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Phase Equilibria of the Binary Systems 1-Hexene with *o*-Xylene, *m*-Xylene, *p*-Xylene, Toluene, and Ethylbenzene at 101.3 kPa

C. Díaz, A. Dominguez, and J. Tojo*

Departamento de Ingeniería Química, Facultad de Ciencias, Universidad de Vigo, 36200 Vigo, Spain

Isobaric vapor−liquid equilibria are measured for 1-hexene + *o*-xylene, + *m*-xylene, + *p*-xylene, + toluene, and + ethylbenzene at 101.3 kPa, using a dynamic still with circulation in both of the phases. The experimental data are tested for thermodynamic consistency and could be represented well by the Wilson and UNIQUAC equations, with the latter being far better. A comparative analysis of the application of the group contribution methods ASOG, original UNIFAC, modified UNIFAC-Dortmund, and modified UNIFAC-Lyngby to the mixtures of this study showed that UNIFAC-Lyngby gives better results.

1. Introduction

Distillation is the most common operation used in the petroleum and chemical industries for the separation of liquid mixtures, and the accurate design of distillation columns requires a knowledge of phase equilibrium behavior. The planned research in this work aims to improve weaknesses of group contribution methods such as the description of isomeric compounds (e.g., xylenes). We determined isobaric (101.3 kPa) vapor−liquid equilibrium (VLE) data for the binary systems 1-hexene + *o*-xylene, + *m*-xylene, + *p*-xylene, + toluene, and + ethylbenzene. The results are correlated by means of models by Wilson[1] and UNIQUAC.[2] We are unaware of previously published VLE data for these systems. This work has also served to test the predictive capacity of the group contribution methods ASOG-KT,[3] UNIFAC,[4] UNIFAC-Dortmund,[5,6] and UNIFAC-Lyngby.[7]

2. Experimental Section

Materials. The chemical substances employed were supplied by Aldrich, Fluka, and Merck and subjected to no further purification. The pure components were degassed ultrasonically, dried over molecular sieves of type 4 A (Aldrich catolog no. 20,8640-4), and kept in an argon (<3 ppmv in water) atmosphere, as soon as the bottles were opened. Purities of the chemicals were checked by gas chromatography. The physical properties of these components are compared with the literature data in Table 1.

Apparatus and Procedure. The apparatus used in this work was an all-glass, dynamic recirculating still, described by Walas,[11] equipped with a Cottrell pump. The still (Labodest model 602), manufactured by Fischer Labor und Verfahrenstechnik (Germany), is capable of handling pressures *P* from 0.25 to 400 kPa and temperatures *T* of up to 523.15 K. The vapor−liquid mixture flows through the Cottrell pump that guarantees an intense phase exchange and then enters a separation chamber shaped in such a manner as prevent an entrainment of liquid particles into the vapor phase.

The equilibrium temperature was measured with a Yokogawa 7563 digital thermometer with a precision of ±0.01 K, and the pressure was measured with a Fischer digital manometer with a precision of ±0.01 kPa. On the average, the systems reached equilibrium conditions after 1 h of operation; the experimental method was difficult because of the highly differing relative volatility values of the components. The compositions of the liquid and condensed vapor samples were determined by measuring their refractive indices at 298.15 K with an automatic refractometer ABBEMAT-HP Dr. Kernchen (accuracy of ±0.00005) and thermostated with a PolyScience controller bath model 9010 with a temperature stability of $\pm 10^{-2}$ K. The composition dependence of refractive indices has previously been reported.[12,13] The estimated uncertainty in the determination of both liquid and vapor phase mole fractions is ±0.002.

