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Vapor−Liquid Equilibria and Excess Enthalpy Data for the Binary Systems Benzene + Benzonitrile and Toluene + Benzonitrile Covering the Temperature Range from 323.15 to 413.15 K

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Isothermal $P-x$ data (VLE) and excess enthalpy (H^E) data for the two binary systems benzene + benzonitrile and toluene + benzonitrile have been measured by means of a computer-operated static apparatus and an isothermal flow calorimeter. Activity coefficients at infinite dilution γ_i^∞ have been derived by fitting a flexible Legendre polynomial to the experimental VLE data. Temperature-dependent interaction parameters for different excess Gibbs energy (G^E) models have been fitted simultaneously to the experimental VLE and H^E data. The experimental results have been compared with the data of other authors.

Introduction

For the description of the phase equilibrium behavior, G^E models can be used, which allow the prediction of multicomponent systems from binary data alone. If no experimental data are available, group contribution methods, such as ASOG, UNIFAC, mod. UNIFAC (Dortmund), or mod. UNIFAC (Lyngby), can be employed. For the revision and extension of these methods, a systematic extension of the existing database is desired.

For the systems benzene + benzonitrile toluene + benzonitrile, respectively, only one isothermal VLE data set at 343.15 K (Martin and Collie (1932)) and one isobaric data set at atmospheric pressure (Ezhov et al. (1976)) are reported. In this paper isothermal $P-x$ data measured with a computer-operated static apparatus are presented for the systems benzene + benzonitrile and toluene + benzonitrile at 323.15 K and 353.15 K and compared with published data.

The temperature dependence of the excess Gibbs energy (G^E) is related with the Gibbs−Helmholtz equation to the excess enthalpy (H^E). Since the published H^E data (Amaya (1961), Fedorova and Sumarokova (1978), Kedrina et al. (1981), Lutsky et al. (1958), Tanaka et al. (1974)) and activity coefficients at infinite dilution (Park et al. (1987), Pul'tsin et al. (1973), Vernier et al. (1969)) for these systems cover only the range from 293.15 K to 303.15 K, additional H^E data were measured with an isothermal flow calorimeter at 323.15 K, 363.15 K, and 413.15 K.

The experimental VLE and H^E data of this work are presented together with the derived activity coefficients at infinite dilution and the temperature-dependent interaction parameters for the Wilson, NRTL, and UNIQUAC models.

Experimental Section

Purity of Materials. Benzene and toluene were purchased from Scharlau while benzonitrile was supplied by BASF. For the VLE measurements all chemicals were dried over molecular sieves, degassed, and distilled as described by Fischer and Gmehling (1994). For the H^E measurements the compounds were used without degassing. The suppliers and final purities as determined by gas chromatography and Karl Fischer titration are listed in Table 1.

Table 1. Suppliers, Purities, and Water Contents of the Chemicals Used

	benzene	toluene	benzonitrile
supplier	Scharlau	Scharlau	BASF
purity/% GC	99.99	99.97	99.98
water content/mass ppm	20	70	35

Apparatus and Procedure. The VLE measurements (isothermal $P-x$ data) were performed with a computer driven static apparatus following the principle proposed by Gibbs and Van Ness (1972). In this device the total pressure P is measured for different overall compositions at constant temperature T. The apparatus and measurement procedure have been described previously (Rarey and Gmehling, 1993, Rarey et al., 1998). It can be applied at temperatures between 278 K and 368 K and pressures from 0 to 0.3 MPa. The thermostated, purified, and degassed compounds are filled into the thermostated and evacuated equilibrium cell. The pressure inside the cell is monitored using a Digiquartz pressure sensor (Model 245A, Paroscientific) and the temperature is measured with a Pt100 resistance thermometer (Model 1506, Hart Scientific). The total compositions can be determined from exactly known volumes of liquids injected into the cell using stepping motor-driven injection pumps and valves. From the total compositions the liquid-phase compositions are obtained by solving the mass and volume balance, taking into account the vapor−liquid equilibrium. Due to the low system pressures of the investigated systems, the calculated liquid-phase compositions are nearly identical with the feed compositions. The experimental uncertainties of this apparatus are as follows: $\sigma(T) = 0.03$ K, $\sigma(P) = 20$ Pa $+ 0.0001$ (P/Pa), $\sigma(x_i) = 0.0001$.

