data for chloroalkane (1) + cycloketone (2) binary mixture and the standard deviation σ_P at working temperatures

T (K)	A_1 or A_{12}	A_2 or A_{21}	A_3	σ_P (kPa)
1,2-Dichloroethane (1) + cyclohexanone (2)				
Redlich–Kister equation (3rd order)				
298.15	-0.57793	-0.05774		0.05
308.15	-0.56454	-0.05243		0.08
318.15	-0.59132	0.00323		0.08
Redlich–Kister equation (4th order)				
298.15	-0.54188	-0.12721	0.10190	0.05
308.15	-0.56942	-0.04013	-0.02262	0.08
318.15	-0.57641	-0.03474	0.06850	0.06
Wilson equation				
298.15	-296.0560	426.8772		0.05
308.15	-294.3043	399.5419		0.09
318.15	-285.3492	353.6879		0.07
NRTL equation ($\alpha = 0.3$)				
298.15	-532.7307	881.6913		0.05
308.15	-542.3221	825.3849		0.10
318.15	-555.0909	810.2770		0.10
UNIQUAC equation				
298.15	-34.4351	-125.6505		0.06
308.15	-28.5708	-131.1834		0.08
318.15	-93.2159	-82.8894		0.08
Chloroform (1) + cyclopentanone (2)				
Redlich–Kister equation (3rd order)				
298.15	-1.38080	-0.21169		0.17
308.15	-1.31000	-0.21599		0.19
318.15	-1.20854	-0.18056		0.14
Redlich–Kister equation (4th order)				
298.15	-1.34122	-0.31173	0.14682	0.16
308.15	-1.29443	-0.25519	0.05745	0.19
318.15	-1.19596	-0.21447	0.05177	0.12
NRTL equation ($\alpha = 0.3$)				
298.15	-678.6816	1815.0591		0.41
308.15	-695.6593	1794.8213		0.57
318.15	-717.4989	1634.6071		0.69
UNIQUAC equation				
298.15	-427.7783	1186.9956		0.35
308.15	-435.9326	1133.0496		0.49
318.15	-435.4019	954.4778		0.58
Chloroform (1) + cyclohexanone (2)				
Redlich–Kister equation (3rd order)				
298.15	-1.68517	-0.18531		0.21
308.15	-1.56570	-0.24445		0.19
318.15	-1.45283	-0.20618		0.28
Redlich–Kister equation (4th order)				
298.15	-1.54786	-0.43436	0.30393	0.13
308.15	-1.48903	-0.38839	0.18093	0.11
318.15	-1.39424	-0.31878	0.14598	0.22
NRTL equation ($\alpha = 0.3$)				
298.15	-661.9026	2051.0034		0.51
308.15	-683.4300	2054.6581		0.75
318.15	-713.7991	2020.7192		0.88
UNIQUAC equation				
298.15	-426.5114	1029.9519		0.22
308.15	-435.7848	1032.3536		0.32
318.15	-436.7939	913.3378		0.41

Parameters A_{ij} for NRTL, Wilson and UNIQUAC equations are expressed in J mol^{-1} .

In both situations, the positive value of H^E is a consequence of the positive slope of the variation G^E/T vs. $1/T$, although G^E values are negative. Anyhow, it is well known that the calculation of excess enthalpy from vapour pressure data implies a great uncertainty [31], which was also mentioned by other authors, too (e.g. very recently by those of Ref. [32]).

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

4.1. DISQUAC model

This model, 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 and the equations for G^E and H^E calculation are the same as those previously used [33–35].

In the DISQUAC model formulation, the interaction terms in the expression for the excess thermodynamic properties, contain a dispersive term (dis) and a quasichemical term (quac) which are calculated independently and then simply added. Each contact (st) is thus characterized by two dispersive interchange parameters and two quasichemical interchange parameters. The temperature dependence of the interaction parameters has been expressed in terms of the interchange coefficients, $C_{st,i}^{dis}$ and $C_{st,i}^{quac}$, where s and t are the types of contact groups surfaces and $i = 1, 2$ (1, for Gibbs energy and 2, for enthalpy).

In the framework of the DISQUAC model, the mixtures of linear/cyclic ketones with chloroalkanes are regarded as possessing four types of surfaces: (I) type a, aliphatic (CH₃, CH₂, CH, C, which are assumed to exert the same force field), (II) type c, cyclic (c-CH₂), (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.

4.1.1. Assessment of geometrical parameters

The total relative molecular volume, r_i , the total surfaces, q_i , and the molecular surface fractions, α_{si} , for the compounds presented in mixtures are usually calculated additively on the basis of the group volumes and surfaces recommended by Bondi [36], arbitrarily taking the volume and surface of methane as unity [33]. The geometrical parameters of the groups appearing in the studied systems have been estimated previously [34,37–39] and cumulated in Ref. [40]. The geometrical parameters used in this paper are presented in Tables 4 and 5.

