EVALUATION OF THE CARBONYL/CHLORINE INTERACTION PARAMETERS IN PENTAN-3-ONE–CHLOROALKANE MIXTURES USING THE DISQUAC GROUP CONTRIBUTION MODEL

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Received September 29, 1999
Accepted March 25, 2000

Dedicated to Dr Henry V. Kehiaian on the occasion of his 70th birthday.

Thermodynamic behaviour of the eight systems containing pentan-3-one and a chloroalkane, namely 1-chlorobutane, 1,2-dichloroethane, 1,3-dichloropropane, 1,4-dichlorobutane, trichloromethane, 1,1,1-trichloroethane, tetrachloromethane and 1,1,2,2-tetrachloroethane was interpreted in terms of the DISQUAC group contribution model. It was found that quasichemical term for the contact C=O/Cl in the pentan-3-one–α,ω-dichloroalkane and pentan-3-one–1,1,1-trichloroethane systems is not negligible. The DISQUAC dispersive interchange parameters for C=O/Cl contact in these systems were evaluated from literature data on linear ketone + 1-chloroalkane systems. It was found that the best description of experimental data for systems containing 1-chlorobutane, trichloromethane, tetrachloromethane, and 1,1,2,2-tetrachloroethane is provided using only dispersive contribution of the C=O/Cl contact. The vapour–liquid equilibrium, G^E, and H^E data were calculated using the DISQUAC model and compared with experimental data. The model provides a fairly consistent description. The relation between the DISQUAC interchange parameters for C=O/Cl contact and the chloroalkane chain length was established.

Key words: Ketones; Pentan-3-one; Chloroalkanes; DISQUAC group contribution model; Binary mixtures; Thermodynamics.

One of the most interesting applications of group contribution models is prediction of thermodynamic properties of mixtures for which no experimental data are available. In other group contribution methods, the interaction parameters – reported as constant – are in fact average values which

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depend on the number and nature of the systems considered in the averaging. The DISQUAC model interprets the properties of organic mixtures in terms of surface interactions using the theory which is an extension of the quasichemical theory by Kehiaian[1] where every molecule is characterized by geometrical and interchange parameters. Calculation of both the geometrical and interchange parameters is presented in detail elsewhere[1–3]. In the DISQUAC model, there is a physically reasonable assumption that the parameters may vary with molecular structure. A basic requirement is that the variation is regular and that similar classes of compounds follow the same rules. The final selection of parameters is achieved by plotting – usually few – adjusted values on smooth curves and estimation of other values by interpolation or extrapolation. The main advantage of the DISQUAC method is the possibility to treat systems containing an arbitrary number of types of groups of different polarities[4,5].

The aim of this work is to evaluate the interchange parameters for C=O/Cl contact in pentan-3-one–chloroalkane mixtures and to test the DISQUAC model for consistent description of phase equilibria and related excess functions of those mixtures using the set of new structure-dependent parameters. The calculations have been performed using selected literature data on vapour–liquid equilibrium (VLE), G^E, and H^E for mixtures of linear ketone–1-chloroalkane or pentan-3-one–polychloroalkane including VLE data measured recently[6,7].

THEORETICAL

The molar excess functions can be expressed as the sum of contributions, namely combinatorial ($G^{E,comb}$), dispersive ($G^{E,dis}$, $H^{E,dis}$) and quasichemical ($G^{E,quac}$, $H^{E,quac}$) ones, thus

$$G^E = G^{E,comb} + G^{E,dis} + G^{E,quac} \tag{1}$$

$$H^E = H^{E,dis} + H^{E,quac} \; . \tag{2}$$

For the system consisting of two component i = 1 or 2, the Flory–Huggins combinatorial term can be used

$$G^{E,comb} = RT\left[x_1 \ln\left(\phi_1/x_1\right) + x_2 \ln\left(\phi_2/x_2\right)\right] \tag{3}$$

with the volume fraction

$$\phi_i = r_i x_i / (r_1 x_1 + r_2 x_2) \,, \tag{4}$$

where x_i is the mole fraction and r_i is the total relative molecular volume of component *i*.