For the measurements of the H^E data a commercial isothermal flow calorimeter (Model 7501, Hart Scientific, Provo, UT) described by Gmehling (1993) and Gardeler et al. (1998) was used. In this type of calorimeter two syringe pumps (Model LC-2600, ISCO) provide a flow of constant composition through a thermostated flow cell equipped with

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Table 2. Pure Component Parameters:[a] Relative van der Waals Volumes r_i and Surfaces q_i, Antoine Coefficients A_i, B_i, and C_i, and Molar Volumes v_i

component	benzene	toluene	benzonitrile
r_i	3.1878	3.9228	3.9900
q_i	2.400	2.968	3.010
A_i	6.00477	6.07577	6.79506
B_i/K	1196.76	1342.31	2066.71
C_i/K	−53.989	−53.963	−32.190
v_i/dm^3 mol^{-1}	0.08941	0.10685	0.10307

[a] DDB (1998).

Table 3. Experimental $P-x$ Data for the System Benzene (1) + Benzonitrile (2) at 323.15 K

x_1	P/kPa	x_1	P/kPa	x_1	P/kPa	x_1	P/kPa
0.000 00	0.588	0.174 79	7.971	0.549 74	21.733	0.928 54	33.900
0.002 42	0.699	0.211 99	9.447	0.558 85	22.044	0.947 84	34.525
0.005 26	0.825	0.250 00	10.927	0.580 00	22.753	0.962 83	35.016
0.008 08	0.953	0.289 97	12.458	0.585 64	22.943	0.974 45	35.400
0.010 91	1.080	0.329 20	13.924	0.611 78	23.815	0.981 98	35.653
0.014 20	1.229	0.368 57	15.375	0.643 85	24.874	0.986 77	35.818
0.017 48	1.380	0.403 58	16.641	0.675 74	25.914	0.990 62	35.954
0.024 00	1.672	0.437 15	17.837	0.708 26	26.966	0.993 55	36.060
0.030 78	1.973	0.470 20	19.000	0.744 09	28.110	0.995 50	36.129
0.040 99	2.412	0.494 48	19.841	0.778 77	29.208	0.997 45	36.196
0.058 51	3.155	0.502 32	20.116	0.813 27	30.288	0.998 74	36.237
0.080 00	4.078	0.522 49	20.805	0.845 06	31.288	0.999 37	36.252
0.106 33	5.174	0.532 31	21.142	0.875 32	32.232	1.000 00	36.276
0.139 24	6.532			0.903 34	33.104		

a pulsed heater and a Peltier cooler. The use of a Peltier cooler allows the measurement of endothermal as well as exothermal heat effects. A back-pressure regulator serves to keep the pressure at a level at which evaporation effects can be prevented. The experimental uncertainties of this device are as follows: $\sigma(T) = 0.03$ K, $\sigma(H^E) = 0.01$ (H^E/J mol^{-1}), $\sigma(x_i) = 0.0001$.

Results

The experimental $P-x$ and H^E data for the investigated systems are listed in Tables 3−8. For both systems temperature dependent G^E model parameters for the Wilson (Wilson, 1964), NRTL (Renon and Prausnitz, 1968), and UNIQUAC (Abrams and Prausnitz, 1975) models were fitted simultaneously to the experimental data (VLE, H^E) including additional H^E data from Wilhelm et al. (1998) measured between 293.15 K and 303.15 K. Because of the unusual H^E behavior, the weighting factor for these data was set to a small value. The following expression was used to describe the temperature dependence of the interaction parameters:

$$A_{ij}/\mathrm{J\ mol^{-1}} = a_{ij} + b_{ij}(T/\mathrm{K}) + c_{ij}(T/\mathrm{K})^2 \qquad (1)$$

where $A_{ij} = \lambda_{ij} - \lambda_{ii}$ (Wilson), $A_{ij} = g_{ij} - g_{jj}$ (NRTL), or $A_{ij} = u_{ij} - u_{jj}$ (UNIQUAC). The obtained parameters are listed in Tables 9 and 10.