4.1.2. Assessment of interchange parameters

The general procedure for the estimation of the interaction parameters has been explained in details in other papers [33–35,40].

DISQUAC interchange parameters for the CO–Cl contact for entire class of binary mixtures of linear ketones with

Table 4

Total relative molecular volume r_i , total surface q_i , and molecular surface fractions α_{ai} (CH₃, CH₂, C groups) and α_{di} (Cl group) for chloroalkanes, calculated from group increments

Chloroalkanes	r_i	q_i	α_{ai}	α_{di}
1,2-Dichloroethane	2.5526	2.1724	0.4286	0.5714
Chloroform	2.5409	2.2828	0.1752	0.8248

Table 5

Total relative molecular volume r_i , total surface q_i , and molecular surface fractions α_{ci} (c-CH₂ groups) and α_{ki} (CO groups) for cycloketone, calculated from group increments

Cycloketone	r_i	q_i	α_{ci}	α_{ki}
Cyclopentanone	3.0292	2.4368	0.2264	0.7736
Cyclohexanone	3.6157	2.7156	0.2032	0.7968

1-chloroalkanes, α,ω -dichloroalkanes and several polychloroalkanes have been already published [40]. The determined $C_{kd,i}^{dis}$ and $C_{kd,i}^{quac}$ coefficients ($i = 1, 2$) follow quite simple rules: (a) the $C_{kd,1}^{dis}$ and $C_{kd,2}^{dis}$ coefficients for the 1-chloroalkane + ketone [CH₃(CH₂)_{u-1}CO(CH₂)_{v-1}CH₃] mixtures, vary regularly with the $u + v$ size of the hydrocarbon chain of a ketone; (b) for the small molecules of α,ω -dichloroalkanes, where the proximity effects are great, the $C_{kd,i}^{dis}$ coefficients vary with the length of the aliphatic chain m between the chlorine groups (for $m \leq 10$ the $C_{kd,i}^{quac}$ coefficients are independent of the nature of ketone).

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

In the DISQUAC predictions of this work, the contact kd of cyclohexanone and cyclopentanone was considered to be identical to that of 3-pentanone. Table 6 lists the dispersive, $C_{st,i}^{dis}$ and the quasichemicals, $C_{st,i}^{quac}$, interchange coefficients for all the st-contacts of the compounds referred to in this paper.

Using these coefficients, we predicted the VLE, G^E and H^E data that are presented in Table 9. According to some authors [42], the VLE prediction performances by using this model, are comparable only with those realized with modified UNIFAC model.

4.2. Modified UNIFAC (Do) model

The modified UNIFAC model (Dortmund) [43] differs from the original UNIFAC [44] by one combinatorial term and the tempera-

Table 6
Dispersive $C_{st,i}^{dis}$ and quasichemical $C_{st,i}^{quac}$ interchange coefficients

Compounds (contact)	Dispersive		Quasichemical		Ref.
	$C_{st,1}^{dis}$	$C_{st,2}^{dis}$	$C_{st,1}^{quac}$	$C_{st,2}^{quac}$	
Cycloalkanes + n-alkanes (contact ac)	0.034 ^{a,b}	0.124 ^{a,b}	0 ^{a,b}	0 ^{a,b}	[41]
Chloroalkanes + n-alkanes (contact ad)	0.093 ^a	0.180 ^a	1.67 ^a	3.20 ^a	[34]
	0.026 ^b	0.05 ^b	0.335 ^b	0.639 ^b	
Chloroalkanes + cycloalkanes (contact cd)	0.49 ^a	1.05 ^a	1.67 ^a	3.20 ^a	[34]
	0.02 ^b	0.03 ^b	0.335 ^b	0.639 ^b	
Cyclic ketones + cycloalkanes/cyclohexane (contact ck)	3.69 ^a	6.26 ^a	4.95 ^a	5.50 ^a	[37]
	3.20 ^b	5.50 ^b	5.41 ^b	6.10 ^b	
Cyclic ketones + n-alkanes (contact ak)	3.69 ^a	6.51 ^a	4.95 ^a	5.50 ^a	[37]
	3.80 ^b	6.80 ^b	5.41 ^b	6.10 ^b	
Linear ketones + chloroalkanes (contact kd)	2.04 ^a	2.18 ^a	-1.04 ^a	-1.29 ^a	[40]
	1.07 ^b	-5.62 ^b	0 ^b	0 ^b	

^a For 1,2-dichloroethane.

^b For chloroform.