Table 1. Densities ρ, Refractive Indices n_D, and Normal Boiling Temperatures T_b of the Pure Components

	ρ(298.15 K)/kg·m^{-3}		n_D(298.15 K)		T_b(101.3 kPa)/K	
component	exptl	lit.	exptl	lit.	exptl	lit.
1-hexene	668.5	668.48[b]	1.38517	1.38502[b]	336.64	336.635[b]
o-xylene	875.5	875.82[a] 875.90[b] 875.49[c]	1.50177	1.50252[a] 1.50295[b] 1.5029[c]	417.55	417.579[b] 417.55[c]
m-xylene	859.8	860.00[b] 859.66[c]	1.49443	1.49464[b] 1.49466[c]	412.22	412.45[a] 412.27[b]
p-xylene	856.5	856.70[b] 856.55[c]	1.49286	1.49325[b] 1.4930[c]	411.38	411.509[b] 411.15[c]
toluene	862.3	862.20[b]	1.49413	1.49396[b]	383.77	383.78[b]
ethylbenzene	862.6	862.60[b]	1.49298	1.49320[b]	409.31	409.352[b]

[a] Tanaka et al.[8] [b] *TRC Thermodynamic Tables.*[9] [c] Lores et al.[10]

3. Results and Discussion

The temperature, *T*, liquid-phase, x_1, and vapor-phase, y_1, mole fraction measurements, activity coefficients, γ_i, excess free energies, g^E, and fugacity coefficients, φ_i, at $P = 101.3$ kPa are shown in Table 2. The activity coefficients, γ_i, were calculated by taking into account the nonideality of the vapor phase, from the following equations:

$$\gamma_i = \frac{y_i P}{x_i P_i^0} \exp\left[\frac{(B_{ii} - v_i^L)(P - P_i^0) + (1 - y_i)^2 P \delta_{ij}}{RT}\right] \quad (1)$$

$$\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj} \quad (2)$$

Here x_i and y_i are the liquid- and vapor-phase compositions, *P* is the total pressure, P_i^0 is the pure-component vapor pressure calculated using the Antoine equation

$$\log P_i^0\ (\text{kPa}) = A_i - \frac{B_i}{T\ (\text{K}) + C_i} \quad (3)$$

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* To whom correspondence should be addressed. Fax: +34 986 812382. E-mail: jtojo@uvigo.es.

