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Isobaric Vapor−Liquid Equilibria of the Binary Systems Cyclohexane with *o*-Xylene, *m*-Xylene, *p*-Xylene, and Ethylbenzene at 101.3 kPa

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Isobaric vapor−liquid equilibria were measured for cyclohexane + *o*-xylene, + *m*-xylene, + *p*-xylene, and + ethylbenzene at 101.3 kPa using a dynamic still with circulation of both phases. Experimental data were tested for thermodynamic consistency and satisfactorily correlated by different equations. The four systems exhibit positive deviations from ideal behavior. A comparative analysis was performed by application of the ASOG, original UNIFAC, modified UNIFAC (Dortmund), and modified UNIFAC (Lyngby) systems, and low root-mean-square deviations of vapor mole fraction and temperature were computed.

Introduction

The study of systems containing xylenes is of great interest in the field of thermodynamics of mixtures for the optimal design of distillation columns and condensers. This work will lead to improvements in group contribution methods in order to better describe isomeric compounds (e.g. xylenes). The literature consulted does not make reference to VLE isobaric data; only isotherm data have been reported previously.[1−4] Good agreement was found between our values of the activity coefficients and corresponding bibliographic values. As a continuation of our previous paper,[5] we will report vapor−liquid equilibrium data at 101.3 kPa of binary systems containing cyclohexane, *o*-xylene, *m*-xylene, *p*-xylene, and ethylbenzene. The results were correlated by the equations of Wilson[6] and UNIQUAC.[7] This work has also served to test the predictive capacity of the group contribution methods ASOG,[8] UNIFAC,[9] UNIFAC-Dortmund,[10,11] and UNIFAC-Lyngby.[12]

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 type 4 Å (Aldrich cat. no 20,8640-4), and stored in an argon (<3 ppm by volume in water) atmosphere, as soon as the bottles were opened. The purity of chemicals was checked by gas chromatography. Their mass fraction purities were at least 0.999 for cyclohexane, 0.986 for *o*-xylene, 0.996 for *m*-xylene, and 0.999 for *p*-xylene and ethylbenzene. The maximun water contents of the cyclohexane, *o*-xylene, *m*-xylene, *p*-xylene, and ethylbenzene (determined with a coulometric moisture model CA-06) were 1.0×10^{-4}, 1.0×10^{-4} 1.3×10^{-2}, 1.0×10^{-4}, and 1.3×10^{-2} mass %, respectively. The physical properties of these components are listed in Table 1.

Apparatus and Procedure. The apparatus used in this work was an all-glass, dynamic recirculating still manufactured by Fischer Labor und Verfahrenstechnik (Germany) (Labodest model 602). It is capable of handling pressures from 0.25 to 400 kPa and temperatures 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 whose shape prevents an entrainment of liquid particles into the vapor phase.

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.
cyclohexane	773.8	773.87[a]	1.42354	1.423 53[a]	353.88	353.929[a]
o-xylene	875.5	875.90[a]	1.50177	1.502 95[a]	417.55	417.579[a]
		875.49[b]		1.502 9[b]		417.55[b]
		875.82[c]		1.502 52[c]		
m-xylene	859.8	860.00[a]	1.49443	1.494 64[a]	412.22	412.27[a]
		859.66[b]		1.494 66[b]		412.45[b]
p-xylene	856.5	856.70[a]	1.49286	1.493 25[a]	411.38	411.509[a]
		856.55[b]		1.493 0[b]		411.15[b]
ethylbenzene	862.6	862.60[a]	1.49298	1.493 20[a]	409.31	409.352[a]

[a] *TRC Thermodynamic Tables.*[14] [b] Lores et al.[15] [c] Tanaka et al.[16]

The equilibrium temperature was measured with a Yokogawa 7563 digital thermometer with a precision of ±0.01 K, and pressure was measured with a Fischer digital manometer with a precision of ±0.01 kPa. The system was kept at the boiling point for 30 min to ensure a stationary state. 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 $\pm10^{-2}$ K. The composition dependence of refractive indices has previously been reported.[13] The greatest uncertainty in the determination of both liquid and vapor phase was ±0.002 in mole fraction.