Table 7
Geometrical parameters R_k and Q_k corresponding to constitutive sub-groups of studied compounds

Main group	Sub-group	R_k	Q_k
1 "CH ₂ "	CH	0.6325	0.3554
9 "CH ₂ CO"	CH ₂ CO	1.7048	1.5542
21 "CCl"	CH ₂ Cl	0.9919	1.3654
23 "CCl ₃ "	CCl ₃	2.6500	2.3778
42 "c-CH ₂ "	c-CH ₂	0.7136	0.8635

ture dependence of group interaction parameters:

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

The UNIFAC model, as a model based on group contribution methods, 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 assumed that for this model, the CO group in cyclohexanone and cyclopentanone is identical to the CO group in a linear ketone, i.e. 3-pentanone.

For the investigated mixtures the *geometrical parameters* of volume, R_k , and of area surface, Q_k , as well as the *interaction parameters* of groups, a_{nm} and a_{mn} , b_{nm} and b_{mn} , c_{nm} and c_{mn} , where k , n and m denote the different structural groups of the investigated mixtures, were taken from the 1993 version of modified UNIFAC (Do [43]) (Tables 7 and 8).

The UNIFAC calculations have been made by using the software package PHEQ (Phase Equilibria database and calculation program) elaborated by Geana [45].

4.3. Comparison with experiment

A detailed comparison of experimental data and calculated values of the molar excess Gibbs energy, G^E , from DISQUAC and mod. UNIFAC (Do) is presented in Figs. 4–6 and Table 9.

In Table 9, the comparison between experimental data and those obtained by DISQUAC and modified UNIFAC is presented, for VLE (standard deviations of pressure), equimolar excess Gibbs energy, $G_{0.5}^E$, and equimolar excess enthalpy, $H_{0.5}^E$, for the systems of cycloketone + chloroalkanes studied in this work.

The experimental vapour pressures of these mixtures are generally well predicted by both models. Although in the UNIFAC model a small number of parameters is used, which 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).

The assumption of considering cyclic ketones as a linear ketone (cyclization effect being neglected) gave good results, for the G^E prediction with the DISQUAC model. The G^E prediction by the UNI-

Table 8
Modified UNIFAC (Do) interaction parameters for the studied systems

n	m	a_{nm} (K)	b_{nm}	c_{nm} (K ⁻¹)	a_{mn} (K)	b_{mn}	c_{mn} (K ⁻¹)
1	9	433.60	0.1473	0.0	199.00	-0.8709	0.0
1	21	401.00	-0.7277	0.0	-65.685	0.07409	0.0
1	23	-653.74	4.5311	-0.008735	1302.6	-8.4270	0.01442
1	42	-680.95	4.0194	-0.006878	1020.8	-6.0746	0.01015
9	21	-99.976	0.0	0.0	55.270	0.0	0.0
9	23	810.17	-3.2209	0.002144	-48.641	-0.7950	0.003713
9	42	156.53	-0.7135	0.0	498.92	-0.04400	0.0
21	23	592.40	-4.2459	0.006905	603.29	-3.9770	0.006248
21	42	-65.685	0.07409	0.0	401.00	-0.7277	0.0
23	42	0.0	0.0	0.0	0.0	0.0	0.0

Table 9
Excess Gibbs energy, G^E , excess enthalpy, H^E at equimolar composition and standard deviations in pressure obtained for the chloroalkanes + cycloketones mixtures, at different temperatures, by DISQUAC and UNIFAC models

Mixture	T (K)	N	Experimental		DISQUAC		UNIFAC		$\sigma(P)$ (kPa)
			$G_{0.5}^E$ (J mol ⁻¹)	$H_{0.5}^E$ (J mol ⁻¹)	$G_{0.5}^E$ (J mol ⁻¹)	$H_{0.5}^E$ (J mol ⁻¹)	$G_{0.5}^E$ (J mol ⁻¹)	$H_{0.5}^E$ (J mol ⁻¹)	
1,2-Dichloroethane + cyclohexanone	298.15	14	-336	-	-435	-441	-35	-70	0.65
	303.15	-	-	-741 [30]	-	-	-	-	-
	308.15	14	-365	342 ^a	-434	-428	-35	-33	1.03
	318.15	14	-381	-	-435	-415	-36	2	1.54
Chloroform + cyclopentanone	298.15	13	-831	-2366 [29]	-936	-2751	-680	-1777	0.52
	308.15	13	-829	-1436 ^a	-875	-2773	-644	-1726	0.28
	318.15	13	-790	-	-813	-2794	-610	-1693	0.39
	298.15	16	-959	-2586 [29]	-1028	-2814	-703	-1681	0.81
Chloroform + cyclohexanone	308.15	16	-954	-1506 ^a	-968	-2832	-671	-1628	1.33
	318.15	16	-922	-	-907	-2849	-641	-1593	1.90

The standard deviations of pressure are defined as $\sigma(P) = \left[\frac{\sum (P_{\text{exp}} - P_{\text{calc}})^2 / N}{N} \right]^{1/2}$, where N is the number of experimental points.

