



Vapour–liquid equilibria, azeotropic data, excess enthalpies, activity coefficients at infinite dilution and solid–liquid equilibria for binary alcohol–ketone systems

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ABSTRACT

Isothermal vapour–liquid equilibria (VLE), solid–liquid equilibria and excess enthalpies have been measured for the systems cyclohexanone+cyclohexanol and 2-octanone+1-hexanol. Additionally in this paper binary azeotropic data at different pressures for 1-pentanol+2-heptanone and 1-hexanol+2-octanone have been determined with the help of a wire band column. Furthermore activity coefficients at infinite dilution for methanol, ethanol, 1-butanol and 1-propanol in 2-octanone at different temperatures have been measured with the help of the dilutor technique. These data together with literature data for alcohol–ketone systems were used to fit temperature-dependent group interaction parameters for the group contribution method modified UNIFAC (Dortmund) and the group contribution equation of state VTPR.

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1. Introduction

The group contribution method modified UNIFAC (Dortmund) [1] and the group contribution equation of state VTPR [2] are continuously revised and extended because of their importance for the synthesis and design of chemical processes. The required group interaction parameters of these models are fitted simultaneously to a comprehensive data base with reliable experimental information, e.g. vapour–liquid equilibria (VLE), solid–liquid equilibria of eutectic systems (SLE), activity coefficients at infinite dilution (γ^∞), excess enthalpies (H^E) and azeotropic data (AZD). While solid–liquid equilibria (SLE) of eutectic systems provide supporting information at low temperatures, H^E data provide reliable information about the temperature dependence and at 140 °C supporting data at high temperatures. VLE and azeotropic data are most important to get reliable information about the composition dependence of the activity coefficients. Activity coefficients at infinite dilution deliver the required information in the dilute composition range [1,3].

2. Experimental

2.1. Chemicals

All the chemicals used in this work were distilled and dried over molecular sieve. The water content was less than 100 ppm. The purities of these chemicals were better than 99.8%. For VLE measurements, the chemicals were distilled and degassed. The chemicals used including their purity are summarized in Table 1.

2.2. Measurement of SLE

Solid–liquid equilibria are important for the design of crystallization processes. Moreover, SLE data for the required eutectic systems are important for fitting temperature-dependent g^E model [4] and group interaction parameters for UNIFAC or modified UNIFAC or the group contribution equation of state VTPR [2]. The experimental data in this work and the reliable experimental data stored in the Dortmund Data Bank (DDB) [5] were used to fit simultaneously the group interaction parameters between the keton- and the alcohol group with the help of a non-linear regression method.

SLE data in this work were measured with the visual technique [6]. The equilibrium cell of this equipment consists of a three-jacket vessel made of glass. The exterior vacuum jacket is evacuated in order to prevent condensation of water on the glass surface at low temperature. The cryostat medium flows through the central jacket

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Table 1
Some physico-chemical data from literature for the chemicals used

Compound	Melting point (K)	Purity (%)	Water content (ppm)
1-Hexanol	229.15	>99.8	90.6
2-Octanone	253.41	>99.9	75.5
Methanol	175.25	>99.8	80.3
Ethanol	158.65	>99.8	65.6
Cyclohexanone	242	>99.9	40.5
Cyclohexanol	298.61	>99.9	70.3
1-Propanol	147.05	>99.8	56.4
1-Butanol	183.35	>99.8	30.8
1-Pentanol	194.25	>99.9	50.1
2-Heptanone	237.65	>99.8	55.7

and transfers the heat to the equilibrium cell. The temperature is measured with a platinum resistance thermometer. The accuracy of the melting temperature is determined to be ± 0.05 K and the accuracy of the composition is ± 0.005 in mole fraction. Measurements can be carried out between 190 and 290 K.

The obtained experimental solid–liquid equilibrium data for the two binary systems 1-hexanol + 2-octanone and cyclohexanone + cyclohexanol are listed in Table 2.

2.3. Measurement of azeotropic data

The knowledge of azeotropic data as a function of pressure or temperature is of great importance for the synthesis and design of distillation processes [7] and the selection of suitable solvents for azeotropic distillation. At the same time azeotropic data are of importance for fitting reliable model parameters.

Azeotropic data were measured with the help of a commercially available micro-spinning band column [8]. With this apparatus azeotropic points up to 3.5 bar can be measured. A nitrogen reservoir, with a pressure of ~ 5 bar can be used for measurements at higher pressures. A vacuum pump is used to work below atmospheric pressures.

During the experiments, the temperature was measured with the help of a resistance thermometer with an accuracy of ± 0.1 K and the pressure by means of a sensor (Druck Limited, type PDRC) with an accuracy of ± 0.05 kPa. A more detailed description of the apparatus is given by Gmehling and Böltz [8]. The composition of the azeotropic mixture was measured with the help of gas–liquid chromatography. The experimental data obtained for 1-hexanol + 2-octanone and 1-pentanol + 2-heptanone are listed in Table 3.