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

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Table 2. Experimental Vapor−Liquid Equilibrium Data: Temperature, *T*, Liquid Phase, x_1, and Vapor Phase, y_1, Mole Fraction, Activity Coefficient, γ_i, Excess Free Energy, 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
Cyclohexane (1) + *o*-Xylene (2)															
413.11	0.0230	0.1316	1.413	0.997	15.6	0.9808	0.9592	371.73	0.4498	0.8458	1.159	1.077	332.1	0.9684	0.9440
406.35	0.0598	0.2994	1.412	1.000	69.3	0.9786	0.9569	369.91	0.4840	0.8627	1.151	1.088	344.2	0.9678	0.9432
398.98	0.1091	0.4578	1.376	1.003	123.0	0.9764	0.9545	368.27	0.5282	0.8776	1.120	1.123	350.3	0.9673	0.9424
395.69	0.1340	0.5193	1.363	1.005	151.1	0.9754	0.9534	365.91	0.5819	0.8995	1.108	1.130	337.5	0.9665	0.9413
392.98	0.1583	0.5683	1.340	1.006	166.3	0.9746	0.9524	363.42	0.6656	0.9210	1.060	1.213	313.0	0.9657	0.9400
389.98	0.1862	0.6170	1.321	1.009	192.2	0.9738	0.9514	361.27	0.7404	0.9396	1.031	1.292	266.9	0.9649	0.9389
386.87	0.2181	0.6635	1.302	1.014	220.9	0.9729	0.9502	359.06	0.8215	0.9579	1.007	1.420	202.9	0.9641	0.9378
384.63	0.2460	0.6960	1.275	1.019	235.4	0.9722	0.9494	356.83	0.8952	0.9751	1.001	1.554	139.4	0.9634	0.9365
380.00	0.3100	0.7576	1.228	1.028	261.1	0.9709	0.9476	355.14	0.9524	0.9887	1.001	1.655	7.8	0.9627	0.9356
376.68	0.3590	0.7957	1.208	1.039	288.0	0.9699	0.9462	353.99	0.9956	0.9990	1.000	1.655	5.6	0.9623	0.9350
374.83	0.3908	0.8151	1.190	1.051	306.5	0.9693	0.9454								
Cyclohexane (1) + *m*-Xylene (2)															
408.93	0.0207	0.1010	1.325	1.001	21.1	0.9807	0.9587								
403.85	0.0558	0.2420	1.300	1.002	54.6	0.9779	0.9572	368.19	0.5264	0.8616	1.108	1.083	279.7	0.9638	0.9476
400.36	0.0824	0.3294	1.288	1.004	79.7	0.9762	0.9562	366.01	0.5788	0.8836	1.095	1.094	274.8	0.9630	0.468
394.81	0.1300	0.4562	1.268	1.004	112.5	0.9737	0.9548	364.37	0.6317	0.9019	1.068	1.126	258.5	0.9624	0.9463
389.59	0.1818	0.5583	1.244	1.010	154.7	0.9716	0.9535	362.13	0.6935	0.9237	1.058	1.140	238.3	0.9616	0.9455
384.53	0.2396	0.6440	1.220	1.021	202.6	0.9697	0.9522	360.65	0.7458	0.9380	1.040	1.177	212.1	0.9610	0.9450
378.76	0.3211	0.7328	1.187	1.028	232.3	0.9676	0.9507	358.83	0.8176	0.9545	1.015	1.286	173.0	0.9603	0.9443
376.29	0.3630	0.7664	1.165	1.037	246.6	0.9667	0.9500	356.79	0.8873	0.9719	1.008	1.385	130.0	0.9595	0.9435
