



*Dedicated to the memory of  
Dr. Henry V. Kehiaian (1929–2009)*

VAPOUR-LIQUID EQUILIBRIA FOR THE BINARY MIXTURES  
OF METHYL ETHYL KETONE (2-BUTANONE) + SOME CHLOROALKANES  
AT TEMPERATURES FROM 298.15 TO 318.15 K.  
COMPARISONS WITH DISQUAC MODEL PREDICTION

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The vapour pressures of binary mixtures of methyl ethyl ketone (2-butanone) + chloroalkanes (1-chloropentane, + 1,1,1-trichloroethane, + 1,1,2,2-tetrachloroethane) were measured by a static total pressure method, at temperatures between 298.15 K and 318.15 K. The vapour pressures vs. liquid phase composition data have been used to calculate the activity coefficients of the two components, and the excess molar Gibbs energies  $G^E$  for the mixtures, using Barker's method. Redlich-Kister, Wilson and NRTL equations have represented the  $G^E$  values, and the vapour phase imperfection was taken into account in terms of the 2<sup>nd</sup> virial coefficients. The studied systems behave differently: for the first and second mixtures, the deviations from Raoult's law are positive, while for the third mixture, the deviations from ideality are negative and large. These experimental VLE and  $G^E$  results and the literature  $H^E$  data for the linear ketone + chloroalkane mixtures, are examined on the basis of DISQUAC (DISpersive-QUAsiChemical) group-contribution model.

## INTRODUCTION

Ketones and chloroalkanes represent classes of technically important compounds used in industry as intermediates or as final products. In view of the variety of possible mixtures, a large number of systems should be investigated experimentally in order to have the data needed for the design of distillation columns and other stills for chemical plants. On the other hand, these experimental data are absolutely necessary for the development of new predictive methods of thermodynamic properties and testing of relevant theories of liquids.

As a continuation of a research project on vapour-liquid equilibria (VLE) in linear ketone +

chloroalkane mixtures, the present paper presents the isothermal VLE measurements in mixtures of methyl ethyl ketone (2-butanone) + 1-chloropentane, + 1,1,1-trichloroethane, + 1,1,2,2-tetrachloroethane, for which no such experimental data are available.<sup>1, 2</sup> In previous papers<sup>3-7</sup> we have reported experimental VLE data for linear ketones + some chloroalkanes mixtures that were used for characterization of the carbonyl-chlorine interactions according to the DISQUAC (DISpersive-QUAsiChemical) model.

To correlate the experimental VLE data Redlich-Kister,<sup>8</sup> Wilson,<sup>9</sup> and NRTL<sup>10</sup> expressions for excess Gibbs energy,  $G^E$ , were used.

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## EXPERIMENTAL

### Apparatus and procedure

The vapour pressure,  $P$ , measurements of pure compounds and binary mixtures were carried out by a static method, in which total pressure is measured as a function of the overall composition in the equilibrium cell.

Use has been made of an isoteniscope based on Surovy's design.<sup>11</sup> The working procedure and the performance of the apparatus were described in previous papers.<sup>12-14</sup>

The equilibrium cell with a total volume of 80 m<sup>3</sup> 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 actual equilibrium temperature,  $T$ , while the temperature of the jacket of the null manometer is maintained (1 to 2 K) higher in order to prevent the partial condensation of the vapours in the upper part of the apparatus. The isoteniscope 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 on a precision Hg manometer, connected to the apparatus. The manometric readings were performed with a Griffin and George Ltd. (London, UK) Type 4214 cathetometer to within  $\pm 0.01$  mm, equivalent to an uncertainty of  $\pm 3$  Pa. 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 cm<sup>3</sup>).

Mixtures of known composition of about 10 cm<sup>3</sup> were prepared by weighting, measured to within 10<sup>-7</sup> kg, and thoroughly degassed in the equilibrium cell by alternate freezing, high vacuum pumping and thawing, as described by Ronc<sup>15</sup> and Young.<sup>16</sup> 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 (International Temperature Scale of 1990) by means of mercury thermometers previously checked at the National Institute of Metrology Bucharest.

The experimental uncertainties are:  $\pm 0.1$  K,  $\pm 0.02$  kPa, and  $\pm 0.001$  for temperature, pressure and liquid phase molar fraction, respectively.

### Materials

The substances used (2-butanone, 1-chloropentane and 1,1,1-trichloroethane) were commercial products from E. Merck A G (Darmstadt and Schuchardt) of the first grade purity. The liquids were dried and stored over 4A molecular sieves and used without further purification. The purity of these substances, checked by gas chromatography, was not less than 99.8 mole %. 1,1,2,2-Tetrachloroethane, purum material ( $\sim 98$  % Fluka) was rectified on a 30-plate column packed with glass helices. Purity determined by gas-chromatography was better than 99.4 %. After rectification it was stored in a refrigerator.

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 pressure with the literature values (see Table 1).

Table 1

Physical properties of pure compounds

Compound/Property	Temperature	2-butanone		1-chloropentane		1,1,1-trichloroethane		1,1,2,2-Tetrachloroethane	
		This work	Lit.	This work	Lit.	This work	Lit.	This work	Lit.
$n_D^{298.15\text{ K}}$		1.3755	1.3764 <sup>17</sup>	1.4101	1.4099 <sup>18</sup>	1.4350	1.4358 <sup>18</sup>	1.4917	1.4918 <sup>6</sup>
$\rho^{298.15\text{ K}}$ (kg/m <sup>3</sup> )		799.6	799.5 <sup>17</sup>	879.8	876.9 <sup>18</sup>	1331.3	1330.3 <sup>18</sup>	1587.6	1586.8 <sup>6</sup>
$P$ (kPa)	298.15 K	12.67	12.63 <sup>19</sup>	4.25	4.02 <sup>20</sup>	16.62	16.49 <sup>21</sup>	0.96	0.69 <sup>22</sup>
	303.15 K	15.94	15.83 <sup>19</sup>	5.43	5.19 <sup>20</sup>	20.43	20.49 <sup>21</sup>	1.41	0.95 <sup>22</sup>
	308.15 K	19.85	19.84 <sup>19</sup>	6.89	6.64 <sup>20</sup>	24.97	25.25 <sup>21</sup>	1.80	1.28 <sup>22</sup>
	313.15 K	24.52	24.28 <sup>19</sup>	8.65	8.42 <sup>20</sup>	30.36	30.86 <sup>21</sup>	2.13	1.72 <sup>22</sup>
	318.15 K	30.04	29.73 <sup>19</sup>	10.78	10.56 <sup>20</sup>	36.71	37.44 <sup>21</sup>	2.41	2.26 <sup>22</sup>

## RESULTS AND DISCUSSION

The vapour pressures of the pure components were measured in the same apparatus at the

working temperatures and are in good agreement with the literature values in majority of the cases (Table 1). The literature values for vapour pressures shown in Table 1 are calculated by using

specific equations as given in the mentioned references.