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Table 2. Experimental VLE Data: Temperature T, Liquid Phase x_1, and Vapor-Phase y_1 Mole Fraction, Activity Coefficient γ_i, Excess Free Energie g^E, and Vapor Fugacity Coefficient φ_i, for the Binary Systems at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2	g^E/J·mol^{-1}	φ_1	φ_2	T/K	x_1	y_1	γ_1	γ_2	g^E/J·mol^{-1}	φ_1	φ_2
1-Hexene (1) + *o*-Xylene (2)								1-Hexene (1) + Toluene (2)							
414.60	0.0094	0.0830	1.476	0.998	7.2	0.9788	0.9596	381.30	0.0222	0.0881	1.258	0.998	9.7	0.9687	0.9624
413.18	0.0161	0.1218	1.296	0.999	9.9	0.9785	0.9591	380.27	0.0312	0.1207	1.255	0.999	20.2	0.9686	0.9621
405.07	0.0508	0.3174	1.237	0.999	32.5	0.9771	0.9561	378.81	0.0450	0.1673	1.246	1.000	31.4	0.9685	0.9615
398.01	0.0876	0.4611	1.190	0.999	47.6	0.9757	0.9532	375.31	0.0826	0.2753	1.208	1.001	51.1	0.9681	0.9600
393.87	0.1118	0.5345	1.172	0.999	56.2	0.9748	0.9514	373.51	0.1039	0.3259	1.185	1.004	65.9	0.9679	0.9592
390.95	0.1295	0.5813	1.166	1.000	64.5	0.9741	0.9501	371.10	0.1334	0.3918	1.174	1.005	79.8	0.9675	0.9581
385.95	0.1658	0.6549	1.138	1.001	71.0	0.9729	0.9478	368.85	0.1652	0.4502	1.149	1.009	92.1	0.9671	0.9570
378.99	0.2252	0.7416	1.102	1.005	80.5	0.9711	0.9443	366.91	0.1930	0.4978	1.139	1.011	102.3	0.9666	0.9560
377.10	0.2448	0.7622	1.086	1.009	84.1	0.9706	0.9434	364.56	0.2302	0.5528	1.123	1.014	112.6	0.9661	0.9547
372.61	0.2897	0.8065	1.076	1.013	93.0	0.9694	0.9409	362.31	0.2708	0.6027	1.100	1.020	120.6	0.9655	0.9535
369.62	0.3248	0.8330	1.063	1.018	96.9	0.9685	0.9393	360.55	0.3035	0.6398	1.089	1.023	125.3	0.9651	0.9525
364.07	0.3980	0.8760	1.043	1.029	101.7	0.9667	0.9360	358.43	0.3486	0.6822	1.067	1.033	129.9	0.9644	0.9513
361.33	0.4393	0.8945	1.032	1.037	103.0	0.9658	0.9342	356.27	0.3921	0.7227	1.063	1.036	133.8	0.9638	0.9500
357.09	0.5086	0.9202	1.022	1.046	97.9	0.9644	0.9315	353.77	0.4493	0.7668	1.051	1.044	135.3	0.9630	0.9485
352.93	0.5844	0.9419	1.015	1.054	90.0	0.9629	0.9286	350.90	0.5250	0.8143	1.032	1.061	130.0	0.9620	0.9467
350.28	0.6381	0.9540	1.012	1.062	84.4	0.9619	0.9266	347.31	0.6268	0.8683	1.017	1.083	116.6	0.9606	0.9443
346.80	0.7140	0.9682	1.010	1.066	72.5	0.9605	0.9240	345.57	0.6800	0.8928	1.012	1.093	104.9	0.9600	0.9432
343.25	0.8059	0.9809	1.002	1.089	52.3	0.9590	0.9211	344.00	0.7315	0.9139	1.007	1.106	91.4	0.9593	0.9421
340.12	0.8924	0.9904	1.001	1.124	37.1	0.9577	0.9185	341.98	0.7981	0.9388	1.005	1.124	77.4	0.9585	0.9407
338.58	0.9382	0.9948	1.000	1.131	25.0	0.9570	0.9172	339.54	0.8878	0.9688	1.000	1.156	45.5	0.9574	0.9389
337.27	0.9792	0.9983	1.000	1.162	9.6	0.9564	0.9160	337.37	0.9715	0.9920	0.999	1.232	13.4	0.9564	0.9373
1-Hexene (1) + *m*-Xylene (2)								1-Hexene (1) + Ethylbenzene (2)							
408.23	0.0195	0.1171	1.122	0.999	5.6	0.9775	0.9584	403.55	0.0290	0.1666	1.109	0.998	9.7	0.9764	0.9573
404.11	0.0403	0.2243	1.121	1.001	18.7	0.9768	0.9568	400.85	0.0457	0.2367	1.095	1.000	16.3	0.9760	0.9562
400.00	0.0628	0.3226	1.118	1.001	27.6	0.9760	0.9552	395.72	0.0774	0.3586	1.091	1.001	26.0	0.9750	0.9540
