

Vapor–Liquid Equilibria of Binary and Ternary Mixtures of Benzene, Cyclohexane, and Chlorobenzene at 40.0 kPa and 101.3 kPa

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Vapor–liquid equilibrium data were measured at isobaric conditions for the binary mixtures of benzene + cyclohexane, benzene + chlorobenzene, and cyclohexane + chlorobenzene, and one ternary mixture of benzene + cyclohexane + chlorobenzene. The measurements were made in an equilibrium still with circulation of both the vapor and liquid phases. Thermodynamic consistency for the three binary mixtures was tested using the area and point-to-point test. The second virial coefficients obtained by the Tsonopoulos method were used to calculate the vapor-phase fugacity coefficients. The parameters of the Wilson, UNIQUAC, and NRTL equations were obtained by fitting to the binary and ternary data.

Introduction

The current environmental concern imposes a strong interest in studies of pollutants including solvents and pesticides. Benzene and cyclohexane are common solvents employed in a number of processes. Chlorobenzene is used in the production of some pesticides; it acts as an intermediary in the production of DDT with benzene and cyclohexane. Experimental vapor–liquid equilibria data for the systems benzene + cyclohexane and benzene + chlorobenzene were found in the literature, but some were measured in a narrow pressure band and others were not thermodynamically consistent. In this study, the isobaric vapor–liquid equilibria for three binary systems and one ternary system of benzene, cyclohexane, and chlorobenzene were measured and correlated with the Wilson, UNIQUAC, and NRTL models. The systems found to not be thermodynamically consistent were benzene + cyclohexane at 40 kPa¹ and cyclohexane + chlorobenzene at 101.3 kPa.² The system benzene + cyclohexane at 101.3 kPa has a lot of published data that are considered to be thermodynamically consistent. This system was used for testing the apparatus, and the data obtained in this work were compared to the reported data of Sieg³ and Chao.⁴ The system benzene + chlorobenzene at 101.3 kPa⁵ was also thermodynamically consistent, and it was used for comparison with the data of this work.

Experimental Section

Materials. Benzene, cyclohexane, and chlorobenzene (all analytical grade, Merck) were used without further purification. The products used in the present study were analyzed by gas chromatography and showed major peak areas consistent with more than 99% purities.

Apparatus and Procedure. The VLE data were measured by a dynamic method with a NORMAG ebulliometer, which is a commercial version of a Röck and Siege two-phase recirculating still.⁶ The apparatus consists of the ebulliometer, a thermostat bath filled with 8 L of triethyl-

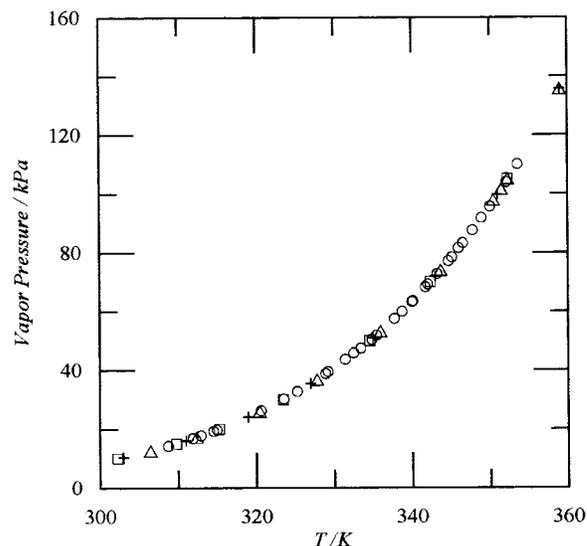


Figure 1. Vapor pressure diagram for ethanol: (○) this work; (□) Thermodynamics Research Center;⁷ (△) Ambrose and Sprake;⁸ (+), Smith and Srivastava.⁹