The pure component properties used for the calculations were taken from the Dortmund Data Bank (DDB 1998) and are given in Table 2, where the Antoine coefficients A_i, B_i, and C_i are expressed by the following equation:

$$\log(P_i^{\mathrm{s}}/\mathrm{kPa}) = A_i - \frac{B_i}{C_i + T/\mathrm{K}} \qquad (2)$$

Table 4. Experimental $P-x$ Data for the System Benzene (1) + Benzonitrile (2) at 353.15 K

x_1	P/kPa	x_1	P/kPa	x_1	P/kPa	x_1	P/kPa
0.000 00	2.437	0.178 27	22.979	0.561 82	61.842	0.947 67	96.292
0.002 34	2.721	0.215 96	27.082	0.579 72	63.411	0.962 65	97.675
0.003 63	2.887	0.254 12	31.161	0.588 58	64.341	0.974 22	98.731
0.005 58	3.132	0.293 92	35.361	0.611 47	66.365	0.981 97	99.458
0.008 16	3.448	0.333 09	39.403	0.643 52	69.309	0.987 26	99.962
0.011 51	3.850	0.372 40	43.410	0.675 43	72.149	0.990 83	100.31
0.015 13	4.288	0.407 32	46.909	0.707 96	75.086	0.993 49	100.56
0.021 70	5.069	0.440 79	50.215	0.743 80	78.280	0.996 19	100.81
0.028 57	5.894	0.473 70	53.428	0.778 50	81.353	0.997 84	100.98
0.039 92	7.257	0.505 61	56.506	0.813 01	84.373	0.998 96	101.09
0.058 60	9.436	0.522 25	57.994	0.844 87	87.173	0.999 47	101.15
0.081 07	12.042	0.535 42	59.346	0.875 12	89.826	1.000 00	101.23
0.107 95	15.109	0.549 48	60.578	0.903 17	92.290		
0.141 95	18.953			0.928 37	94.546		

Table 5. Experimental H^E Data for the System Benzene (1) + Benzonitrile (2)

323.15 K and 1.48 MPa		363.15 K and 1.48 MPa		413.15 K and 1.55 MPa	
x_1	H^E/J mol^{-1}	x_1	H^E/J mol^{-1}	x_1	H^E/J mol^{-1}
0.0575	10.050	0.0575	4.805	0.0286	−1.895
0.1140	15.878	0.1140	9.431	0.0569	−4.231
0.1697	20.318	0.1697	11.539	0.1130	−7.175
0.2246	23.337	0.2246	12.689	0.1683	−11.538
0.2786	26.297	0.2786	12.713	0.2228	−13.962
0.3581	27.469	0.3581	12.072	0.2766	−16.348
0.4358	25.421	0.4358	10.346	0.3295	−18.249
0.5367	21.559	0.5367	9.187	0.3818	−19.985
0.6348	16.185	0.6348	8.141	0.4333	−21.627
0.7064	13.554	0.7064	8.355	0.4841	−21.031
0.7766	11.822	0.7766	11.450	0.5342	−20.302
0.8225	12.963	0.8225	13.641	0.5836	−17.206
0.8678	13.753	0.8678	16.138	0.6324	−14.872
0.9125	13.618	0.9125	17.596	0.6805	−10.281
0.9565	11.824	0.9565	13.994	0.7280	−5.773
				0.7748	1.519
				0.8210	7.568
				0.8666	12.766
				0.9117	18.695
				0.9561	18.097
				0.9781	14.126

