

PHASE EQUILIBRIA IN 4-METHYLPENTAN-2-ONE-WATER AND 4-METHYLPENTAN-2-ONE-4-METHYLPENTAN-2-OL SYSTEMS AND THEIR THERMODYNAMIC DESCRIPTION

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Liquid-liquid equilibrium and excess enthalpies at 25, 40 and 60 °C were measured for the 4-methylpentan-2-one-water system. Vapour-liquid equilibrium at 115 °C and 99.96 kPa, and excess enthalpies at 25, 40 and 60 °C were determined for the 4-methylpentan-2-one-4-methylpentan-2-ol system. The data obtained were correlated together with those given in literature using the superposition of the Wilson and Redlich-Kister equation. The correlation procedure utilised also the data on excess enthalpy measured in a heterogeneous region.

Key words: Liquid-liquid equilibrium; Vapour-liquid equilibrium; Excess enthalpy; Ketones; 4-Methylpentan-2-one; 4-Methylpentan-2-ol; Water; Chemical thermodynamics.

In the framework of thermodynamic studies of heterogeneous systems, correlation of experimental data has been extended by the procedure employing data on excess enthalpy for a heterogeneous region¹. The reason for this approach to handling of experimental data is to bring correlation as close to the reality as possible. The systems under investigation in this work, *i.e.* 4-methylpentan-2-one-water and 4-methylpentan-2-one-4-methylpentan-2-ol, served for testing the new calculation procedure. Besides, knowledge of the thermodynamic behaviour of these systems is useful for product separation when manufacturing 4-methylpentan-2-one.

Some phase equilibrium data for the 4-methylpentan-2-one-water system exist in literature. There are data on liquid-liquid equilibrium (LLE) measured by several authors²⁻¹¹. Some of them, however, differ significantly⁸⁻¹¹. Data on vapour-liquid equilibrium (VLE) can be also found in litera-

ture^{4,5,12,13}. For the 4-methylpentan-2-one–4-methylpentan-2-ol system, a measurement of VLE has been reported¹⁴. No data on excess enthalpy for both systems have been found. Therefore, LLE in the 4-methylpentan-2-one–water system, and VLE at 99.96 kPa in the 4-methylpentan-2-one–4-methylpentan-2-ol system and excess enthalpies at 25, 40 and 60 °C in both systems were measured in this work. The data obtained together with those given in literature^{2–7} were correlated on the basis of the superposition of the Wilson equation¹⁵ and the Redlich–Kister expansion¹⁶.

THEORETICAL

For the thermodynamic description of the systems studied, a modified Wilson equation was applied in the same way as it has been already introduced¹. The modification consists of the superposition of the Wilson equation¹⁵ and the Redlich–Kister expansion¹⁶.

$$Q = \frac{G^E}{RT} = Q_{\text{Wilson}} + Q_{\text{RK}} \quad (1)$$

with

$$Q_{\text{Wilson}} = -x_1 \ln(x_1 + A_{12} x_2) - x_2 \ln(x_2 + A_{21} x_1) \quad (2)$$

$$A_{ij} = \frac{V_j}{V_i} \exp\left(-\frac{a_{ij}}{T_R}\right) \quad (3)$$

$$a_{ij} = \alpha_{ij} + \beta_{ij} T_R + \frac{\gamma_{ij}}{T_R} \quad (4)$$

$$Q_{\text{RK}} = x_1 x_2 \sum_{k=0}^r a_{12k} (x_1 - x_2)^k \quad (5)$$

$$a_{12k} = \alpha_{12k} + \beta_{12k} T_R + \frac{\gamma_{12k}}{T_R} \quad (6)$$

Equations (4) and (6) give the temperature dependence of the model parameters in a general form. For a particular system, these relations are al-

ways used with β or γ (or both) equal to zero. The character of the temperature dependence of the model parameters is determined by the sign of the molar excess heat capacity $c_{pm}^E = (\partial H^E / \partial T)_p$ for the system to be correlated (see also ref.¹⁷). The reciprocal function of temperature ($a = \alpha + \gamma/T$) is more flexible, since it can describe both systems with $c_{pm}^E > 0$ and systems with $c_{pm}^E < 0$. The other possibility, the linear temperature function ($a = \alpha + \beta T$), can be successfully used only for systems exhibiting $c_{pm}^E > 0$.

In addition, for numerical reasons, the temperature transformation was chosen so that the actual temperature T was divided by a reference temperature T_{ref} :

$$T_{\text{R}} = \frac{T}{T_{\text{ref}}} \quad (7)$$

$T_{\text{ref}} = 300$ K was applied in this paper.

