

DISQUAC CHARACTERIZATION OF THE CARBONYL–CHLORINE INTERACTIONS IN BINARY MIXTURES OF LINEAR KETONE WITH CHLOROALKANE

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Both the published and our new data on vapour–liquid equilibrium, excess Gibbs energy G^E and excess enthalpy H^E for the linear ketone–chloroalkane binary mixtures are interpreted in terms of the DISQUAC group contribution model. The components are characterized by three types of contact surfaces: chlorine (Cl), carbonyl (C=O) and alkyl (CH₃, CH₂, CH, C). The Cl/alkyl and C=O/alkyl contact parameters are known from the literature. The parameters for C=O/Cl are re-evaluated here using extensive data on linear ketone–chloroalkane mixtures. It was found that the best description of ketone mixtures with 1-chloroalkane, trichloromethane, 1,1,1-trichloroethane, tetrachloromethane and 1,1,2,2-tetrachloroethane is obtained using a dispersive contribution of the C=O/Cl contact only. On the other hand the quasichemical term cannot be neglected for the ketone– α,ω -dichloroalkane systems. The newly evaluated interaction parameters for DISQUAC model enable good prediction of phase equilibrium and thermodynamic properties G^E and H^E as well as the temperature dependence of G^E .

Keywords: DISQUAC group contribution model; Thermodynamics; Chloroalkanes; Linear ketones; Binary mixtures; Phase equilibria.

The prediction of thermodynamic properties of mixtures for which no experimental data are available is the main goal of any group contribution model. The DISQUAC, an extended quasichemical pseudo-lattice group contribution model^{1,2}, has been successfully applied for the evaluation of thermodynamic properties of mixtures of different classes of organic substances^{3–9}. In contrast to other group contribution methods where resulting interaction parameters are the average values dependent on the number and nature of the systems involved in the averaging, the DISQUAC model is based on a physically reasonable assumption that the parameters may

also vary with molecular structure. The basic assumption is that the variation is "regular" in the sense that similar classes of compounds follow the same rules. The final selection of DISQUAC parameters is achieved by plotting the known adjusted values allowing thus the estimation of values to be evaluated by interpolation or extrapolation. Therefore, the proximity effects due to specific inter- or intramolecular interactions are reflected in the variation of parameters with molecular structure. The main advantage of the DISQUAC model consists in the possibility to treat systems containing arbitrary number of group types of different polarity. The DISQUAC is an alternative model which may be used when other group contribution models fail or do not predict thermodynamic properties with sufficient accuracy.

The paper is aimed at the evaluation of interchange parameters for the C=O/Cl contact in linear ketone–chloroalkane mixtures, further we test quality of DISQUAC model for the prediction of phase equilibrium and excess functions using a set of new structure-dependent parameters. For this purpose, both the new and literature experimental data on vapour–liquid equilibrium (VLE), molar excess Gibbs energy G^E and molar excess enthalpy H^E were analyzed by the DISQUAC approach.

The DISQUAC model was applied to three types of chlorine groups in chloroalkanes: (i) 1-chloroalkane, (ii) α,ω -dichloroalkane and (iii) polychloroalkane. Subsequently, the variation of these parameters with the chloroalkane and ketone chain length as well as with the number of chlorine atoms is taken into account.

THE MODEL

The DISQUAC model explains the properties of organic mixtures in terms of surface interactions using the approach that consists in the extension of the quasichemical theory where each molecule is characterized by geometrical and interaction parameters. The equations used for the calculation of G^E and H^E are the same as described in the first part¹⁰ and need not be repeated here.

The temperature dependence of interaction parameters can be expressed in terms of the dispersive and quasichemical interchange coefficients $C_{st,n}^{\text{dis}}$ and $C_{st,n}^{\text{quac}}$, respectively,

$$g_{st}^{\text{dis|quac}} / RT = C_{st,1}^{\text{dis|quac}} + C_{st,2}^{\text{dis|quac}} [(298.15 / T) - 1] \quad (1)$$

$$h_{st}^{\text{dis|quac}} / RT = C_{st,2}^{\text{dis|quac}} (298.15 / T), \quad (2)$$

where s and t denote the type of group surface (namely: a for alkyl, d for chlorine and k for carbonyl).

The ketone–chloroalkane mixtures are described using the interchange 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 $C_{ad,1}^{\text{quac}}$, $C_{ak,1}^{\text{quac}}$, $C_{kd,1}^{\text{quac}}$, $C_{ad,2}^{\text{quac}}$, $C_{ak,2}^{\text{quac}}$, $C_{kd,2}^{\text{quac}}$. The ad and ak coefficients are already known from the literature; the only remaining kd coefficients are re-evaluated in this work.