Table 1. Critical Temperature (T_c), Critical Pressure (P_c), Critical Volume (V_c), Critical Compressibility Factor (Z_c), Rackett's Parameter (Z_{RA}), Acentric Factor (ω), UNIQUAC Parameters (r , q), and Parameters of the Antoine Equation (A , B , C)

parameter	Bz ^b	Chex ^b	ClBz ^b
T_c /K	562.2	553.5	632.4
P_c /bar	48.9	40.7	45.2
Z_c	0.274	0.271	0.265
Z_{RA}	0.270	0.273	0.265
ω	0.212	0.212	0.249
r	3.1878	4.0464	3.8127
q	2.400	3.240	2.844
A^a	6.00477	5.97636	6.08681
B^a	1196.76	1206.47	1419.92
C^a	-53.989	-50.014	-56.925

^a A , B , and C are parameters in the vapor pressure equation: $\log(P^s/\text{kPa}) = A - B/(C + T/\text{K})$. ^b Bz = benzene, Chex = cyclohexane, ClBz = chlorobenzene.

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Table 2. Experimental VLE Data and Activity Coefficients (γ) for the System Benzene + Cyclohexane at 40.0 kPa and 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2
40.0 kPa				
325.75	0.000	0.000		1.000
324.30	0.112	0.125	1.180	1.041
323.65	0.208	0.238	1.239	1.040
323.50	0.237	0.262	1.204	1.052
322.95	0.388	0.423	1.212	1.046
322.85	0.432	0.454	1.172	1.070
322.90	0.637	0.616	1.077	1.175
323.10	0.708	0.672	1.049	1.239
323.20	0.724	0.687	1.045	1.246
323.55	0.807	0.765	1.030	1.321
325.55	1.000	1.000	1.000	
101.3 kPa				
353.80	0.000	0.000		1.000
352.55	0.125	0.144	1.176	1.016
352.50	0.132	0.154	1.193	1.014
351.85	0.210	0.235	1.167	1.027
351.65	0.229	0.252	1.154	1.034
351.30	0.278	0.293	1.117	1.055
351.20	0.310	0.332	1.139	1.046
350.75	0.412	0.428	1.119	1.065
350.55	0.552	0.549	1.078	1.109
350.60	0.579	0.565	1.056	1.136
350.75	0.645	0.624	1.042	1.160
350.90	0.706	0.687	1.044	1.160
351.20	0.758	0.726	1.018	1.223
351.40	0.803	0.772	1.016	1.243
351.60	0.839	0.808	1.012	1.274
352.05	0.893	0.868	1.007	1.300
353.25	1.000	1.000	1.000	

Table 3. Experimental VLE Data and Activity Coefficients (γ) for the System Benzene + Chlorobenzene at 40.0 kPa and 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2
40.0 kPa				
373.45	0.000	0.000		1.000
365.35	0.090	0.307	0.976	0.996
362.05	0.143	0.405	0.887	1.017
357.45	0.197	0.535	0.970	0.996
351.60	0.275	0.660	1.019	0.998
346.05	0.378	0.759	1.011	1.017
342.20	0.462	0.825	1.017	0.993
339.40	0.536	0.863	1.004	1.008
337.05	0.595	0.892	1.011	1.002
334.55	0.675	0.922	1.003	1.000
333.95	0.695	0.926	0.998	1.037
330.20	0.817	0.963	1.007	1.014
328.30	0.900	0.980	0.995	1.089
325.75	1.000	1.000	1.000	
101.3 kPa				
404.75	0.000	0.000		1.000
397.10	0.090	0.259	0.941	1.001
388.95	0.193	0.483	0.983	0.989
382.65	0.279	0.612	0.999	0.999
376.90	0.391	0.717	0.962	1.028
372.65	0.462	0.782	0.990	1.025
369.15	0.549	0.830	0.969	1.067
367.25	0.600	0.856	0.962	1.085
363.65	0.710	0.900	0.942	1.172
360.90	0.801	0.935	0.936	1.220
357.10	0.884	0.967	0.978	1.213
356.45	0.922	0.974	0.962	1.454
355.05	0.972	0.985	0.961	2.457
353.25	1.000	1.000	1.000	

eneglycol (TEG), a small compressor (Dental compressor, SCHULZ), a vacuum pump (C560488, Edwards), and a manostat to control the pressure. A flask with silica gel was connected in the line that links the ebulliometer to the vacuum pump. The equilibrium temperature was measured with a calibrated glass thermometer. Pressure