Table 2
Experimental SLE data, temperature T (K) as a function of the mole fraction x_1^L , for binary alcohol + ketone systems

T (K)	x_1^L	T (K)	x_1^L	T (K)	x_1^L
1-Hexanol (1) + 2-octanone (2)					
253.4	0.000	247.9	0.350	241.1	0.700
252.7	0.053	247	0.402	239.4	0.750
251.9	0.102	246.4	0.450	237.7	0.799
251	0.153	245.6	0.499	234.5	0.847
250.3	0.201	244.8	0.550	229.7	0.898
249.5	0.250	243.7	0.598	226.7	0.947
248.7	0.301	242.9	0.650	229	1.000
Cyclohexanone (1) + cyclohexanol (2)					
297.2	0.000	273.7	0.350	258	0.699
293.7	0.048	271.2	0.400	255.9	0.750
289.4	0.103	268.8	0.450	253.5	0.802
286.6	0.152	267.3	0.502	251.4	0.853
282.8	0.202	264.1	0.550	249.2	0.903
279.7	0.250	260.7	0.618	247.1	0.953
276.6	0.301	259.7	0.649	245.9	1.000

Table 3
Experimental azeotropic data for the binary alcohol + ketone systems

T (K)	P (mbar)	$y_{1, az}$
1-Hexanol (1) + 2-octanone (2)		
430.95	1033.9	0.901
379.25	159.3	0.782
321.75	9.65	0.496
1-Pentanol (1) + 2-heptanone (2)		
409.7	1009.55	0.938
350	127.5	0.524
314.35	15.85	0.281

Table 4
Infinite dilution activity coefficients for different alcohols in 2-octanone

Solvent	Solute	T (K)	γ^∞	T (K)	γ^∞
2-Octanone	Methanol	303.17	3.14	323.16	2.78
		313.15	2.95	333.18	2.62
2-Octanone	Ethanol	303.15	3.27	323.14	2.87
		313.16	3.07	333.15	2.73
2-Octanone	1-Propanol	303.15	3.31	323.15	2.94
		313.16	3.08	333.16	2.80
2-Octanone	1-Butanol	303.14	3.30	323.17	3.10
		313.15	3.19	333.15	3.00

2.4. Measurement of activity coefficients at infinite dilution

Activity coefficients at infinite dilution deliver the required information for the selection of selective solvents, to improve the knowledge of the phase equilibrium behavior and for the proper

Table 5
Experimental H^E data for binary alcohol + ketone systems at 363.15 and 413.15 K

H^E (J/mol)	x_1	H^E (J/mol)	x_1	H^E (J/mol)	x_1
Cyclohexanone (1) + cyclohexanol (2) at $T = 363.15$ K and $P = 16.51$ bar					
272.1	0.051	1344.9	0.406	1019.6	0.754
520.5	0.102	1378.8	0.456	869.8	0.803
733.9	0.153	1395.8	0.506	688.1	0.853
919.5	0.204	1370.7	0.555	482.3	0.902
1068.6	0.254	1323.5	0.605	249.1	0.951
1191.3	0.305	1250.1	0.655		
1282.8	0.355	1148.9	0.705		
Cyclohexanone (1) + cyclohexanol (2) at $T = 413.15$ K and $P = 15.82$ bar					
162.5	0.051	831.5	0.405	620.7	0.754
311.1	0.102	852.3	0.455	526.2	0.803
443.7	0.153	863.2	0.505	412	0.853
561.3	0.203	846.4	0.555	284.9	0.902
656.7	0.254	816.5	0.605	146.3	0.951
732.7	0.304	766	0.655		
794.3	0.355	701.4	0.704		
1-Hexanol (1) + 2-octanone (2) at 363.15 K and $P = 16.17$ bar					
342.6	0.062	1440.9	0.455	947.8	0.79
635.1	0.122	1445	0.506	793.1	0.833
878	0.181	1427.4	0.557	618.3	0.876
1073.6	0.238	1369.4	0.605	427.2	0.918
1221.4	0.294	1297.3	0.652	219.8	0.96
1333.2	0.349	1202.7	0.699		
1403	0.402	1084.4	0.745		
1-Hexanol (1) + 2-octanone (2) at 413.15 K and $P = 16.17$ bar					
247	0.062	1121.7	0.455	758.3	0.79
467.8	0.122	1134.5	0.506	636.7	0.833
655.1	0.181	1126.2	0.556	501.5	0.876
812.2	0.238	1086.1	0.605	350.8	0.918
927.6	0.294	1032.7	0.652	179.7	0.96
1022.3	0.349	960.2	0.699		
1083.2	0.402	863.6	0.745		

Table 6
Experimental P-x data for cyclohexanone (1)+cyclohexanol (2) at 323.15 K

P (kPa)	x_1	P (kPa)	x_1	P (kPa)	x_1	P (kPa)	x_1
0.555	0.0000	0.803	0.110	1.282	0.507	1.638	0.943
0.561	0.0011	0.854	0.141	1.330	0.548	1.648	0.960
0.571	0.0032	0.913	0.181	1.363	0.599	1.657	0.974
0.58	0.0056	0.972	0.223	1.402	0.647	1.662	0.983
0.592	0.0092	1.031	0.269	1.441	0.694	1.671	0.998
0.606	0.0138	1.088	0.316	1.48	0.740	1.672	0.999
0.621	0.0198	1.143	0.364	1.516	0.785	1.673	1.000
0.644	0.0287	1.194	0.412	1.551	0.827		
0.674	0.0425	1.243	0.440	1.581	0.865		
0.711	0.0602	1.244	0.464	1.605	0.895		
0.754	0.0827	1.288	0.505	1.622	0.922		