The direct experimental values ( $P$ ,  $T$ ,  $x$ ) and calculated vapour phase compositions,  $y$ , and the

derived thermodynamic quantities (activity coefficients,  $\gamma_1$ ,  $\gamma_2$ , excess Gibbs energy,  $G^E$ ), for the binary systems at temperatures from 298.15 to 318.15 K are presented in Tables 2-4 and Figs. 1-4.

Table 2

Experimental VLE data for 2-butanone (1) + 1-chloropentane (2)

$x_1$	$y_1$ calc	$P_e$ (kPa)	$P_c$ (kPa)	$P_e - P_c$ (kPa)	$\gamma_1$	$\gamma_2$	$G^E$ (J/mol)
<b>T = 298.15 K</b>							
0.0000	0.0000	4.24	4.24	0.00	2.3631	1.0000	0
0.0442	0.2257	5.28	5.26	0.02	2.1384	1.0023	89
0.1089	0.3989	6.34	6.39	-0.05	1.8637	1.0137	198
0.1137	0.4080	6.45	6.47	-0.02	1.8456	1.0150	205
0.2052	0.5304	7.71	7.57	0.14	1.5536	1.0486	317
0.3045	0.6085	8.27	8.38	-0.11	1.3297	1.1057	388
0.3985	0.6632	8.94	8.98	-0.04	1.1848	1.1768	410
0.4843	0.7082	9.55	9.46	0.09	1.0957	1.2514	396
0.5710	0.7542	9.92	9.92	0.00	1.0380	1.3287	355
0.6570	0.8028	10.37	10.40	-0.03	1.0057	1.3964	293
0.7676	0.8697	11.07	11.05	0.02	0.9907	1.4459	195
0.8690	0.9317	11.70	11.72	-0.02	0.9932	1.4254	100
0.9660	0.9844	12.36	12.41	-0.05	0.9993	1.3240	22
1.0000	1.0000	12.66	12.66	0.00	1.0000	1.2678	0
<b>T = 303.15 K</b>							
0.0000	0.0000	5.43	5.43	0.00	3.0125	1.0000	0
0.0442	0.2535	6.93	6.99	-0.06	2.5393	1.0038	113
0.1089	0.4151	8.38	8.48	-0.10	2.0449	1.0219	245
0.1137	0.4229	8.85	8.57	0.28	2.0153	1.0237	253
0.2052	0.5254	9.69	9.79	-0.10	1.5834	1.0712	376
0.3045	0.5922	10.45	10.65	-0.20	1.3073	1.1430	440
0.3985	0.6444	11.49	11.32	0.17	1.1534	1.2226	448
0.4843	0.6912	11.88	11.88	0.00	1.0696	1.2971	420
0.5710	0.7426	12.53	12.47	0.06	1.0212	1.3651	367
0.6570	0.7964	13.20	13.08	0.12	0.9976	1.4158	297
0.7676	0.8680	13.74	13.92	-0.18	0.9900	1.4404	194
0.8690	0.9313	14.74	14.77	-0.03	0.9943	1.4094	101
0.9660	0.9841	15.55	15.63	-0.07	0.9995	1.3253	23
1.0000	1.0000	15.94	15.94	0.00	1.0000	1.2833	0
<b>T = 308.15 K</b>							
0.0000	0.0000	6.89	6.89	0.00	2.8661	1.0000	0
0.0442	0.2429	8.74	8.75	-0.01	2.4471	1.0035	110
0.1089	0.4050	10.53	10.57	-0.04	1.9988	1.0204	239
0.1137	0.4130	10.62	10.68	-0.06	1.9716	1.0221	247
0.2052	0.5189	12.22	12.22	0.00	1.5682	1.0671	369
0.3045	0.5880	13.47	13.32	0.15	1.3031	1.1362	434
0.3985	0.6411	14.11	14.14	-0.03	1.1521	1.2141	443
0.4843	0.6888	14.84	14.84	0.00	1.0684	1.2880	416
0.5710	0.7397	15.67	15.56	0.11	1.0195	1.3564	363
0.6570	0.7937	16.20	16.30	-0.10	0.9955	1.4077	293
0.7676	0.8662	17.21	17.34	-0.13	0.9881	1.4313	190
0.8690	0.9306	18.44	18.39	0.05	0.9933	1.3944	97
0.9660	0.9841	19.26	19.46	-0.20	0.9994	1.2976	21
1.0000	1.0000	19.85	19.85	0.00	1.0000	1.2495	0
<b>T = 313.15 K</b>							
0.0000	0.0000	8.65	8.65	0.00	2.6274	1.0000	0
0.0442	0.2272	10.77	10.76	0.01	2.2823	1.0032	103
0.1089	0.3897	12.58	12.92	-0.33	1.9047	1.0182	224
0.2052	0.5101	14.81	14.98	-0.17	1.5315	1.0600	348

Table 2 (continued)

0.3045	0.5850	16.36	16.41	-0.05	1.2947	1.1222	413
0.3985	0.6417	17.47	17.49	-0.02	1.1559	1.1928	426
0.4843	0.6911	18.39	18.41	-0.02	1.0769	1.2609	405
0.5710	0.7423	19.51	19.33	0.18	1.0291	1.3259	358
0.6570	0.7955	20.26	20.26	0.00	1.0040	1.3782	293
0.7676	0.8662	21.42	21.53	-0.11	0.9934	1.4126	196
0.8690	0.9294	22.84	22.79	0.05	0.9954	1.3966	104
0.9660	0.9835	23.97	24.06	-0.09	0.9995	1.3288	24
1.0000	1.0000	24.52	24.52	0.00	1.0000	1.2923	0
<b>T = 318.15 K</b>							
0.0000	0.0000	10.78	10.78	0.00	2.6775	1.0000	0
0.0442	0.2260	13.28	13.39	-0.11	2.3103	1.0033	106
0.1089	0.3861	15.71	16.02	-0.31	1.9127	1.0190	231
0.1137	0.3941	16.68	16.19	0.49	1.8884	1.0207	239
0.2052	0.5038	18.38	18.49	-0.11	1.5250	1.0625	356
0.3045	0.5772	20.13	20.17	-0.04	1.2827	1.1267	420
0.3985	0.6336	21.33	21.44	-0.11	1.1430	1.1988	429
0.4843	0.6836	22.61	22.53	0.08	1.0650	1.2670	404
0.5710	0.7362	23.91	23.63	0.28	1.0191	1.3302	352
0.6570	0.7912	24.63	24.75	-0.12	0.9965	1.3778	285
0.7676	0.8645	26.24	26.30	-0.06	0.9892	1.4005	185
0.8690	0.9294	27.77	27.86	-0.09	0.9939	1.3681	94
0.9660	0.9838	29.47	29.47	0.00	0.9994	1.2808	21
1.0000	1.0000	30.04	30.04	0.00	1.0000	1.2370	0