Table 4. Experimental VLE Data and Activity Coefficients (γ) for the System Cyclohexane + Chlorobenzene at 40.0 kPa

T/K	x_1	y_1	γ_1	γ_2
40.0 kPa				
373.45	0.000	0.000		1.000
369.25	0.021	0.160	2.023	0.986
362.45	0.060	0.351	1.861	0.997
348.25	0.228	0.640	1.343	1.125
344.95	0.277	0.690	1.319	1.174
340.55	0.376	0.773	1.250	1.185
337.25	0.457	0.826	1.223	1.193
334.35	0.560	0.869	1.156	1.250
330.35	0.666	0.923	1.182	1.148
328.70	0.780	0.944	1.093	1.361
328.10	0.826	0.953	1.064	1.483
326.65	0.919	0.979	1.034	1.517
325.95	1.000	1.000	1.000	
101.3 kPa				
404.75	0.000	0.000		1.000
391.35	0.105	0.362	1.334	1.027
378.75	0.280	0.638	1.180	1.050
372.55	0.375	0.760	1.224	0.973
369.60	0.458	0.810	1.152	0.977
365.75	0.600	0.850	1.020	1.187
362.35	0.694	0.892	1.014	1.253
360.95	0.777	0.914	0.964	1.436
359.35	0.842	0.928	0.944	1.793
356.05	0.953	0.970	0.956	2.822
353.80	1.000	1.000	1.000	

Table 5. Average Deviation in Vapor Phase Calculated by the Point-to-Point Test¹⁵ for the Systems Cyclohexane + Benzene, Cyclohexane + Chlorobenzene, and Benzene + Chlorobenzene

pressure (kPa)	cyclohexane + benzene			cyclohexane + chlorobenzene		benzene + chlorobenzene	
	$ \Delta y ^a$	$ \Delta y ^b$	$ \Delta y ^c$	$ \Delta y ^d$	$ \Delta y ^e$	$ \Delta y ^f$	$ \Delta y ^g$
40.0	0.005	0.020			0.010		0.001
101.3	0.009		0.003	0.002	0.010	0.046	0.010

^a This work. ^b Morachevsky and Zharov.¹ ^c Sieg.³ ^d Chao.⁴ ^e Rao and Rao.² ^f Serwinski and Michalowski.⁵

Table 6. Experimental VLE Data and Activity Coefficients (γ) for the System Benzene + Cyclohexane + Chlorobenzene at 40.0 kPa

T/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
326.70	0.748	0.149	0.777	0.204	1.006	1.327	1.078
325.55	0.459	0.445	0.483	0.504	1.062	1.144	0.833
326.65	0.157	0.746	0.190	0.785	1.174	1.022	1.509
335.25	0.429	0.155	0.603	0.294	1.008	1.371	1.002
334.75	0.146	0.436	0.207	0.680	1.034	1.146	1.117
355.35	0.094	0.090	0.233	0.319	0.941	1.376	1.018
343.05	0.198	0.200	0.336	0.442	0.940	1.241	1.088
328.80	0.395	0.384	0.451	0.501	1.025	1.174	1.157
331.25	0.346	0.353	0.426	0.500	1.013	1.171	1.178

Table 7. Experimental VLE Data and Activity Coefficients (γ) for the System Benzene + Cyclohexane + Chlorobenzene at 101.3 kPa