Table 7
Experimental P-x data for cyclohexanone (1)+cyclohexanol (2) at 363.15 K

P (kPa)	x_1	P (kPa)	x_1	P (kPa)	x_1	P (kPa)	x_1
5.162	0.0000	6.076	0.110	8.148	0.507	9.598	0.943
5.185	0.0012	6.280	0.141	8.297	0.552	9.649	0.960
5.224	0.0035	6.524	0.180	8.453	0.599	9.695	0.973
5.257	0.0061	6.770	0.223	8.610	0.647	9.721	0.982
5.301	0.0100	7.028	0.269	8.766	0.694	9.740	0.988
5.344	0.0140	7.274	0.316	8.922	0.740	9.752	0.991
5.406	0.0198	7.512	0.364	9.074	0.785	9.764	0.995
5.484	0.0290	7.739	0.412	9.214	0.826	9.775	0.998
5.596	0.0427	7.954	0.459	9.343	0.864	9.778	0.999
5.731	0.0604	8.007	0.464	9.441	0.895	9.786	1.000
5.891	0.0828	8.155	0.505	9.527	0.921		

Table 8
Experimental P-x data for 1-hexanol (1)+2-octanone (2) at 323.15 K

P (kPa)	x_1	P (kPa)	x_1	P (kPa)	x_1	P (kPa)	x_1
0.653	0.0000	0.695	0.131	0.685	0.688	0.558	0.983
0.656	0.0015	0.701	0.168	0.672	0.732	0.554	0.988
0.657	0.0030	0.707	0.213	0.659	0.774	0.551	0.991
0.659	0.0065	0.712	0.261	0.644	0.813	0.548	0.994
0.661	0.0100	0.713	0.311	0.629	0.850	0.545	0.997
0.664	0.0151	0.715	0.362	0.614	0.882	0.542	0.999
0.666	0.0227	0.717	0.413	0.601	0.909	0.542	1.000
0.669	0.0338	0.715	0.463	0.589	0.931		
0.674	0.0507	0.713	0.511	0.577	0.949		
0.681	0.0722	0.711	0.556	0.570	0.964		
0.688	0.0991	0.696	0.644	0.563	0.975		

Table 9
Experimental P-x data for 1-hexanol (1)+2-octanone (2) at 363.15 K

P (kPa)	x_1	P (kPa)	x_1	P (kPa)	x_1	P (kPa)	x_1
4.798	0.0000	5.161	0.131	5.730	0.600	5.489	0.963
4.801	0.0015	5.244	0.168	5.727	0.644	5.469	0.974
4.808	0.0030	5.335	0.213	5.715	0.689	5.457	0.982
4.820	0.0065	5.423	0.261	5.698	0.732	5.448	0.987
4.831	0.0100	5.501	0.311	5.679	0.774	5.439	0.991
4.848	0.0152	5.570	0.363	5.654	0.813	5.433	0.994
4.872	0.0228	5.628	0.413	5.625	0.849	5.426	0.997
4.905	0.0339	5.677	0.463	5.596	0.882	5.426	0.999
4.956	0.0508	5.714	0.511	5.565	0.908	5.422	1.000
5.014	0.0722	5.713	0.513	5.537	0.930		
5.083	0.0992	5.726	0.556	5.511	0.949		

design of separation processes. In particular reliable γ^∞ information can avoid over-sizing of distillation columns. In addition, these data are required for fitting reliable parameters for mod. UNIFAC [1,4] and VTPR [2,9] and can be used for the selection of selective solvents for extractive distillation.

In this work, the dilutor technique was used to determine activity coefficient at infinite dilution for various alcohols in 2-octanone. The accuracy of the temperature is determined to be ± 0.05 K. The relative error for the measurements carried out using the dilutor technique is approximately $\pm 2.5\%$. More details about the dilutor technique and the measurement procedure have been published by Krummen et al. [10]. The experimental γ^∞ data obtained for the four binary systems methanol in 2-octanone, ethanol in 2-octanone, 1-propanol in 2-octanone and 1-butanol in 2-octanone are listed in Table 4. In all cases the γ^∞ values decrease with increasing temperature.

2.5. Measurement of excess enthalpies

The knowledge of excess enthalpies is of great interest, because they deliver the required information for fitting temperature-dependent parameters. In this work, excess enthalpies were determined for two alcohol–ketone systems at two temperatures, with the help of a commercially available isothermal flow calorimeter. The experimental procedure was described in detail in [11]. The temperature of the thermostat is measured with a Hart Scientific platinum resistance calibrated thermometer with an accuracy of ± 0.05 K [11].

In Table 5 the experimental excess enthalpies are listed for the systems cyclohexanone (1)+cyclohexanol (2) and 1-hexanol (1)+2-octanone (2) at different temperatures.