To assess the corrections for nonideal behaviour of the vapour phase, the virial equation with the second virial coefficient B was employed. The compressibility factor z is given by the equation

$$z = 1 + \frac{Bp}{RT} \quad (8)$$

with

$$B = B_{11}y_1^2 + B_{22}y_2^2 + 2B_{12}y_1y_2 \quad (9)$$

The values B_{11} and B_{22} represent the second virial coefficients of pure substances. They were calculated from the relations

$$B_{11} = \alpha_{B1} + \beta_{B1}/T, \quad B_{22} = \alpha_{B2} + \beta_{B2}/T, \quad (10)$$

where α_{B1} , β_{B1} , α_{B2} and β_{B2} are constants determined from temperature dependence of the second virial coefficients of pure substances. The value B_{12} is the cross virial coefficient calculated from the relation

$$B_{12} = \text{sign}(B_{11})\sqrt{(B_{11}B_{22})} \quad (11)$$

with the condition

$$\text{sign}(B_{11}) = \text{sign}(B_{22}) \quad (12)$$

which was fulfilled for all binary systems studied in this work.

The correction of vapour nonideal behaviour is performed by means of fugacity coefficients calculated from the equation

$$\ln \Phi_i = \frac{p}{RT} \left(2 \sum_{j=1}^2 y_j B_{ij} - B \right), \quad i = 1, 2. \quad (13)$$

Fugacity coefficients are then introduced into the VLE condition

$$x_i \gamma_i f_i^* = y_i \Phi_i p, \quad i = 1, 2.$$

To calculate the model parameters, the procedure described previously¹⁸ was applied. For the description of the system 4-methylpentan-2-one–water, the experimental data on excess enthalpy in the heterogeneous region were employed as shown previously¹.

EXPERIMENTAL

Chemicals

All chemicals were supplied by Merck. 4-Methylpentan-2-one and 4-methylpentan-2-ol were “reagents for synthesis”, dried over molecular sieve A5. For LLE and VLE measurements, both substances were additionally fractionated. Water was distilled from KMnO_4 . Purities, densities and refractive indices of the reagents are summarised in Table I.

Measurements

A direct analytical method²² was used to determine LLE in the 4-methylpentan-2-one–water system. This method consisted in intensive stirring of a heterogeneous mixture at constant temperature (± 0.05 K) and then analysing samples of both liquid phases. The aqueous phase was analysed with a gas chromatograph Chrom 5 with a thermal-conductivity detector, connected to a 3 m long glass column packed with Chromosorb 101. Hydrogen was used as carrier gas with a flow rate of $40 \text{ cm}^3 \text{ min}^{-1}$. Temperature in the chromatograph oven was 180°C . The water content in the ketone phase was determined either by Fischer titration or by gas chromatography.

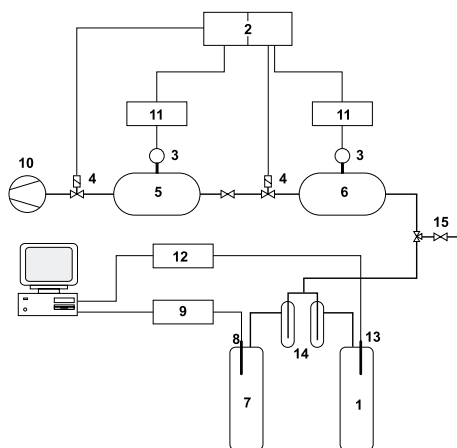
VLE in the 4-methylpentan-2-one–4-methylpentan-2-ol was measured in a modified Kay's circulation still²³. The whole apparatus is schematically shown in Fig. 1. A constant temper-

ature in the VLE still 1 was maintained by means of a self-made vacuum/pressure controller 2 connected with pressure transducers 3 and electromagnetic valves 4. The controlling system consisted of two independent units. The first controlled a forward vacuum/pressure in the reservoir 5 and the other maintained a desired vacuum/pressure in the reservoir 6 connected with the VLE still and the ebullimeter 7. The pressure set points in the controllers were adjusted manually by an operator taking into account the still temperature. The controller compared the desired value of pressure (the set point) with the actual pressure (the signal from the pressure transducer) and responded by switching the corresponding electromagnetic valve. The temperature in the VLE still was monitored by means of a PC and a calibrated platinum resistance thermometer 8. The pressure in the system was calculated (using the Antoine equation) from the boiling temperature of water. This temperature was mea-

TABLE I
Properties and purity of the compounds used

Compound	Density at 20 °C g cm ⁻³		Refractive index at 20 °C		GC purity %	Water content mass, %
	measured	literature	measured	literature		
4-Methylpentan-2-one	0.8005	0.8004 (ref. ¹⁹)	1.3972	1.3959 (ref. ¹⁹)	99.81	0.007
4-Methylpentan-2-ol	0.8067	0.8075 (ref. ²⁰)	1.4122	1.4122 (ref. ²¹)	99.75	0.002
Water	Conductivity less than $5.6 \cdot 10^{-6}$ S m ⁻¹					

FIG. 1
Schematic diagram of VLE apparatus: 1 VLE still, 2 vacuum/pressure controller, 3 pressure transducers, 4 electromagnetic valves, 5 forward vacuum/pressure reservoir, 6 vacuum/pressure reservoir, 7 ebullimeter, 8 platinum resistance thermometer, 9 resistance bridge, 10 pump, 11 display, 12 multimeter, 13 temperature sensor, 14 cooling traps, 15 air-inlet valve



sured in the ebulliometer 7 connected in parallel with a precise calibrated platinum resistance thermometer (Sensing Devices Limited) and a resistance bridge ASL F26 9. In equilibrium, the temperature fluctuations were ± 0.03 K in the VLE still and ± 0.01 K in the ebulliometer. The latter value corresponds to the pressure fluctuations of ± 32 Pa. The system was maintained in equilibrium for about 1 h and then samples of vapour and liquid phases were withdrawn with syringes for analyses, performed at 100 °C with a gas chromatograph with a 3 m long glass column packed with Chromosorb HP + 10% Carbowax 20M.