The calculations were performed using selected data on VLE, G^E and H^E for ketone–chloroalkane mixtures including the previously evaluated C=O/Cl interchange parameters for the propan-2-one–chloroalkane¹¹ and pentan-3-one–chloroalkane¹⁰ mixtures. Besides the literature data on ketone–chloroalkane systems, we used our G^E data resulting from VLE measurements on the following binary mixtures of propan-2-one with 1-chloropentane, 1,3-dichloropropane, 1,4-dichlorobutane, 1,1,2,2-tetrachloroethane and 1,1,1-trichloroethane^{12,13}; butan-2-one with 1-chloropentane, 1,3-dichloropropane, 1,4-dichlorobutane¹⁴, 1,1,1-trichloroethane and 1,1,2,2-tetrachloroethane¹⁵; pentan-3-one with 1,2-dichloroethane, 1,3-dichloropropane¹⁶, 1,4-dichlorobutane, trichloromethane, 1,1,1-trichloroethane and 1,1,2,2-tetrachloroethane¹⁷. The H^E data are rather scarce; only the mixtures of propan-2-one–chloroalkane^{18–25}, butan-2-one–chloroalkane^{26–30} and pentan-3-one–chloroalkane^{22,30,31} were found.

Estimation of DISQUAC Interchange Parameters

The necessary geometric parameters for the evaluation of the relative molecular volume r_i , the relative molecular surface q_i and the molecular surface fractions $\alpha_{s,i}$ of all molecular species have been calculated on the basis of the group volumes and surfaces³² arbitrarily setting the molecular volume and surface of methane to unity¹. The geometric parameters of groups existing in the studied mixtures have been estimated earlier^{3,4} and summarized elsewhere^{10,11}.

The ketone–chloroalkane mixtures possess three types of surfaces: (i) type a, aliphatic (CH₃, CH₂, CH, C; all these groups are assumed to exert the same force field), (ii) type d, chlorine (Cl) and (iii) type k, carbonyl (C=O). The three types of surfaces a, d and k form three pairs of contacts: ad, ak and kd. The dispersive and quasichemical interchange parameters for ad and ak contacts have been critically evaluated from thermodynamic proper-

ties of chloroalkane-*n*-alkane and ketone-*n*-alkane mixtures and published by Kehiaian *et al.*^{4,6}

Since the ad- and ak-contact parameters are known, only the kd-contact parameters have to be determined. The C=O/Cl contact in linear ketone-chloroalkane mixtures is of similar polarity as COO/Cl contact in *n*-alkyl alkanoate + chloroalkane mixtures. Therefore, taking into account the expected structural effects, the DISQUAC parameters for the kd contact have been determined using the same procedure as that of Avedis *et al.*⁸ For this purpose, the equimolar experimental values for G^E and H^E have been used from both the literature and our recent measurements.

For the *linear ketone-1-chloroalkane* mixtures, preliminary calculations were performed under the assumption that the kd contact is either entirely dispersive or entirely quasichemical. The parameters were adjusted to experimental equimolar values of both G^E and H^E . In the case of H^E data, it was shown that their dependence on composition is best modelled when the kd contact is described using only the dispersive coefficients. The data used for the adjustment of parameters were: G^E data (at $x = 0.5$) for the propan-2-one with 1-chlorobutane¹⁸ and 1-chloropentane¹² systems, for the butan-2-one with 1-chlorobutane³⁶ and 1-chloropentane¹⁴ systems; H^E data (at $x = 0.5$) for the 1-chlorobutane with propan-2-one¹⁸, butan-2-one²⁶, pentan-2-one³¹ and pentan-3-one³¹ systems, for the butan-2-one with 1-chloropentane, 1-chlorohexane and 1-chlorooctane systems²⁶, for the pentan-2-one with 1-chloropentane, 1-chlorohexane and 1-chlorooctane systems²⁶, and for the hexan-2-one with 1-chlorohexane system²⁶. The dispersive parameters have been determined systematically starting with systems for which the experimental data were available. These parameters were used for the estimation of dispersive parameters of remaining systems considering the observed structure effects. The obtained dispersive parameters for the kd contact and their dependence on the chain length of 1-chloroalkane are given in Table I.

It was found that for the *ketone- α,ω -dichloroalkane* mixtures, the kd contact contributes with a non-negligible quasichemical term similarly as in the *n*-alkyl alkanoate- α,ω -dichloroalkane mixtures⁸. Assuming that the dispersive kd-contact parameters of α,ω -dichloroalkane are the same as for 1-chloroalkane ($m \geq 7$, Table I), we adjusted the quasichemical interchange parameters $C_{kd,n}^{quac}$ using the most reliable equimolar G^E and H^E data available. Table II summarizes the obtained values and Fig. 1 illustrates the change of $C_{kd,n}^{quac}$ parameters with aliphatic chain length m between the chlorine groups in α,ω -dichloroalkanes. It was observed that $C_{kd,n}^{quac}$ coefficients are independent of the nature of ketone for $m \leq 10$.

