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Vapor–liquid equilibria of the binary mixtures of tetrahydrofuran with 2,2,4-trimethylpentane, methylcyclohexane and *n*-heptane at 101.3 kPa

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Abstract

Vapor–liquid equilibrium (VLE) data have been measured at 101.3 kPa for three binary mixtures of tetrahydrofuran with 2,2,4-trimethylpentane, methylcyclohexane and *n*-heptane. The isobaric *T*–*x*–*y* data have been reported and the thermodynamic consistency has been examined. The non-ideal behavior of the vapor phase has been considered by using the Soave–Redlich–Kwong (SRK) equation of state in calculating the fugacity coefficient. The Wilson, NRTL and UNIQUAC activity coefficient models have been employed to correlate the experimental VLE data. The correlation results are satisfactory and the optimally fitted binary parameters of various activity coefficient models are presented. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Vapor–liquid equilibria; Mixture; Data

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1. Introduction

The experimental data of vapor–liquid equilibrium (VLE) are essential to the design of chemical and separation processes. VLE data have been measured in our laboratory [1,2] for binary and ternary systems. The VLE data for three binary mixtures of tetrahydrofuran with 2,2,4-trimethylpentane, methylcyclohexane and *n*-heptane have been measured at 101.3 kPa in this study. The VLE data for the binary system of tetrahydrofuran + *n*-heptane at 94 kPa have been shown by Wisniak et al. [3]. To our knowledge, no isobaric experimental data at 101.3 kPa of these mixtures have been presented in literature. Binary and ternary VLE data for tetrahydrofuran with other components at either isothermal or isobaric conditions have also been presented previously [4–8]. An all-glass recirculating still has been employed in the experiment, and the equilibrium temperatures and compositions of the coexisting vapor and liquid phases

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have been measured. Various thermodynamic consistency tests have been examined for the measured results. The experimental data have also been correlated using various activity coefficient models.

2. Experimental

2.1. Chemicals

All the chemicals were high-purity grade purchased from the Merck. These chemicals were used without further purification. No detectable impurity was observed in the gas chromatography (GC) analyses. The purity of all chemicals was better than 99.8 mass%. The pure fluid properties were measured in this study, and the comparison with literature data is shown in Table 1. The refractive indices of the pure components were measured at 293.15 ± 0.1 K by an Abbe refractometer, Atago 3T (Japan), with an accuracy of ±0.0001. The densities of the pure components were measured at 293.15 ± 0.01 K using an Anton Paar DMA 60/602 density meter (Austria) with an accuracy of $\pm 1.0 \times 10^{-5}$ g cm^{-3}.

2.2. Apparatus and procedures

The apparatus used was an all-glass recirculating still described by Paul [9]. The equipment has a side-heating unit, which ensures complete mixing of the liquid mixtures. This design also prevents liquid droplet entrainment and partial condensation of the vapor phase. A digital quartz thermometer (DMT-610, Tokyo Electrical, Japan), with an accuracy of ±0.01 K, was used to measure the equilibrium temperatures. A mercury barometer was used to measure the pressure of the system. The slight oscillation of the pressure was observed with a dibutyl phthalate manometer. The experimental temperatures were taken at this constant pressure of 101.3 kPa. The accuracy of the pressure control was within ±0.05%.

In each experiment, the liquid mixture was heated in the recirculating still at a fixed pressure of 101.3 kPa. Equilibrium was usually reached after 1 h, when the temperatures of the liquid and vapor phases were constant and their difference was within ±0.02 K. Small amount of samples of the equilibrium phases were then taken and analysed in a GC.

A Shimadzu GC, type 8A, equipped with a thermal conductivity detector, was used to determine the compositions of the equilibrium phases. The GC was calibrated with solutions of known compositions for

Table 1
Comparison of the measured normal boiling temperatures (T_b), refractive indices (n_D (at 293.15 K)), and densities (ρ (at 293.15 K)) of pure fluids in this work with literature data [20]