The measurements of excess enthalpies were carried out with a commercial Hart Scientific flow calorimeter and two Varian 8500 metering pumps. Details about calorimetric equipment are given elsewhere²⁴. Since the 4-methylpentan-2-one-water system exhibits a rather wide region of limited miscibility, the measurements were performed either by direct mixing pure components or by diluting a homogenous mixture with water. The mixture used in the latter procedure (designed as an initial mixture with the 4-methylpentan-2-one mole fraction, $x^{(i)} = 0.0021$) was prepared by direct mixing pure components with the pumps and the corresponding heat of mixing was determined. The composition ensured that the mixture remained homogeneous at all temperatures.

The excess enthalpy of a final mixture (obtained by diluting the initial mixture with water) was then evaluated using the formula

$$H^E(x^{(f)}) = Q^D + \frac{x^{(f)}}{x^{(i)}} H^E(x^{(i)}), \quad (15)$$

where $H^E(x^{(f)})$ and $H^E(x^{(i)})$ are excess molar enthalpies at the composition of the final mixture $x^{(f)}$ and of the initial mixture $x^{(i)}$, respectively. Q^D is the heat released by dilution and related to the total mole amount of the components.

Preliminary tests of the calorimetric apparatus were performed using the ethanol-water and tetrahydrofuran-water systems. According to the measurements, the relative accuracy of the direct excess enthalpy results is about 2%.

RESULTS AND DISCUSSION

4-Methylpentan-2-one-Water

The LLE data for the 4-methylpentan-2-one-water system are given in Table II and in Fig. 2. Solubilities of 4-methylpentan-2-one in the aqueous phase are found to be almost independent of temperature, which was confirmed by many investigators²⁻⁷. The solubility data in the ketone phase measured by different authors are rather contradictory (see Fig. 2 right). This fact shows that LLE measurements in this system require special attention. The results obtained from our measurements follow almost smooth lines lying within the other data.

Excess enthalpies of this system were measured at 25, 40 and 60 °C (Table III, Figs 3 and 4). The system exhibits a wide region of limited miscibility.

Therefore, measurements in the dilute region (at low concentrations of 4-methylpentan-2-one) were performed either by direct mixing of pure components or by the dilution method described above.

To correlate thermodynamic behaviour of the 4-methylpentan-2-one-water system, a modified Wilson equation was employed. The system required as much as seven parameters (four in the Wilson term and three in the

TABLE II
Experimental LLE data for the 4-methylpentan-2-one (1)-water (2) system and deviations of the experimental from calculated data

$t, ^\circ\text{C}$	x_1	z_1	Δx_1	Δz_1	$\Delta T, \text{K}$
0.00	0.0054	0.8969	0.0004	0.0011	0.00
20.00	0.0041	0.8896	0.0006	-0.0021	-0.01
30.00	0.0030	0.8825	0.0000	-0.0016	-0.01
40.35	0.0028	0.8710	0.0001	-0.0027	-0.03
43.20	0.0027	0.8675	0.0004	-0.0029	-0.03
50.00	0.0026	0.8600	0.0001	-0.0021	-0.03
58.30	0.0025	0.8488	0.0001	-0.0022	-0.03
60.00	0.0025	0.8383	0.0001	-0.0100	-0.14
79.00	0.0025	0.8161	0.0002	-0.0029	-0.05
90.60	0.0030	0.7953	0.0007	-0.0035	-0.06
94.50	0.0030	0.7827	0.0006	-0.0088	-0.16

FIG. 2
Liquid-liquid equilibrium for the 4-methylpentan-2-one (1)-water (2) system. ● Our experimental data; literature experimental data included in the correlation: Δ ref.², ∇ ref.³, \circ ref.⁴, \blacktriangle ref.⁵, ∇ ref.⁶, \star ref.⁷; literature data not included in the correlation: \square ref.⁸, \star ref.⁹, \blacksquare ref.¹⁰, \diamond ref.¹¹; — correlation

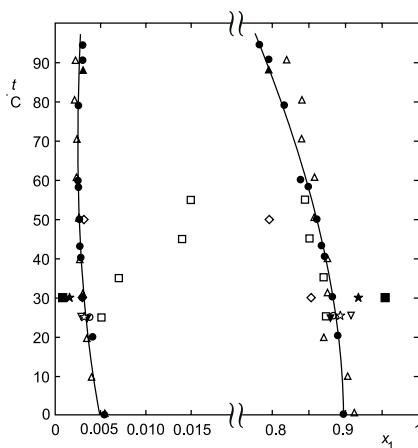


TABLE III
 Experimental data on excess enthalpies H^E (in J mol⁻¹) for the 4-methylpentan-2-one (1)-
 water (2) system