397.83	0.0763	0.3711	1.103	1.002	30.8	0.9756	0.9542	391.93	0.1025	0.4390	1.086	1.002	34.3	0.9742	0.9524
394.57	0.0971	0.4381	1.090	1.004	40.6	0.9749	0.9529	386.83	0.1395	0.5358	1.067	1.003	44.8	0.9731	0.9500
389.54	0.1311	0.5328	1.087	1.005	47.9	0.9738	0.9506	377.62	0.2203	0.6813	1.055	1.006	59.5	0.9707	0.9455
383.74	0.1748	0.6268	1.082	1.006	59.9	0.9724	0.9479	371.35	0.2870	0.7609	1.049	1.009	67.4	0.9690	0.9421
378.41	0.2218	0.7012	1.071	1.009	69.1	0.9710	0.9452	367.96	0.3278	0.7978	1.040	1.013	74.1	0.9680	0.9402
370.59	0.3041	0.7912	1.054	1.017	84.5	0.9688	0.9410	363.88	0.3831	0.8375	1.036	1.019	80.4	0.9667	0.9378
367.03	0.3476	0.8258	1.047	1.021	89.2	0.9677	0.9390	361.71	0.4151	0.8566	1.032	1.022	83.1	0.9660	0.9365
360.36	0.4413	0.8810	1.037	1.028	94.4	0.9655	0.9350	359.41	0.4516	0.8755	1.025	1.026	84.7	0.9652	0.9350
356.36	0.5087	0.9079	1.028	1.035	91.9	0.9641	0.9324	355.97	0.5112	0.9012	1.021	1.034	85.7	0.9640	0.9327
352.33	0.5854	0.9332	1.021	1.045	87.9	0.9627	0.9296	352.81	0.5711	0.9224	1.017	1.039	83.0	0.9628	0.9306
348.32	0.6728	0.9542	1.013	1.058	78.0	0.9611	0.9267	350.61	0.6174	0.9359	1.010	1.045	78.5	0.9620	0.9290
347.05	0.7030	0.9602	1.010	1.065	74.1	0.9606	0.9257	348.69	0.6626	0.9469	1.006	1.056	72.1	0.9613	0.9276
343.60	0.7904	0.9752	1.006	1.078	57.8	0.9592	0.9230	345.60	0.7376	0.9630	1.000	1.066	59.7	0.9600	0.9253
341.90	0.8412	0.9821	0.999	1.100	41.5	0.9585	0.9216	342.34	0.8263	0.9779	1.000	1.094	45.0	0.9586	0.9227
339.60	0.9074	0.9903	0.999	1.123	28.0	0.9574	0.9197	340.11	0.8900	0.9870	1.000	1.112	33.4	0.9577	0.9209
338.26	0.9490	0.9948	0.999	1.156	16.7	0.9568	0.9186	338.61	0.9356	0.9925	1.000	1.164	27.6	0.9570	0.9196
337.36	0.9779	0.9977	0.998	1.225	7.9	0.9564	0.9178	337.53	0.9703	0.9966	1.000	1.197	14.7	0.9565	0.9187
1-Hexene (1) + *p*-Xylene (2)															
408.91	0.0128	0.0765	1.103	1.000	4.3	0.9775	0.9591								
402.51	0.0464	0.2467	1.103	1.000	16.5	0.9764	0.9566								
398.80	0.0676	0.3338	1.099	1.001	25.5	0.9757	0.9552								
397.03	0.0790	0.3727	1.088	1.003	29.9	0.9753	0.9544								
392.30	0.1091	0.4693	1.087	1.003	38.6	0.9743	0.9524								
388.40	0.1361	0.5402	1.086	1.004	47.8	0.9735	0.9507								
381.15	0.1929	0.6547	1.083	1.005	61.0	0.9717	0.9473								
376.99	0.2322	0.7109	1.071	1.008	68.3	0.9706	0.9452								
373.79	0.2654	0.7492	1.062	1.013	78.1	0.9697	0.9435								
370.17	0.3051	0.7888	1.058	1.015	85.2	0.9686	0.9416								
367.35	0.3382	0.8169	1.056	1.016	89.0	0.9678	0.9400								
364.28	0.3824	0.8445	1.041	1.027	96.3	0.9668	0.9382								
358.23	0.4744	0.8921	1.031	1.037	100.4	0.9648	0.9345								
354.94	0.5345	0.9143	1.022	1.048	98.9	0.9636	0.9323								
349.98	0.6353	0.9434	1.013	1.064	92.8	0.9618	0.9289								
346.79	0.7089	0.9595	1.008	1.079	83.3	0.9605	0.9266								
343.77	0.7851	0.9732	1.006	1.089	65.1	0.9593	0.9243								
342.02	0.8346	0.9806	1.002	1.099	49.9	0.9585	0.9229								
339.83	0.8990	0.9889	1.000	1.126	34.3	0.9575	0.9211								
338.05	0.9549	0.9953	0.999	1.149	15.1	0.9567	0.9196								