Component	T_b (K)		n_D		ρ (g cm^{-3})		GC purity
	Experimental	Literature	Experimental	Literature	Experimental	Literature	(mass%)
Tetrahydrofuran	339.12	339.12	1.4064	1.4071	0.8875	0.8867	>99.9
2,2,4-Trimethylpentane	372.33	372.38	1.3902	1.3914	0.6920	0.6920	>99.9
Methylcyclohexane	374.02	374.09	1.4229	1.4231	0.7695	0.7694	>99.8
n-Heptane	371.51	371.57	1.3872	1.3876	0.6843	0.6838	>99.9

each binary mixture that were prepared gravimetrically. The relationship between the peak area and the composition was determined for each binary mixture. The GC column was made of a 3 m length stainless steel tube of 3 mm diameter. The column was packed with Porapak Q. The temperature of the injection port of the GC was maintained at 493 K. The oven temperature of the GC was 463 K. The carrier gas was helium with a purity of 99.9% and a flow rate of 30 $\mathrm{cm}^3\,\mathrm{min}^{-1}$. The GC response peaks were integrated using a Shimadzu C-R3A integrator. At least four analyses were made for each liquid and vapor sample, respectively. With these repeated procedures, the accuracy of equilibrium composition measurement was within ±0.001 mol fraction.

3. Results and discussion

The VLE data for three binary mixtures of tetrahydrofuran with 2,2,4-trimethylpentane, methylcyclohexane and *n*-heptane, have been measured at 101.3 kPa in this study. The results are shown in Tables 2–4, respectively. The liquid phase activity coefficients γ_i were calculated by the classical equation

$$\gamma_i = \frac{\hat{\phi}_i y_i P}{x_i P_i^{\mathrm{sat}} \phi_i^{\mathrm{sat}} \exp[V_i^{\mathrm{L}}(P - P_i^{\mathrm{sat}})/RT]} \tag{1}$$

where ϕ_i^{sat} is the fugacity coefficient of pure component i in its saturated state; $\hat{\phi}_i$ the fugacity coefficient of component i in the vapor mixture, and x and y are the equilibrium mole fractions in the liquid and vapor phases, respectively. The saturated vapor pressure is denoted by P^{sat}, and V^{L} is the saturated liquid molar volume.

Table 2
Experimental VLE data for tetrahydrofuran(1) + 2,2,4-trimethylpentane(2) at 101.3 kPa

T (K)	x_1	y_1	γ_1	γ_2
372.33	0.0000	0.0000		1.0000
368.01	0.0471	0.1580	1.4394	1.0005
366.89	0.0639	0.1991	1.3788	1.0008
365.89	0.0764	0.2314	1.3758	1.0024
364.08	0.1016	0.2879	1.3514	1.0072
362.37	0.1303	0.3434	1.3168	1.0099
361.25	0.1506	0.3799	1.3001	1.0102
360.78	0.1595	0.3945	1.2914	1.0113
359.11	0.1881	0.4414	1.2837	1.0163
356.19	0.2503	0.5268	1.2507	1.0212
354.75	0.2831	0.5659	1.2382	1.0253
351.65	0.3648	0.6481	1.2049	1.0362
348.44	0.4670	0.7266	1.1621	1.0659
346.41	0.5376	0.7721	1.1406	1.0965
344.78	0.6193	0.8154	1.0994	1.1400
342.88	0.7234	0.8653	1.0601	1.2219
340.34	0.9036	0.9492	1.0091	1.4449
339.42	0.9769	0.9876	1.0002	1.5229
339.12	1.0000	1.0000	1.0000	–

Table 3
Experimental VLE data for tetrahydrofuran(1) + methylcyclohexane(2) at 101.3 kPa

T (K)	x_1	y_1	γ_1	γ_2
374.02	0.0000	0.0000		1.0000
372.71	0.0128	0.0508	1.4620	1.0000
371.64	0.0247	0.0909	1.4069	0.9999
369.72	0.0460	0.1578	1.3951	1.0000
368.94	0.0556	0.1852	1.3809	1.0002
367.33	0.0759	0.2374	1.3637	1.0008
365.56	0.1008	0.2956	1.3417	1.0008
363.35	0.1313	0.3604	1.3352	1.0040
361.22	0.1624	0.4207	1.3345	1.0070
359.33	0.1995	0.4748	1.2952	1.0103
357.92	0.2232	0.5110	1.2939	1.0148
356.94	0.2471	0.5372	1.2650	1.0215
355.55	0.2739	0.5732	1.2642	1.0235
354.72	0.2970	0.5939	1.2392	1.0304
352.95	0.3404	0.6393	1.2253	1.0326
350.44	0.4251	0.7010	1.1590	1.0656
348.87	0.4784	0.7362	1.1335	1.0914
347.22	0.5443	0.7759	1.1041	1.1212
345.77	0.6060	0.8090	1.0809	1.1606
344.55	0.6652	0.8408	1.0629	1.1865
343.28	0.7358	0.8724	1.0375	1.2584
342.33	0.7900	0.8990	1.0260	1.2952
341.40	0.8502	0.9269	1.0123	1.3581
340.62	0.9022	0.9509	1.0032	1.4369
340.12	0.9354	0.9676	1.0006	1.4606
339.50	0.9738	0.9868	1.0000	1.5016
339.12	1.0000	1.0000	1.0000	–