25 °C			40 °C			60 °C		
x_1	H^E	ΔH^E	x_1	H^E	ΔH^E	x_1	H^E	ΔH^E
0.0002	-1.6	0.2 ^a	0.0002	-1.2	0.1 ^a	0.0002	-0.4	0.2 ^a
0.0004	-3.4	0.1 ^a	0.0004	-2.4	0.2 ^a	0.0004	-0.5	0.7 ^a
0.0007	-6.4	-0.2	0.0007	-4.0	0.5	0.0008	-0.7	1.6 ^a
0.0008	-7.0	0.1 ^a	0.0008	-4.6	0.5 ^a	0.0010	-0.4	2.3
0.0010	-8.7	0.7 ^a	0.0010	-5.4	1.0	0.0013	-0.8	2.7 ^a
0.0010	-8.1	0.1	0.0013	-6.8	1.5 ^a	0.0015	-0.8	3.2
0.0013	-10.6	0.9 ^a	0.0015	-7.9	1.6	0.0017	-1.0	3.5 ^a
0.0015	-12.9	0.3	0.0017	-9.0	1.8 ^a	0.0019	-1.1	3.9 ^a
0.0017	-14.1	0.8 ^a	0.0019	-10.1	1.9 ^a	0.0019	-1.0	3.9
0.0021	-17.8	0.6	0.0021	-11.0	2.2	0.0021	-0.8	4.6
0.0029	-21.2	7.1 ^a	0.0024	-12.2	5.2 ^b	0.0029	-0.1	5.4 ^b
0.0060	-18.9	7.4 ^b	0.0030	-10.1	6.7 ^b	0.0059	3.0	4.4 ^b
0.0091	-17.1	7.4 ^b	0.0060	-7.9	6.1 ^b	0.0088	6.2	3.6 ^b
0.0124	-15.9	6.6 ^b	0.0091	-5.4	5.8 ^b	0.0158	14.7	2.7 ^b
0.0158	-14.2	6.1 ^b	0.0124	-2.7	5.5 ^b	0.0878	99.6	-9.9 ^b
0.0878	27.7	3.7 ^b	0.0158	0.4	5.4 ^b	0.1780	206.2	-25.4 ^b
0.1780	92.0	12.6 ^b	0.0878	60.9	-0.4 ^b	0.3660	431.9	-54.1 ^b
0.3660	217.2	22.0 ^b	0.1780	140.7	-3.7 ^b	0.5907	702.9	-87.2 ^b
0.5907	373.6	40.2 ^b	0.3660	298.6	-19.0 ^b	0.8761	1 030.7	71.6
0.8491	513.3	21.0 ^b	0.5907	503.6	-21.0 ^b	0.8949	798.9	-30.0
0.8761	515.6	-41.9	0.8761	711.8	-63.6	0.9087	702.8	-26.9
0.8949	496.3	3.5	0.8949	693.9	18.1			
0.9087	464.6	23.8	0.9087	655.0	56.4			

^a Heterogeneous region. ^b Data obtained by diluting.

Redlich–Kister term) to achieve reasonable thermodynamic description. When calculating the parameters, the data listed in Tables IV and V were used.

The solid lines in Figs 2–4 represent data on LLE and excess enthalpies modelled by the modified Wilson equation. They are a result of simultaneous correlation of LLE, VLE and excess enthalpy data. The representation of LLE and VLE is very good. The experimental data on LLE which were not included in correlation^{8–11} lie out of a trend of the other data so that they were probably erroneous. Representation of excess enthalpy data can be

TABLE IV
Pure component constants used in calculation

Compound	V $\text{cm}^3 \text{mol}^{-1}$	A^a	B^a	C^a	α_B $\text{cm}^3 \text{mol}^{-1}$	β_B $\text{cm}^3 \text{mol}^{-1} \text{K}$
4-Methylpentan-2-one	125.82	14.07841 ^b	3 103.029 ^b	212.046 ^b	3 043 ^c	-1 864 300 ^c
4-Methylpentan-2-ol	127.33	17.48113 ^d	5 007.820 ^d	257.780 ^d	4 395 ^e	-2 487 200
Water	18.07	16.26205 ^f	3 799.887 ^f	226.346 ^f	1 510 ^g	-7 583 300 ^g

^a Constants of the Antoine equation $\ln p = A - B/(t + C)$. ^b Ref.²⁵. ^c Determined from data reported by Malijevský *et al.*²⁶. ^d Ref.²⁷. ^e Data estimated using the method of McCann and Danner²⁸. ^f Ref.²⁹. ^g Determined from data reported by Dymond and Smith³⁰.