Table 3

Experimental VLE data for 2-butanone (1) + 1,1,1-trichloroethane (2)

$x_1$	$y_1$ calc	$P_e$ (kPa)	$P_c$ (kPa)	$P_e - P_c$ (kPa)	$\gamma_1$	$\gamma_2$	$G^E$ (J/mol)
<b>T = 298.15 K</b>							
0.0000	0.0000	16.60	16.60	0.00	1.2661	1.0000	0
0.0513	0.0476	16.53	16.57	-0.04	1.2052	1.0013	27
0.0955	0.0857	16.49	16.51	-0.01	1.1613	1.0042	45
0.1083	0.0964	16.48	16.49	-0.01	1.1499	1.0053	49
0.2136	0.1805	16.26	16.23	0.03	1.0750	1.0182	73
0.3333	0.2746	15.89	15.83	0.06	1.0226	1.0372	79
0.4035	0.3322	15.53	15.54	-0.01	1.0040	1.0483	74
0.5027	0.4198	15.07	15.09	-0.02	0.9892	1.0610	59
0.6063	0.5216	14.56	14.57	-0.01	0.9843	1.0671	40
0.6732	0.5938	14.13	14.21	-0.08	0.9853	1.0653	26
0.7621	0.6977	13.84	13.75	0.09	0.9894	1.0536	10
0.8087	0.7552	13.54	13.51	0.03	0.9922	1.0427	4
0.8466	0.8032	13.28	13.32	-0.04	0.9945	1.0312	0
0.8664	0.8286	13.24	13.23	0.01	0.9956	1.0242	-1
0.9219	0.9003	13.00	12.99	0.01	0.9983	1.0008	-4
0.9422	0.9265	12.92	12.91	0.01	0.9990	0.9908	-3
1.0000	1.0000	12.70	12.70	0.00	1.0000	0.9583	0
<b>T = 303.15 K</b>							
0.0000	0.0000	20.43	20.43	0.00	1.3804	1.0000	0
0.0513	0.0516	20.49	20.47	0.02	1.2900	1.0018	37
0.0955	0.0914	20.48	20.45	0.02	1.2259	1.0058	62
0.1083	0.1023	20.47	20.44	0.03	1.2094	1.0073	68
0.2136	0.1859	20.37	20.23	0.14	1.1028	1.0251	102
0.3333	0.2768	19.74	19.79	-0.05	1.0299	1.0513	109
0.5027	0.4175	18.98	18.89	0.09	0.9843	1.0843	81
0.6063	0.5184	18.20	18.21	-0.01	0.9780	1.0925	54
0.6732	0.5911	17.77	17.75	0.02	0.9794	1.0896	35
0.7621	0.6966	17.18	17.14	0.04	0.9852	1.0728	13
0.8087	0.7553	16.89	16.84	0.05	0.9891	1.0573	4

Table 3 (continued)

0.8466	0.8041	16.62	16.61	0.01	0.9923	1.0410	-1
0.8664	0.8299	16.40	16.49	-0.09	0.9939	1.0311	-3
0.9219	0.9020	16.22	16.20	0.02	0.9976	0.9985	-6
0.9422	0.9181	16.12	16.11	0.01	0.9987	0.9847	-5
1.0000	1.0000	15.89	15.89	0.00	1.0000	0.9401	0
<b>T = 308.15 K</b>							
0.0000	0.0000	24.96	24.96	0.00	1.3409	1.0000	0
0.0513	0.0518	25.08	25.02	0.06	1.2618	1.0016	34
0.0955	0.0921	25.05	25.00	0.05	1.2053	1.0052	58
0.1083	0.1032	25.04	24.99	0.05	1.1907	1.0066	63
0.2136	0.1891	24.78	24.75	0.03	1.0956	1.0225	95
0.3333	0.2827	24.26	24.27	-0.01	1.0298	1.0463	102
0.4035	0.3396	23.84	23.89	-0.05	1.0065	1.0602	96
0.5027	0.4262	23.23	23.26	-0.03	0.9878	1.0765	78
0.6063	0.5273	22.56	22.52	0.04	0.9815	1.0846	53
0.6732	0.5993	21.93	22.00	-0.07	0.9824	1.0826	36
0.7621	0.7030	21.34	21.33	0.01	0.9873	1.0688	16
0.8087	0.7604	20.96	20.99	-0.03	0.9906	1.0556	7
0.8466	0.8081	20.75	20.73	0.02	0.9933	1.0417	1
0.8664	0.8332	20.65	20.60	0.05	0.9947	1.0331	-0.5
0.9219	0.9036	20.31	20.27	0.04	0.9980	1.0047	-4
0.9422	0.9292	20.19	20.16	0.03	0.9988	0.9927	-4
1.0000	1.0000	19.90	19.90	0.00	1.0000	0.9534	0
<b>T = 313.15 K</b>							
0.0000	0.0000	30.36	30.36	0.00	1.4631	1.0000	0
0.0513	0.0561	30.56	30.58	-0.02	1.3511	1.0021	45
0.0955	0.0981	30.66	30.66	0.00	1.2724	1.0068	76
0.1083	0.1095	30.67	30.67	0.00	1.2523	1.0086	83
0.2136	0.1946	30.55	30.52	0.03	1.1233	1.0296	124
0.3333	0.2848	30.09	30.01	0.08	1.0363	1.0607	133
0.4035	0.3395	29.47	29.57	-0.10	1.0060	1.0791	124
0.5027	0.4238	28.74	28.80	-0.06	0.9822	1.1003	100
0.6063	0.5241	27.79	27.84	-0.05	0.9746	1.1103	67
0.6732	0.5967	27.25	27.18	0.07	0.9761	1.1071	44
0.8087	0.7607	25.88	25.87	0.01	0.9873	1.0692	6
0.8664	0.8346	25.43	25.39	0.04	0.9929	1.0385	-3
0.9219	0.9055	25.01	25.01	0.00	0.9973	1.0003	-6
0.9422	0.9308	24.88	24.89	-0.01	0.9984	0.9842	-6
1.0000	1.0000	24.62	24.62	0.00	1.0000	0.9324	0
<b>T = 318.15 K</b>							
0.0000	0.0000	36.71	36.71	0.00	1.3814	1.0000	0
0.0513	0.0546	36.90	36.90	0.00	1.2993	1.0016	39
0.0955	0.0968	36.97	36.96	0.01	1.2402	1.0053	67
0.2136	0.1972	36.84	36.79	0.04	1.1240	1.0232	114
0.3333	0.2921	36.26	36.25	0.01	1.0520	1.0487	128
0.4035	0.3490	35.78	35.78	0.00	1.0252	1.0645	125
0.5027	0.4344	34.93	34.97	-0.04	1.0019	1.0846	109
0.6063	0.5332	34.00	33.97	0.03	0.9912	1.0988	84
0.7621	0.7042	32.25	32.29	-0.04	0.9913	1.0965	40
0.8466	0.8071	31.39	31.39	0.00	0.9951	1.0786	20
0.8664	0.8319	31.14	31.19	-0.05	0.9961	1.0725	15
0.9219	0.9021	30.69	30.67	0.02	0.9984	1.0509	6
0.9422	0.9278	30.51	30.49	0.02	0.9991	1.0413	4
1.0000	1.0000	30.04	30.04	0.00	1.0000	1.0094	0