The fugacity coefficient was calculated using the Soave–Redlich–Kwong (SRK) equation of state [10]

$$P = \frac{RT}{v-b} - \frac{a\alpha(T)}{v(v+b)} \tag{2}$$

$$a = 0.42748\frac{R^2{T_c}^2}{P_c} \tag{3}$$

$$b = 0.08664\frac{RT_c}{P_c} \tag{4}$$

$$\alpha(T) = [1 + (0.48 + 1.574\omega - 0.176\omega^2)(1 - T_r^{0.5})]^2 \tag{5}$$

The simple van der Waals mixing rules were used to evaluate the mixture parameters

$$a_m = \sum\sum y_i y_j (a_i a_j)^{0.5} \tag{6}$$

$$b_m = \sum y_i b_i \tag{7}$$

Table 4
Experimental VLE data for tetrahydrofuran(1) + n-heptane(2) at 101.3 kPa

T (K)	x_1	y_1	γ_1	γ_2
371.51	0.0000	0.0000		1.0000
370.16	0.0136	0.0503	1.4993	1.0028
368.46	0.0331	0.1131	1.4477	1.0049
365.56	0.0722	0.2199	1.3957	1.0050
363.73	0.1001	0.2843	1.3672	1.0056
361.95	0.1279	0.3435	1.3574	1.0056
360.07	0.1634	0.4029	1.3126	1.0116
358.41	0.1949	0.4538	1.2984	1.0137
357.00	0.2218	0.4916	1.2872	1.0214
355.41	0.2597	0.5368	1.2558	1.0300
353.95	0.2966	0.5750	1.2290	1.0434
352.39	0.3388	0.6148	1.2042	1.0593
351.20	0.3773	0.6487	1.1818	1.0679
349.74	0.4197	0.6858	1.1729	1.0766
348.53	0.4559	0.7171	1.1710	1.0774
347.54	0.4941	0.7407	1.1499	1.0991
346.37	0.5443	0.7704	1.1254	1.1248
345.40	0.5870	0.7942	1.1084	1.1507
343.82	0.6662	0.8344	1.0777	1.2114
343.06	0.7092	0.8549	1.0622	1.2517
342.09	0.7742	0.8833	1.0365	1.3429
341.37	0.8216	0.9059	1.0248	1.4067
340.83	0.8591	0.9241	1.0172	1.4646
340.39	0.8924	0.9407	1.0109	1.5230
339.97	0.9249	0.9574	1.0072	1.5619
339.50	0.9634	0.9806	1.0033	1.5782
339.12	1.0000	1.0000	1.0000	–

The critical constants were taken from the literature [11]. The vapor pressures of the pure components were expressed by the Antoine equation

$$\log P_i^{\mathrm{sat}}\ (\mathrm{kPa}) = a_i - \frac{b_i}{T\ (\mathrm{K}) + c_i} \tag{8}$$

The constants a, b and c in Eq. (8) were taken from literature [12]. Values for the various pure fluids are shown in Table 5. The liquid molar volumes were approximated by the Rackett equation [13]. The calculated activity coefficients for each binary mixture are also listed in Tables 2–4. Plots of the activity coefficients against mole fraction for three binary systems are shown in Figs. 1–3, respectively. All binary mixtures show positive deviations. The activity coefficients were then examined for thermodynamic consistency by the Kojima's method [14] and Van Ness's method [15]. These methods include point test, integral area test and direct test, which have been used by various authors to examine experimental data. The Kojima's method includes both the point and integral tests. In the Kojima's point test, a parameter δ

Table 5
Pure component properties used in this work[a]

Component	T_c (K)	P_c (kPa)	ω	a	b	c
Tetrahydrofuran	540.15	5188	0.2264	6.12052	1202.561	−46.863
2,2,4-Trimethylpentane	543.96	2568	0.3031	5.93034	1254.146	−52.831
Methylcyclohexane	572.19	3471	0.2350	5.94280	1266.954	−52.282
n-Heptane	540.26	2736	0.3511	6.02633	1268.583	−56.054

[a] The critical constants and acentric factor were taken from [11]. The parameters in the vapor pressure equation ($\log P_i^{\text{sat}}\ (\text{kPa}) = a_i - b_i/[T\ (\text{K}) + c_i]$) were taken from [12].