Dispersive terms can be expressed as

$$G^{\mathrm{E,dis}} = (q_1 x_1 + q_2 x_2) \xi_1 \xi_2 g_{12}^{\mathrm{dis}} \tag{5}$$

$$H^{\mathrm{E,dis}} = (q_1 x_1 + q_2 x_2) \xi_1 \xi_2 h_{12}^{\mathrm{dis}} \tag{6}$$

with

$$g_{12}^{\mathrm{dis}} = -\frac{1}{2} \sum_s \sum_t (\alpha_{s1} - \alpha_{s2})(\alpha_{t1} - \alpha_{t2}) g_{st}^{\mathrm{dis}} \tag{7}$$

$$h_{12}^{\mathrm{dis}} = -\frac{1}{2} \sum_s \sum_t (\alpha_{s1} - \alpha_{s2})(\alpha_{t1} - \alpha_{t2}) h_{st}^{\mathrm{dis}} \,, \tag{8}$$

where q_i is the total relative molecular surface of molecule *i*, $\xi_i = q_i x_i / (q_1 x_1 + q_2 x_2)$ is the surface fraction of component *i* in the mixture 1–2, α_{si} is the molecular surface fraction of the group *s* in molecule *i*, and g_{st}^{dis}, h_{st}^{dis} are the dispersive interchange parameters of the *st*-contact.

Qusichemical terms are given as follows:

$$G^{\mathrm{E,quac}} = x_1 \mu_1^{\mathrm{E,quac}} + x_2 \mu_2^{\mathrm{E,quac}} \tag{9}$$

$$H^{\mathrm{E,quac}} = \frac{1}{2} (q_1 x_1 + q_2 x_2) \sum_s \sum_t \left[X_s X_t - (\xi_1 X_{s1} X_{t1} + \xi_2 X_{s2} X_{t2}) \eta_{st} h_{st}^{\mathrm{quac}} \right] \tag{10}$$

with

$$\mu_i^{\mathrm{E,quac}} = z q_1 RT \sum_s \alpha_{si} \ln \left(X_s \alpha_{si} / X_{si} \alpha_s \right) \tag{11}$$

$$\eta_{st} = \exp\left(-g_{st}^{\text{quac}} / zRT\right) , \qquad (12)$$

where g_{st}^{quac}, h_{st}^{quac} are the quasichemical interchange parameters of the *st*-contact, and coordination number $z = 4$. The quantities X_s and X_t can be obtained by solving the system of n (total number of diferrent contact surfaces) equations

$$X_s\left(X_s + \sum_t X_t \eta_{st}\right) = \alpha_s \qquad (13)$$

and X_{si} and X_{ti} are solutions of the same set for pure components.

As a rule, the following simple temperature dependences of both the dispersive (j = dis) and quasichemical (j = quac) interchange parameters are used as follows

$$g_{st}^{\text{j}} \; / \; RT = C_{st,1}^{\text{j}} + C_{st,2}^{\text{j}}\left[\left(298.15/T\right) - 1\right] \qquad (14)$$

$$h_{st}^{\text{j}} / RT = C_{st,2}^{\text{j}}\left(298.15/T\right) . \qquad (15)$$

Parameters $C_{st,1}^{\text{j}}$ and $C_{st,2}^{\text{j}}$ are called (dispersive or quasichemical) interchange coefficients.

For the particular case studied here, the chloroalkane–ketone binary systems consist of three types of surface: type *a* (alkyl), type *d* (chlorine), and type *k* (carbonyl). Therefore, the coefficients $C_{ad,1}^{\text{dis}}, C_{ak,1}^{\text{dis}}, C_{kd,1}^{\text{dis}}, C_{ad,2}^{\text{dis}}, C_{ak,2}^{\text{dis}}, C_{kd,2}^{\text{dis}}$ and $C_{ad,1}^{\text{quac}}, C_{ak,1}^{\text{quac}}, C_{kd,1}^{\text{quac}}, C_{ad,2}^{\text{quac}}, C_{ak,2}^{\text{quac}}, C_{kd,2}^{\text{quac}}$ describing systems of this type should be determined. All *ad* and *ak* coefficients are already known from the literature; the only remaining *kd* coefficients are estimated in this work.