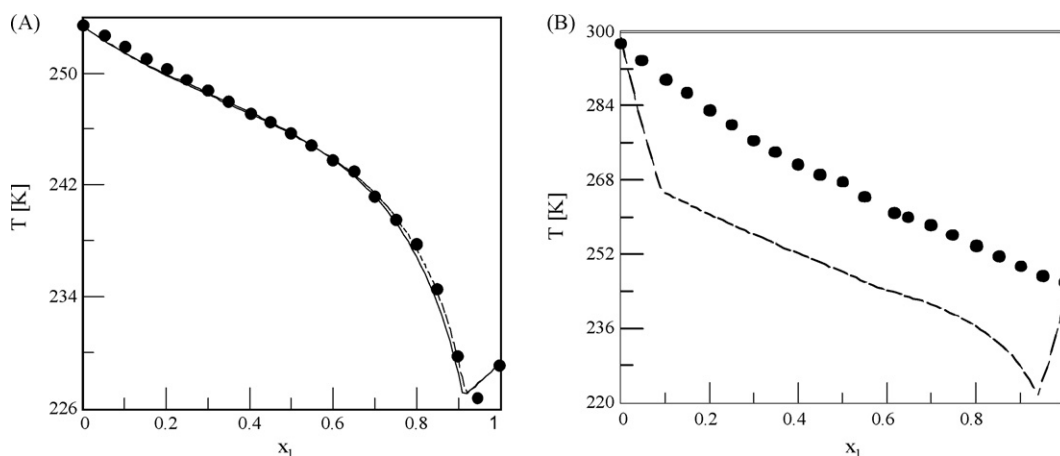


Fig. 1. Experimental and predicted SLE data for alcohol + ketone systems. (A) solid–liquid equilibria for 1-hexanol + 2-octanone. (B) Solid–liquid equilibria for cyclohexanone (1)+cyclohexanol (2) assuming eutectic behavior, and (●) experimental data. (---) Published mod. UNIFAC parameters. (—) New mod. UNIFAC parameters.

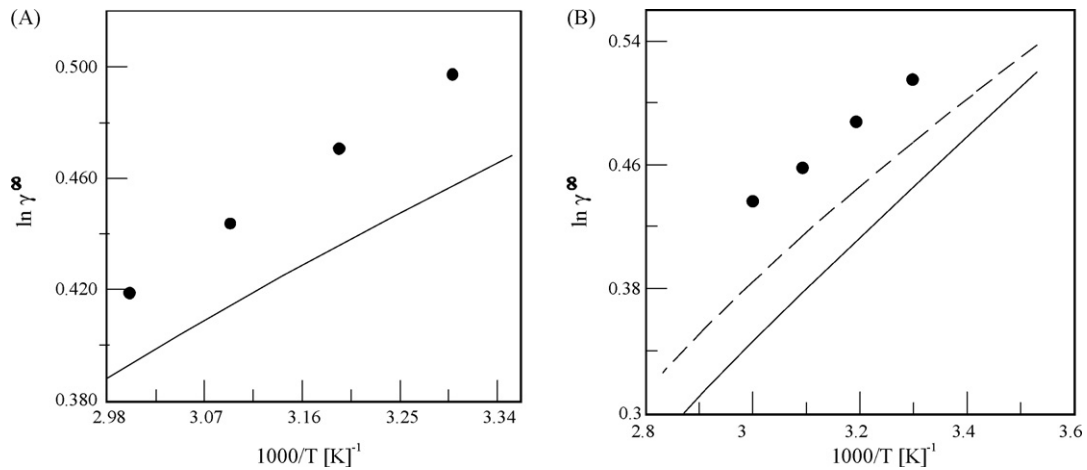


Fig. 2. Experimental and predicted activity coefficient at infinite dilution for alcohol+ketone systems. (A) Methanol in 2-octanone. (B) Ethanol in 2-octanone. (---) Published mod. UNIFAC parameters. (—) New mod. UNIFAC parameters.

2.6. Measurement of vapour–liquid equilibria (VLE)

For the extensions of thermodynamic models (g^E models, equation of state, and group contribution methods), a reliable knowledge of the phase equilibrium behavior is required. Hence, VLE data are of particular importance, isothermal P-x data were measured with a computer driven static apparatus. The degassed,

purified and thermostated compounds are charged into the evacuated measurement cell. The cell is kept at constant temperature using a thermostatic oil bath. With the help of a Digiquartz pressure sensor, the pressure is monitored (model 245A, Paroscientific). The temperature is measured with a Pt100 resistance thermometer. The compositions of the system can be determined from known quantities of the liquids injected into the equilibrium cell