374.11	0.4023	0.7947	1.154	1.043	257.9	0.9659	0.9494	355.63	0.9325	0.9828	1.002	1.478	83.8	0.9591	0.9431
371.91	0.4436	0.8195	1.138	1.054	267.9	0.9651	0.9487	354.48	0.9743	0.9933	1.002	1.579	39.2	0.9586	0.9426
370.08	0.4807	0.8410	1.128	1.064	276.4	0.9645	0.9482								
Cyclohexane (1) + *p*-Xylene (2)															
406.93	0.0289	0.1422	1.388	0.995	14.3	0.9795	0.9585	373.32	0.4073	0.7920	1.155	1.064	296.1	0.9656	0.9494
403.28	0.0520	0.2349	1.370	1.002	60.0	0.9777	0.9574	371.19	0.4508	0.8184	1.138	1.076	302.9	0.9649	0.9488
397.74	0.0945	0.3712	1.335	1.004	100.6	0.9751	0.9559	369.35	0.4974	0.8400	1.109	1.101	307.1	0.9642	0.9482
394.43	0.1215	0.4420	1.326	1.008	135.3	0.9737	0.9550	367.34	0.5480	0.8630	1.089	1.123	303.0	0.9635	0.9476
390.56	0.1586	0.5220	1.305	1.009	160.0	0.9720	0.9541	364.40	0.6295	0.8960	1.064	1.151	275.4	0.9624	0.9466
387.83	0.1886	0.5725	1.279	1.014	185.8	0.9710	0.9534	361.32	0.7298	0.9283	1.033	1.212	227.0	0.9613	0.9456
384.18	0.2337	0.6365	1.247	1.019	211.5	0.9696	0.9524	359.36	0.7954	0.9478	1.021	1.250	185.5	0.9605	0.9449
381.42	0.2730	0.6808	1.235	1.022	230.3	0.9686	0.9517	357.32	0.8721	0.9667	1.005	1.374	133.7	0.9597	0.9441
379.63	0.2968	0.7069	1.213	1.032	249.9	0.9679	0.9512	356.16	0.9142	0.9782	1.002	1.399	91.6	0.9593	0.9437
377.80	0.3332	0.7327	1.192	1.042	267.1	0.9672	0.9507	354.77	0.9740	0.9929	0.993	1.583	15.9	0.9587	0.9432
375.29	0.3670	0.7664	1.181	1.049	285.7	0.9663	0.9500								
Cyclohexane (1) + Ethylbenzene (2)															
404.99	0.0301	0.1339	1.306	1.000	26.7	0.9796	0.9580	371.29	0.4428	0.8062	1.138	1.057	271.8	0.9650	0.9492
398.64	0.0790	0.3054	1.290	1.002	74.0	0.9762	0.9561	369.55	0.4824	0.8282	1.122	1.068	275.7	0.9643	0.9487
393.26	0.1278	0.4334	1.268	1.004	111.5	0.9736	0.9548	367.76	0.5258	0.8496	1.106	1.084	278.9	0.9637	0.9482
387.38	0.1906	0.5546	1.239	1.010	156.5	0.9711	0.9533	366.17	0.5679	0.8681	1.090	1.102	276.8	0.9631	0.9477
384.90	0.2228	0.6017	1.216	1.013	171.1	0.9701	0.9527	363.02	0.6590	0.9025	1.062	1.151	264.1	0.9619	0.9467
381.98	0.2610	0.6514	1.203	1.019	197.3	0.9690	0.9520	360.37	0.7505	0.9310	1.034	1.222	224.2	0.9609	0.9458
379.64	0.2930	0.6887	1.197	1.023	216.6	0.9681	0.9514	358.18	0.8328	0.9540	1.014	1.315	170.7	0.9601	0.9451
377.53	0.3281	0.7212	1.178	1.030	230.8	0.9673	0.9509	356.20	0.9118	0.9753	1.001	1.438	97.1	0.9593	0.9445
373.84	0.3936	0.7736	1.153	1.043	253.8	0.9659	0.9499	355.06	0.9642	0.9892	0.991	1.616	26.1	0.9589	0.9442