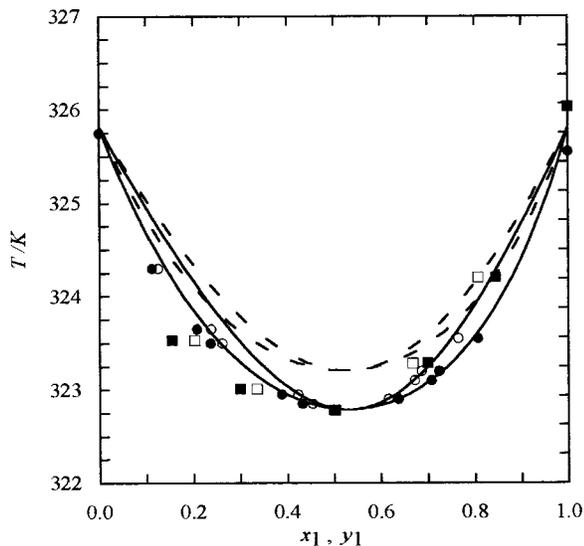
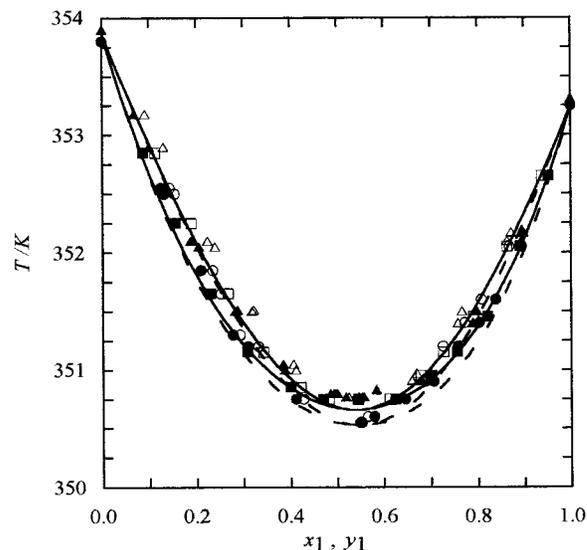
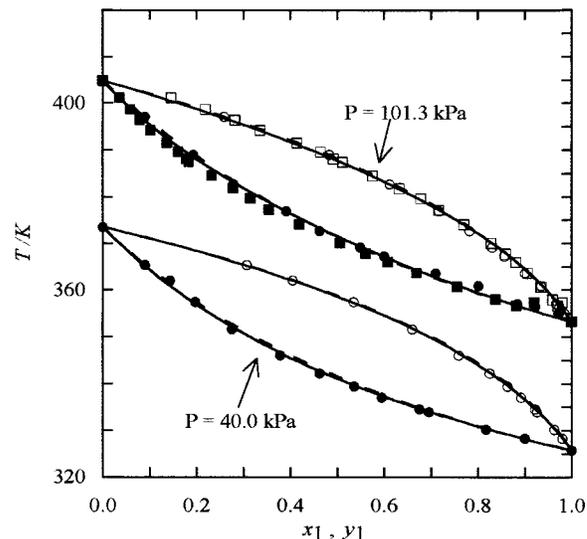
T/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
354.75	0.772	0.156	0.782	0.196	0.969	1.225	1.416
353.65	0.473	0.467	0.488	0.493	1.020	1.062	1.526
354.55	0.157	0.772	0.187	0.786	1.146	0.998	1.774
365.10	0.446	0.157	0.599	0.272	0.959	1.269	1.051
364.60	0.150	0.456	0.206	0.660	0.995	1.075	1.119
387.35	0.093	0.089	0.219	0.277	0.960	1.317	0.996
374.75	0.186	0.179	0.329	0.402	0.980	1.283	1.002
357.50	0.412	0.414	0.454	0.492	0.974	1.072	1.304
360.55	0.347	0.354	0.431	0.485	1.006	1.135	1.061