For the *ketone–polychloroalkane* (namely trichloromethane, 1,1,1-trichloroethane, tetrachloromethane and 1,1,2,2-tetrachloroethane) mixtures, a good description of experimental data was found using only the dispersive contribution of kd contact. The parameters obtained are presented in Table III. However, the polychloroalkanes under study are the first members of different series according to the classification by Kehiaian and Marongiu⁴. The estimation of predictive parameters for these series of chloroalkanes would require much more additional input data. For the time being, the results are in agreement with those reported for the contact COO/Cl in mixtures of 1,1,2,2-tetrachloroethane with *n*-alkyl alkanooates^{33,34}.

TABLE I

Dispersive interchange coefficients for the C=O group (type k) in linear ketone $\text{CH}_3(\text{CH}_2)_{u-1}\text{CO}(\text{CH}_2)_{v-1}\text{CH}_3$ with Cl atom (type d) in 1-chloroalkane $\text{CH}_3(\text{CH}_2)_{m-2}\text{CH}_2\text{Cl}^a$

<i>u</i>	<i>v</i>	<i>m</i>	$C_{\text{kd},1}^{\text{dis}}$	$C_{\text{kd},2}^{\text{dis}}$	<i>u</i>	<i>v</i>	<i>m</i>	$C_{\text{kd},1}^{\text{dis}}$	$C_{\text{kd},2}^{\text{dis}}$		
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	2	2	4	1.54 ^b	1.68		
		5	2.21 ^b	2.37			≥7	2.38 ^b	2.51		
		6	2.27 ^b	2.43			5	1.73 ^b	1.87 ^b		
		≥7	2.57 ^b	2.73				6	1.79 ^b	1.93 ^b	
1	3	4	2.09 ^b	2.23	≥7	2.04 ^b	2.18 ^b				
		5	2.22 ^b	2.36							

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

TABLE II

Quasichemical interchange coefficients for C=O group (type k) in linear ketone $\text{CH}_3(\text{CH}_2)_{u-1}\text{CO}(\text{CH}_2)_{v-1}\text{CH}_3$ with Cl atom (type d) in α,ω -dichloroalkane $\text{ClCH}_2(\text{CH}_2)_{m-2}\text{CH}_2\text{Cl}$. Values for $m \geq 5$ are estimated

<i>m</i>	1	2	3	4	5	6	7	8	9	10
$C_{\text{kd},1}^{\text{quac}}$	-2.15	-1.04	-0.67	-0.49	-0.38	-0.29	-0.20	-0.12	-0.05	0
$C_{\text{kd},2}^{\text{quac}}$	-2.26	-1.29	-0.85	-0.65	-0.48	-0.37	-0.26	-0.17	-0.10	0

RESULTS AND DISCUSSION

Examples of the comparison of predicted data (using the newly estimated DISQUAC interchange parameters) with experimental data for VLE and the equimolar G^E and H^E for the chloroalkane with propan-2-one, butan-2-one and pentan-3-one mixtures are presented in Tables IV–VII; the agreement is quite good. The VLE data are represented very well for most of ketone–chloroalkane systems with both positive and large negative deviations from ideality. The P - x diagrams for the propan-2-one–1,1,1-trichloroethane and

TABLE III

Dispersive interchange coefficients for C=O group (type k) in linear ketone $\text{CH}_3(\text{CH}_2)_{u-1}\text{CO}(\text{CH}_2)_{v-1}\text{CH}_3$ with Cl atom (type d) in polychloroalkane mixtures

$u + v$	CHCl_3		CH_3CCl_3		CCl_4		$\text{Cl}_2\text{CHCHCl}_2$	
	$C_{\text{kd},1}^{\text{dis}}$	$C_{\text{kd},2}^{\text{dis}}$	$C_{\text{kd},1}^{\text{dis}}$	$C_{\text{kd},2}^{\text{dis}}$	$C_{\text{kd},1}^{\text{dis}}$	$C_{\text{kd},2}^{\text{dis}}$	$C_{\text{kd},1}^{\text{dis}}$	$C_{\text{kd},2}^{\text{dis}}$
1 + 1	-1.22	-5.98	2.38	1.91	0.02	-1.00	-1.50	-6.13
1 + 2	-2.59	-7.86	1.10	0.77	-0.59	-2.80	-2.21	-6.84
2 + 2	1.07	-5.62	4.77	5.37	7.40	7.36	1.21	-1.65