Table 6. Experimental $P-x$ Data for the System Toluene (1) + Benzonitrile (2) at 323.15 K

x_1	P/kPa	x_1	P/kPa	x_1	P/kPa	x_1	P/kPa
0.000 00	0.485	0.128 71	2.446	0.504 94	7.182	0.937 14	11.598
0.001 49	0.509	0.162 65	2.928	0.535 62	7.520	0.954 76	11.779
0.003 02	0.534	0.198 47	3.427	0.568 21	7.872	0.968 55	11.924
0.004 44	0.558	0.235 47	3.928	0.601 48	8.226	0.977 94	12.025
0.007 35	0.608	0.274 72	4.444	0.634 96	8.577	0.983 96	12.092
0.011 68	0.678	0.313 39	4.939	0.669 48	8.934	0.988 83	12.146
0.015 98	0.747	0.352 52	5.427	0.708 00	9.325	0.992 46	12.185
0.020 44	0.817	0.387 43	5.853	0.745 77	9.703	0.994 87	12.211
0.026 78	0.916	0.421 07	6.253	0.783 84	10.081	0.996 56	12.229
0.037 67	1.085	0.449 74	6.561	0.819 36	10.430	0.998 29	12.248
0.053 43	1.329	0.454 12	6.638	0.853 54	10.764	0.999 15	12.255
0.073 07	1.623	0.477 59	6.875	0.885 61	11.078	1.000 00	12.268
0.097 55	1.992			0.914 67	11.366		

For the components benzene and toluene the deviations between experimental pure component vapor pressures P_i^{s} and calculated values using the Antoine coefficients from the DDB are smaller than 0.3%. Due to the small absolute values for the vapor pressures of benzonitrile, the deviations for this component are up to 16% but not bigger than 0.17 kPa. These discrepancies may result from the fact that the chemicals were degassed in different charges. To account only for the excess Gibbs energy G^E, the Antoine coefficients A_i were adjusted to the experimental data during the parameter-fitting procedure.

Figures 1−4 show the experimental $P-x$ and H^E data from this work together with the data from Wilhelm et al. (1998) and values calculated with the NRTL parameters given in Tables 9 and 10. Figure 1 also contains the isothermal $P-x-y$ data set for the system benzene + benzonitrile from Martin and Collie (1932), which was not included in the data regression. In Figure 5 a comparison

Table 7. Experimental $P-x$ Data for the System Toluene (1) + Benzonitrile (2) at 353.15 K

x_1	P/kPa	x_1	P/kPa	x_1	P/kPa	x_1	P/kPa
0.000 00	2.439	0.146 95	9.267	0.478 79	22.218	0.937 69	36.834
0.004 01	2.646	0.179 44	10.669	0.506 14	23.165	0.955 22	37.397
0.005 11	2.705	0.213 29	12.094	0.536 83	24.210	0.968 98	37.850
0.006 21	2.765	0.249 63	13.592	0.569 40	25.302	0.978 28	38.160
0.008 81	2.900	0.285 73	15.039	0.602 65	26.398	0.984 19	38.360
0.012 55	3.087	0.322 74	16.492	0.636 10	27.476	0.988 99	38.523
0.016 22	3.268	0.356 08	17.768	0.670 60	28.568	0.992 61	38.651
0.019 90	3.449	0.388 54	18.982	0.709 04	29.779	0.994 99	38.734
0.025 45	3.710	0.409 31	19.756	0.746 75	30.948	0.99 664	38.793
0.034 82	4.137	0.420 94	20.173	0.784 75	32.116	0.998 36	38.853
0.048 36	4.778	0.429 12	20.461	0.820 19	33.201	0.999 19	38.883
0.066 24	5.629	0.450 94	21.240	0.854 28	34.239	1.000 00	38.914
0.088 94	6.673	0.452 78	21.322	0.886 26	35.218		
0.116 52	7.919			0.915 27	36.121		

Table 8. Experimental H^E Data for the System Toluene (1) + Benzonitrile (2)