Table 8. Correlation Parameters and the Absolute Average Deviations in Boiling Points and Vapor-Phase Mole Fractions for the Binary Systems

model	A_{12}	A_{21}	$(\Delta y)_{av}$	$(\Delta T)_{av}$
$P = 40.0$ kPa				
Benzene + Cyclohexane				
Wilson	57.194	107.33	0.007	0.09
UNIQUAC	11.450	41.656	0.007	0.09
NRTL	214.73	-49.942	0.007	0.09
Benzene + Chlorobenzene				
Wilson	-212.78	372.07	0.004	0.26
UNIQUAC	0.4804	-0.4725	0.004	0.31
NRTL	-60.687	53.624	0.004	0.33
Cyclohexane + Chlorobenzene				
Wilson	-100.25	469.54	0.019	0.51
UNIQUAC	321.99	-163.53	0.019	0.53
NRTL	480.95	-150.66	0.019	0.59
$P = 101.3$ kPa				
Benzene + Cyclohexane				
Wilson	87.351	40.292	0.006	0.05
UNIQUAC	-39.085	87.376	0.006	0.05
NRTL	134.95	-81.406	0.006	0.05
Benzene + Chlorobenzene				
Wilson	-102.47	110.36	0.009	0.52
UNIQUAC	-216.57	301.34	0.009	0.55
NRTL	166.37	-167.67	0.009	0.52
Cyclohexane + Chlorobenzene				
Wilson	245.36	-60.114	0.014	0.61
UNIQUAC	-93.585	157.85	0.014	0.61
NRTL	169.91	377.96	0.014	0.61

Table 9. Correlation Parameters and the Absolute Average Deviations in Boiling Points and Vapor-Phase Mole Fractions for the Binary Systems (Data Reduction at Both 40.0 and 103.3 kPa)

model	A_{12}	A_{21}	$(\Delta y)_{av}$	$(\Delta T)_{av}$
Benzene + Cyclohexane				
Wilson	79.264	54.975	0.007	0.23
UNIQUAC	-14.952	62.533	0.007	0.23
NRTL	134.39	-3.1131	0.007	0.23
Benzene + Chlorobenzene				
Wilson	-20.439	-0.9730	0.007	0.52
UNIQUAC	3.3577	-10.842	0.007	0.51
NRTL	44.302	-64.884	0.007	0.50
Cyclohexane + Chlorobenzene				
Wilson	192.69	-3.6237	0.012	1.13
UNIQUAC	-25.369	77.422	0.012	1.13
NRTL	-74.767	262.31	0.012	1.13

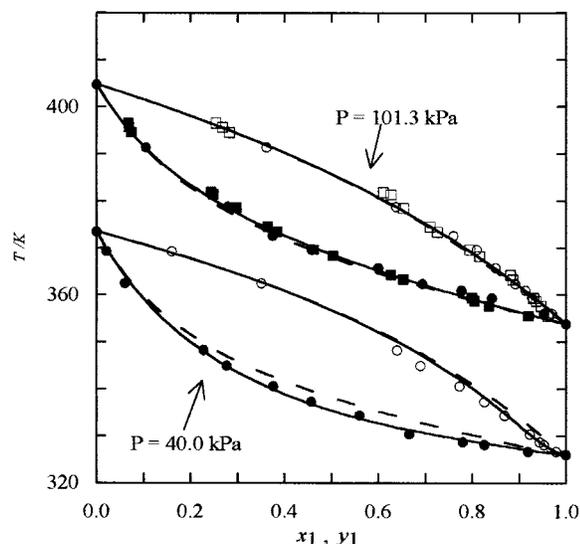
**Figure 2.** T - x - y diagram for benzene (1) + cyclohexane (2) at 40.0 kPa: (●) x_1 , (○) y_1 this work; (■) x_1 , (□) y_1 Morachevsky and Zharov;¹ (—) for 40.0 kPa and (---) for both data sets with the UNIQUAC equation.**Figure 3.** T - x - y diagram for benzene (1) + cyclohexane (2) at 101.3 kPa: (●) x_1 , (○) y_1 this work; (▲) x_1 , (△) y_1 Siege;³ (■) x_1 , (□) y_1 Chao;⁴ (—) for 101.3 kPa and (---) for both data sets with the UNIQUAC equation.**Figure 4.** T - x - y diagram for benzene (1) + chlorobenzene (2): (●) x_1 , (○) y_1 this work at 40.0 kPa and 101.3 kPa; (■) x_1 , (□) y_1 Rao² at 101.3 kPa; (—) for 40.0 or 101.3 kPa and (---) for both data sets with the UNIQUAC equation.