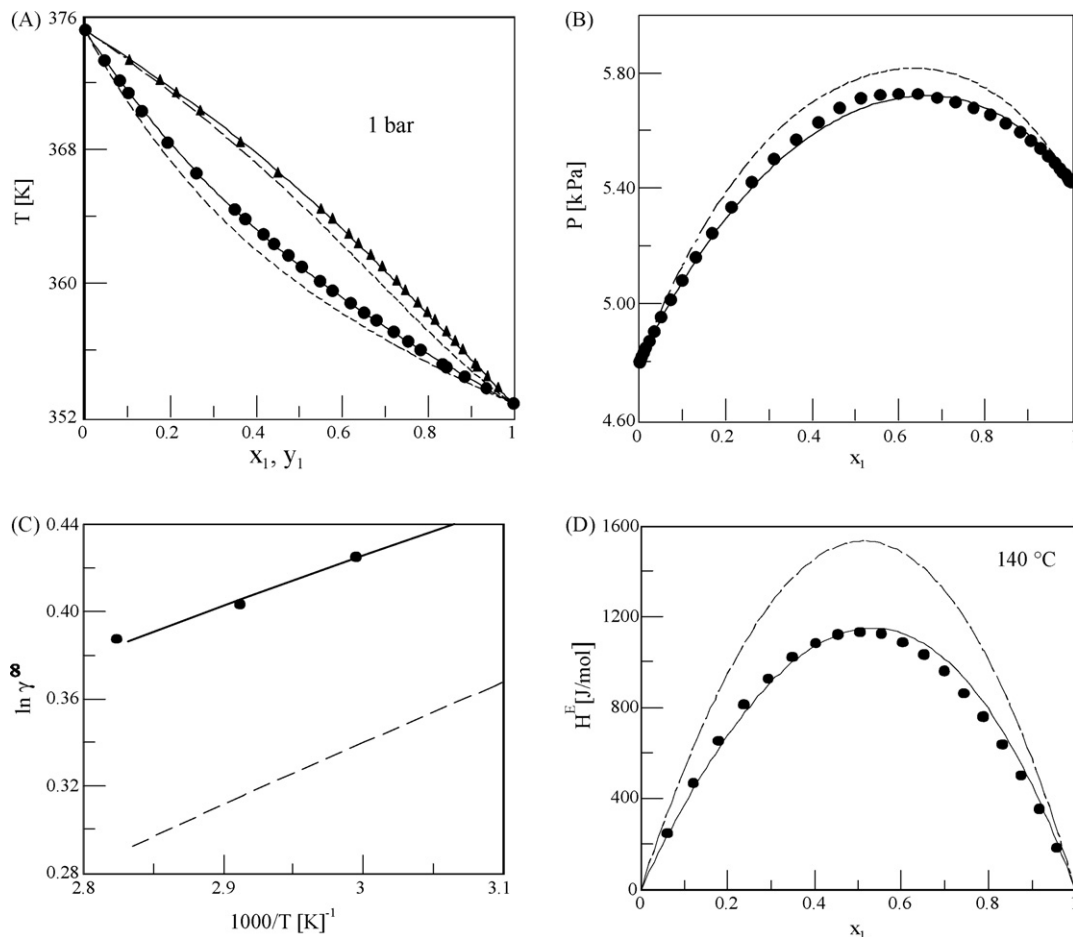


Fig. 3. Experimental and predicted mixture properties for alcohol+ketone systems. (A) Vapour–liquid equilibria for 2-butanone (1)+tert-pentanol (2) [15]. (B) Vapour–liquid equilibria for 1-hexanol+2-octanone at 363.15 K. (C) Activity coefficients at infinite dilution for 2-butanone in 1,6-hexanediol [16]. (D) Excess enthalpies for 1-hexanol+2-octanone. (●, ▲, and ◆) Experimental data. (---) Published mod. UNIFAC parameters. (—) New modified UNIFAC parameters.

(feed composition) taking into account the amount evaporated. All measurements were performed at low temperature (low system pressure). At this low pressure, the calculated liquid phase composition is nearly identical to the feed composition within ± 0.0005 . The experimental uncertainties of this device are as follows: $\sigma(T) = 0.03$ K, $\sigma(P) = (20 \text{ Pa}) + 0.0001 (P \text{ (Pa)})$, $\sigma(x_i) = 0.0001$. More details about the computer driven static apparatus and the measurement procedure can be found in [12,13]. The VLE data

measured are given in Tables 6–9 for the systems cyclohexanone (1) + cyclohexanol (2) and 1-hexanol (1) + 2-octanone (2) at different temperatures.

3. Results and discussion

In Fig. 1 a comparison of the measured SLE data and the results of mod. UNIFAC for the system 1-hexanol + 2-octanone are shown.