was defined as

$$\delta = 100\sum_{j=1}^{n}\frac{|\delta_j|}{n} \tag{9}$$

The summation was calculated over all the data points where

$$\delta_j = \frac{\partial(\Delta G_{\mathrm{m}}/RT)}{\partial x_1} - \ln\left(\frac{\gamma_1}{\gamma_2}\right) - \varepsilon \tag{10}$$

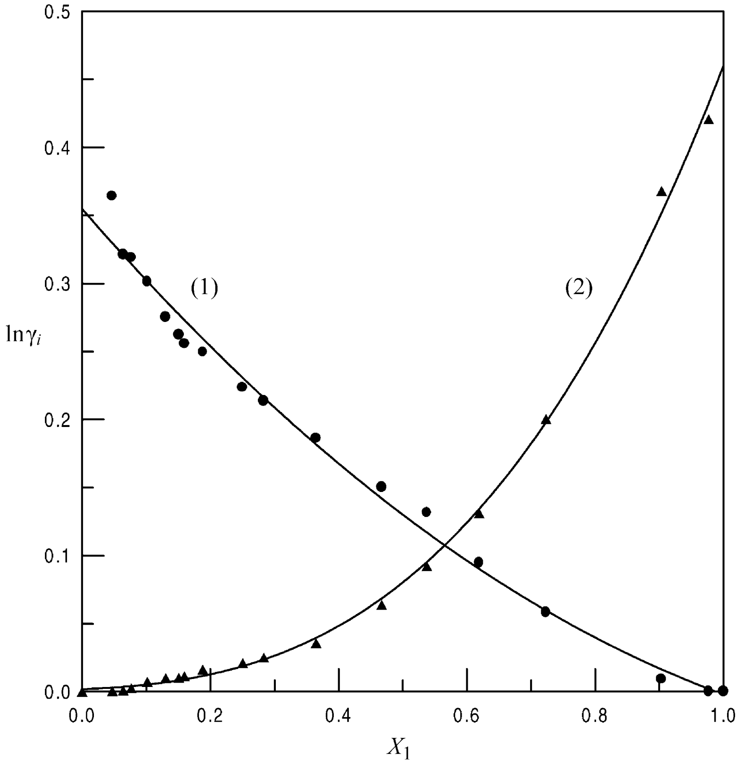

Fig. 1. Activity coefficients for the system tetrahydrofuran(1) + 2,2,4-trimethylpentane(2) at 101.3 kPa (●,▲: experimental data; —: smoothed curve using the Wilson equation).

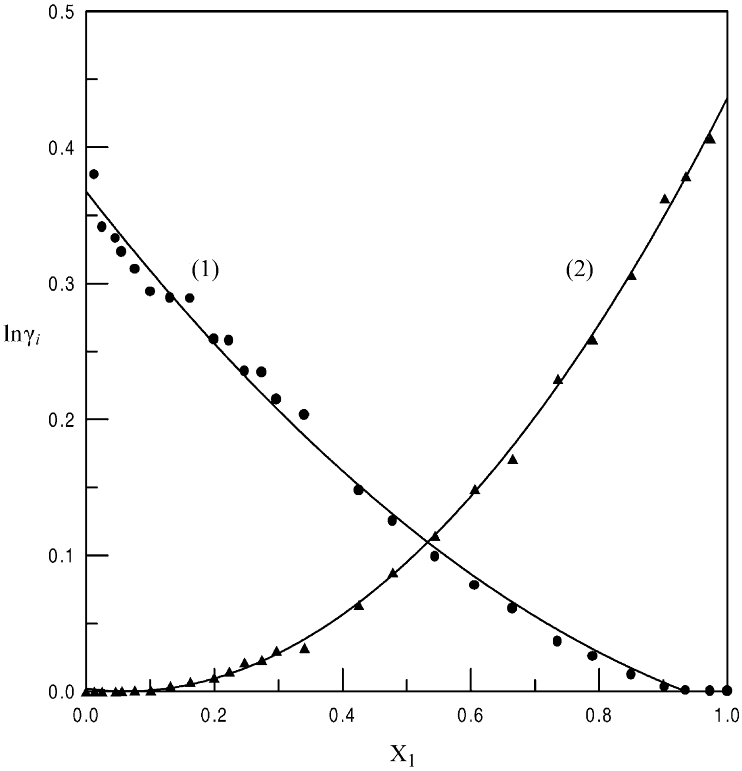

Fig. 2. Activity coefficients for the system tetrahydrofuran(1) + methylcyclohexane(2) at 101.3 kPa (●,▲: experimental data; —: smoothed curve using the Wilson equation).