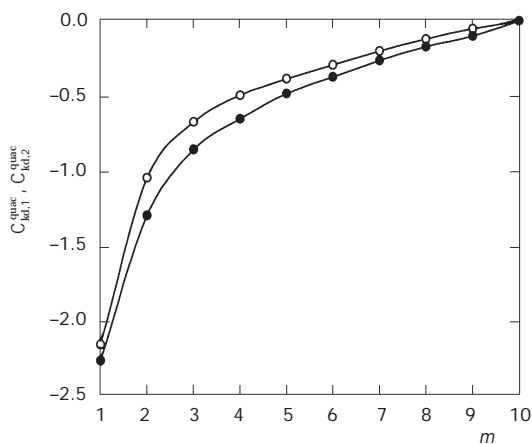


FIG. 1

Dependence of $C_{\text{kd},1}^{\text{quac}}$ (○) and $C_{\text{kd},2}^{\text{quac}}$ (●) interchange coefficients on m in the α,ω -dichloroalkane $\text{ClCH}_2(\text{CH}_2)_{m-2}\text{CH}_2\text{Cl}$ -ketone mixtures

TABLE IV
Excess Gibbs energy and excess enthalpy for the propan-2-one–chloroalkane mixtures at equimolar composition

Chloroalkane	T, K	$G^E(x = 0.5), J \text{ mol}^{-1}$		$H^E(x = 0.5), J \text{ mol}^{-1}$	
		calc.	exp.	calc.	exp.
1-Chlorobutane	298.15	333	333 ¹⁸	455	455 ¹⁸
1-Chloropentane	298.15	419	405 ¹²		
	303.15	417	392 ¹²		
	308.15	414	386 ¹²		
	313.15	412	376 ¹²		
Dichloromethane	303.15	-537	-406 ¹⁹	-873	-896 ¹⁹
1,2-Dichloroethane	273.15	-145	-226 ²⁰		
	298.15			-321	-405 ²²
1,3-Dichloropropane	298.15	-25	-9 ¹²	-113	-50 ²³
	303.15	-24	-16 ¹²		
	308.15	-22	-16 ¹²		
	313.15	-21	-28 ¹²		
1,4-Dichlorobutane	298.15	25	36 ¹³	7	-7 ²³
	303.15	25	26 ¹³		
	308.15	26	24 ¹³		
	313.15	26	25 ¹³		
Trichloromethane	298.15			-1921	-1925 ¹⁹
	323.15	-510	-510 ¹⁹		
1,1,1-Trichloroethane	298.15	271	265 ¹²		
	303.15	272	269 ¹²		
	308.15	272	275 ¹²		
	313.15	273	280 ¹²		
	363.15			227	228 ²⁴
1,1,2,2-Tetrachloroethane	298.15	-792	-779 ¹³	-2183	-2146 ²⁵
	303.15	-769	-798 ¹³		
	308.15	-746	-754 ¹³		
	313.15	-724	-699 ¹³		
Tetrachloromethane	318.15	131	131 ²¹	264	264 ³⁵

TABLE V
Excess Gibbs energy and excess enthalpy for the butan-2-one-chloroalkane mixtures at equimolar composition

Chloroalkane	T, K	$G^E(x = 0.5), J \text{ mol}^{-1}$		$H^E(x = 0.5), J \text{ mol}^{-1}$	
		calc.	exp.	calc.	exp.
1-Chlorobutane	298.15			233	197 ²⁶
	350.30	220	177 ³⁶		
1-Chloropentane	298.15	267	391 ¹⁴	311	289 ²⁶
	303.15	267	412 ¹⁴		
	308.15	266	408 ¹⁴		
	313.15	265	398 ¹⁴		
	318.15	264	396 ¹⁴		
Dichloromethane	288.15	-558	-640 ²⁷		
1,2-Dichloroethane	333.15	-132	-208 ²⁸		
1,3-Dichloropropane	298.15	-82	75 ¹⁴	-295	-216 ²⁹
	303.15	-78	76 ¹⁴		
	308.15	-74	82 ¹⁴		
	313.15	-71	83 ¹⁴		
	318.15	-67	66 ¹⁴		
1,4-Dichlorobutane	298.15	-44	44 ¹⁴	-200	-181 ²⁹
	303.15	-42	50 ¹⁴		
	308.15	-39	20 ¹⁴		
	313.15	-36	46 ¹⁴		
	318.15	-34	71 ¹⁴		
Trichloromethane	303.15	-702	-603 ¹⁹		
	318.15	-632	-735 ¹⁹		
	308.15			-2118	-2106 ¹⁹
1,1,1-Trichloroethane	298.15	84	60 ¹⁵		
	303.15	86	82 ¹⁵		
	313.15	90	101 ¹⁵		
	318.15	91	110 ¹⁵		
	363.15			-36	-27 ²⁴
1,1,2,2-Tetrachloroethane	298.15	-632	-615 ¹⁵	-2023	-2965
	303.15	-609	-649 ¹⁵		
	313.15	-563	-562 ¹⁵		
	318.15	-540	-456 ¹⁵		
Tetrachloromethane	298.15			-73	-80 ³⁰