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	$P_c{}^a$/MPa	$10^{10}R_D{}^b$/m	$10^{30}\mu^a$/C·m	$T_c{}^a$/K	$Z_c{}^b$	*A*	*B*	*C*	*T* range/K
cyclohexane	4.0750	3.2420	0.00	553.54	0.273	6.22416	1380.54	−26.624	352.15−553.15
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
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.[17] [b] Daubert and Danner.[18] [c] Gmehling et al.[19]

= 101.3 kPa are reported in Table 2. The activity coefficients, γ_i, in the liquid phase for each equilibrium stage were calculated by

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

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

where x_i and y_i are the liquid- and vapor-phase compositions, *P* is the total pressure, and P_i° represents the vapor pressures of the pure components, which were obtained by use of the Antoine equation, with the constants A_i, B_i, and C_i reported in Table 3, given by

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

The second virial coefficients of the pure gases, B_{ii} and B_{jj}, and the cross second virial coefficient, B_{ij}, calculated according to Hayden and O'Connell empirical correlations,[20] the values used for the critical constants, the acentric factor, the dipole moment, and the association parameter are also shown in Table 3. The molar volumes, $v_i^{\rm L}$, of the saturated liquid were estimated by the Yen and Woods[21] equation.

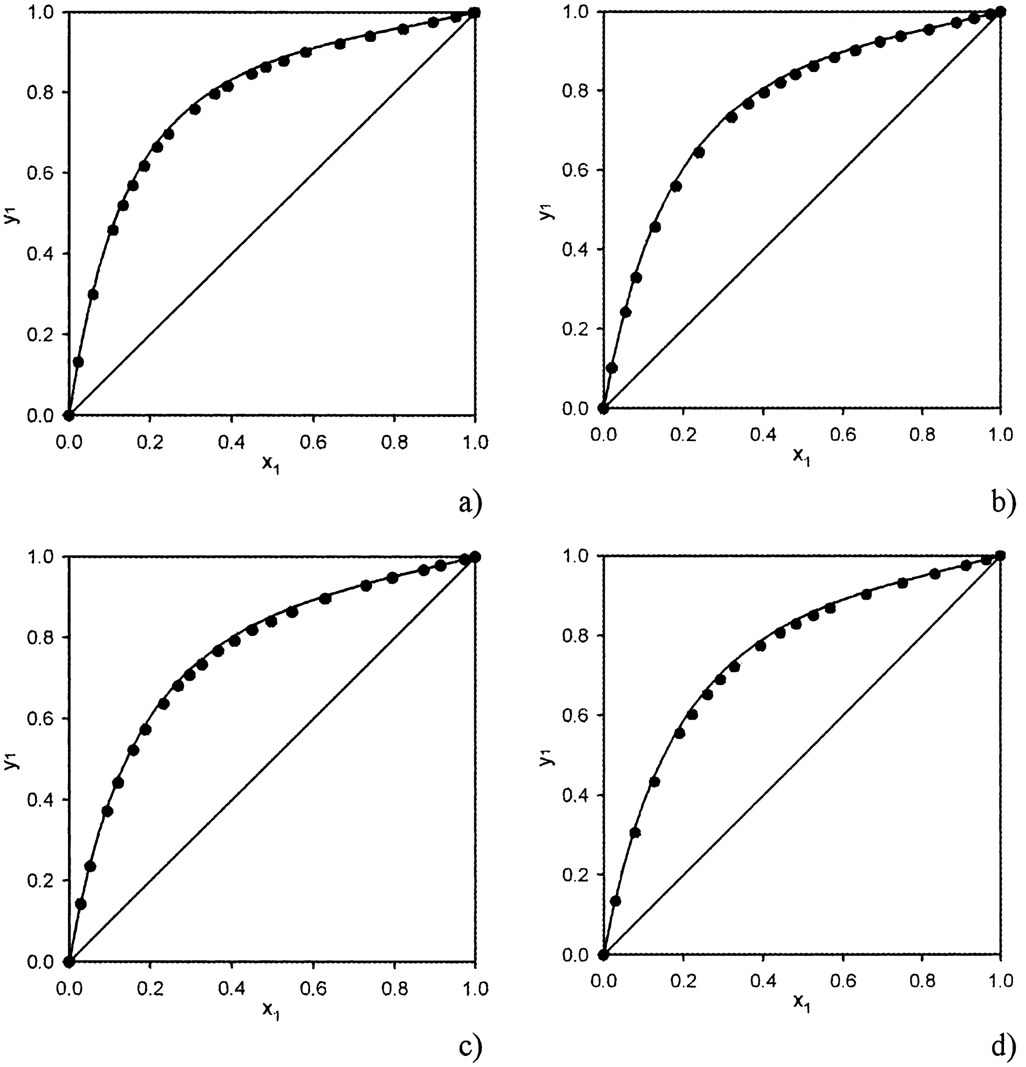

Figure 1. Experimental $y-x$ diagram for the binary systems at 101.3 kPa: ●, this work; —, UNIQUAC equation; (a) cyclohexane (1) + *o*-xylene (2); (b) cyclohexane (1) + *m*-xylene (2); (c) cyclohexane (1) + *p*-xylene (2); (d) cyclohexane (1) + ethylbenzene (2).