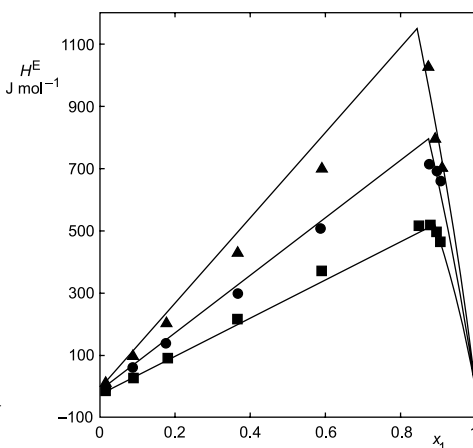


FIG. 3
Excess enthalpies for the 4-methylpentan-2-one (1)–water (2) system. Experimental data: ■ 25, ● 40, ▲ 60 °C; — correlation

TABLE V
Survey of data used for the correlation and resulting RMSD

Data type	Data range	n	Standard deviation	RMSD
4-methylpentan-2-one-water				
LLE(refs ²⁻⁷)	0-95 °C	26	$\sigma_x = 0.0005$ $\sigma_z = 0.0005$ $\sigma_T = 0.05$ K	$S_x = 0.0003$ $S_z = 0.0102$ $S_T = 0.1$ K
VLE(refs ^{4,5}) ^a	101.32 kPa 25 °C	55	$\sigma_x = 0.0005$ $\sigma_y = 0.0010$ $\sigma_T = 0.05$ K $\sigma_p = 0.02$ p	$S_x = 0.0012$ $S_y = 0.0032$ $S_T = 0.01$ K $S_p = 1.5$ kPa
H^E -(homogeneous)	25, 40, 60 °C	39	$\sigma_{H^E} = 2$ J mol ⁻¹	$S_{H^E} = 20$ J mol ⁻¹
H^E -(heterogeneous)	25, 40, 60 °C	28	$\sigma_{H^E} = 5$ J mol ⁻¹	$S_{H^E} = 23$ J mol ⁻¹
4-methylpentan-2-one-4-methylpentan-2-ol				
VLE ^b	115 °C 99.65 kPa	18	$\sigma_x = 0.0010$ $\sigma_y = 0.0010$ $\sigma_T = 0.05$ K $\sigma_p = 0.02$ p	$S_x = 0.0022$ $S_y = 0.0019$ $S_T = 0.01$ K $S_p = 0.57$ kPa
H^E	25, 40, 60 °C	57	$\sigma_{H^E} = 15$ J mol ⁻¹	$S_{H^E} = 15$ J mol ⁻¹

^a Data in ref.¹² are inaccessible. Data in ref.¹³ have not been trusted due to relatively complicated analytical procedure. Deviation in liquid mole fractions from the data given in ref.⁵ are up to $\Delta x_1 = 0.035$. ^b Data in ref.¹⁴ are inaccessible.

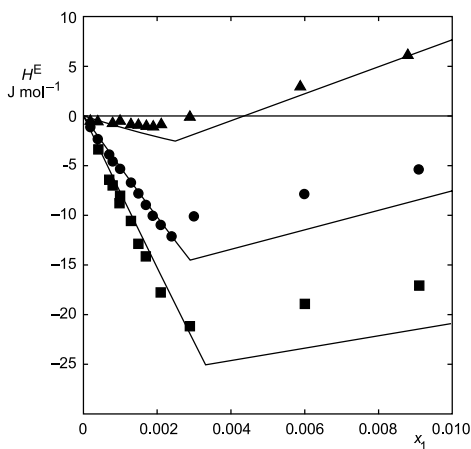


FIG. 4
Excess enthalpies for the 4-methylpentan-2-one (1)-water (2) system for low concentration of 4-methylpentan-2-one. Experimental data: ■ 25, ● 40, ▲ 60 °C; — correlation

considered also as successful in spite of slight deviations (up to -87 J mol^{-1}) of the experimental from modelled data at 60°C (see Fig. 3). The same deviations noticeable in the Fig. 4 are actually smaller than 5 J mol^{-1} . It can be pointed out that for some binary systems, simultaneous correlation of VLE and excess enthalpies by the NRTL model resulted in much higher deviation (up to 300 J mol^{-1}) for the excess enthalpy data in the heterogeneous regions³¹.

4-Methylpentan-2-one–4-Methylpentan-2-ol

Excess enthalpies for the 4-methylpentan-2-one–4-methylpentan-2-ol system were determined at 25, 40 and 60°C (Table VI and Fig. 5). To extend the experimental data for thermodynamic modelling, the VLE for this system was measured at a pressure of 99.65 kPa and at a constant temperature of 115°C . The results along with the deviations of the experimental from the calculated data are summarised in Table VII.

The thermodynamic modelling of the system by means of the modified Wilson equation did not required the Redlich–Kister term. Four parameters in the Wilson's part were sufficient enough. In this case the energy parameters were considered to be the reciprocal function of temperature. The parameters are given in Table VIII. The simultaneous correlation of the VLE and excess enthalpy fits our experimental data with good agreement.