TABLE VI
Excess Gibbs energy and excess enthalpy for the pentan-3-one–chloroalkane mixtures at equimolar composition

Chloroalkane	T, K	$G^E(x = 0.5), J \text{ mol}^{-1}$		$H^E(x = 0.5), J \text{ mol}^{-1}$	
		calc.	exp.	calc.	exp.
1-Chlorobutane	298.15			36	36 ²⁶
1,2-Dichloroethane	298.15			-434	-433 ³⁰
	323.15	-341	-213 ¹⁶		
	333.15	-339	-214 ¹⁶		
	343.15	-337	-194 ¹⁶		
1,3-Dichloropropane	353.15	-336	-204 ¹⁶		
	343.15	-144	-147 ¹⁶		
	353.15	-140	-138 ¹⁶		
	363.15	-137	-131 ¹⁶		
	373.15	-133	-133 ¹⁶		
1,4-Dichlorobutane	358			-285	-318 ³⁷
	343.15	-83	-89 ¹⁷		
	353.15	-78	-86 ¹⁷		
	363.15	-74	-82 ¹⁷		
	373.15	-70	-78 ¹⁷		
Trichloromethane	358			-226	-216 ³⁷
	313.15	-848	-800 ¹⁷		
	323.15	-784	-736 ¹⁷		
	333.15	-720	-698 ¹⁷		
	343.15	-656	-658 ¹⁷		
1,1,1-Trichloroethane	358			-2881	-2848 ³⁷
	323.15	-18	-20 ¹⁷		
	333.15	-13	-11 ¹⁷		
	343.15	-7	-8 ¹⁷		
	353.15	-2	-3 ¹⁷		
Tetrachloromethane	338			-200	-200 ³⁷
	298.15			-160	-160 ³⁷
1,1,2,2-Tetrachloroethane	353.15	604	604 ²²		
	343.15	-713	-712 ¹⁷		
	353.15	-678	-672 ¹⁷		
	363.15	-644	-644 ¹⁷		
	373.15	-610	-608 ¹⁷		
	358			-1893	-1892 ³⁷

TABLE VII

Deviations of experimental pressures P and vapour phase compositions y from values predicted using the DISQUAC model for the ketone–chloroalkane mixtures

System ^{ref}	T , K	AD_p , kPa	SD_p , kPa	SRD_p , %	AD_y	SD_y
		Propan-2-one with				
1-Chloropentane ¹²	298.15	0.19	0.22	1.2		
	303.15	0.29	0.34	1.4		
	308.15	0.38	0.46	1.5		
	313.15	0.52	0.65	1.8		
1,3-Dichloropropane ¹²	298.15	0.56	0.69	3.2		
	303.15	0.28	0.30	1.8		
	308.15	0.37	0.41	1.8		
	313.15	0.29	0.32	1.3		
1,4-Dichlorobutane ¹³	298.15	0.08	0.10	1.8		
	303.15	0.08	0.10	1.9		
	308.15	0.06	0.06	2.2		
	313.15	0.07	0.09	0.6		
1,1,1-Trichloroethane ¹²	298.15	0.16	0.19	0.8		
	303.15	0.28	0.35	1.1		
	308.15	0.27	0.34	0.9		
	313.15	0.40	0.47	1.0		
1,1,2,2-Tetrachloroethane ¹³	298.15	0.68	0.89	6.3		
	303.15	0.78	1.0	5.9		
	308.15	0.88	1.1	5.1		
	313.15	0.98	1.4	4.4		
		Butan-2-one with				
1-Chloropentane ¹⁴	298.15	0.37	0.45	6.3		
	303.15	0.56	0.73	8.2		
	308.15	0.70	0.86	7.7		
	313.15	0.73	0.95	6.9		
	318.15	0.93	1.20	6.9		
1,3-Dichloropropane ¹⁴	298.15	0.35	0.40	7.2		
	303.15	0.41	0.48	6.5		
	308.15	0.54	0.60	6.2		
	313.15	0.64	0.69	5.8		
	318.15	0.66	0.75	5.0		
1,4-Dichlorobutane ¹⁴	298.15	1.30	3.50	3.0		
	303.15	0.17	0.23	4.5		
	308.15	0.17	0.20	3.1		
	313.15	0.23	0.30	3.9		
	318.15	0.39	0.47	5.1		