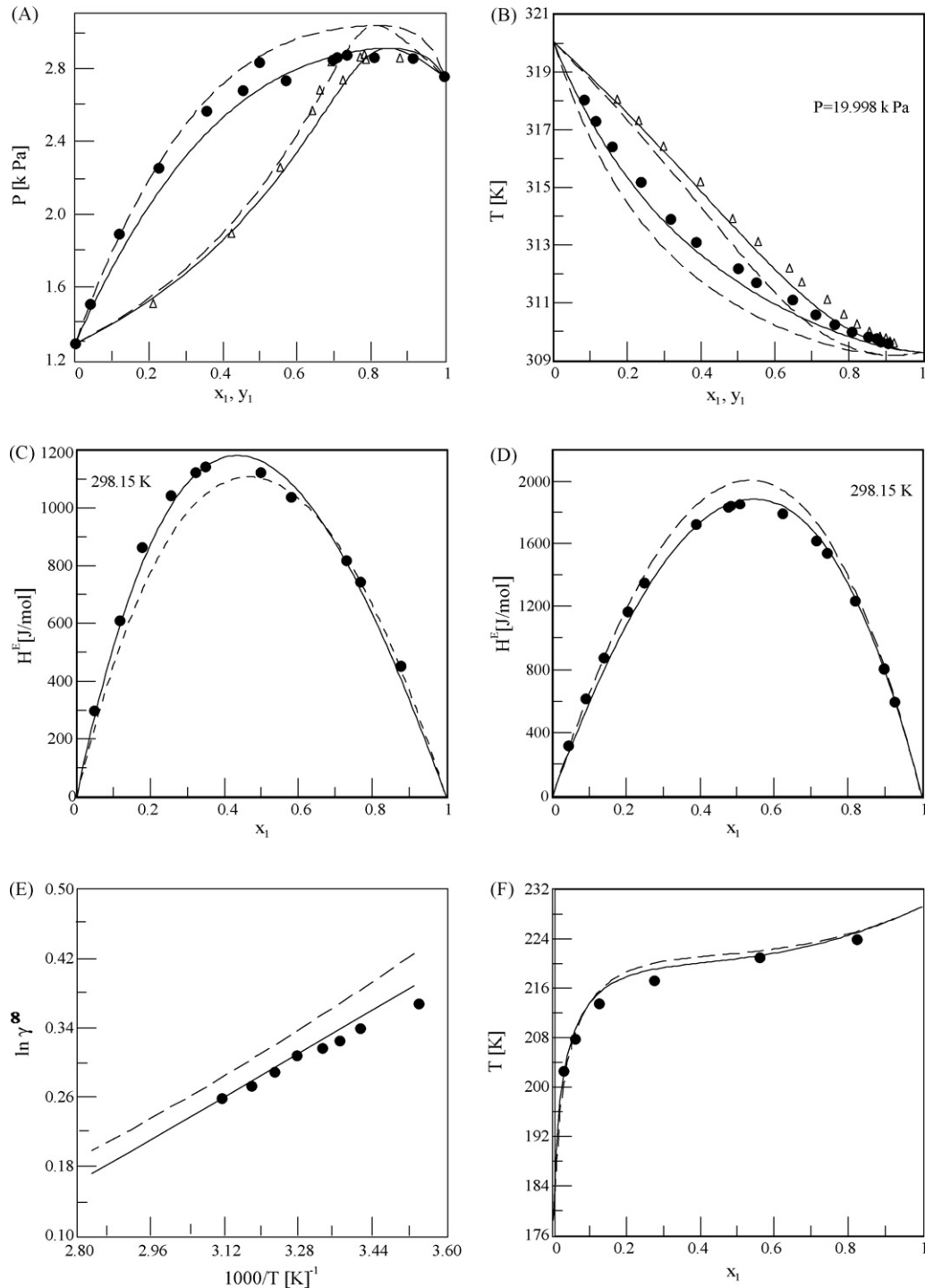


Fig. 4. Experimental and predicted mixture properties for alcohol + ketone systems. (A) Vapour–liquid equilibria for 1-propanol + 2,4-pentanedione [17]. (B) Vapour–liquid equilibria for 2-butanone + *tert*-butanol [18]. (C) Excess enthalpies for 1-propanol + 4-heptanone [19]. (D) Excess enthalpies for 2-butanone + 1-decanol [20]. (E) Activity coefficients at infinite dilution for acetone in 1-butanol [21]. (F) Solid–liquid equilibria for 1-hexanol + acetone [22] (● and ▲) experimental data. (---) Published mod. UNIFAC parameters. (—) Fitted mod. UNIFAC parameters.

Table 10
Group interaction parameters for modified UNIFAC (Dortmund)

n/m	a_{nm} (K)	b_{nm}	c_{nm} (K ⁻¹)	a_{mn} (K)	b_{mn}	c_{mn} (K ⁻¹)
Alcohol/ketone	-68.502	0.8252	-0.0015	821.59	-1.7539	0.0001

Table 11
Group interaction parameter for the VTPR equation

n	m	a_{nm} (K)	b_{nm}	a_{mn} (K)	b_{mn}
Alcohol	Ketone	495.39	-1.1522	244.66	-0.12527

While excellent agreement between the predicted and experimental data is achieved, poor results are obtained for the system cyclohexanone (1)+cyclohexanol (2). The reason is that, for the prediction of the SLE data using mod. UNIFAC eutectic behavior was assumed. But as can be seen from the experimental data, the system cyclohexanone + cyclohexanol obviously does not show eutectic behavior.

Fig. 2A shows a comparison of the experimental activity coefficients at infinite dilution for methanol in 2-octanone system measured in this work and the values predicted with the parameters already published for mod. UNIFAC. The deviations between the predicted and experimental data are acceptable. In Fig. 2B a comparison between the predicted and the experimental data for the system ethanol in 2-octanone are presented. In this case the

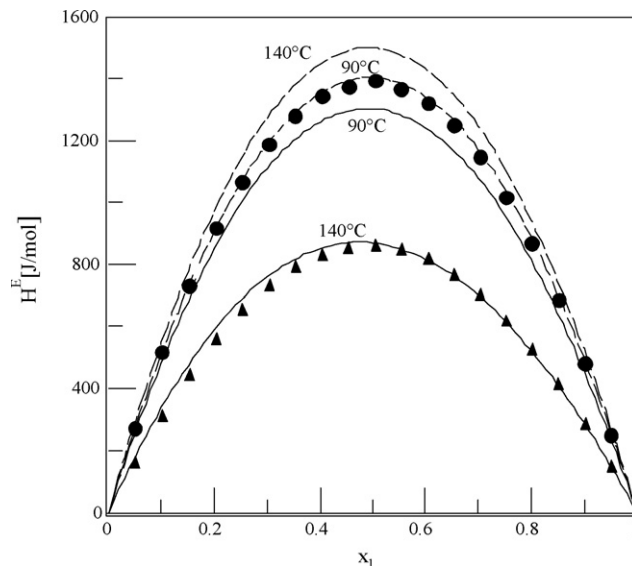


Fig. 5. Experimental and predicted excess enthalpies for alcohol + ketone systems. (---) Mod. UNIFAC old parameters for cyclohexanone (1)+cyclohexanol (2). (—) Mod. UNIFAC new parameters for cyclohexanone (1)+cyclohexanol (2). (●) Experimental data at 90 °C. (▲) Experimental data at 140 °C.