Table 3. Physical Properties of the Pure Components: Critical Presure P_C, Mean Gyration Radius R_D, Dipole Moment μ, Critical Temperature T_C, Critical Compressibility Factor Z_C, and Antoine Parameters A, B, and C

						Antoine constants[c]			
component	P_C/MPa[a]	$10^{10}R_D$[b]/m	$10^{30}\mu$[a]/C·m	T_C/K[a]	Z_C[b]	A	B	C	range T/K
1-hexene	3.1720	3.6600	1.67	504.03	0.265	5.93649	1073.08	−63.779	335.15−499.15
o-xylene	3.7330	3.8360	2.07	630.37	0.263	6.12644	1476.39	−59.278	336.15−418.15
m-xylene	3.5410	3.9370	1.33	617.05	0.259	6.13399	1462.270	−58.039	302.15−439.15
p-xylene	3.5110	3.8310	0.00	616.26	0.260	6.11543	1453.43	−57.840	300.15−439.15
toluene	4.1090	3.4720	1.20	591.79	0.264	6.07577	1342.31	−53.963	246.15−384.15
ethylbenzene	3.6090	3.8970	1.93	617.17	0.263	6.09070	1429.55	−59.383	263.15−409.15

[a] Prausnitz et al.[14] [b] Daubert and Danner.[15] [c] Gmehling et al.[16]

where the constants A_i, B_i, and C_i are reported in Table 3, B_{ii} and B_{jj} are the second virial coefficients of the pure gases, and B_{ij} is the cross second virial coefficient. Second virial coefficients were estimated by the Hayden and O'Connell method.[17] The values used for the critical constants, acentric factor, dipole moment, and association parameter are listed in Table 3. The liquid molar volume, v_i^L, was calculated by the Yen and Woods[18] equation.