The free energy change on mixing ΔG_m was calculated by summing up the activity coefficient for each component in a mixture. The ε term was related to the heat of mixing in the isobaric experiment. An estimated value of 0.03 was used for ε according to the suggestion of Kojima et al. [14]. For the Kojima's area test, a parameter A was defined as

$$A = 100\left[\int_0^1 \ln\left(\frac{\gamma_1}{\gamma_2}\right)\,\mathrm{d}x_1 + \int_0^1 (\varepsilon)\,\mathrm{d}x_1\right] \tag{11}$$

Kojima et al. [14] also proposed an infinite dilution test. The following terms were calculated at the infinite dilution conditions

$$I_1 = 100\left|\frac{(G^\mathrm{E}/x_1x_2RT)_{x_1=0} - (\ln(\gamma_1/\gamma_2))_{x_1=0}}{(\ln(\gamma_1/\gamma_2))_{x_1=0}}\right| \tag{12}$$

$$I_2 = 100\left|\frac{(G^\mathrm{E}/x_1x_2RT)_{x_2=0} - (\ln(\gamma_2/\gamma_1))_{x_2=0}}{(\ln(\gamma_2/\gamma_1))_{x_2=0}}\right| \tag{13}$$

A direct thermodynamic consistency test has been recently presented by Van Ness [15]. The activity coefficients calculated from the experiment were fitted by an excess Gibbs free energy function, such as the Wilson equation [16] in this study. At each data point, the residual between the calculated and

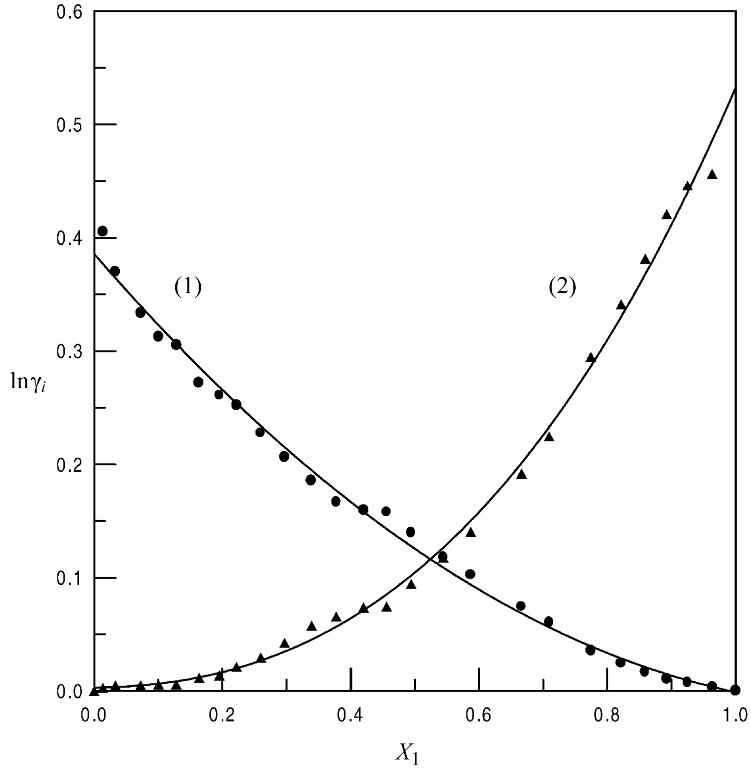

Fig. 3. Activity coefficients for the system tetrahydrofuran(1) + *n*-heptane(2) at 101.3 kPa (●,▲: experimental data; —: smoothed curve using the Wilson equation).

experimental activity coefficient ratios was evaluated. The root mean squares (RMS) deviations for the residual values were determined. According to the suggestion of Van Ness [15], the RMS value should be as small as possible. The criteria of thermodynamic consistency of each method and the results for various tests of this study are shown in Table 6. It is demonstrated that all these binary systems satisfy the requirements for the various thermodynamic consistency test methods.