TABLE VII
(Continued)

System ^{ref}	<i>T</i> , K	AD _{<i>p</i>} , kPa	SD _{<i>p</i>} , kPa	SRD _{<i>p</i>} , %	AD _{<i>y</i>}	SD _{<i>y</i>}
1,1,1-Trichloroethane ¹⁵	298.15	0.10	0.12	0.9		
	303.15	0.16	0.17	1.0		
	308.15	0.15	0.17	0.8		
	313.15	0.36	0.46	1.6		
	318.15	0.23	0.28	0.8		
1,1,2,2-Tetrachloroethane ¹⁵	298.15	0.06	0.08	3.8		
	303.15	0.09	0.11	3.0		
	313.15	0.13	0.17	3.5		
	318.15	0.28	0.32	6.3		
Pentan-3-one with						
1,2-Dichloroethane ¹⁶	323.15	0.72	0.76	3.5	0.0130	0.0140
	333.15	1.10	1.10	3.4	0.0120	0.0130
	343.15	1.70	1.70	3.7	0.0130	0.0140
	353.15	2.10	2.20	3.2	0.0086	0.0110
1,3-Dichloropropane ¹⁶	343.15	0.06	0.07	0.3	0.0027	0.0040
	353.15	0.12	0.15	0.4	0.0055	0.0065
	363.15	0.13	0.18	0.3	0.0079	0.0089
	373.15	0.28	0.49	0.9	0.0100	0.0110
1,4-Dichlorobutane ¹⁷	343.15	0.04	0.05	0.4	0.0057	0.0075
	353.15	0.09	0.10	0.6	0.0052	0.0078
	363.15	0.11	0.13	0.5	0.0045	0.0064
	373.15	0.21	0.25	0.6	0.0058	0.0082
Trichloromethane ¹⁷	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 ¹⁷	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 ¹⁷	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

butan-2-one–1,1,2,2-tetrachloroethane systems are shown as two typical examples in Figs 2 and 3, respectively.

The temperature dependence of G^E is fairly well described by the DISQUAC model as can be seen from Tables IV–VI. The dependence of G^E on composition is shown in Figs 4 and 6 for the propan-2-one–chloroalkane

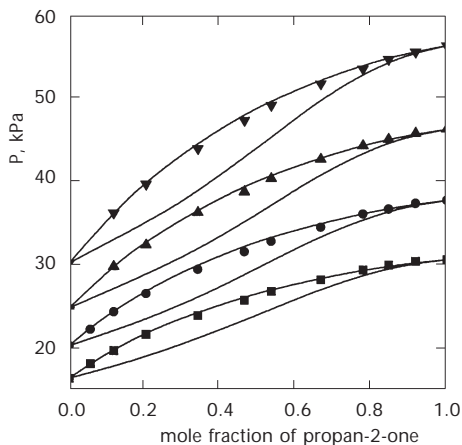


FIG. 2

VLE diagram for the propan-2-one–1,1,1-trichloroethane mixture at 298.15 (■), 303.15 (●), 308.15 (▲) and 313.15 K (▼). The lines are predicted using the DISQUAC model; points denote experimental values¹²

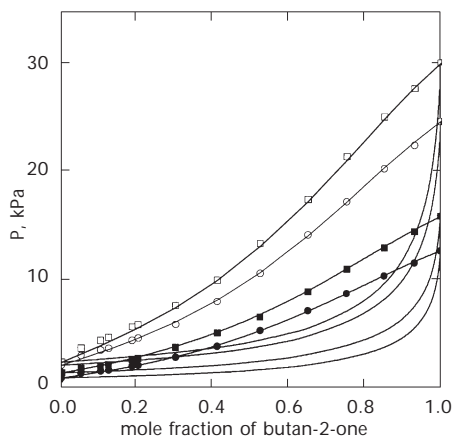


FIG. 3

VLE diagram for the butan-2-one–1,1,2,2-tetrachloroethane mixture at 298.15 (●), 303.15 (■), 313.15 (○) and 318.15 K (□). The lines are predicted using the DISQUAC model; points denote experimental values¹⁵