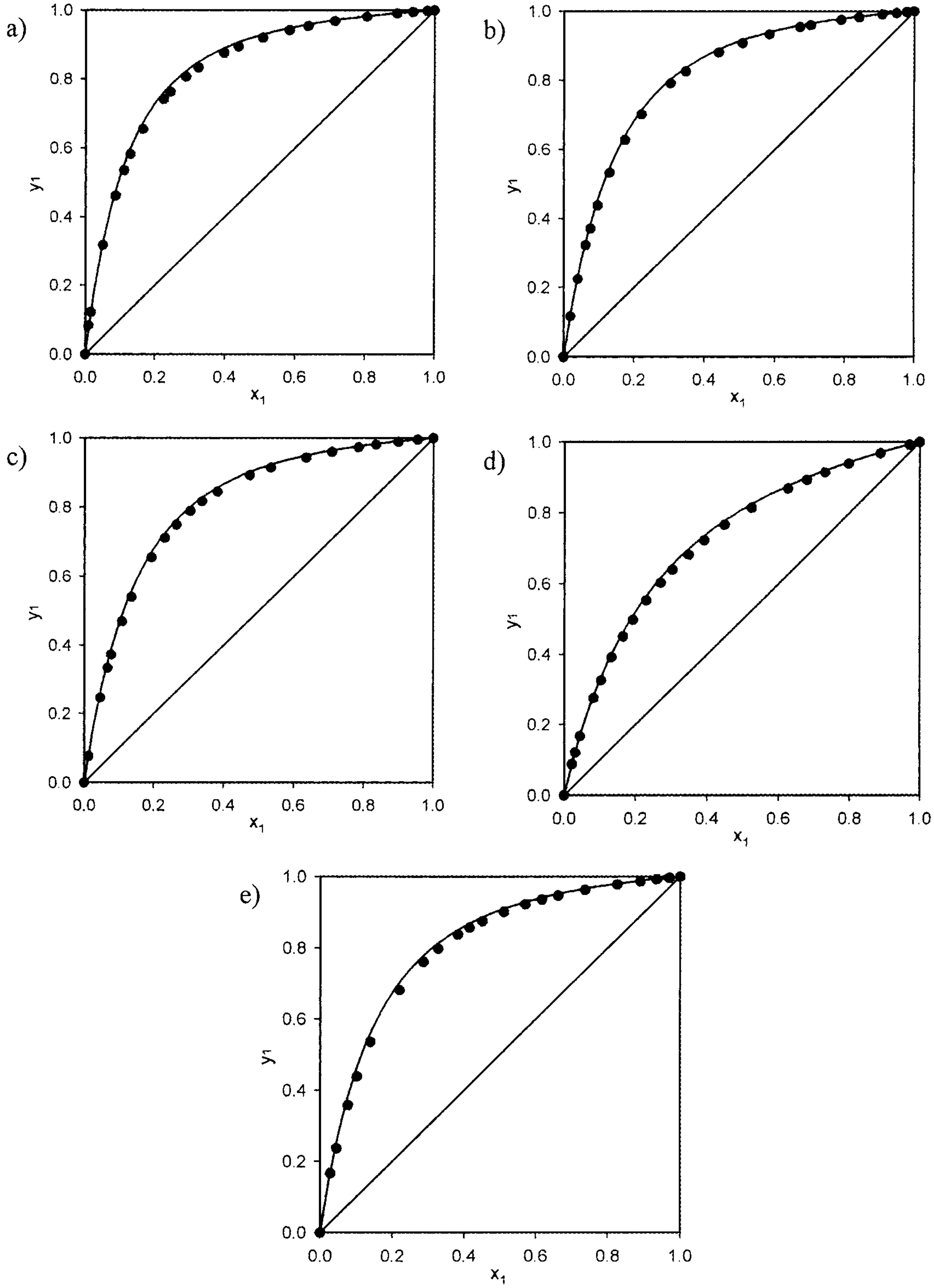

Figure 1. Experimental *y*–*x* diagram for the binary systems at 101.3 kPa: ●, this work; —, UNIQUAC equation; (a) 1-hexene (1) + *o*-xylene (2); (b) 1-hexene (1) + *m*-xylene (2); (c) 1-hexene (1) + *p*-xylene (2); (d) 1-hexene (1) + toluene (2); (e) 1-hexene (1) + ethylbenzene (2).

The systems present positive deviations from ideality, and the excess free energies, calculated from activity coefficients, are positive over the entire range of composition.

The VLE data were found to be thermodynamically consistent by means of the point-to-point test of Van Ness et al.[19] as modified by Fredenslund et al.[4] Consistency criteria were met using a three-parameter Legendre polynomial. Table 4 presents the mean absolute deviations in vapor-phase composition, Δy, and in pressure, ΔP. The L/W point-to-point method of Wisniak[20] showed good consistency (all of the values of L/W are between 0.9 and 1.0 for the binary systems), and according to the McDermott–Ellis method,[21] as modified by Wisniak and Tamir,[22] all experimental points were considered to be thermodynamically consistent. In terms of consistency criteria ($D < D_{\max}$), for the experimental data reported here, D never exceeded 0.006, while the smallest value of $D_{\max}$ was 0.029.

Correlation. The activity coefficients were correlated with both the Wilson[1] and UNIQUAC[2] equations. An automatic implementation of thermodynamic models, a