323.15 K and 1.41 MPa		363.15 K and 1.48 MPa		413.15 K and 1.48 MPa	
x_1	H^E/J mol^{-1}	x_1	H^E/J mol^{-1}	x_1	H^E/J mol^{-1}
0.0485	4.397	0.0485	9.472	0.0481	10.432
0.0972	7.793	0.0972	16.299	0.0963	22.433
0.1706	11.129	0.1461	22.152	0.1448	29.387
0.2442	13.035	0.1951	26.778	0.1935	41.166
0.3182	13.355	0.2442	31.295	0.2423	47.362
0.3926	12.534	0.3182	36.957	0.2914	54.969
0.4922	11.098	0.3926	41.631	0.3407	62.323
0.5925	11.991	0.4922	47.106	0.3901	68.596
0.6681	13.934	0.5925	51.233	0.4398	75.510
0.7441	17.405	0.6681	53.668	0.4897	80.665
0.8205	21.194	0.7441	55.222	0.5398	84.335
0.8972	21.305	0.7950	55.260	0.5901	89.854
0.9485	16.506	0.8460	51.909	0.6406	92.812
		0.8972	46.091	0.6913	93.599
		0.9485	31.448	0.7422	94.141
				0.7933	90.032
				0.8447	83.053
				0.8962	68.788
				0.9480	43.306

Table 9. Temperature Dependent G^E Model Interaction Parameters for the System Benzene (1) + Benzonitrile (2)

model	i	j	a_{ij}/J mol^{-1}	b_{ij}/J mol^{-1} K^{-1}	c_{ij}/J mol^{-1} K^{-2}	
Wilson	1	2	1609.43	−10.4797	0.012 672 06	
	2	1	−2283.23	17.9209	−0.018 464 79	
NRTL	1	2	−3261.07	27.9210	−0.026 059 02	$\alpha_{12} = 0.2311$
	2	1	2414.24	−19.1382	0.018 972 90	
UNIQUAC	1	2	−1922.76	13.9825	−0.015 525 53	
	2	1	1554.60	−10.5577	0.012 418 38	

Table 10. Temperature Dependent G^E Model Interaction Parameters for the System Toluene (1) + Benzonitrile (2)

model	i	j	a_{ij}/J mol^{-1}	b_{ij}/J mol^{-1} K^{-1}	c_{ij}/J mol^{-1} K^{-2}	
Wilson	1	2	488.91	−5.5536	0.005 384 60	
	2	1	−1525.31	16.6656	−0.016 479 66	
NRTL	1	2	−1937.87	20.3545	−0.020 449 17	$\alpha_{12} = 0.3224$
	2	1	830.27	−8.7289	0.008 763 89	
UNIQUAC	1	2	−898.79	10.2637	−0.009 576 26	
	2	1	454.28	−5.5709	0.004 854 85	

is given between the NRTL correlation and the isobaric $T-x-y$ data set for the system toluene + benzonitrile from Ezhov et al. (1976), which was not used for fitting the temperature dependent G^E model parameters. As can be seen, good agreement between the correlation and the published VLE data is obtained.

The H^E data from this work and Wilhelm et al. (1998) are consistent with the data from Lutsky et al. (1958) and Tanaka et al. (1974) whereas the data from Amaya (1961), Fedorova and Sumarokova (1978), and Kedrina et al. (1981) seem to be of lower quality. The small H^E values are described qualitatively using quadratic temperature dependent G^E model parameters even though the G^E models do not describe the observed unusual H^E behavior.

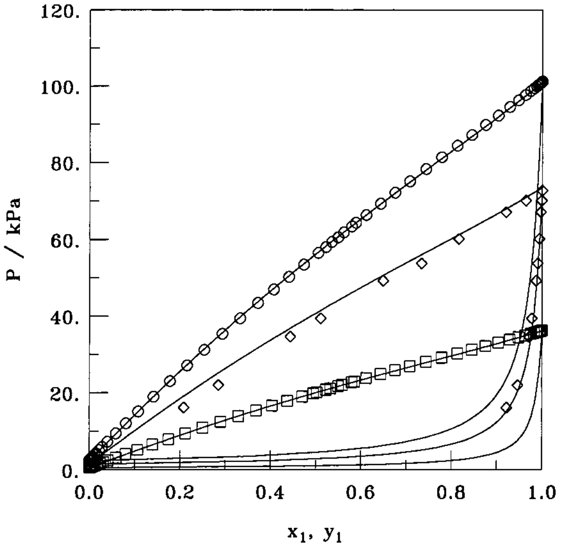

Figure 1. Experimental and predicted $P-x(y)$ behavior of the system benzene (1) + benzonitrile (2): this work at (□) 323.15 K and (○) 353.15 K; (◇) Martin and Collie (1932) at 343.15 K; (—) NRTL.