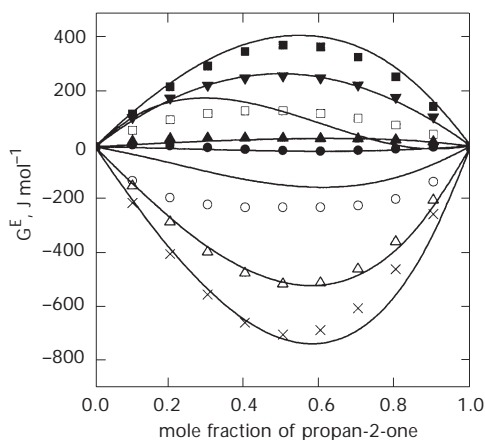


FIG. 4

Molar excess Gibbs energy G^E for the systems of propan-2-one with 1-chloropentane at 308.15 (\blacksquare)¹², 1,2-dichloroethane at 273.15 (\circ)²⁰, 1,3-dichloropropane at 303.15 (\bullet)¹², 1,4-dichlorobutane at 303.15 (\blacktriangle)¹³, trichloromethane at 323.15 (\triangle)¹⁹, 1,1,1-trichloroethane at 303.15 (\blacktriangledown)¹², tetrachloromethane at 318.15 (\square)²¹ and 1,1,2,2-tetrachloroethane at 313.15 K (\times)¹³. The lines are predicted using the DISQUAC model; points denote experimental values

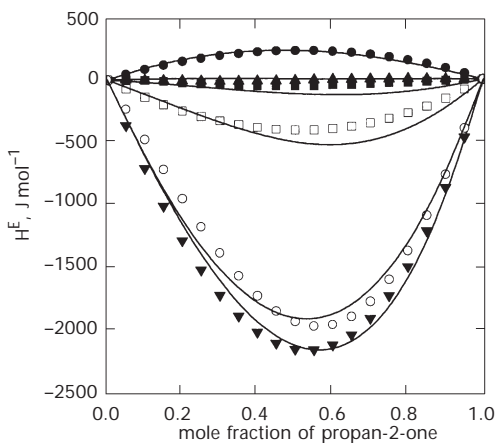


FIG. 5

Molar excess enthalpy H^E at 298.15 K for the systems of propan-2-one with 1,2-dichloroethane²² (\square), 1,3-dichloropropane²³ (\blacksquare), 1,4-dichlorobutane²³ (\blacktriangle), trichloromethane¹⁹ (\circ), 1,1,1-trichloroethane²⁴ (\bullet) (at 363.15 K) and 1,1,2,2-tetrachloroethane²⁵ (\blacktriangledown). The lines are predicted using the DISQUAC model; points denote experimental values

and butan-2-one-chloroalkane mixtures, respectively. Significant differences between calculated and experimental G^E values for the propan-2-one-1,2-dichloroethane (Table IV and Fig. 4) and butan-2-one with 1,2-dichloroethane, 1,3-dichloropropane and 1,4-dichlorobutane mixtures (Table V and Fig. 6) are due to the inaccuracy of experimental data, *i.e.* they are not to the model imperfection. For the propan-2-one-tetrachloromethane system, the dependence of experimental G^E on composition is positive and symmetrical in contrast to the S-shaped curve resulting from the prediction. The experimental H^E are in a good agreement with predicted values. The dependence of H^E on the composition is shown in Figs 5 and 7.

Analogously to the COO/Cl contact in the 1-chloroalkane-*n*-alkyl alkanoate systems⁸, the C=O/Cl contact in ketone-1-chloroalkane mixtures is best described by the dispersive parameter only. For the mixtures with α,ω -dichloroalkanes, the interaction energy of the C=O/Cl or COO/Cl contact is much stronger than the average energies of Cl/Cl, C=O/C=O or COO/COO contacts. The H atoms in CH₂Cl groups interact specifically with C=O (or COO) group (weak H-bond) due to the inductive effects of two Cl atoms. This may explain both the negative quasichemical interchange coefficients for short chain α,ω -dichloroalkanes (Table II) and the observed proximity effect. The inductive effect of Cl atoms is more evident

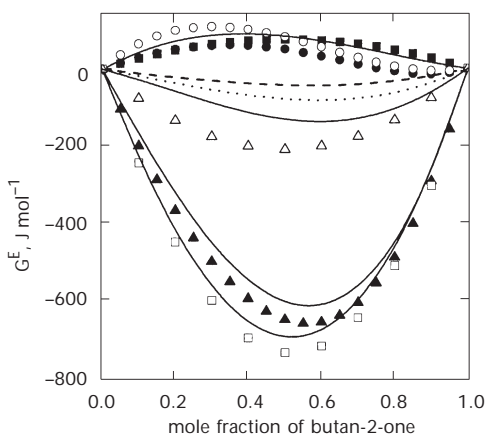


FIG. 6

Molar excess Gibbs energy G^E at 303.15 K for the systems of butan-2-one with 1,3-dichloropropane¹⁴ (■, ····), 1,4-dichlorobutane¹⁴ (●, - - - -), trichloromethane¹⁹ (□, - · - ·), 1,1,1-trichloroethane¹⁵ (○, - - - -), 1,1,2,2-tetrachloroethane¹⁵ (▲, - · - ·) and 1,2-dichloroethane²⁸ (at 333.15 K) (△, - · - ·). The lines are predicted using the DISQUAC model; points denote experimental values

in ketone (or *n*-alkyl alkanoate³³)–trichloromethane or –1,1,2,2-tetrachloroethane systems where the specific interactions between unlike molecules are stronger.