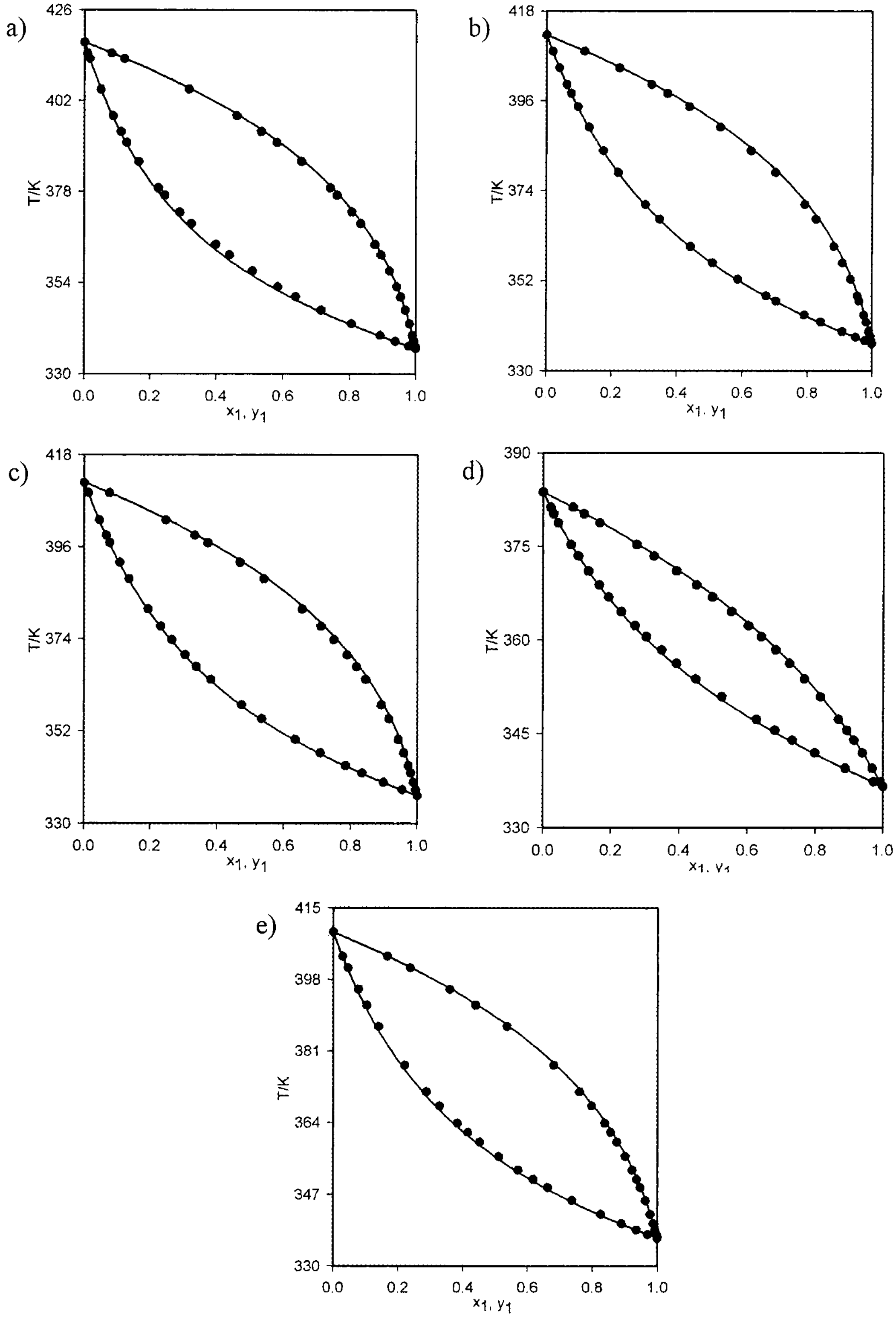

Figure 2. Temperature composition diagram for the binary systems at 101.3 kPa: ●, this work; —, UNIQUAC equation; (a) 1-hexene (1) + *o*-xylene (2); (b) 1-hexene (1) + *m*-xylene (2); (c) 1-hexene (1) + *p*-xylene (2); (d) 1-hexene (1) + toluene (2); (e) 1-hexene (1) + ethylbenzene (2).

computational package Thermath extended by Castier,[23] was used. This program allows the generation of a code that is compatible with the Schenepper and Stadtherr[24] version of the INTLIB/INTBIS[25] for interval arithmetic and guarantees that the global minimum of the objective function was achieved within an initially specified range for each model parameter. Estimation of the parameters for the equations studied was based on minimization of the objective function F in terms of experimental and

Table 4. Consistency Test for the Binary Systems

system	$100\Delta y_1$[a]	$100\Delta P$/kPa[b]
1-hexene (1) + *o*-xylene (2)	0.22	0.24
1-hexene (1) + *m*-xylene (2)	0.08	0.19
1-hexene (1) + *p*-xylene (2)	0.10	0.16
1-hexene (1) + toluene (2)	0.09	0.13
1-hexene (1) + ethylbenzene (2)	0.07	0.16

[a] Average absolute deviation in vapor-phase composition. [b] Average absolute deviation in pressure.