Table 4

Experimental VLE data for 2-butanone (1) + 1,1,2,2-tetrachloroethane (2)

$x_1$	$y_1$ calc	$P_e$ (kPa)	$P_c$ (kPa)	$P_e - P_c$ (kPa)	$\gamma_1$	$\gamma_2$	$G^E$ (J/mol)
<b>T = 298.15 K</b>							
0.0000	0.0000	0.96	0.96	0.00	0.5413	1.0000	0
0.0509	0.2710	1.37	1.25	0.12	0.5325	1.0004	-79
0.1022	0.4408	1.60	1.55	0.05	0.5320	1.0004	-159
0.1233	0.4944	1.67	1.67	0.00	0.5340	0.9999	-192
0.1853	0.6189	2.04	2.05	-0.01	0.5463	0.9956	-287
0.2019	0.6462	2.10	2.16	-0.06	0.5511	0.9935	-311
0.3008	0.7733	2.87	2.89	-0.02	0.5913	0.9698	-445
0.4106	0.8664	3.86	3.91	-0.05	0.6556	0.9153	-559
0.5239	0.9274	5.31	5.25	0.06	0.7372	0.8250	-623
0.6503	0.9669	7.16	7.09	0.07	0.8354	0.6897	-612
0.7528	0.9845	8.77	8.79	-0.02	0.9092	0.5648	-528
0.8518	0.9939	10.40	10.48	-0.08	0.9648	0.4433	-375
0.9113	0.9980	11.58	11.75	-0.17	0.9921	0.3522	-196
1.0000	1.0000	12.71	12.71	0.00	1.0000	0.2815	0
<b>T = 303.15 K</b>							
0.0000	0.0000	1.41	1.41	0.00	0.4278	1.0000	0
0.0509	0.2137	1.82	1.70	0.12	0.4554	0.9984	-105
0.1022	0.3808	1.99	2.03	-0.04	0.4833	0.9935	-202
0.1233	0.4383	2.20	2.18	0.02	0.4948	0.9905	-240
0.1853	0.5773	2.65	2.66	-0.01	0.5292	0.9784	-342
0.2019	0.6082	2.76	2.80	-0.04	0.5386	0.9743	-367
0.3008	0.7514	3.75	3.75	0.00	0.5963	0.9414	-498
0.4106	0.8529	5.10	5.03	0.07	0.6653	0.8859	-602
0.5239	0.9183	6.55	6.66	-0.11	0.7424	0.8042	-655
0.6503	0.9617	8.95	8.88	0.07	0.8326	0.6821	-637
0.7528	0.9818	11.02	10.95	0.07	0.9031	0.5627	-552
0.8518	0.9929	12.96	13.05	-0.09	0.9602	0.4379	-396
0.9113	0.9977	14.47	14.67	-0.20	0.9906	0.3382	-210
1.0000	1.0000	15.89	15.89	0.00	1.0000	0.2579	0
<b>T = 308.15 K</b>							
0.0000	0.0000	1.79	1.79	0.00	0.4639	1.0000	0
0.0509	0.2192	2.31	2.18	0.13	0.4798	0.9991	-98
0.1022	0.3832	2.51	2.60	-0.09	0.4987	0.9959	-192
0.1233	0.4390	2.79	2.79	0.00	0.5072	0.9937	-228
0.1853	0.5741	3.36	3.38	-0.02	0.5352	0.9840	-330
0.2019	0.6043	3.56	3.56	0.00	0.5433	0.9804	-356
0.3008	0.7467	4.82	4.72	0.10	0.5976	0.9493	-490
0.4106	0.8501	6.23	6.34	-0.11	0.6681	0.8922	-597
0.5239	0.9174	8.43	8.42	0.01	0.7491	0.8064	-650
0.6503	0.9614	11.28	11.24	0.04	0.8423	0.6818	-629
0.7528	0.9815	13.92	13.84	0.08	0.9118	0.5652	-539
0.8518	0.9926	16.26	16.42	-0.16	0.9652	0.4483	-382
1.0000	1.0000	19.90	19.90	0.00	1.0000	0.2844	0
<b>T = 313.15 K</b>							
0.0000	0.0000	2.13	2.13	0.00	0.6524	1.0000	0
0.0509	0.2729	2.99	2.78	0.21	0.6181	1.0013	-60
0.1022	0.4351	3.49	3.40	0.09	0.5992	1.0038	-127
0.1233	0.4857	3.64	3.65	-0.01	0.5952	1.0046	-156
0.1853	0.6036	4.37	4.41	-0.04	0.5937	1.0049	-241
0.2019	0.6296	4.59	4.62	-0.03	0.5957	1.0041	-264
0.3008	0.7546	5.86	6.02	-0.16	0.6238	0.9880	-391
0.4106	0.8509	7.98	7.97	0.01	0.6812	0.9403	-505
0.5239	0.9169	10.63	10.54	0.09	0.7588	0.8545	-571
0.6503	0.9611	14.17	14.07	0.10	0.8525	0.7233	-565
0.7528	0.9812	17.26	17.28	-0.02	0.9210	0.6027	-487

Table 4 (continued)

0.8518	0.9923	20.29	20.43	-0.14	0.9705	0.4871	-344
0.9313	0.9973	22.44	22.80	-0.36	0.9936	0.4014	-179
1.0000	1.0000	24.62	24.62	0.00	1.0000	0.3355	0
<b>T = 318.15 K</b>							
0.0000	0.0000	2.41	2.41	0.00	0.8734	1.0000	0
0.0509	0.3360	3.67	3.46	0.21	0.7774	1.0029	-27
0.1022	0.4957	4.39	4.35	0.04	0.7165	1.0096	-67
0.1233	0.5416	4.66	4.68	-0.02	0.6993	1.0127	-87
0.1853	0.6444	5.63	5.66	-0.03	0.6688	1.0207	-153
0.2019	0.6667	5.83	8.93	-0.10	0.6648	1.0222	-172
0.3008	0.7741	7.63	7.66	-0.03	0.6684	1.0193	-285
0.4106	0.8596	10.01	10.05	-0.04	0.7121	0.9831	-395
0.5239	0.9202	13.37	13.20	0.17	0.7828	0.9038	-467
0.6503	0.9619	17.46	17.51	-0.05	0.8710	0.7756	-473
0.7528	0.9812	21.40	21.37	0.03	0.9339	0.6580	-410
0.8518	0.9919	25.04	25.10	-0.06	0.9769	0.5484	-288
0.9313	0.9971	27.64	27.87	-0.23	0.9953	0.4707	-148
1.0000	1.0000	30.04	30.04	0.00	1.0000	0.4140	0

In Figs. 1-3, the experimental VLE data are presented together with those predicted using DISQUAC model; a good agreement between the data is observed.