Table 4. Consistency Test for the Binary Systems

system	$100\Delta y_1{}^{a}$	$100\Delta P^{b}$/kPa
cyclohexane (1) + *o*-xylene (2)	0.25	0.82
cyclohexane (1) + *m*-xylene (2)	0.09	0.17
cyclohexane (1) + *p*-xylene (2)	0.11	0.21
cyclohexane (1) + ethylbenzene (2)	0.08	0.21

[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
	Cyclohexane (1) + *o*-Xylene (2)			
Wilson	$\Delta\lambda_{12} = -233.68$	$\Delta\lambda_{21} = 2033.93$	0.45	0.010
UNIQUAC	$\Delta u_{12} = 1289.59$	$\Delta u_{21} = -723.83$	0.44	0.011
	Cyclohexane (1) + *m*-Xylene (2)			
Wilson	$\Delta\lambda_{12} = -747.76$	$\Delta\lambda_{21} = 2563.45$	1.11	0.017
UNIQUAC	$\Delta u_{12} = 1769.08$	$\Delta u_{21} = -1121.35$	0.32	0.010
	Cyclohexane (1) + *p*-Xylene (2)			
Wilson	$\Delta\lambda_{12} = -227.78$	$\Delta\lambda_{21} = 1736.40$	0.29	0.010
UNIQUAC	$\Delta u_{12} = 1074.87$	$\Delta u_{21} = -630.99$	0.23	0.009
	Cyclohexane (1) + Ethylbenzene (2)			
Wilson	$\Delta\lambda_{12} = -808.89$	$\Delta\lambda_{12} = 2690.14$	0.40	0.011
UNIQUAC	$\Delta u_{12} = 1793.64$	$\Delta u_{21} = -1132.65$	0.34	0.011

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

The thermodynamic consistency of the data was tested by using the point-to-point procedure of Van Ness et al.[22] as described by Fredenslund et al.,[9] using a third-order Legendre polynomial. According to this test, the data point is considered consistent if the average absolute deviation in the vapor-phase composition is smaller than 0.01. 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[23] got positive consistency (all the values of L/W are between 0.9 and 1.1 for the binary systems), and according to the McDermott-Ellis method[24] as modified by Wisniak and Tamir,[25] all experimental points were considered thermodynamically consistent. On the basis of consistency criteria ($D < D_{\max}$), for the experimental data reported here, D never exceeded 0.016, while the smallest value of $D_{\max}$ was 0.068.

Correlation. The reduction of the equilibrium data was carried out for the activity coefficients versus liquid-phase mole fraction with the Wilson[6] and UNIQUAC[7] equations. To ease automatic implementation of thermodynamic models, the computational package Thermath, extended by Castier,[26] was used. This program allows the generation of code that is compatible with the Schnepper and