The basic thermodynamical data for this evaluation were taken from literature. For linear ketone–1-chloroalkane mixtures, reliable sources were used as follows: VLE and G^{E} data for propan-2-one–1-chlorobutane[8], propan-2-one–1-chloropentane[9], and butan-2-one–1-chlorobutane[10] systems; H^{E} data for propan-2-one or pentan-3-one–1-chlorobutane[11] and butan-2-one or pentan-2-one–1-chlorobutane or 1-chloropentane or 1-chlorohexane or 1-chlorooctane, and hexan-2-one–1-chlorohexane[12] systems. For mixtures of pentan-3-one–polychloroalkane, one set of isobaric

VLE data has been reported for tetrachloromethane[13] and two sets of experimental data on H^E were available, namely for 1,2-dichloroethane[14] and for tetrachloromethane[15]. The accurate data of VLE and G^E reported recently for the pentan-3-one systems with 1,2-dichloroethane or 1,3-dichloropropane[6] and with 1,4-dichlorobutane, trichloromethane, 1,1,1-trichloroethane or 1,1,2,2-tetrachloroethane[7] complete the list. For these last systems, the H^E calculated from temperature dependence of G^E were used as reported in ref.[16].

Estimation of Interaction Parameters

The ketone–chloroalkane system is characterized by three types of surfaces: type *a*, alkyl (CH_3, CH_2, CH, C), type *d*, chlorine (Cl), and type *k*, carbonyl (C=O). These three types of surfaces form three pairs of contacts, namely *ak* (alkyl/C=O), *ad* (alkyl/Cl), and *kd* (C=O/Cl). The interchange parameters for alkyl/C=O contact[17] as well as for alkyl/Cl contact[18] have been already determined.

The parameters for the contact COO/Cl in mixtures of 1-chloroalkane or α,ω-dichloroalkane with n-alkyl n-alkanoate have been obtained earlier[19] and for 1,1,2,2-tetrachloroethane with n-alkyl n-alkanoate have also been reported[5]. In this work, the parameters for contact of similar polarity, C=O/Cl, in pentan-3-one–chloroalkane mixtures have been determined using an analogous procedure taking into account the expected structural effects.

The geometric parameters, namely the relative molecular volume r_i, the relative molecular surface q_i and the molecular surface fractions α_{si} for all molecules in pentan-3-one–chloroalkane mixtures under study were calculated from the group increments using the method developed in ref.[20]. These parameters necessary for calculation of the combinatorial term are summarized in Table I.

The dispersive and quasichemical interchange parameters for the *ak*-contact in n-alkane–pentan-3-one mixtures were recommended by Kehiaian *et al.*[17] as $C_{ak,1}^{\text{dis}} = 3.60$, $C_{ak,2}^{\text{dis}} = 7.27$, $C_{ak,1}^{\text{quac}} = 4.62$, $C_{ak,2}^{\text{quac}} = 4.46$. The dispersive and quasichemical interchange parameters for the *ad*-contact have been evaluated for mixtures of n-alkane–chloroalkane with different chlorine atom(s) location[18]. These parameters are listed in Table II for the investigated chloroalkanes.

For linear ketone–1-chloroalkane mixtures, preliminary calculations were performed assuming that *kd*-contact is either entirely dispersive or entirely quasichemical. The parameters were adjusted to represent the experimental equimolar values of G^E and H^E. It appeared that the concentration depend-

TABLE I
Relative molecular volume r_i, relative moleculare surface q_i and molecular surface fractions α_{ai}, α_{ki}, α_{di} calculated from the group increments[17,18] by method[20]

Compound, *i*	r_i	q_i	α_{ai}	$\alpha_{di}(\alpha_{ki})$
Pentan–3-one	3.4755	2.9448	0.8126	(0.1874)
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
Trichloromethane	2.5409	2.2828	0.1752	0.8248
1,1,1-Trichloroethane	3.1378	2.6138	0.2797	0.7203
Tetrachloromethane	3.0543	2.5104	0.0000	1.0000
1,1,2,2-Tetrachloroethane	3.6519	2.9035	0.1354	0.8646

TABLE II
Dispersive and quasichemical interchange coefficients for mixtures of n-alkane (type *a*) with different types of Cl atoms (type *d*) in chloroalkane