Table 5. Interaction Parameters and Root-Mean-Square Deviations from the UNIQUAC and Wilson Equations at 101.3 kPa

model	parameters/J·mol^{-1}		rms T	rms y_1
	1-Hexene (1) + o-Xylene (2)			
Wilson	$\Delta\lambda_{12} = -70.71$	$\Delta\lambda_{21} = 525.76$	0.82	0.008
UNIQUAC	$\Delta u_{12} = 31.17$	$\Delta u_{21} = -11.80$	0.80	0.007
	1-Hexene (1) + m-Xylene (2)			
Wilson	$\Delta\lambda_{12} = 1740.29$	$\Delta\lambda_{21} = 746.55$	1.17	0.020
UNIQUAC	$\Delta u_{12} = -113.05$	$\Delta u_{21} = 82.17$	0.52	0.013
	1-Hexene (1) + p-Xylene (2)			
Wilson	$\Delta\lambda_{12} = -433.09$	$\Delta\lambda_{21} = 667.22$	0.37	0.012
UNIQUAC	$\Delta u_{12} = -158.91$	$\Delta u_{21} = 107.07$	0.28	0.012
	1-Hexene (1) + Toluene (2)			
Wilson	$\Delta\lambda_{12} = -278.32$	$\Delta\lambda_{21} = 815.71$	0.32	0.010
UNIQUAC	$\Delta u_{12} = 144.64$	$\Delta u_{12} = 92.55$	0.25	0.009
	1-Hexene (1) + Ethylbenzene (2)			
Wilson	$\Delta\lambda_{12} = -945.25$	$\Delta\lambda_{12} = 1484.99$	0.83	0.015
UNIQUAC	$\Delta u_{12} = -39.75$	$\Delta u_{21} = 26.94$	0.64	0.013

Table 6. Root-Mean-Square-Deviations in Equilibrium Temperature and Vapor-Phase Composition from the ASOG, UNIFAC, UNIFAC-Dortmund, and UNIFAC-Lyngby Group Contribution Methods

	rms T/K				rms y_1			
system	ASOG	original UNIFAC	UNIFAC-Dortmund	UNIFAC-Lyngby	ASOG	original UNIFAC	UNIFAC-Dortmund	UNIFAC-Lyngby
1-hexene (1) + o-xylene (2)	1.03	1.08	3.30	0.88	0.014	0.014	0.036	0.012
1-hexene (1) + m-xylene (2)	1.24	1.41	3.39	1.07	0.022	0.008	0.047	0.020
1-hexene (1) + p-xylene (2)	1.34	1.38	3.66	1.16	0.023	0.023	0.048	0.021
1-hexene (1) + toluene (2)	0.46	1.06	1.56	0.51	0.012	0.019	0.025	0.012
1-hexene (1) + ethylbenzene (2)	1.24	2.25	2.02	1.40	0.020	0.030	0.027	0.021

calculated γ_i values

$$F = \sum_{j=1}^{n_{\mathrm{DAT}}} \sum_{i=1}^{N} \left(\frac{\gamma_{ij}^{\mathrm{exp}} - \gamma_{ij}^{\mathrm{calc}}}{\gamma_{ij}^{\mathrm{exp}}} \right)^2 \tag{4}$$

where n_{DAT} is the number of experimental data, γ^{exp} is the coefficient calculated from the experimental data, γ^{calc} is the activity coefficient calculated from the y and T correlations, and N is the number of components. Optimized parameter sets and the root-mean-square deviations of T and y_1 from the equations of Wilson and UNIQUAC are shown in Table 5. The UNIQUAC equation represents the data better. Figures 1 and 2 show the y_1−x_1 and T−x_1−y_1 diagrams and the correlated line corresponding to the best model for each binary system.

Predictive Models. Prediction of VLE for the binary systems at 101.3 kPa has been carried out by the ASOG-KT[3] and UNIFAC[4] methods and their modifications by UNIFAC-Dortmund[5,6] and UNIFAC-Lyngby. The group interaction parameters were those published by Kojima and Tochigi,[3] Hansen et al.,[26] Gmehling et al.,[6] and Larsen et al.[7] for these methods. The root-mean-square deviations between the experimental VLE data and those predicted for the temperature, $\sigma(T)$, and the composition of the vapor phase, $\sigma(y_1)$, are shown in Table 6. It can be observed that the description of these systems by the UNIFAC-Lyngby method shows better agreement with the experimental data. The difficulties in representation of these systems are to be expected because a simple group contribution model like ASOG, UNIFAC, or modified UNIFAC is not able to account for isomeric effects (e.g., ortho, meta, or para substitution) in the case of the different benzene derivatives. Of course, new main groups can be included, which would improve the prediction results.

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