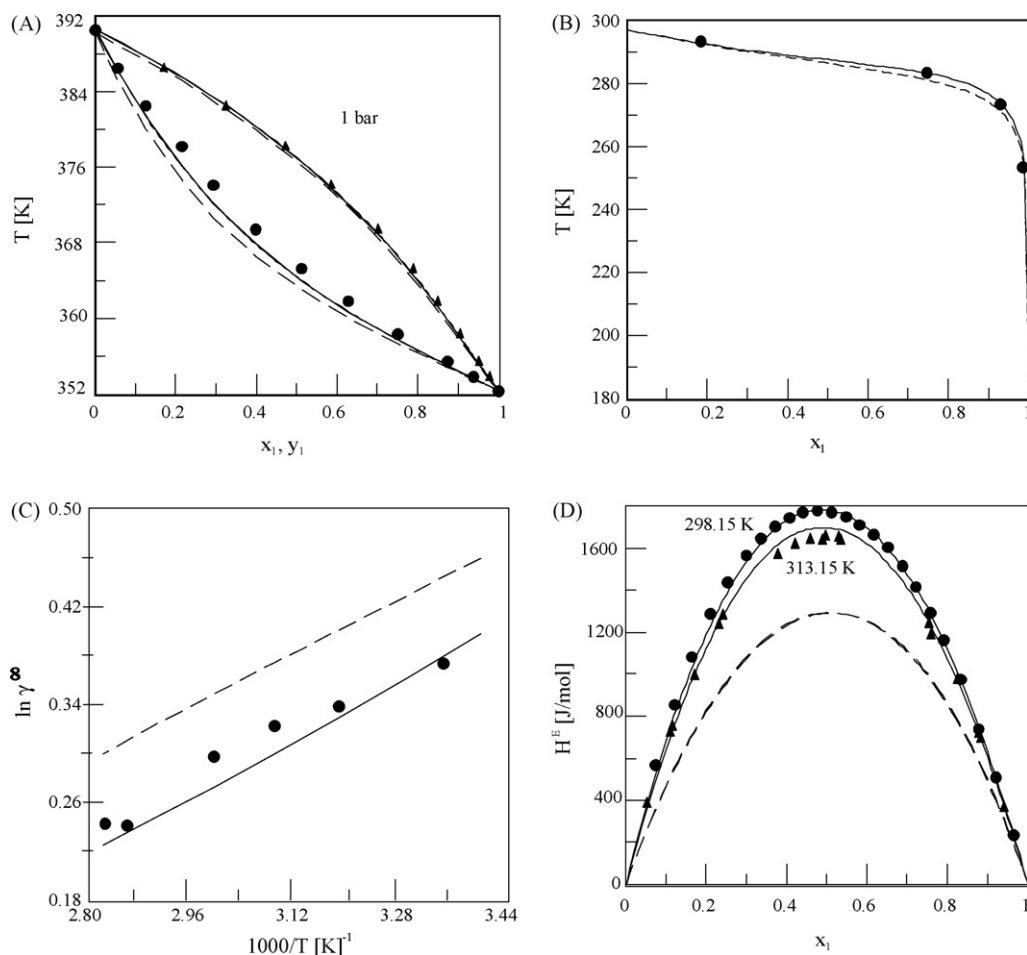


Fig. 6. Experimental and predicted mixture properties for alcohol + ketone systems. (A) Vapour-liquid equilibria for 2-butanone (1)+1-butanol (2) [23]. (B) Solid-liquid equilibria for 2-butanone (1)+1-dodecanol (2) [24]. (C) Activity coefficients at infinite dilution for ethanol in 2-butanone [25–28]. (D) Excess enthalpies for 2-butanone (1)+2-butanol (2) [29,30]. (●) Experimental data. (---) Mod. UNIFAC. (—) VTPR.

prediction using the already published parameters shows a slightly better description of the experimental data than the new ones.

Most of the data measured in this work together with the data stored in the Dortmund Data Bank [5] have been used for fitting the group interaction parameters of the group contribution method modified UNIFAC with the help of a sophisticated software program package connected to the DDB. Seven types of thermody-

namic mixture data (VLE, H^E , C_p^E , LLE, SLE, AZD, γ^∞) are used in the fitting procedure of modified UNIFAC. In the case of the VTPR equation, four type of thermodynamic mixture properties (VLE, H^E , SLE, γ^∞) are used to determine the group interaction parameters for alcohol–ketone systems. More about the fitting procedure can be found in [14]. The parameters obtained for mod. UNIFAC are listed in Table 10.