Table 6
Consistency test results of the binary VLE experimental data

Method of test	Criterion of consistency	Tetrahydrofuran(1) + 2,2,4-trimethylpentane(2)	Tetrahydrofuran(1) + methylcyclohexane(2)	Tetrahydrofuran(1) + *n*-heptane(2)
Van Ness direct test	[RMS of $\Delta\ln(\gamma_1/\gamma_2)$] < 0.025	0.024 (+)	0.014 (+)	0.019 (+)
Kojima method				
(a)Point test	$\delta < 5$	2.83(+)	3.02(+)	4.61(+)
(b)Area test	$A < 3$	0.44(+)	1.66(+)	2.91(+)
(c)Infinite dilution test	$I_1 < 30$	13.96(+)	4.89(+)	27.39(+)
	$I_2 < 30$	3.23(+)	14.56(+)	2.33(+)

Table 7

Correlation parameters and absolute average deviations in boiling temperature (ΔT) and vapor phase mole fraction (Δy) for the binary mixtures

Equations	A_{12} ($\mathrm{J\,mol^{-1}}$)	A_{21} ($\mathrm{J\,mol^{-1}}$)	B_{12}	Δy	ΔT (K)
Tetrahydrofuran(1) + 2,2,4-trimethylpentane(2)					
UNIQUAC	1540.38	−776.00		0.0034	0.19
Wilson	−679.01	1986.63		0.0035	0.19
NRTL	−943.57	2324.16	0.2	0.0031	0.19
Tetrahydrofuran(1) + methylcyclohexane(2)					
UNIQUAC	1103.44	−482.29		0.0017	0.11
Wilson	−195.88	1483.14		0.0015	0.10
NRTL	−466.92	1765.83	0.2	0.0017	0.12
Tetrahydrofuran(1) + *n*-heptane(2)					
UNIQUAC	1214.38	−534.62		0.0031	0.16
Wilson	−142.29	1636.29		0.0031	0.16
NRTL	−907.54	2434.35	0.2	0.0033	0.18

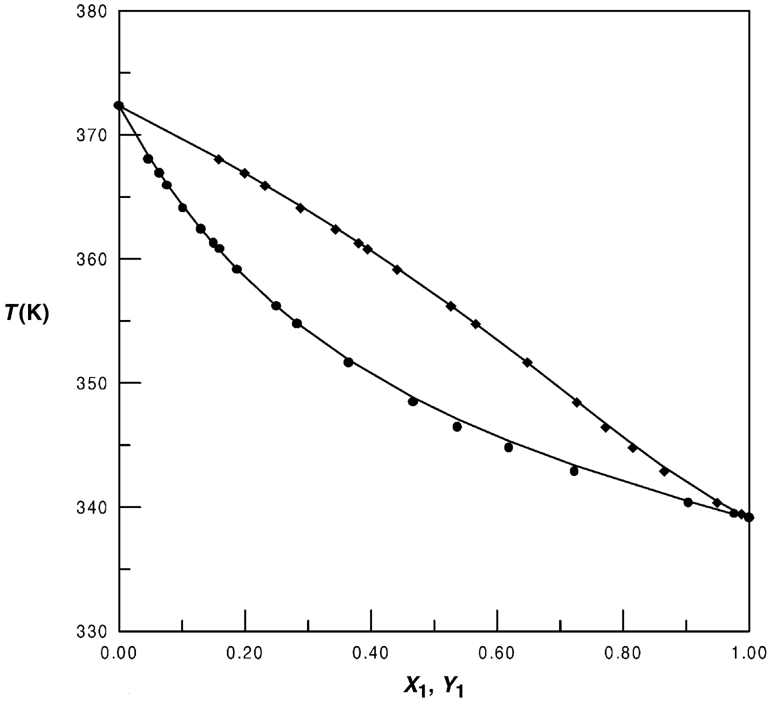

Fig. 4. T–x–y curve for tetrahydrofuran(1) + 2,2,4-trimethylpentane(2) at 101.3 kPa (—: smoothed curve using the Wilson equation; experimental data: ● (liquid phase), ◆ (vapor phase)).

The experimental results were then used to obtain the binary parameters in various activity coefficient models of Wilson [16], NRTL [17] and UNIQUAC [18]. The expressions for the activity coefficients for each model are listed in the literature [19]. The following objective function was minimized in the regressions:

$$Q = \sum_n \sum_i \left(\frac{\gamma_i^{\mathrm{exp}} - \gamma_i^{\mathrm{cal}}}{\gamma_i^{\mathrm{exp}}} \right)^2 \qquad (14)$$

The regression results are shown in Table 7. The deviations in vapor phase compositions and equilibrium temperatures are reasonably small, and it is indicated that all these activity coefficient models are suitable to represent the binary experimental data. The *T–x–y* diagrams of three binary systems are shown in Figs. 4–6, respectively. No azeotrope was found for these binary systems. The calculated *T–x–y* curves agree satisfactorily with the experimental data for all three binary mixtures. Comparison of the composition dependence of the activity coefficient and the *T–x–y* curve for the binary system of tetrahydrofuran + n-heptane with those from Wisniak et al. at 94 kPa [3] indicates that both experimental data sets show similar and consistent behavior.