Chloroalkane	$C_{ad,1}^{\mathrm{dis}}$	$C_{ad,2}^{\mathrm{dis}}$	$C_{ad,1}^{\mathrm{quac}}$	$C_{ad,2}^{\mathrm{quac}}$
1-Chlorobutane	0.093	0.180	2.34	3.75
1,2-Dichloroethane	0.093	0.180	1.67	3.20
1,3-Dichloropropane	0.093	0.180	2.08	3.46
1,4-Dichlorobutane	0.093	0.180	2.28	3.68
Trichloromethane	0.026	0.050	0.335	0.639
1,1,1-Trichloroethane	0.093	0.180	0.203	0.413
Tetrachloromethane	0.093	0.180	0.000	0.000
1,1,2,2-Tetrachloroethane	0.093	0.180	0.442	0.843

ences of H^E are best reproduced when the *kd*-contact is described using the dispersive coefficients only. The data used for this purpose were the equimolar G^E and H^E for the propan-2-one or butan-2-one–1-chlorobutane mixtures and the data for equimolar H^E for butan-2-one–1-chloropentane or 1-chlorohexane or 1-chlorooctane, pentan-2-one–1-chlorobutane or 1-chloropentane or 1-chlorohexane or 1-chlorooctane, and hexan-2-one–1-chlorohexane mixtures. The values of dispersive parameters for the *kd*-contact and their dependence on the 1-chloroalkane chain length are given in Table III and Fig. 1. The dispersive parameters have been determined systematically starting with systems for which the experimental data were available. These parameters were used for estimation of the dispersive parameters for the remaining systems taking also into account the observed structure effects. The extrapolated dispersive interchange coefficients for the *kd*-contact in the mixture of pentan-3-one–long-chain 1-chloroalkane were estimated as $C^{\text{dis}}_{kd,1}$ = 2.04 and $C^{\text{dis}}_{kd,2}$ = 2.18. The best description of the experimental data for trichloromethane, tetrachloromethane, 1-chlorobutane or 1,1,2,2-tetrachloroethane–pentan-3-one mixtures was found using only the dispersive contribution of the *kd*-contact. Our results are in

TABLE III
Dispersive interchange coefficients for the C=O group (type *k*) in straight-chain ketone $CH_3(CH_2)_{u-1}CO(CH_2)_{v-1}CH_3$ with Cl atom (type *d*) in 1-chloroalkane $CH_3(CH_2)_{m-2}CH_2Cl$[a]

u	*v*	*m*	$C^{\text{dis}}_{ad,1}$	$C^{\text{dis}}_{ad,2}$	*u*	*v*	*m*	$C^{\text{dis}}_{ad,1}$	$C^{\text{dis}}_{ad,2}$
1	1	4	2.55	2.97	1	3	6	2.25[b]	2.39
		5	2.74	3.16[b]			≥7	2.38[b]	2.52
		6	2.84[b]	3.26[b]	1	4	4	2.08[b]	2.22[b]
		≥7	2.92[b]	3.34[b]			5	2.22[b]	2.36[b]
1	2	4	2.06	2.22			6	2.25[b]	2.51
		5	2.21[b]	2.37			≥7	2.38[b]	1.51[a]
		6	2.27[b]	2.43	2	2	4	1.54[b]	1.68
		≥7	2.57[b]	2.73			5	1.73[b]	1.87[b]
1	3	4	2.09[b]	2.23			6	1.79[b]	1.93[b]
		5	2.22[b]	2.36			≥7	2.04[b]	2.18[b]

[a] The quasichemical interchange coefficients $C^{\text{quac}}_{kd,1} = C^{\text{quac}}_{kd,2} = 0$. [b] Estimated value.

agreement with those reported[5] for the contact COO/Cl in mixtures of 1,1,2,2-tetrachloroethane with n-alkyl n-alkanoates.

In agreement with results[19] for the contact COO/Cl in n-alkyl n-alkanoate–α,ω-dichloroalkane mixtures, it was found that the contact C=O/Cl in the pentan-3-one–α,ω-dichloroalkane system contributes a non-negligible quasichemical term and a similar proximity effect was also observed. For the pentan-3-one–1,1,1-trichloroethane system, it was also found that the best description of VLE and G^E experimental data is obtained when a quasichemical contribution for the C=O/Cl contact is considered. In both these cases, we have assumed that the dispersive contribution is the same as that for long-chain 1-chloroalkanes in mixtures with pentan-3-one. Both the dispersive and quasichemical parameters for the *kd*-contact in pentan-3-one–chloroalkane mixtures under study are given in Table IV.