These isotherms show that the studied systems behave differently: for the first and second mixtures, the deviations from Raoult's law are positive, while for the third mixture, the deviations from ideality are negative and large.

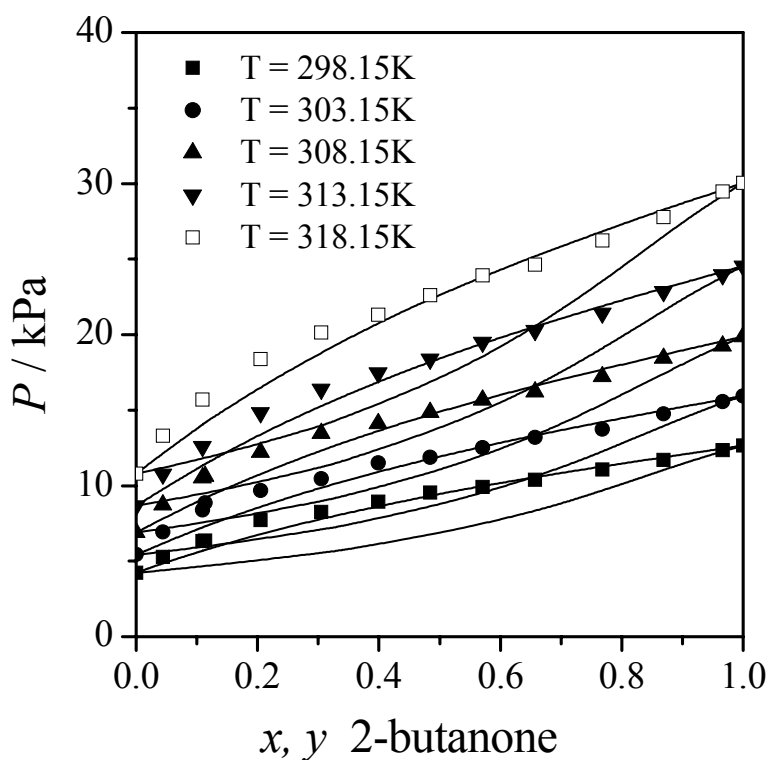


Fig. 1 – VLE diagram for 2-butanone + 1-chloropentane mixture.

The lines are predicted using the DISQUAC model; points denote experimental values.

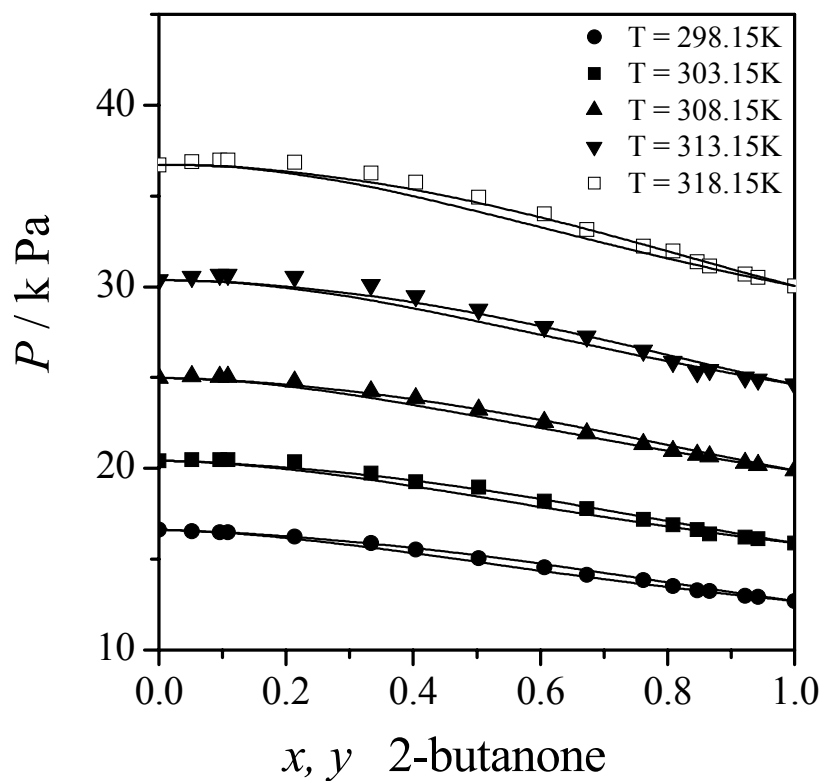


Fig. 2 – VLE diagram for 2-butanone + 1,1,1-trichloroethane mixture. The lines are predicted using the DISQUAC model; points denote experimental values.

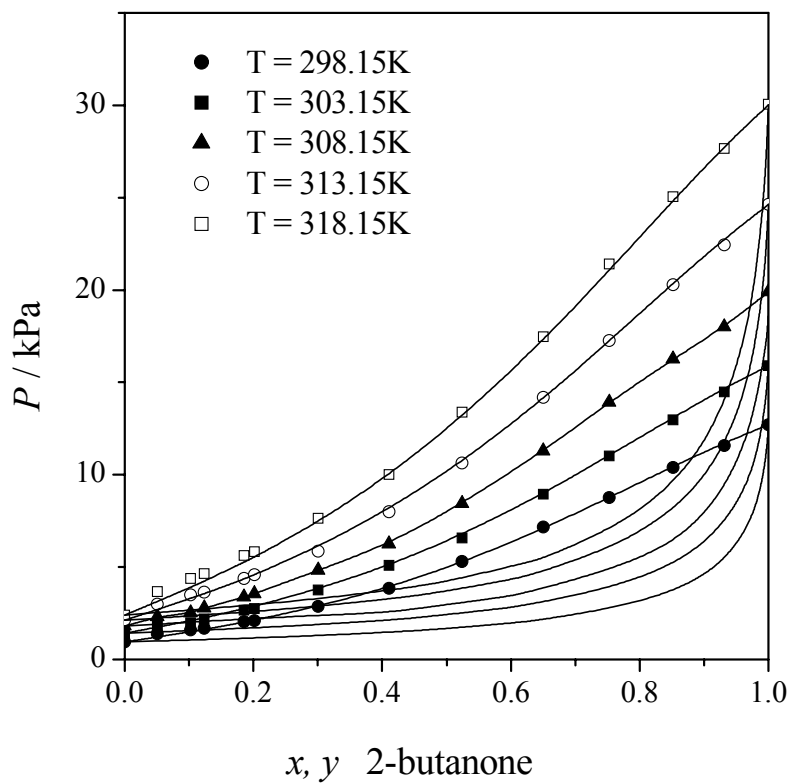


Fig. 3 – VLE diagram for 2-butanone + 1,1,2,2-tetrachloroethane mixture. The lines are predicted using the DISQUAC model; points denote experimental values.