was determined by measuring differences in the height of the mercury in a U-tube manometer with a cathetometer. The calibration of both the apparatus and the analytical measurements was done by measuring the vapor pressure of pure ethanol in the range 309.75 K to 353.60 K with the Normag apparatus and by measuring the VLE data of benzene + cyclohexane at 101.3 kPa. The vapor pressure data obtained were compared with the data of refs 7–9 and are shown in Figure 1. The equilibrium compositions of sample liquid and condensed vapor phases were analyzed with a gas chromatograph (CG3537, Instrumentos Científicos CG-Brazil). A thermal conductivity detector was used along with a column (1.5 m by 3.125 mm) packed by carbowax and connected to an integrator (CDS 111, Varian). The gas carrier was hydrogen flowing at 4.7×10^{-7} $\text{m}^3 \cdot \text{s}^{-1}$ with a column temperature of 390 K.

The uncertainty in the pressure measurements was about ± 0.07 kPa, and the temperature uncertainty was about ± 0.05 K. The uncertainty in the final mole fractions

Table 10. Correlation Parameters and the Absolute Average Deviations in Boiling Points and Vapor-Phase Mole Fractions for the Ternary Systems Benzene + Cyclohexane + Chlorobenzene

model	A_{12}	A_{21}	A_{13}	A_{31}	A_{23}	A_{32}	$(\Delta y)_{av}$	$(\Delta T)_{av}$
Data Reduction at 40.0 kPa								
Wilson	174.24	-44.532	-1.1821	-7.5481	50.108	107.05	0.004	0.23
UNIQUAC	-91.641	160.15	-3.3976	0.96346	72.927	-24.025	0.004	0.23
NRTL	-8.4545	137.39	43.005	-51.829	84.186	69.441	0.004	0.23
Data Reduction at 101.3 kPa								
Wilson	47.234	27.541	10.034	-37.672	174.46	-10.067	0.008	0.31
UNIQUAC	-123.77	182.11	-198.95	263.45	-63.379	112.56	0.006	0.32
NRTL	132.4	-55.942	-14.516	-14.301	-93.854	262.9	0.008	0.31
Data Reduction at Both 40.0 and 101.3 kPa								
Wilson	86.321	8.1274	-6.2904	-14.664	97.445	54.736	0.005	0.48
UNIQUAC	-22.88	58	-17.778	9.5564	28.388	14.617	0.005	0.49
NRTL	44.828	47.281	-21.87	0.05214	9.7038	139.76	0.005	0.48

**Figure 5.** T - x - y diagram for cyclohexane (1) + chlorobenzene (2): (●) x_1 , (○) y_1 this work at 40.0 and 101.3 kPa; (■) x_1 , (□) y_1 Serwinski and Michalowski⁵ at 101.3 kPa; (—) for 40.0 or 101.3 kPa and (---) for both data sets with the UNIQUAC equation.