RESULTS AND DISCUSSION

A comparison of the calculated data (using the coefficients reported in Table IV) with experimental data for VLE and the equimolar G^E and H^E for pentan-3-one–chloroalkane mixtures are presented in Tables V and VI.

Negative or largely negative values of G^E and H^E with a well defined minimum around equimolar composition clearly indicate formation of a complex between the two components in mixture. We have tested the flexibility of the model by means of a comparison of calculated and experimental values of VLE, molar excess Gibbs energies and molar excess enthalpies. The VLE data are reproduced very well for the pentan-3-one–

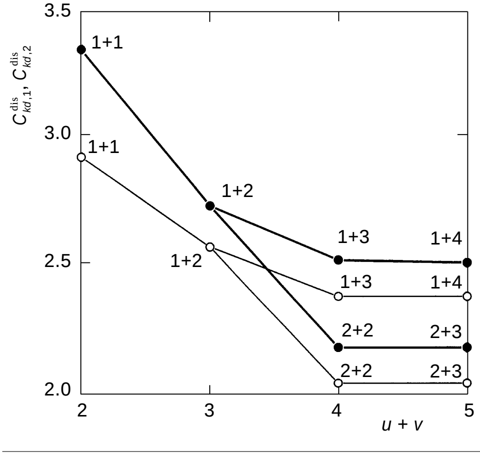

FIG. 1

Change of the $C^{\text{dis}}_{kd,1}$ (❍) and $C^{\text{dis}}_{kd,2}$ (●) interchange coefficients for 1-chlorooctane–linear ketone $CH_3(CH_2)_{u-1}CO(CH_2)_{v-1}CH_3$ with $u + v$ (individual $u + v$ are indicated inside the diagram) α,ω-dichloroalkane mixtures (up to 0.9% in pressure and molar fraction 0.0100 in vapour composition), which exhibit negative deviations from ideal behaviour. An excellent agreement was obtained for the ideal mixture with 1,1,1-trichloroethane (up to 0.3% in pressure and molar fraction 0.0060 in vapour phase). For mixtures with large negative deviations from ideality such as those containing trichloromethane or 1,1,2,2-tetrachloroethane, VLE is also well described by the DISQUAC with deviations up to 1.7% for pressure and up to molar fraction 0.0130 in vapour phase. As ex-

TABLE IV
Dispersive and quasichemical interchange coefficients for the C=O group (type *k*) in pentan-3-one with Cl atom (type *d*) in chloroalkane

Chloroalkane	$C_{kd,1}^{\mathrm{dis}}$	$C_{kd,2}^{\mathrm{dis}}$	$C_{kd,1}^{\mathrm{quac}}$	$C_{kd,2}^{\mathrm{quac}}$
1-Chlorobutane	1.54	1.68	0	0
1,2-Dichloroethane	2.04	2.18	–0.692	–1.662
1,3-Dichloropropane	2.04	2.18	–0.687	–0.969
1,4-Dichlorobutane	2.04	2.18	–0.502	–0.455
Trichloromethane	1.07	–5.62	0	0
1,1,1-Trichloroethane	2.04	2.18	2.20	2.40
Tetrachloromethane	7.40	7.36	0	0
1,1,2,2-Tetrachloroethane	1.21	–1.65	0	0