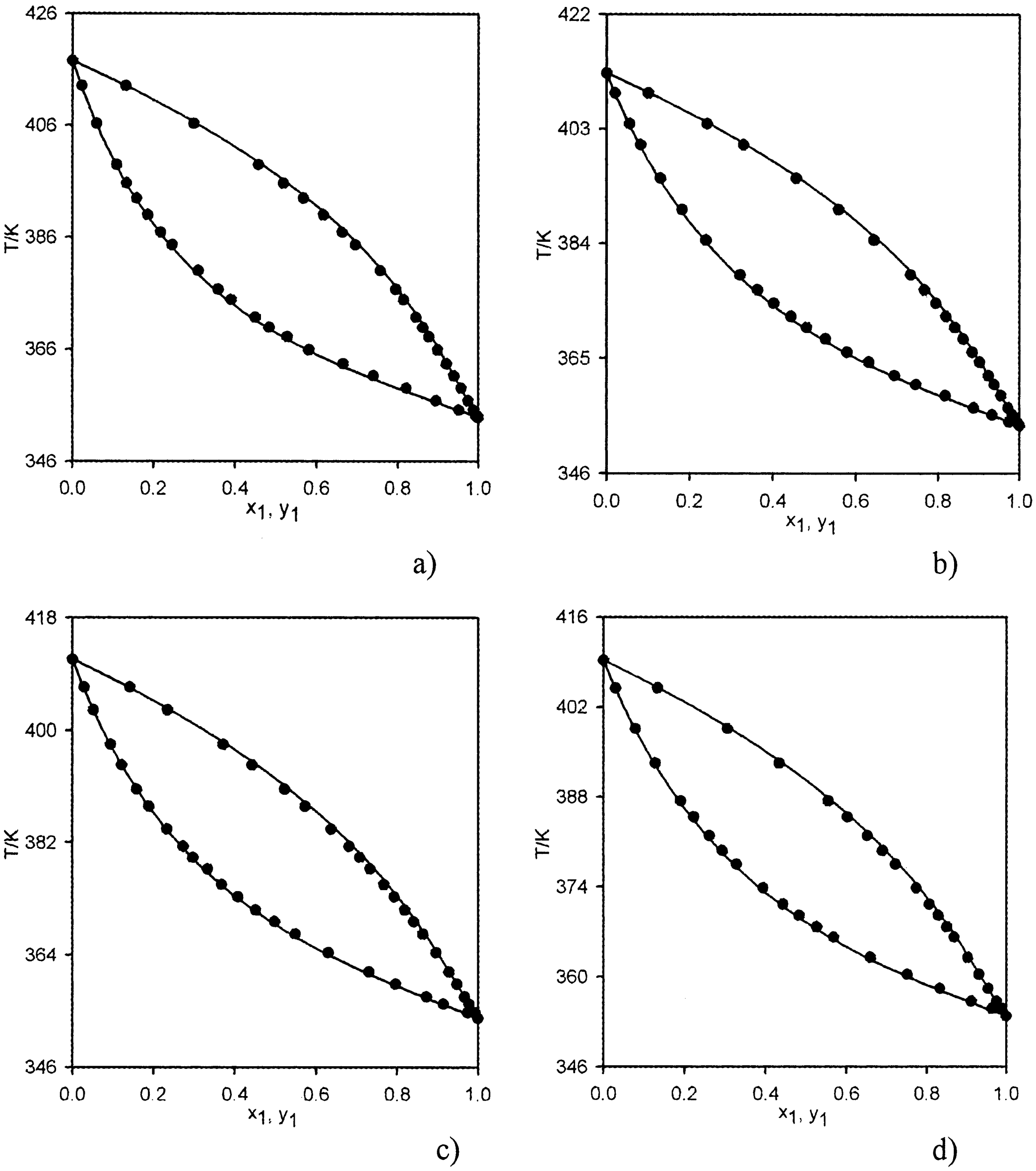

Figure 2. Temperature composition diagram for the binary systems at 101.3 kPa: ●, this work; —, UNIQUAC equation; (a) cyclohexane (1) + *o*-xylene (2); (b) cyclohexane (1) + *m*-xylene (2); (c) cyclohexane (1) + *p*-xylene (2); (d) cyclohexane (1) + ethylbenzene (2).

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
cyclohexane (1) + *o*-xylene (2)	3.02	2.18	2.64	3.17	0.026	0.017	0.022	0.026
cyclohexane (1) + *m*-xylene (2)	1.82	1.14	1.57	2.03	0.014	0.005	0.010	0.013
cyclohexane (1) + *p*-xylene (2)	2.37	1.56	2.03	2.50	0.021	0.011	0.016	0.020
cyclohexane (1) + ethylbenzene (2)	1.92	1.10	1.60	1.79	0.014	0.005	0.111	0.011

Stadtherr[27] version of the INTLIB/INTBIS (Kearfott and Novoa[28]) for interval arithmetic and guarantees that the global minimum of the objective function was achieved inside an initially specified range for each model parameter. The parameters obtained were based on minimization of the objective function *F* in terms of experimental and calculated γ_i values, given by

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

where n_{DAT} is the number of experimental data, γ_{exp} is the coefficient calculated from the experimental data, and γ_{calc} is the activity coefficient calculated from the y_1 and *T* correlations. Optimized parameter sets and the root-mean-square deviations of *T* and y_1 from the equations of Wilson and UNIQUAC are presented in Table 5. Although the correlations obtained on both models appear to be acceptable, the UNIQUAC equation represents the data successfully. 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. Widely used group-contribution models were applied, such as ASOG[8] and UNIFAC[9] and their modifications UNIFAC-Dortmund[10,11] and UNIFAC-Lyngby.[12] In all cases, the predictions were evaluated by comparison with the temperature and the concentration values of the vapor phase. Table 6 gives root-mean-square deviations between the experimental VLE data and those predicted for the temperature, $\sigma(T)$, and the composition of the vapor phase, $\sigma(y_1)$. The group interaction parameters were those published by Tochigi et al.,[8] Hansen et al.,[29] Gmehling et al.,[11] and Larsen et al.[12] for these methods. It can be observed that the description of these systems by the original UNIFAC method shows good agreement with the experimental data.

Remarkably high temperature deviations were observed for all the predictive models. This fact can be attributed to significant differences in the boiling points of these components. On the other hand, the group contribution models today are unable to distinguish details in the molecular structures such as isomers.

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