To evaluate precision of the parameters obtained is very difficult mathematical task so that the constants in Table VIII are reported with five digits. This digit number resulted from our former empirical experience.

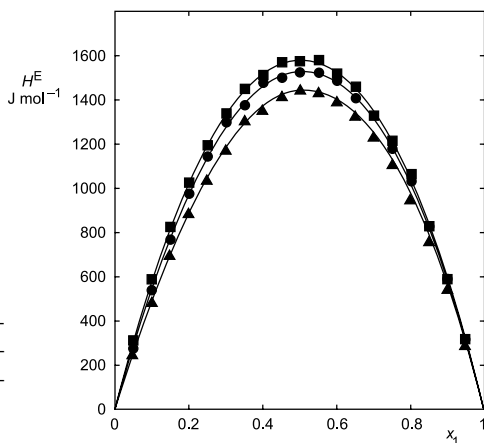


FIG. 5
Excess enthalpies for the 4-methylpentan-2-one (1)–4-methylpentan-2-ol (2) system. Experimental data: ■ 25, ● 40, ▲ 60°C ; — correlation

TABLE VI
 Experimental data on excess enthalpies H^E (in J mol⁻¹) for the 4-methylpentan-2-one (1)-
 4-methylpentan-2-ol (2) system

25 °C			40 °C			60 °C		
x_1	H^E	ΔH^E	x_1	H^E	ΔH^E	x_1	H^E	ΔH^E
0.0506	311.2	8.5	0.0506	274.3	-10.1	0.0506	246.8	-14.8
0.1012	588.7	16.5	0.1012	538.2	-1.5	0.1012	479.8	-18.5
0.1517	826.8	18.1	0.1517	766.2	0.8	0.1517	695.9	-13.3
0.2021	1 026.3	13.8	0.2021	974.8	12.9	0.2021	884.2	-10.1
0.2525	1 194.6	9.7	0.2525	1 143.5	14.2	0.2525	1 034.9	-18.6
0.3027	1 336.1	10.7	0.3027	1 297.8	30.5	0.3027	1 171.8	-14.1
0.3530	1 451.0	15.8	0.3530	1 375.1	-1.5	0.3530	1 302.6	10.5
0.4031	1 504.4	-9.5	0.4031	1 478.6	22.3	0.4031	1 349.5	-21.5
0.4532	1 569.7	7.6	0.4532	1 498.2	-8.6	0.4532	1 413.7	-8.8
0.5033	1 568.2	-11.5	0.5033	1 524.5	-3.2	0.5033	1 443.8	-2.4
0.5532	1 579.8	13.2	0.5532	1 522.3	3.6	0.5532	1 430.4	-10.9
0.6031	1 510.6	-12.2	0.6031	1 490.9	11.5	0.6031	1 388.7	-18.8
0.6530	1 459.5	11.6	0.6530	1 407.5	-2.0	0.6530	1 325.8	-18.1
0.7027	1 328.8	-13.0	0.7027	1 328.7	20.1	0.7027	1 230.7	-19.5
0.7524	1 214.6	11.0	0.7524	1 180.1	4.4	0.7524	1 104.2	-21.2
0.8021	1 060.1	27.5	0.8021	1 038.5	28.6	0.8021	945.5	-22.9
0.8517	830.2	2.2	0.8517	827.7	17.0	0.8517	754.3	-24.1
0.9012	590.6	1.9	0.9012	587.2	10.3	0.9012	539.3	-15.4
0.9506	306.6	-7.0	0.9506	315.7	8.3	0.9506	286.1	-9.7

TABLE VII
Experimental VLE data for the 4-methylpentan-2-one (1)–4-methylpentan-2-ol (2) system and the deviations of the experimental from the calculated data

x_1	y_1	t , °C	p , kPa	Δx_1	Δy_1	ΔT , K	Δp , kPa
0.0833	0.1464	115.0	61.33	-0.0003	0.0002	0.00	-0.33
0.1984	0.3125	115.0	66.33	-0.0003	0.0002	0.00	-1.07
0.2852	0.4101	115.0	70.69	0.0036	-0.0032	-0.02	-0.67
0.2947	0.4221	115.0	71.22	0.0030	-0.0027	-0.01	-0.59
0.5081	0.6421	115.0	81.02	-0.0027	0.0032	0.01	-0.16
0.5508	0.6700	115.0	82.17	-0.0012	-0.0015	-0.01	-0.61
0.7100	0.7977	115.0	88.59	-0.0009	0.0012	0.00	-0.26
0.7484	0.8267	115.0	89.60	-0.0014	0.0020	0.00	-0.64
0.0795	0.1325	129.4	99.65	-0.0044	0.0030	0.01	0.21
0.2525	0.3662	126.1	99.65	-0.0017	0.0043	0.02	0.10
0.3536	0.4755	124.2	99.65	-0.0015	0.0016	0.01	0.66
0.4219	0.5459	123.1	99.65	-0.0005	0.0016	0.01	0.34
0.4862	0.6061	121.9	99.65	-0.0005	0.0005	0.00	0.93
0.5805	0.6892	120.5	99.65	-0.0002	0.0003	0.00	0.76
0.6879	0.7750	119.0	99.65	-0.0002	-0.0003	0.00	0.63
0.7795	0.8452	117.9	99.65	-0.0005	0.0007	0.00	0.40
0.8900	0.9249	116.5	99.65	-0.0009	0.0013	0.00	0.43
0.9607	0.9737	115.7	99.65	-0.0006	0.0009	0.00	0.35