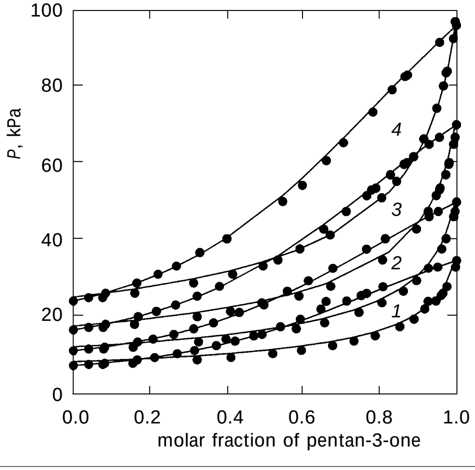

FIG. 2
P–*x*–*y* diagram for the pentan-3-one–1,1,2,2-tetrachloroethane system at 343.15 K (*1*), 353.15 K (*2*), 363.15 K (*3*) and 373.15 K (*4*). The lines denote calculated values using the DISQUAC; the points denote experimental values[7]

amples, four VLE isotherms are plotted in Fig. 2 for the mixture containing 1,1,2,2-tetrachloroethane. The curve shapes and values for G^E are well fitted for chloroalkanes under study, which is shown in Fig. 3. From Table VI it is clear that the temperature dependence of G^E is also well described by the DISQUAC model. The experimental values of H^E are in a good agreement

TABLE V
Deviations of experimental pressures (P) and vapour phase compositions (y) from values calculated using the coefficients (see Table IV) for pentan-3-one–chloroalkane mixtures

Chloroalkane	T, K	AD_P, kPa	SD_P, kPa	SRD_P, %	AD_y	SD_y
1,2-Dichloroethane	323.15	0.13	0.16	0.6	0.0053	0.0063
	333.15	0.18	0.26	0.6	0.0052	0.0057
	343.15	0.34	0.39	0.7	0.0034	0.0047
	353.15	0.27	0.32	0.4	0.0032	0.0037
1,3-Dichloropropane	343.15	0.06	0.08	0.3	0.0027	0.0040
	353.15	0.12	0.15	0.4	0.0055	0.0065
	363.15	0.12	0.17	0.3	0.0079	0.0089
	373.15	0.29	0.50	0.9	0.0100	0.0110
1,4-Dichlorobutane	343.15	0.09	0.09	0.7	0.0064	0.0088
	353.15	0.12	0.13	0.8	0.0061	0.0092
	363.15	0.14	0.17	0.7	0.0053	0.0079
	373.15	0.24	0.27	0.8	0.0071	0.0098
Trichloromethane	313.15	0.22	0.25	1.7	0.0100	0.0130
	323.15	0.32	0.37	1.5	0.0065	0.0081
	333.15	0.38	0.57	1.2	0.0071	0.0080
	343.15	0.60	0.74	1.1	0.0100	0.0110
1,1,1-Trichloroethane	323.15	0.05	0.06	0.3	0.0041	0.0049
	333.15	0.08	0.10	0.2	0.0034	0.0044
	343.15	0.11	0.14	0.2	0.0041	0.0049
	353.15	0.21	0.25	0.3	0.0044	0.0056
1,1,2,2-Tetrachloroethane	343.15	0.17	0.25	1.1	0.0018	0.0022
	353.15	0.21	0.28	1.0	0.0027	0.0036
	363.15	0.47	0.63	1.4	0.0049	0.0070
	373.15	0.64	0.86	1.5	0.0064	0.0089

with those calculated by the model as is shown in Fig. 4. In the case of tetrachloromethane, the S-shape is fairly represented even though the calculated values are lower than experimental ones within the molar fraction of pentan-3-one range of 0–0.5. Generally, it can be concluded that the experimental data are well described by the DISQUAC model.

The relation between the interchange parameters for the C=O/Cl contact and the chain length of the chloroalkane or ketone was evaluated from 1-chloroalkane mixtures. As shown in Fig. 1 and Table III, the dispersive parameters for the C=O/Cl (polar/polar) contact decrease with increasing chain length of ketone. This was also found[19] for dispersive parameters for the COO/Cl contact in mixtures of n-alkyl n-alkanoate with 1-chloro-

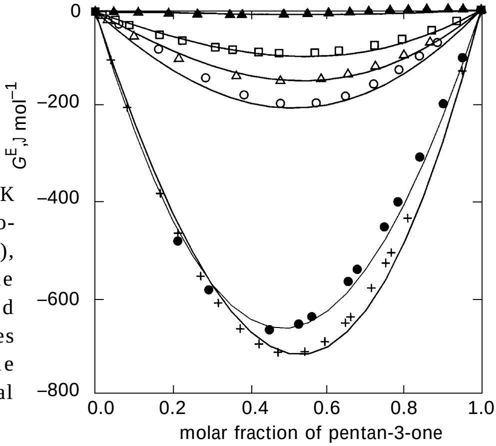

FIG. 3
Molar excess Gibbs energy G^E at 343.15 K for the systems pentan-3-one–1,2-dichloroethane (❍), –1,3-dichloropropane (Δ), –1,4-dichlorobutane (❒), –trichloromethane (●), –1,1,1-trichloroethane (▲), and –1,1,2,2-tetrachloroethane (+). The lines denote calculated values using the DISQUAC; the points denote experimental values[6,7]