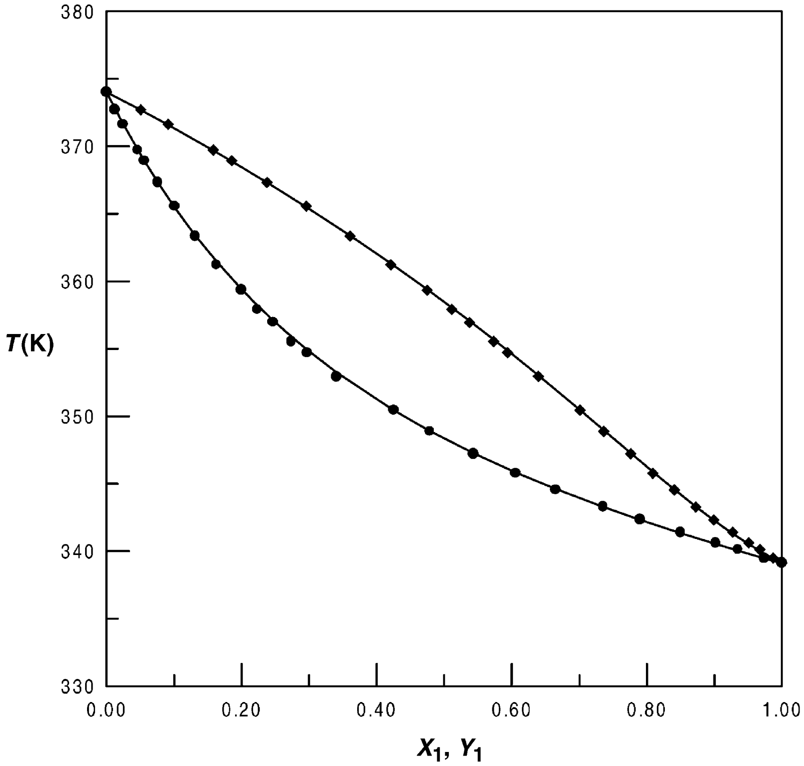

Fig. 5. *T–x–y* curve for tetrahydrofuran(1) + methylcyclohexane(2) at 101.3 kPa (—: smoothed curve using the Wilson equation; experimental data: ● (liquid phase), ◆ (vapor phase)).

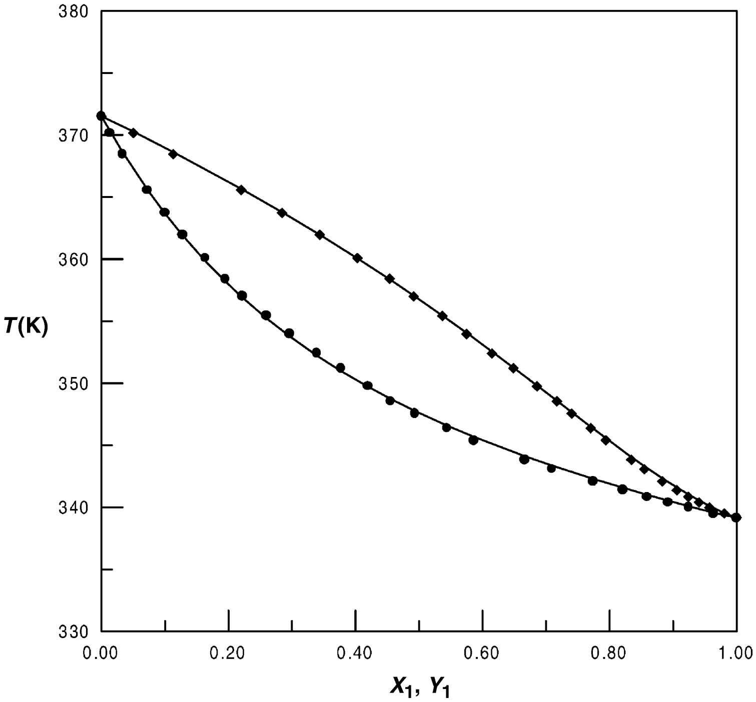

Fig. 6. T–x–y curve for tetrahydrofuran(1) + n-heptane(2) at 101.3 kPa (—: smoothed curve using the Wilson equation; experimental data: ● (liquid phase), ◆ (vapor phase)).