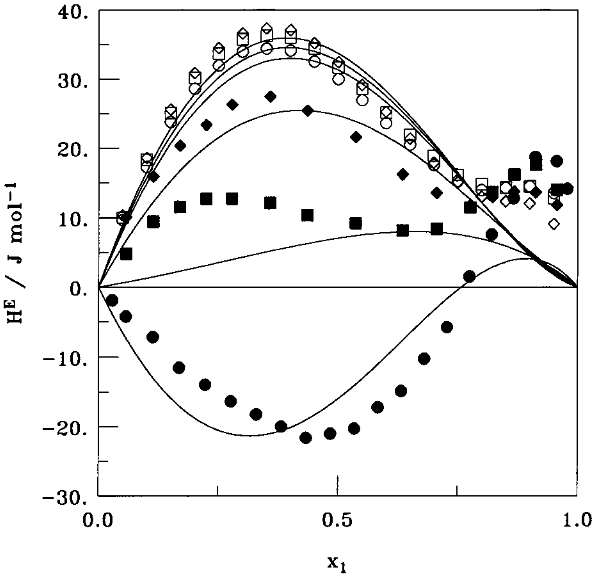

Figure 2. Experimental and predicted excess enthalpy data for the system benzene (1) + benzonitrile (2): this work at (◆) 323.15 K, (■) 363.15 K, and (●) 413.15 K; Wilhelm et al. (1998) at (◇) 293.15 K, (□) 298.15 K, and (○) 303.15 K; (—) NRTL.

From the experimental $P-x$ data from this work, activity coefficients at infinite dilution γ_i^∞ were derived using a Legendre polynomial (Kolbe, 1983), which is more flexible than the mentioned G^E models. The results are given in Table 11 together with published data.

Conclusions

$P-x$ and H^E data for the systems benzene + benzonitrile and toluene + benzonitrile were measured by means of the static method and a flow calorimeter, respectively, at different temperatures. Quadratic temperature dependent G^E model interaction parameters were fitted to the experi-

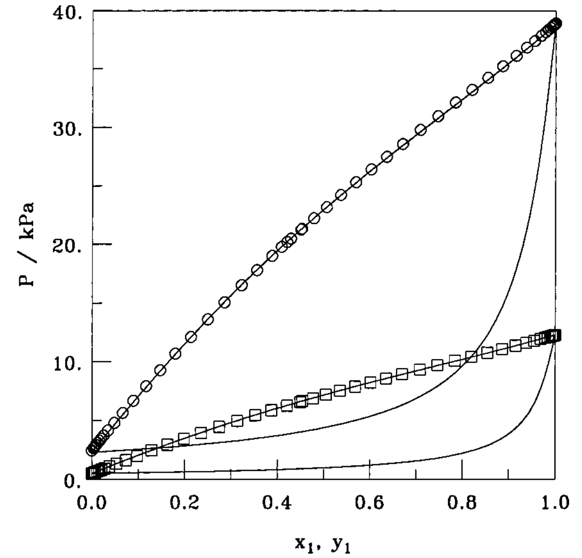

Figure 3. Experimental and predicted $P-x(y)$ behavior of the system toluene (1) + benzonitrile (2): this work at (□) 323.15 K and (○) 353.15 K; (—) NRTL.