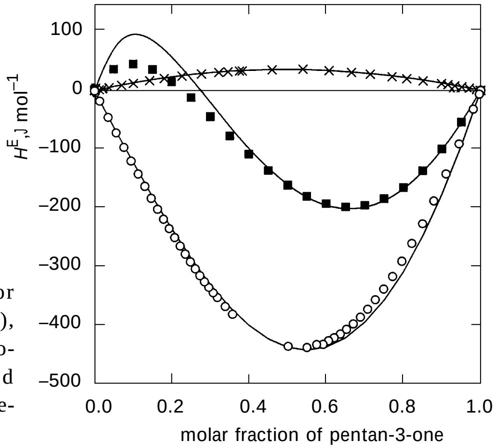

FIG. 4
Molar excess enthalpy H^E at 298.15 K for pentan-3-one–1,2-dichloroethane[14] (❍), –tetrachloromethane[15] (■), and –1-chlorobutane[11] (×). The lines denote calculated values using the DISQUAC; the points denote experimental values from literature

TABLE VI

Molar excess Gibbs energies G^E and molar excess enthalpies H^E for pentan-3-one–chloroalkane mixtures at equimolar composition; comparison of experimental data with values calculated using the coefficients from Table IV

Chloroalkane	$T^{ref.}$, K	G^E(x = 0.5), J mol^{-1}		H^E(x = 0.5), J mol^{-1}	
		calc.	exp.	calc.	exp.
1-Chlorobutane	298.15[12]			36	36
1,2-Dichloroethane	298.15[15]			–434	–433
	323.15[17]	–217	–213		
	333.15[17]	–210	–214		
	343.15[17]	–203	–194		
	353.15[17]	–197	–204		
1,3-Dichloropropane	343.15[17]	–145	–147		
	353.15[17]	–140	–138		
	363.15[17]	–135	–131		
	373.15[17]	–130	–133		
	358[3]			–317	–318
1,4-Dichlorobutane	343.15[2]	–95	–89		
	353.15[2]	–92	–86		
	363.15[2]	–89	–82		
	373.15[2]	–87	–78		
	358[3]			–183	–216
Trichloromethaane	313.15[2]	–848	–800		
	323.15[2]	–784	–736		
	333.15[2]	–720	–698		
	343.15[2]	–656	–658		
	358[3]			–2 881	–2 848
1,1,1-Trichloroethane	323.15[2]	–18	–20		
	333.15[2]	–13	–11		
	343.15[2]	–7	–8		
	353.15[2]	–2	–3		
	338[3]			–200	–200
Tetrachloromethane	298.15[16]			–160	–160
	353.15[14]	604	604		
1,1,2,2-Tetrachloroethane	343.15[2]	–713	–712		
	353.15[2]	–678	–672		
	363.15[2]	–644	–644		
	373.15[2]	–610	–608		
	358[3]			–1 893	–1 892

alkane. It was also determined that the dispersive parameters for the C=O/Cl contact in mixtures of pentan-3-one are slightly smaller than those for pentan-2-one. The increase in the ketone chain length produces a steric effect that is already known from linear ketone–n-alkane studies[6]. In the case of the pentan-3-one–trichloromethane or 1,1,2,2-tetrachloroethane systems, the lower or even negative values of dispersive parameters may be caused by the H-bond between the acid H atoms in chloroalkane and the C=O group in ketone.

It should be pointed out that only the evaluation of new DISQUAC parameters for mixtures of linear ketones with 1-chloroalkanes and of pentan-3-one with some polychloroalkanes has been performed in this work. In future, the study has to be extended to systems containing linear ketones other than pentan-3-one in order to obtain a unique set of DISQUAC parameters capable of providing reliable and more general predictions.