TABLE VIII

Parameters of the modified Wilson equation. The values calculated for the 4-methylpentan-2-one (1)–water (2) and 4-methylpentan-2-one (1)–4-methylpentan-2-ol (2) systems

4-methylpentan-2-one–water	4-methylpentan-2-one–4-methylpentan-2-ol
$\alpha_{12} = -7.600^a$	$\alpha_{12} = -1.5366$
$\beta_{12} = 6.9914$	$\gamma_{12} = 1.7184$
$\alpha_{21} = 4.4187$	$\alpha_{21} = 0.05248$
$\beta_{21} = -2.4176$	$\gamma_{21} = 0.52251$
$\alpha_{120} = 2.4940$	
$\alpha_{121} = -1.3187$	
$\alpha_{122} = 0.52732$	

^a In preliminary calculations, this parameter value was found by way of trial. In the final phase of parameter determination, the value was fixed in order to improve the calculation stability.

CONCLUSION

Liquid–liquid equilibrium and excess enthalpies at 25, 40 and 60 °C were measured for the 4-methylpentan-2-one–water system. Vapour–liquid equilibrium at 115 °C and 99.96 kPa and excess enthalpies at 25, 40 and 60 °C were determined for the 4-methylpentan-2-one–4-methylpentan-2-ol system. Thermodynamic description of these systems is given using a modified Wilson equation. The procedure for parameter calculation also employed data on the excess enthalpy for the 4-methylpentan-2-one–water system measured in the heterogeneous region. The correlation results confirmed the applicability of the calculation procedure introduced previously¹. Parameters of this model were evaluated using our experimental data together with the data taken from literature. The model describes the system with fairly good agreement.

SYMBOLS

a_j	temperature-dependent parameters of the Wilson equation; Eq. (4)
a_{jk}	temperature-dependent parameters of the Redlich–Kister equation; Eq. (6)
A_j	temperature-dependent parameters of the Wilson equation; Eqs (2), (3)
A, B, C	constants of the Antoine equation $\ln p^0 = A - B/(t + C)$
B	the second virial coefficient, $\text{cm}^3 \text{mol}^{-1}$; Eq. (9)
B_{11}, B_{22}	the second virial coefficients of pure compounds, $\text{cm}^3 \text{mol}^{-1}$; Eqs (10)

B_{12}	the second cross virial coefficient, $\text{cm}^3 \text{mol}^{-1}$; Eq. (11)
c_{pm}^E	molar excess heat capacity, $\text{J mol}^{-1} \text{K}^{-1}$
f_i^*	standard fugacity of the i -th compound in the liquid phase
G^E	excess Gibbs energy, J mol^{-1}
H^E	excess enthalpy, J mol^{-1}
n	number of experimental points
p	total pressure, kPa
p^0	vapour pressure of pure component, kPa
Q	dimensionless excess Gibbs energy; Eq. (1)
Q^D	heat of dilution, J mol^{-1}
$Q_{\text{Wilson}}, Q_{\text{RK}}$	contribution to Q based on the Wilson and Redlich–Kister equations; Eqs (2), (5)
r	number of terms in the Redlich–Kister equation
R	gas constant, $\text{J mol}^{-1} \text{K}^{-1}$
S_v	root mean square deviation (RMSD) of the variable v ,

$$S_v = \sqrt{\sum_{i=1}^n (v_{\text{exp}} - v_{\text{calc}})_i^2 / n}$$

t	temperature, $^{\circ}\text{C}$
T	temperature, K
T_R	reduced temperature; Eq. (7)
T_{ref}	reference temperature, K ($T_{\text{ref}} = 300 \text{ K}$ in this paper)
V_i	molar volume of the i -th liquid component, $\text{cm}^3 \text{mol}^{-1}$; Eq. (3)
x_i	mole fraction of the i -th component in liquid phase, $i = 1, 2$
$x^{(i)}, x^{(f)}$	composition of the initial and final mixtures; Eq. (15)
y_i	mole fraction of the i -th component in vapour phase, $i = 1, 2$
z	compressibility factor
z_1	mole fraction of component 1 in liquid phase
$\alpha_{ij}, \beta_{ij}, \gamma_{ij}$	temperature-independent parameters of the Wilson equation; Eq. (4)
$\alpha_{ijk}, \beta_{ijk}, \gamma_{ijk}$	temperature-independent parameters of the Redlich–Kister equation; Eq. (6)
α_{B1}, α_{B2}	parameters of temperature dependence of the second virial coefficients of pure substances, $\text{cm}^3 \text{mol}^{-1}$; Eqs (10)
β_{B1}, β_{B2}	parameters of temperature dependence of the second virial coefficients of pure substances, $\text{cm}^3 \text{mol}^{-1} \text{K}$; Eqs (10)
Δ	deviation of an experimental value from a calculated value of variable v , $\Delta = v_{\text{exp}} - v_{\text{calc}}$
Φ_i	fugacity coefficient of the i -th compound; Eq. (13)
γ_i	activity coefficient of the i -th compound; Eq. (13)
σ_{v_i}	estimated error of experimental data (standard deviation) of the variable v_i