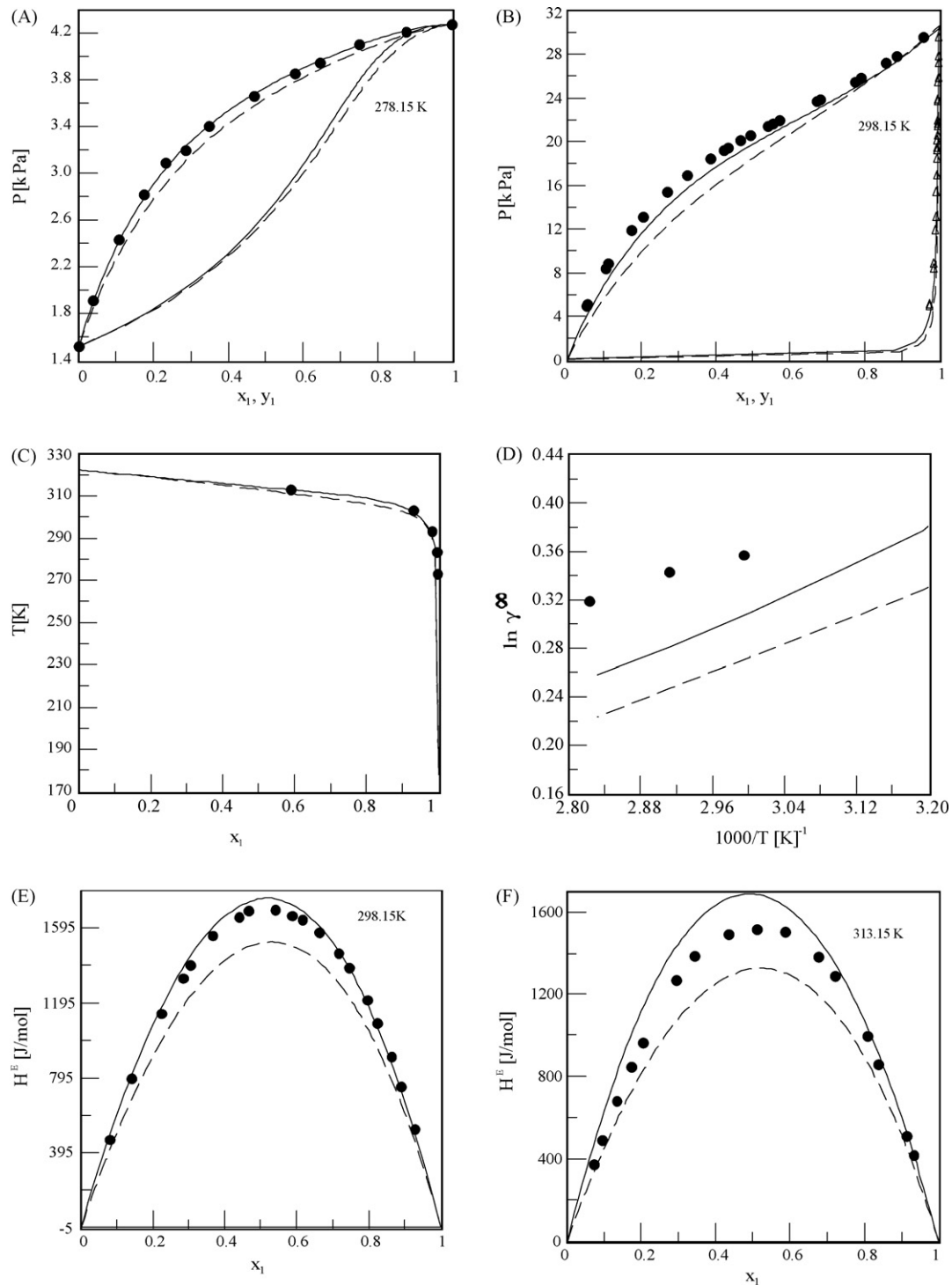


Fig. 7. Experimental and predicted mixture properties for alcohol + ketone systems. (A) Vapour–liquid equilibria for 2-butanone (1)+2-propanol (2) [31]. (B) Vapour–liquid equilibria for acetone (1)+cyclohexanol (2) [32]. (C) Solid–liquid equilibria for acetone (1)+tetradecanol (2) [33]. (D) Activity coefficients at infinite dilution for acetone in 1, 6-hexanediol [34]. (E) Excess enthalpies for 2-hexanone (1)+1-decanol (2) [35]. (F) Excess enthalpies for 2-butanone (1)+*tert*-butanol (2) [36]. (●) Experimental data. (---) Mod. UNIFAC. (–) VTPR.

Fig. 3 shows a comparison of the experimental and the predicted data with the help of mod. UNIFAC using the published temperature-dependent interaction parameters and the new ones for alcohol + ketone systems. Figs. 3B and 4A–B show that a significantly better description of the vapour–liquid equilibria (VLE) is obtained with the help of the new parameters. From Figs. 3C–D and 4C–F it can be seen that a slightly better description for different alcohol–ketone systems is achieved with the help of the new parameters.

In Fig. 5, results are presented for cyclohexanone + cyclohexanol. It can be seen that the new parameters lead to a slightly better description of the excess enthalpies. Moreover, the temperature dependence of the excess enthalpies for this system is predicted correctly with the help of the new parameters. In Table 11 the fitted temperature-dependent interaction parameters of VTPR are listed. Figs. 6 and 7 show a comparison between predicted data using VTPR equation and mod. UNIFAC. These figure show that better results are obtained using VTPR for binary alcohol + ketone systems than for mod. UNIFAC.

4. Conclusion

Using the new experimental data together with data stored in the Dortmund Data Bank temperature-dependent group interaction parameters for alcohol–ketone systems were fitted simultaneously for the group contribution method mod. UNIFAC, and the group contribution equation of state VTPR.

In all cases good agreement between the experimental and calculated values using modified UNIFAC interaction parameters fitted in this work is obtained. Using the new temperature-dependent group interaction parameters for mod. UNIFAC, the description of the thermodynamic mixture properties is a little more accurate than with the published parameters. Using the group contribution equation of state VTPR, better results than for mod. UNIFAC are achieved for alcohol + ketone systems.

List of symbols

a_{nm}	temperature independent group interaction parameter
ACT	activity coefficient at infinite dilution
AZD	azeotropic data
b_{nm}	linear temperature-dependent group interaction parameter
c_{nm}	quadratic temperature-dependent group interaction parameter
DDB	Dortmund Data Bank
H^E	excess enthalpy
m, n	main group m, n
P	pressure
SLE	solid–liquid equilibrium
T	absolute temperature

VTPR	volume translated Peng–Robinson equation of state
VLE	vapour–liquid equilibrium
x	liquid phase mole fraction
y	vapour phase mole fraction

Greek letter

γ^∞	activity coefficient at infinite dilution
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