SYMBOLS

a	alkyl-type surface
ak, ad, kd	contact between types of surfaces a–k, a–d, and k–d, respectively
AD_i	average deviation for property i
$C_{st,1}^{\mathrm{dis}}$, $C_{st,2}^{\mathrm{dis}}$	dispersive interchange coefficients for the st-contact
$C_{st,1}^{\mathrm{quac}}$, $C_{st,2}^{\mathrm{quac}}$	quasichemical interchange coefficients for the st-contact
d	chlorine-type surface
G^{E}	molar excess Gibbs energy, J mol^{-1}
H^{E}	molar excess enthalpy, J mol^{-1}
k	carbonyl-type surface
P	pressure, kPa
q_i	relative molecular surface of molecule i
r_i	relative molecular volume of molecule i
s	(general) s-type surface
SD_i	standard deviation for property i
SRD_P	standard relative deviation for pressure, %
t	(general) t-type surface
T	absolute temperature, K
m, u, v	number of methylene groups in ketone
x, y	liquid and vapour composition, molar fraction
α, ω	terminal positions of chlorine group in the dichloroalkane
α_{si}	molecular surface fraction of the group s in molecule i

The authors would like to acknowledge partial support of the Grant Agency of the Czech Republic (grant No. 104/99/0136). M. T. thanks Dr H. V. Kehiaian (ITODYS, Université de Paris VII – CNRS) for initiating this study and for helpful discussion. Fruitful discussion with Dr A. Barhala (Institute of Physical Chemistry of Romanian Academy, Bucharest) is also acknowledged.

REFERENCES

1. Kehiaian H. V.: *Fluid Phase Equilib.* **1983**, *13*, 243.
2. Kehiaian H. V., Grolier J.-P. E., Benson G. C.: *J. Chim. Phys.* **1978**, *75*, 1031.
3. Kehiaian H. V.: *Pure Appl. Chem.* **1985**, *57*, 15.
4. Tine M. R., Kehiaian H. V.: *Fluid Phase Equilib.* **1987**, *32*, 211.
5. Fárková J., Wichterle I., Kehiaian H. V.: *Fluid Phase Equilib.* **1995**, *112*, 23.
6. Teodorescu M., Barhala A., Landauer O.: *ELDATA: Int. Electron. J. Phys.-Chem. Data* **1997**, *3*, 101.
7. Teodorescu M., Aim K., Wichterle I.: *Fluid Phase Equilib.* **1998**, *147*, 215.
8. Khurma J. R., Muthu O., Munjal S., Smith B. D.: *J. Chem. Eng. Data* **1983**, *28*, 86.
9. Dragoescu D., Barhala A., Vilcu R.: *Fluid Phase Equilib.* **1998**, *146*, 247.
10. Wisniak J.: *Thermochim. Acta* **1995**, *257*, 51.
11. Kechavarz R.: *Ph.D. Thesis*. University of Provence, Aix-Marseille I 1985.
12. Pico J. M., Menaut C. P., Fernandez J., Legido J. L., Paz Andrade M. I.: *J. Solution Chem.* **1991**, *20*, 115.
13. Govindan B., Govindaswamy S., Andiappan A.: *Indian Chem. Eng.* **1988**, *30*, 67.
14. Kechavarz R., Dubes J. P., Tachoire H.: *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1990**, 120.
15. Kiyohara O., Benson G. C., Grolier J.-P. E.: *Int. DATA Ser., Sel. Data Mixtures. Ser. A* **1991**, 64.
16. Teodorescu M.: *Ph.D. Thesis*. Polytechnic University of Bucharest, Bucharest 1998.
17. Kehiaian H. V., Porcedda S., Marongiu S., Lepori L., Matteoli E.: *Fluid Phase Equilib.* **1991**, *63*, 231.
18. Kehiaian H. V., Marongiu B.: *Fluid Phase Equilib.* **1988**, *40*, 23.
19. Avedis G., Grolier J.-P. E., Fernandez J., Kehiaian H. V.: *J. Solution Chem.* **1994**, *23*, 135.
20. Bondi A.: *Physical Properties of Molecular Crystals, Liquids and Glasses*. Wiley, New York 1968.