Abbreviations

LLE	liquid–liquid equilibrium
VLE	vapour–liquid equilibrium
RMSD	root mean square deviation

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REFERENCES

1. Řehák K., Novák J. P., Konetzná J., Heintz A., Voňka P., Matouš J.: *Collect. Czech. Chem. Commun.* **1999**, *64*, 1393.
2. Stephenson R. M.: *J. Chem. Eng. Data* **1992**, *37*, 80.
3. Hlavatý K., Linek J.: *Collect. Czech. Chem. Commun.* **1973**, *38*, 374.
4. Gaube J., Krenzer L., Olf G., Wendel R.: *Fluid Phase Equilib.* **1987**, *35*, 279.
5. Cho T. H., Ochi K., Kojima K.: *Fluid Phase Equilib.* **1983**, *11*, 137.
6. Sherwood T. K., Evans J. E., Longcor J. V. A.: *Ind. Eng. Chem.* **1939**, *39*, 1144.
7. Regna E. A., Bruins P. F.: *Ind. Eng. Chem.* **1956**, *48*, 1268.
8. Arce A., Blanco A., Souza P., Vidal I.: *J. Chem. Eng. Data* **1993**, *38*, 201.
9. Narasimham K. S., Reddy C. C., Chari K. S.: *J. Chem. Eng. Data* **1962**, *7*, 457.
10. Rao D. S., Rao K. V., Prasad A. R., Chiranjivi C.: *J. Chem. Eng. Data* **1979**, *24*, 241.
11. Rajapakse N., Finston H. L., Fried V.: *J. Chem. Eng. Data* **1986**, *31*, 408.
12. Yokoyama K., Nakamura S., Ohe S.: *Ishikawajima-Harima Giho* **1970**, *10(3)*, 217; *Chem. Abstr.* **1970**, *73*, 78939.
13. Rawat B., Krishna S.: *J. Chem. Eng. Data* **1984**, *29*, 403.
14. Lu S., Wang Y., Xu K.: *Gaoxiao Huaxue Gongcheng Xuebao* **1989**, *3(1)*, 9; *Chem. Abstr.* **1991**, *114*, 109602.
15. Wilson G. M.: *J. Am. Chem. Soc.* **1964**, *86*, 127.
16. Redlich O., Kister A. T.: *Ind. Eng. Chem.* **1984**, *40*, 345.
17. Malijevská I., Malijevský A.: *Collect. Czech. Chem. Commun.* **1999**, *64*, 1093.
18. Voňka P., Novák J. P., Matouš J.: *Collect. Czech. Chem. Commun.* **1989**, *54*, 2823.
19. Linek J., Wichterle I.: *Collect. Czech. Chem. Commun.* **1973**, *38*, 1846.
20. Henne A. L., Matuszak A. H.: *J. Am. Chem. Soc.* **1944**, *66*, 1649.
21. Bartok M.: *Acta Phys. Chem.* **1974**, *20*, 443.
22. Novák J. P., Matouš J., Pick J.: *Liquid-Liquid Equilibria*, p. 276. Elsevier, Amsterdam 1987.
23. Kay W. B.: *AIChE J.* **1979**, *25*, 179.
24. Bender M., Hauser J., Heintz A.: *Ber. Bunsen-Ges. Phys. Chem.* **1991**, *95*, 801.
25. Ambrose D., Ghiasee N. B., Tuckerman R.: *J. Chem. Thermodyn.* **1988**, *20*, 767.
26. Malijevský A., Majer V., Vondrák P., Tekáč V.: *Fluid Phase Equilib.* **1986**, *28*, 283.
27. Gmehling J., Onken U., Weidlich U.: *Vapor-Liquid Equilibrium Data Collection (Supplement 2). Chemistry Data Series, Vol. I, Part 2d.* DECHEMA, Frankfurt/Main 1982.
28. McCann D. W., Danner R. P.: *Ind. Eng. Chem. Process Des. Dev.* **1984**, *23*, 529.
29. Boublík T., Fried V., Hála E.: *The Vapour Pressures of Pure Substances.* Elsevier, Amsterdam 1984.
30. Dymond J. H., Smith E. B.: *The Virial Coefficients of Gases.* Clarendon Press, Oxford 1980.
31. de Haan A. B., Heine A., Fischer K., Gmehling J.: *J. Chem. Eng. Data* **1995**, *40*, 1228.