The isothermal vapour-liquid equilibrium data of the mixtures were correlated by Barker's method<sup>23</sup> using well known equations for  $G^E$ , Redlich-Kister,<sup>8</sup> Wilson,<sup>9</sup> and NRTL.<sup>10</sup> Vapour phase imperfection was accounted for in terms of the 2<sup>nd</sup> molar virial coefficient, estimated by the method of Tsonopoulos<sup>24</sup> while the molar volumes were estimated by Rackett<sup>25</sup> equation whose coefficients were taken from Lide and Kehiaian<sup>26</sup>. Critical properties of substances were taken from Ambrose's report.<sup>27</sup> The coefficients  $A_i$  of the mentioned equations were determined by regression through minimization of the objective function  $Q$ , equation (1):

$$Q = \sum_j^N \left[ \frac{(P_{c,j} - P_{e,j})}{P_{e,j}} \right]^2 \quad (1)$$

where the subscripts  $c$  and  $e$  denote calculated and experimental values of pressure of experimental point  $j$ ,  $N$  being the total number of experimental points for one isotherm. For the mixtures under study, the standard deviation  $\sigma(P)$  values are situated between 0.03 kPa and 0.33 kPa (see Table 5).

The binary coefficients  $A_{ij}$  are  $(k_{ij} - k_{ii})$  for the Wilson equation,  $(g_{ij} - g_{ii})$  for the NRTL equation and represent energies of interactions between unlike molecules 1-2 and 2-1 (being expressed in J mol<sup>-1</sup>). For Redlich-Kister equation, they are without physical significance. The third NRTL parameter  $\alpha$ , is related to nonrandomness in the mixtures that for the studied class of systems has a fixed value of 0.3.

In the case of 2-butanone + 1,1,2,2-tetrachloroethane mixture, the correlation with the Wilson equation failed, probably due to some numerical problems in the fitting procedure.

Table 5

Parameters of the equations used to correlate VLE data for 2-butanone + 1-chloropentane, +1,1,1-trichloroethane, and + 1,1,2,2-tetrachloroethane binary mixture and the standard deviation  $\sigma(P)$  at 298.15 K; 303.15 K; 308.15K; 313.15 K; 318.15K

Equation	Parameters and $\sigma(P)$ /kPa				
	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
2-butanone + 1-chloropentane					
Redlich-Kister equation of 4 <sup>th</sup> order					
$A_1$	0.6305	0.6541	0.6378	0.6112	0.5988
$A_2$	-0.3114	-0.4266	-0.4151	-0.3548	-0.3861
$A_3$	-0.0819	-0.0221	—	—	—
$\sigma(P)$ /kPa	0.07	0.14	0.09	0.13	0.20
Wilson					
$A_1$	-97.72	-130.89	-131.43	-119.59	-143.34
$A_2$	431.59	587.70	568.51	482.85	575.30
$\sigma(P)$ /kPa	0.13	0.20	0.24	0.19	0.33
NRTL ( $\alpha = 3$ )					
$A_1$	-191.48	-235.45	-236.99	-217.55	-250.77
$A_2$	530.85	673.26	662.89	580.47	672.41
$\sigma(P)$ /kPa	0.11	0.16	0.18	0.15	0.26
2-butanone + 1,1,1-trichloroethane					
Redlich-Kister equation of 3 <sup>rd</sup> order					
$A_1$	0.0967	0.1303	0.1228	0.1553	0.1662
$A_2$	-0.1393	-0.1921	-0.1705	-0.2253	-0.1569
$\sigma(P)$ /kPa	0.04	0.05	0.04	0.05	0.03
Wilson					
$A_1$	-218.11	-234.98	-237.28	-236.44	-217.17
$A_2$	419.26	503.05	492.76	519.34	450.25
$\sigma(P)$ /kPa	0.06	0.10	0.07	0.15	0.12
NRTL ( $\alpha = 3$ )					
$A_1$	-300.80	-326.88	-325.46	-336.47	-308.10
$A_2$	491.56	576.79	558.14	607.30	534.28
$\sigma(P)$ /kPa	0.05	0.07	0.03	0.09	0.07
2-butanone + 1,1,2,2-tetrachloroethane					
Redlich-Kister equation of 4 <sup>th</sup> order					
$A_1$	-0.9919	-1.0295	-1.0057	-0.8641	-0.6900
$A_2$	-0.3269	-0.2531	-0.2446	-0.3325	-0.3733
$A_3$	0.0513	-0.0727	-0.0070	0.1045	0.1813
$\sigma(P)$ /kPa	0.08	0.09	0.08	0.15	0.11

Table 5 (continued)

NRTL ( $\alpha = 3$ )					
A <sub>1</sub>	-640.81	-664.17	-671.05	293.14	290.23
A <sub>2</sub>	1450.50	1420.69	1398.69	437.91	-431.01
$\sigma(P)$ / kPa	0.15	0.23	0.22	0.18	0.30

$\sigma(P)$ , the average standard deviation of the total vapour pressure is defined as:  $\sigma(P) = \left[ \sum (P_{\text{exp}} - P_{\text{calc}})^2 / (N - m) \right]^{1/2}$  where:  $N$  = nr. of experimental points;  $m$  = nr. of equation parameters

The equimolar excess enthalpies,  $H^E$ , estimated from the temperature dependence of  $G^E$  are: 311 J mol<sup>-1</sup>, for 2-butanone + 1-chloropentane mixture and -2965 J mol<sup>-1</sup>, for 2-butanone + 1,1,2,2-tetrachloroethane mixture at the average temperature of 308.15 K, and -8 J mol<sup>-1</sup>, for 2-butanone + 1,1,1-trichloroethane mixture at an average temperature of 305.15 K, in comparison with the values from direct calorimetric measurements of 289 mol<sup>-1</sup> at 298.15 K, for the first mixture<sup>28</sup> and of -27 J mol<sup>-1</sup> at 363.15 K, for the third mixture<sup>29</sup>, respectively. For the second mixture, there are no calorimetric values available, but we can consider for comparison, the value of -2146 J mol<sup>-1</sup> at 298.15 K for 2-propanone + 1,1,2,2-tetrachloroethane<sup>30</sup> and -2500 J mol<sup>-1</sup> for n-alkanoates + 1,1,2,2-tetrachloroethane<sup>31, 32</sup>.

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 the 2-butanone + 1,1,2,2-tetrachloroethane mixtures specific interactions take place with complex formation between the two components, due to the H-bonds.

The agreement between the estimated and the measured  $H^E$  values is reasonable, if magnification of the errors inherent in the differentiation of the Gibbs-Helmholtz equation is taken into account. Anyhow, it is well known that the calculation of excess enthalpy from vapour pressure data implies a great uncertainty<sup>33</sup>, which was also mentioned by other authors<sup>34</sup>, too.