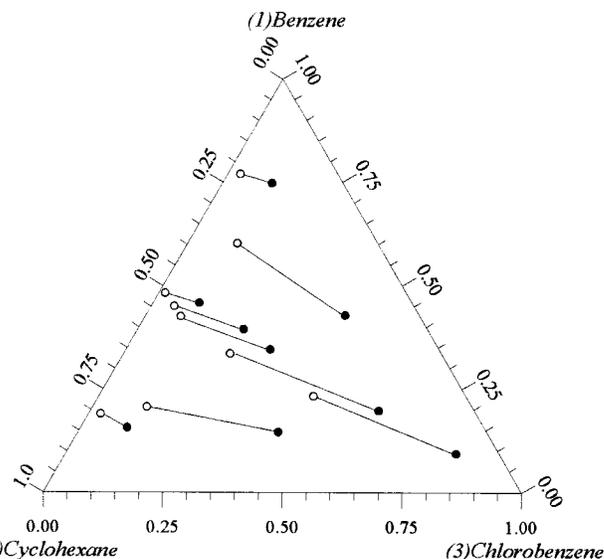
caused by the above uncertainties is estimated to be ± 0.003 .

The experimental procedure consists of heating the sample, reading the equilibrium temperature, and measuring the compositions of the liquid and the vapor phases. The sample was introduced into the reservoir of the ebulliometer and heated under constant pressure. Steady-state conditions were reached in about 1 h, as indicated by the constant boiling temperatures and continuous flow of both phases. The system was allowed to maintain this equilibrium state for about 30 min before samples were taken.

Results and Discussion

The pure component thermodynamic properties used in these calculations are given in Table 1. The critical properties and acentric factors were obtained from the literature¹⁰ as well as the UNIQUAC parameters that depend only on the molecular structure of the pure components.¹¹

Binary Systems. The experimental vapor-liquid equilibrium data for the systems benzene + cyclohexane, benzene + chlorobenzene, and cyclohexane + chlorobenzene are given in Tables 2–4 for pressures of 40.0 kPa and 101.3 kPa. All these systems form a homogeneous liquid phase; a minimum azeotrope was reported only for the benzene + cyclohexane mixture.

**Figure 6.** Vapor-liquid equilibrium tie lines for benzene (1) + cyclohexane (2) + chlorobenzene (3) at 40.0 kPa: (●) liquid phase; (○) vapor phase.

Experimental activity coefficients γ_i were calculated with the following equation:¹²

$$y_i \phi_i^L P = x_i \gamma_i P_i^s \phi_i^s \exp[V_i^L(P - P_i^s)/RT] \quad (1)$$

where y_i is the vapor-phase mole fraction and ϕ_i and ϕ_i^s are the fugacity coefficients of component i in the mixture and in the saturation conditions, respectively; they were calculated by using the second virial coefficient calculated with the Tsonopoulos method.¹³ P is the pressure, T is the temperature, x is the liquid-phase mole fraction, γ_i is the activity coefficient, and P_i^s is the vapor pressure of the pure components calculated with the Antoine equation with constants obtained from the literature for benzene, cyclohexane,¹¹ and chlorobenzene.¹⁰ The liquid molar volumes, V_i^L , were calculated with the modified Rackett equation.¹⁰

The results were tested for thermodynamic consistency by using the area test (Wisniak)¹⁴ and the point-to-point test of Van Ness-Fredenslund (Fredenslund et al.),¹⁵ following the Wilsak and Philip¹⁶ analysis, and were satisfactory, indicating that the measured data are thermodynamically consistent. The results using the point-to-point test of the data of three binaries treated in this work and of the literature data are given in Table 5.