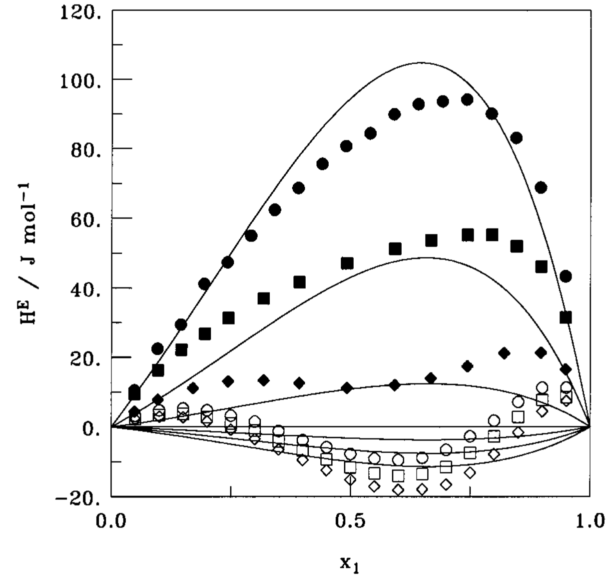

Figure 4. Experimental and predicted excess enthalpy data for the system toluene (1) + benzonitrile (2): this work at (◆) 323.15 K, (■) 363.15 K, and (●) 413.15 K; Wilhelm et al. (1998) at (◇) 293.15 K, (□) 298.15 K, and (○) 303.15 K; (—) NRTL.

mental data, including the H^E data from Wilhelm et al. (1998). Using these parameters, good agreement between calculated and all experimental $P-x$ data is obtained for the temperature range covered.

The quality of the description of these slightly nonideal systems is nearly independent of the selected G^E model. The average relative deviation between experimental pressures and those calculated with the NRTL parameters given in Tables 9 and 10 is 0.0044 for the system benzene + benzonitrile (Wilson, 0.0039; UNIQUAC, 0.004) and 0.0039 for the system toluene + benzonitrile (Wilson, 0.0034; UNIQUAC, 0.0036). Moreover, published VLE data can be described reliably with the fitted G^E model parameters.

Using quadratic temperature dependent interaction parameters, only a qualitative description of the small excess enthalpies at different temperatures is achieved whereby the unusual shape of the H^E curves for these systems cannot be described with the chosen G^E models.

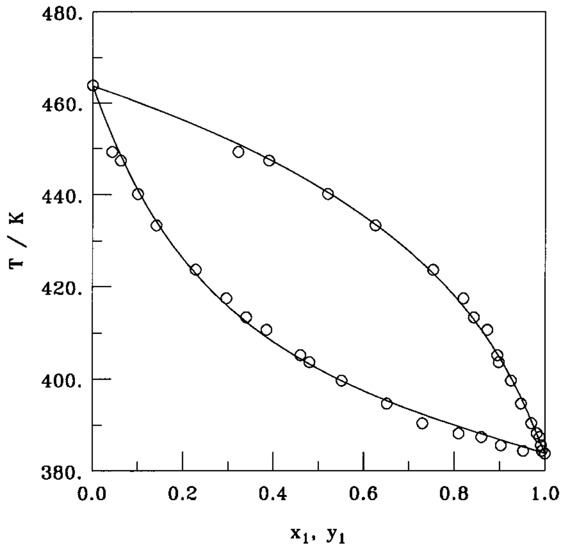

Figure 5. Experimental and predicted $T-x-y$ behavior of the system toluene (1) + benzonitrile (2): (○) Ezhov et al. (1976) at 101.325 kPa; (—) NRTL.

Table 11. Comparison of the Activity Coefficients at Infinite Dilution γ_i^∞ for the Systems Benzene + Benzonitrile and Toluene + Benzonitrile with Published Data

component 1	component 2	T/K	γ_1^∞	γ_2^∞	source
benzene	benzonitrile	298.15	1.240		Vernier et al. (1969)
		303.15	1.170		Pul'tsin et al. (1973)
		323.15	1.252	1.493	this work
		353.15	1.239	1.455	this work
toluene	benzonitrile	298.15	1.310		Park et al. (1987)
		323.15	1.386	1.679	this work
		353.15	1.357	1.616	this work

The temperature dependence of the activity coefficients at infinite dilution estimated from the $P-x$ data is consistent with the measured H^E data. However, the published activity coefficients at infinite dilution are a little smaller than our values.

Due to the good agreement between all experimental and calculated values, the G^E model parameters given in Tables 9 and 10 can be recommended for the investigated systems in the temperature range from 273 K to 453 K.

Acknowledgment

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Literature Cited

Abrams, D. S.; Prausnitz, J. M. Statistical Thermodynamics of Liquid Mixtures: A New Expression for the Excess Gibbs Energy of Partly or Completely Miscible Systems. *AIChE J.* **1975**, *21*, 116−128.