### VLE DATA AND EXCESS THERMODYNAMIC PROPERTIES PREDICTION BY DISQUAC MODEL

The DISQUAC model describes the properties of organic mixtures in terms of surface interactions using an approach that represents extension of the quasichemical theory where each molecule is characterized by geometrical and interaction parameters. The equations used to calculate  $G^E$  and  $H^E$  and the temperature dependence of the

interaction parameters are the same as described in other papers<sup>35-39</sup> and need not to be repeated here.

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 surface 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 dispersive and quasichemical interchange coefficients  $C_{st,i}^{\text{dis}}$  and  $C_{st,i}^{\text{quac}}$ , respectively:

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

$$h_{st}^{\text{dis|quac}} / RT = C_{st,2}^{\text{dis|quac}} (298.15/T) \quad (3)$$

where  $s$  and  $t$  denote 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 ketones with chloroalkanes are regarded as possessing three types of surfaces: (I) type  $a$ , aliphatic (CH<sub>3</sub>, CH<sub>2</sub>, CH, C, which are assumed to exert the same force field), (II) type  $d$ , chloro (Cl) and (III) type  $k$ , carbonyl (CO). The three types of surfaces  $a$ ,  $d$  and  $k$  generate three pairs of contacts:  $ad$ ,  $ak$ , and  $kd$ .

The ketone-chloroalkane mixtures are generally described with use of 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  $C_{ad,1}^{\text{quac}}$ ,  $C_{ak,1}^{\text{quac}}$ ,  $C_{kd,1}^{\text{quac}}$ ,  $C_{ad,2}^{\text{quac}}$ ,  $C_{ak,2}^{\text{quac}}$ ,  $C_{kd,2}^{\text{quac}}$ .

### 1. Assessment of geometrical parameters

The total relative molecular volume,  $r_i$ , the total surfaces,  $q_i$ , and the molecular surface fractions,  $\alpha_{si}$ , for the compounds present in mixtures are usually

calculated additively on the basis of the group volumes and surfaces recommended by Bondi<sup>40</sup>, arbitrarily taking the volume and surface of methane as unity.<sup>35</sup> The geometrical parameters

of the groups appearing in the studied systems have been estimated previously<sup>41</sup> and cumulated in Ref.<sup>42, 43</sup> The geometrical parameters used in this paper are presented in Table 6.

Table 6

Total relative molecular volumes  $r_i$ , total surfaces  $q_i$  and molecular surface fractions  $\alpha_{ai}$  (groups CH<sub>3</sub>, CH<sub>2</sub>, C),  $\alpha_{di}$  (Cl groups) and  $\alpha_{ki}$  (CO group) for chloroalkanes and for 2-butanone, calculated from the group increments

Chloroalkanes	$r_i$	$q_i$	$\alpha_{ai}$	$\alpha_{di}$
1-chloropentane	3.8674	3.2138	0.8069	0.5714
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
2-ketone	$r_i$	$q_i$	$\alpha_{ai}$	$\alpha_{ki}$
2-butanone	2.8779	2.4793	0.7775	0.2225

## 2. Assessment of interchange parameters

The general procedure for the estimation of the interaction parameters has been explained in details in other papers.<sup>33-39, 41-43</sup>

DISQUAC interchange parameters for the CO-Cl contact for a great number of binary mixtures of linear ketones with 1-chloroalkanes,  $\alpha,\omega$ -dichloroalkanes and several polychloroalkanes have been already published.<sup>42</sup> 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 [CH<sub>3</sub>(CH<sub>2</sub>) <sub>$u-1$</sub> CO(CH<sub>2</sub>) <sub>$v-1$</sub> CH<sub>3</sub>] 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  $C_{kd,i}^{quac}$  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 ketone + polychloroalkane (1,1,1-trichloroethane and 1,1,2,2-tetrachloroethane) mixtures, the best description of the experimental data was found using only the dispersive contribution of the  $kd$  contact. The polychloroalkanes under study are the first members from different series according to Kehiaian and Marongiu.<sup>38</sup> The estimation of the predictive parameters for these series of chloroalkanes requires more experimental 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-alkylalkanoates.<sup>39</sup>

Table 7 lists the dispersive  $C_{st,i}^{dis}$ , and the quasichemical  $C_{st,i}^{quac}$ , interchange coefficients for all the  $st$ -contacts of the compounds referred in this paper. Using these coefficients, we predicted the VLE,  $G^E$  and  $H^E$  data that are presented in Table 8.

Table 7

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

Compounds, (contact)	Dispersive		Quasichemical		Ref.
	$C_{st,1}^{dis}$	$C_{st,2}^{dis}$	$C_{st,1}^{quac}$	$C_{st,2}^{quac}$	
chloroalkanes + n-alkanes, (contact $ad$ )	0.093 <sup>a</sup>	0.180 <sup>a</sup>	2.34 <sup>a</sup>	3.75 <sup>a</sup>	[38]
	0.026 <sup>b</sup>	0.05 <sup>b</sup>	0.203 <sup>b</sup>	0.413 <sup>b</sup>	[38]
	0.093 <sup>c</sup>	0.180 <sup>c</sup>	0.442 <sup>c</sup>	0.843 <sup>c</sup>	[38]
linear ketones + n-alkanes, (contact $ak$ )	3.25	6.16	5.35	6.35	[41]
linear ketones + chloroalkanes, (contact $kd$ )	2.57 <sup>a</sup>	2.73 <sup>a</sup>	0 <sup>a</sup>	0 <sup>a</sup>	[43]
	1.10 <sup>b</sup>	0.77 <sup>b</sup>	0 <sup>b</sup>	0 <sup>b</sup>	[43]
	-2.21 <sup>c</sup>	-6.84 <sup>c</sup>	0 <sup>c</sup>	0 <sup>c</sup>	[43]

<sup>a</sup> for 1-chloropentane; <sup>b</sup> for 1,1,1-trichloroethane; <sup>c</sup> for 1,1,2,2-tetrachloroethane

## 3. Comparison with experiment

An example of comparison between the predicted data using the estimated DISQUAC interchange parameters (shown in Table 7) with the experimental data for VLE, the equimolar excess Gibbs energy,  $G^E$  and the equimolar excess enthalpy,  $H^E$  for the studied mixtures, are

presented both in Table 8 and in Figs. 1-5. The experimental vapour pressures of these mixtures are generally well predicted by the model (Figs. 1-3). The model reproduces quite accurately our  $G^E$  values over the entire concentration range (Fig. 4). The  $H^E$  data are also satisfactorily well represented (Fig. 5).