The negative or largely negative values of G^E and H^E and a well-defined minimum of their dependence on composition (around equimolar) indicate that there are specific interactions in these mixtures with formation of complexes between the two components due to H-bonds.

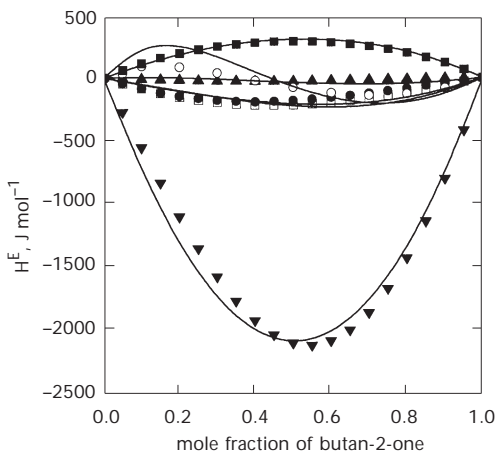


FIG. 7

Molar excess enthalpy H^E at 298.15 K for the systems of butan-2-one with 1-chloropentane²⁶ (■), 1,3-dichloropropane²⁹ (□), 1,4-dichlorobutane²⁹ (●), 1,1,1-trichloroethane²⁴ (▲), trichloromethane¹⁹ (▼) and tetrachloromethane³⁰ (○). The lines are predicted using the DISQUAC model; points denote experimental values

CONCLUSIONS

The previously published DISQUAC interchange parameters for the C=O/Cl contact¹⁰ have been extended to the whole class of linear ketones with 1-chloroalkanes, α,ω -dichloroalkanes and some polychloroalkane binary mixtures.

The determined $C_{kd,n}^{dis}$ and $C_{kd,n}^{quac}$ coefficients obey simple rules: (i) $C_{kd,1}^{dis}$ and $C_{kd,2}^{dis}$ coefficients for the 1-chloroalkane–ketone $[\text{CH}_3(\text{CH}_2)_{u-1}\text{CO}(\text{CH}_2)_{v-1}\text{CH}_3]$ mixtures vary regularly with the $u + v$ length of the hydrocarbon chain of a ketone; (ii) for small molecules of α,ω -dichloroalkanes, where the proximity effects are important, the $C_{kd,n}^{quac}$ coefficients vary with the aliphatic chain length m between the chlorine groups (for $m \leq 10$ the $C_{kd,n}^{quac}$ coefficients are also independent of the nature of ketone).

The estimation of predictive parameters for the series of polychloroalkanes requires more experimental data; the polychloroalkanes under study are only the first members of different series. Nevertheless, the results are in agreement with those reported for the contact COO/Cl in mixtures of 1,1,2,2-tetrachloroethane with *n*-alkyl alkanooates³⁴.

It was shown that the DISQUAC model provides a consistent prediction of phase equilibria and thermodynamic excess functions using the new set of structure-dependent parameters. For mixtures of linear ketones with long chloroalkanes, where proximity effects disappear, the DISQUAC group contribution model can be successfully used for the prediction of thermodynamic properties using a unique set of parameters.

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>i</i>
$C_{st,1}^{dis}, C_{st,2}^{dis}$	dispersive interchange coefficients for st contact
$C_{st,1}^{quac}, C_{st,2}^{quac}$	quasichemical interchange coefficients for st contact
d	chlorine-type surface
$g_{st}^{dis quac}$	dispersive quasichemical interchange parameter for st contact
G^E	molar excess Gibbs energy, J mol ⁻¹
$h_{st}^{dis quac}$	dispersive quasichemical interaction parameter for st contact
H^E	molar excess enthalpy, J mol ⁻¹
k	carbonyl-type surface
<i>P</i>	pressure, kPa
<i>q_i</i>	relative molecular surface of molecule <i>i</i>
<i>r_i</i>	relative molecular volume of molecule <i>i</i>
<i>R</i>	gas constant
s	s-type surface (general)
SD_i	standard deviation for property <i>i</i>
SRD_p	standard relative deviation for pressure, %
t	t-type surface (general)
<i>T</i>	temperature, K
<i>m, u, v</i>	number of methylene groups in chloroalkane or ketone
α, ω	terminal position of chlorine group in dichloroalkane
α_{si}	molecular surface fraction of the group <i>s</i> in molecule <i>i</i>

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