4. Conclusion

Vapor–liquid equilibria of three binary mixtures of tetrahydrofuran with 2,2,4-trimethylpentane, methylcyclohexane and n-heptane have been measured at 101.3 kPa. The results of all binary mixtures satisfy the requirements for various thermodynamic consistency tests. Three activity coefficient models have been employed to correlate the experimental data. The results are satisfactory and the calculated deviations in vapor phase compositions and equilibrium temperatures are reasonably small.

List of symbols

a, b	parameters of the Antoine equation or the SRK equation of state
A	parameter of the Kojima's area test
A_{12}, A_{21}	parameters of the activity coefficient model
B_{12}	nonrandomness parameter of the NRTL model
c	parameters of the Antoine equation
G	Gibbs free energy
I_1, I_2	parameters of the Kojima's infinite dilution test
n	number of data points
n_D	refractive indices
P	pressure

Q	objective function
R	gas constant
T	temperature
v	molar volume
x, y	compositions in the liquid and vapor phases, respectively

Greek letters

α	temperature correction term in the SRK equation of state
δ	parameter of the Kojima's point test
ε	energy term in the Kojima's test
$\hat{\phi}_i$	fugacity coefficient of component *i* in the vapor mixture
ϕ_i^{sat}	fugacity coefficient of pure component *i* in its saturated state
γ	activity coefficient
ρ	density
ω	acentric factor

Subscripts

1, 2, *i*, *j*	components in a mixture, or data points
b	normal boiling state
c	critical state
m	mixture property
r	reduced state

Superscripts

cal	calculated value
exp	experimental value
E	excess property
L	liquid phase
sat	saturated state

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References

[1] L.C. Feng, C.H. Chou, M. Tang, Y.P. Chen, J. Chem. Eng. Data 43 (1998) 658–661.
[2] T.Y. Wen, M. Tang, Y.P. Chen, Fluid Phase Equilib. 163 (1999) 99–108.
[3] J. Wisniak, G. Embon, R. Shafir, J. Chem. Eng. Data 42 (1997) 681–684.
[4] D.D. Deshpande, S.L. Oswal, J. Chem. Thermodyn. 7 (1975) 155–159.
[5] M. Keller, S. Schnabel, A. Heintz, Fluid Phase Equilib. 110 (1995) 231–265.
[6] S. Rodriguez, H. Artigas, C. Lafuente, A.M. Mainar, F.M. Royo, Thermochim. Acta 362 (2000) 153–160.
[7] K. Rehak, J. Matous, J.P. Novak, Fluid Phase Equilib. 109 (1995) 113–129.
[8] J.A. Salas, E.L. Arancibia, M. Katz, Fluid Phase Equilib. 152 (1998) 255–263.

[9] R.N. Paul, J. Chem. Eng. Data 21 (1976) 165–169.
[10] G. Soave, Chem. Eng. Sci. 27 (1972) 1197–1203.
[11] T.E. Daubert, R.P. Danner, Data Compilation, Hemisphere Publishing Company, NY, 1989.
[12] M.S. Richard, M. Stanislaw, Handbook of the Thermodynamics of Organic Compounds, Elsevier, Amsterdam, 1987.
[13] C.F. Spencer, R.P. Danner, J. Chem. Eng. Data 17 (1972) 236–241.
[14] K. Kojima, H.M. Moon, K. Ochi, Fluid Phase Equilib. 56 (1990) 269–284.
[15] H.C. Van Ness, Pure Appl. Chem. 67 (1995) 859–872.
[16] G.M. Wilson, J. Amer. Chem. Soc. 86 (1964) 127–130.
[17] H. Renon, J.M. Prausnitz, AIChE J. 14 (1968) 135–144.
[18] D.S. Abrams, J.M. Prausnitz, AIChE J. 21 (1975) 116–128.
[19] J. Gmehling, U. Onken, W. Arlt, P. Grenzheuzer, U. Weidlich, B. Kolbe, J. Rarey-Nies, Vapor–Liquid Equilibrium Data Collection Chemistry Data Series, Vol. 1, DECHEMA, Frankurt, Germany, 1979.
[20] TRC Data Base for Chemistry and Engineering, Thermodynamic Research Center, Texas A&M University, College Station, TX, 1993.