Table 8

Excess Gibbs energy,  $G^E$ , excess enthalpy,  $H^E$  at equimolar composition and standard deviations in pressure for the 2-butanone + chloroalkane mixtures, at different temperatures, by DISQUAC model

Mixture	T(K)	N	Experimental			DISQUAC		
			$G^E_{0.5}$ J mol <sup>-1</sup>	$H^E_{0.5}$ J mol <sup>-1</sup>	$\sigma(P)$ kPa	$G^E_{0.5}$ J mol <sup>-1</sup>	$H^E_{0.5}$ J mol <sup>-1</sup>	$\sigma(P)$ kPa
2-butanone + 1-chloropentane	298.15	391		289 <sup>28</sup>	0.11	267	311	0.45
	303.15	412			0.16	267		0.73
	308.15	408			0.18	266		0.86
	308.15	398			0.15	265		0.95
	318.15	396			0.26	264		1.20
2-butanone + 1,1,1-trichloroethane	298.15	60			0.05	84		0.12
	303.15	82			0.07	86		0.17
	308.15	79			0.03	88		0.17
	313.15	101			0.09	90		0.46
	318.15	110			0.07	91		0.28
	363.15			-27 <sup>29</sup>			-36	
2-butanone + 1,1,2,2-tetrachloroethane	298.15	-615			0.15	-632		0.08
	303.15	-649			0.23	-609		0.11
	308.15	-644		-2965 <sup>a</sup>	0.22	-586	-2023	0.13
	313.15	-562			0.18	-563		0.17
	318.15	-456			0.30	-540		0.32

<sup>a</sup>estimated value from the variation of  $G^E$  with temperature

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

## CONCLUSIONS

Isothermal vapour-liquid equilibrium measurements ( $P$ - $T$ - $x$ ) for the binary systems methyl ethyl ketone (2-butanone) + 1-chloropentane, + 1,1,1-trichloroethane, + 1,1,2,2-tetrachloroethane, at temperatures from 298.15 to 318.15 K are reported. The experimental data show that the first and the second mixture have positive deviation from Raoult's law, while for the third mixture the deviations from ideality are negative and large.

The vapour pressures vs. liquid phase composition data have been used to calculate the activity coefficients of the two components, and the

excess molar Gibbs energies  $G^E$  for the mixtures, using Barker's method. The  $G^E$  values were represented by the well known Redlich-Kister, Wilson and NRTL equations. No significant difference between  $G^E$  values obtained with these equations has been observed.

We have tested the capacity for prediction of vapour-liquid equilibrium (VLE) and excess quantities ( $G^E$  and  $H^E$ ) data for the studied mixtures by the DISQUAC group contribution model. For the  $G^E$  and  $H^E$  data, as well as for the VLE data, the DISQUAC predictions are good.

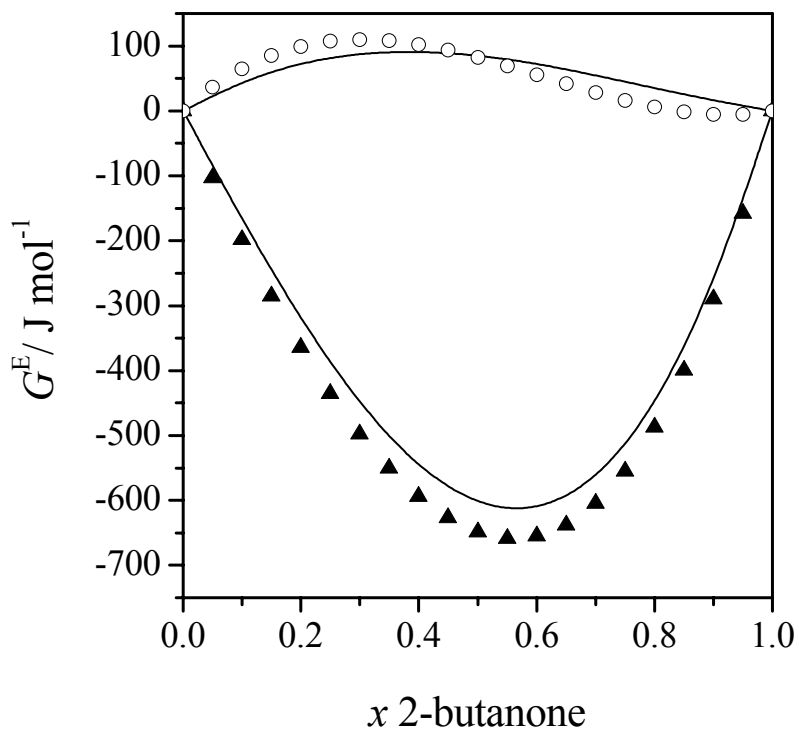


Fig. 4 – Molar excess Gibbs energy  $G^E$  at 303.15K for the mixture of 2-butanone + 1,1,1-trichloroethane (O) and 2-butanone + 1,1,2,2-tetrachloroethane ( $\blacktriangle$ ). The points denote experimental values; the lines denote calculated values using the DISQUAC model.

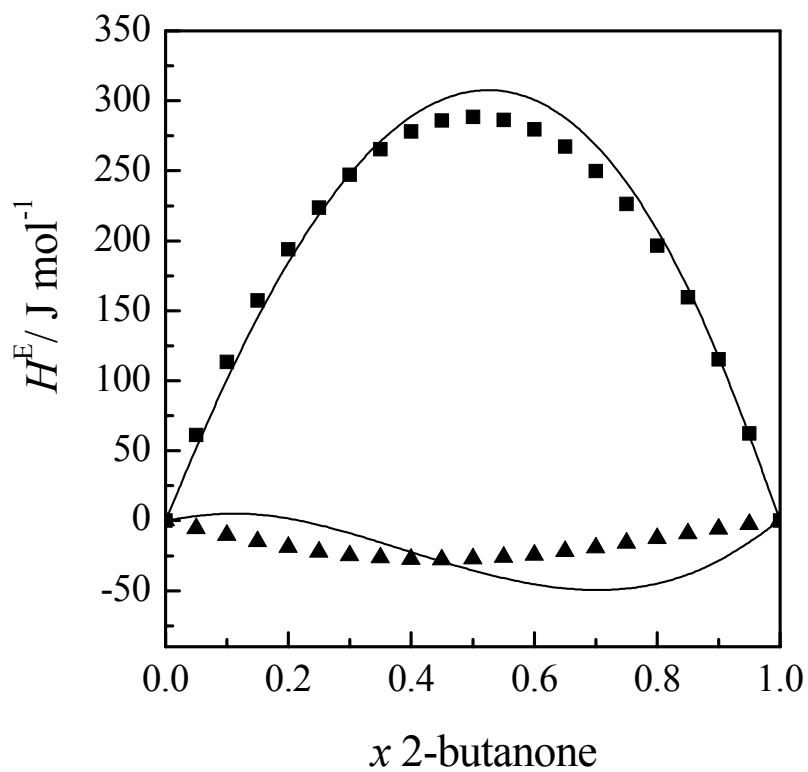


Fig. 5 – Molar excess enthalpy  $H^E$  for the mixture of 2-butanone + 1-chloropentane ( $\blacksquare$ ) at 298.15 K and 2-butanone + 1,1,1-trichloroethane ( $\blacktriangle$ ) at 363.15 K. The points denote experimental values from literature; the lines denote calculated values using the DISQUAC model.

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