Ternary Systems. The experimental data for the ternary systems are presented in Tables 6 and 7 and shown in Figures 6 and 7. The ternary system indicates the formation of just a minimum boiling azeotrope only in the

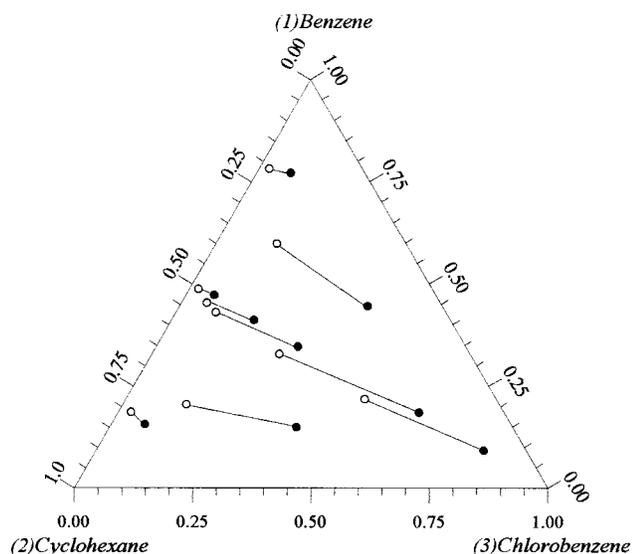


Figure 7. Vapor-liquid equilibrium tie lines for benzene (1) + cyclohexane (2) + chlorobenzene (3) at 101.3 kPa: (●) liquid phase; (○) vapor phase.

region of the mixture of the binary benzene + cyclohexane, confirmed by experimental data for the binary system and, later, for the calculation of the ternary diagram with the models.

Correlation and Prediction

The activity coefficients of the binary and ternary systems were correlated by the Wilson, UNIQUAC, and NRTL equations.¹² The binary adjustable parameters for various models are as follows: Wilson, $A_{ij} = (\lambda_{ij} - \lambda_{ji})/R$; UNIQUAC, $A_{ij} = (u_{ij} - u_{ji})/R$; NRTL, $A_{ij} = (g_{ij} - g_{ji})/R$ with $\alpha_{ij} = 0.3$. The binary parameters for all models, A_{ij} , were evaluated by a nonlinear regression method based on the maximum-likelihood principle,¹⁷ which facilitates the treatment of data involving different numbers of restrictions simultaneously as, for example, the correlation of groups of different data.

The following objective function was minimized during optimization of the parameters in each of the equations:

$$FO = \sum_{k=1}^d \sum_{j=1}^{N_k} \left\{ \left(\frac{P_{jk} - P_{jk}^{\text{exp}}}{\sigma_{P_{jk}}} \right)^2 + \left(\frac{T_{jk} - T_{jk}^{\text{exp}}}{\sigma_{T_{jk}}} \right)^2 + \sum_{i=1}^{C_k-1} \left[\left(\frac{x_{ijk} - x_{ijk}^{\text{exp}}}{\sigma_{x_{ijk}}} \right)^2 + \left(\frac{y_{ijk} - y_{ijk}^{\text{exp}}}{\sigma_{y_{ijk}}} \right)^2 \right] \right\} \quad (2)$$

where d is the number of the data group, N_k is the number of experimental data in each group k , C_k is the number of components of each group k , and σ is the estimated standard deviation of each of the measured variables, that is, pressure, P , temperature, T , and liquid-phase and vapor-phase mole fraction, x and y . The fitted parameters together with the mean values of the absolute deviations in boiling

points, ΔT , and in vapor-phase mole fraction, Δy , for all systems are given in Tables 8–10.

The small deviations of the adjustment and the good agreement of the fit to the experimental points indicate that all the activity coefficient models are adequate to represent the binary experimental data. The UNIQUAC model supplied slightly smaller deviations and was chosen in this work to calculate the equilibrium curves of the binary systems shown in Figures 2–5 together with the data of this work and the literature data. The continuous line represents the regression done with the data of just one group (same pressure). The dotted line represents the regression done with the data at both pressures (40 and 101.3 kPa).

Conclusion

The results from the two consistency tests indicate that all the groups of data for binary systems obtained in this work are thermodynamically consistent. The parameters estimated for the activity coefficient models (Wilson, NRTL, and UNIQUAC) show that all three models were satisfactory for all mixtures.

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