^a Estimated value from the variation of G^E with temperature.

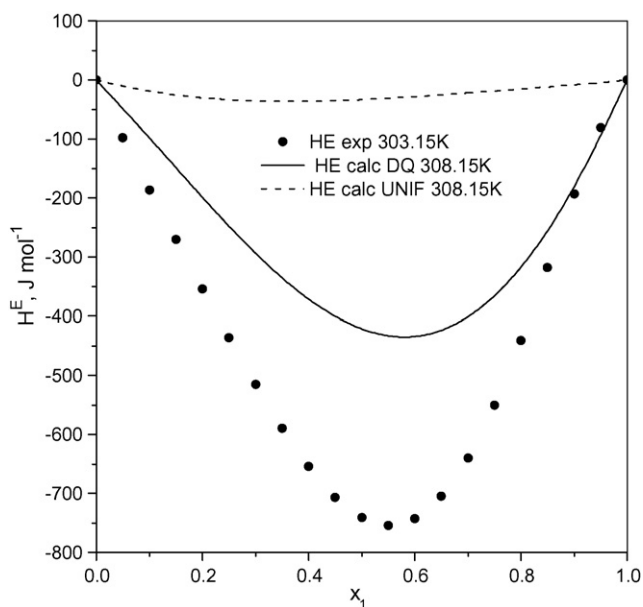


Fig. 7. Molar excess enthalpy for the 1,2-dichloroethane (1) + cyclohexanone (2) system at $T=303.15\text{ K}$. Curves, calculated values with the DQ (—) and UNIFAC (---) models; solid symbol, experimental values [30].

FAC model were unsatisfactory (Fig. 4, even different in sign, for the systems 1,2-dichloroethane + cyclohexanone).

In Fig. 7 the H^E prediction for the 1,2-dichloroethane + cyclohexanone system at 303.15 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-CH₂CO”, in the framework of this model.

It was observed that in the cycloketone + chloroalkane systems the increase of the inductive effect of Cl atoms leads to stronger specific interactions between unlike molecules [3]. A similar situation was also noted in the case of linear ketone mixtures [40], or of *n*-alkyl alkanoates + chloroalkanes [35].

Negative or high negative G^E and H^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.

5. Conclusions

Isothermal vapour–liquid equilibrium measurements (P – T – x) are reported for 1,2-dichloroethane + cyclohexanone, chloroform + cyclopentanone and chloroform + cyclohexanone.

We have tested the capacity of the prediction of vapour–liquid equilibrium (VLE) and excess quantities (G^E and H^E) data for the studied mixtures by two group contribution models, DISQUAC and mod. UNIFAC (Do).

For the vapour–liquid equilibrium, the vapour pressures predictions of these mixtures are well represented by both models. For G^E and H^E , the best results were obtained with the DISQUAC model.

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

List of symbols

$a_{nm}, a_{mn}, b_{nm}, b_{mn}, c_{nm}, c_{mn}$	group interaction parameters for modified UNIFAC (Do) model
A_1, A_2, A_3	parameters of Redlich–Kister equation
A_{12}, A_{21}	binary parameters of Wilson, NRTL and UNIQUAC equations (J mol^{-1})
$C_{st,i}^{\text{dis}}$	dispersive interchange coefficients (DISQUAC model)
$C_{st,i}^{\text{quac}}$	quasichemical interchange coefficients (DISQUAC model)
G^E	molar excess Gibbs energy (J mol^{-1})
H^E	molar excess enthalpy (J mol^{-1})
m	number of equation parameters
$n_D^{298.15\text{ K}}$	refractive index at 298.15 K
N	total number of experimental points for an isotherm
P	vapour pressure (kPa)
Q	objective function in Eq. (2)
r_i, q_i	relative molecular volumes or surfaces, respectively (DISQUAC model)
R_k, Q_k	van der Waals volumes or surfaces, respectively, for modified UNIFAC (Do) model
T	temperature (K)
x, y	liquid and vapour composition mole fraction, respectively

Subscripts

calc	calculated
exp	experimental
j	j th experimental point

Greek letters

α	nonrandomness parameter in the NRTL equation
$\alpha_{ai}, \alpha_{ci}, \alpha_{di}, \alpha_{ki}$	molecular surface fractions of compounds for DISQUAC model
$\rho^{298.15\text{ K}}$	density of liquid (kg/m^3) at 298.15 K
σ_P	average standard deviation of the total vapour pressure
ψ_{nm}	group interaction parameters for modified UNIFAC (Do) model

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