Amaya, K. Thermodynamical Studies on Binary Systems Consisting of Polar and Nonpolar Liquids. II. The Measurement of the Heats of Mixing for Binary Systems of Polar and Nonpolar Liquids. *Bull. Chem. Soc. Jpn.* **1961**, *34*, 1278−1285.

Ezhov, V. S.; Golovko, S. N.; Guseinov, E. M. Determination of Equilibrium Characteristics for the Systems Vapor-Liquid and Liquid−Liquid Corresponding to Products of Oxidation and Ammonolysis of Toluene, α- and β-Picoline. *Khim. Farm. Zh.* **1976**, *10*, 77−79.

Federova, V. I.; Sumarokova, T. H. Thermodynamic Examination of the System $SnCl_4$−C_6H_6, CH_3CN−C_6H_6 and C_6H_5CN−C_6H_6. Communication III. *Izv. Akad. Nauk. Kaz. SSR, Ser. Khim.* **1978**, *28*, 71−73.

Fischer, K.; Gmehling, J. $P-x$ and γ^∞ Data for the Different Binary Butanol−Water Systems at 50 °C. *J. Chem. Eng. Data* **1994**, *39*, 309−315.

Gardeler, H.; Horstmann, S.; Tsuboi, A.; Toba, S.; Rarey, J.; Gmehling, J. Vapor-Liquid Equilibria at Six Temperatures from 313.15 K to 402.15 K and Excess Enthalpy Data at 363.15 K and 1.65 MPa for the System Toluene + 2,2,4-Trimethylpentane (Isooctane). *ELDATA: Int. Electron. J. Phys.—Chem. Data* **1998**, *4*, 1−10.

Gibbs, R. E.; Van Ness, H. C. Vapor-Liquid Equilibria from Total-Pressure Measurements. A New Apparatus. *Ind. Eng. Chem. Fundam.* **1972**, *11*, 410−413.

Gmehling, J. Excess Enthalpies for 1,1,1-Trichloroethane with Alkanes, Ketones, and Esters. *J. Chem. Eng. Data* **1993**, *38*, 143−146.

Kedrina, N. N.; Semenov, L. V.; Gaile, A. A. Heats of Mixing of Hydrocarbons with Polar Solvents. *Deposited Doc. Oniitekhim.* **1981**, 600KHP-D81.

Kolbe, B. Description of the Thermodynamic Properties of Liquid Mixtures Over a Wide Temperature and Pressure Range on the Example of the System Ethanol/Water. Dissertation, Dortmund, 1983.

Lutsky, A. E.; Obukhova, E. T.; Petrenko, B. T. Heats of Mixing and Dipole Moments of Molecular Components. *Zh. Phys. Khim.* **1958**, *32*, 720−721.

Martin, A. R.; Collie, B. Partial Vapour Pressures and Refractivities of Binary Mixtures of Benzene and some of its Polar Derivatives. *J. Chem. Soc. London* **1932**, 2658−2667.

Park, J. H.; Hussam, A.; Couasnon, P.; Fritz, D.; Carr, P. W. Experimental Reexamination of Selected Partition Coefficients from Rohrschneider's Data Set. *Anal. Chem.* **1987**, *59*, 1970−1976.

Pul'tsin, M. N.; Gaile, A. A.; Proskuryakov, V. A. Effect of the Structure of the Solvents and of the Components of a Mixture an Selectivity. IX. Selectivity of Derivatives of Cyclohexane and Cyclohexene. *Zh. Fiz. Khim.* **1973**, *47*, 751.

Rarey, J.; Gmehling, J. Computer-Operated Differential Static Apparatus for the Measurement of Vapor-Liquid Equilibrium Data. *Fluid Phase Equilib.* **1993**, *83*, 279−287.

Rarey, J.; Horstmann, S.; Gmehling J. Vapor-Liquid Equilibria and Vapor Pressure Data for the System Ethyl *tert*-Butyl Ether + Ethanol and Ethyl *tert*-Butyl Ether + Water. *J. Chem. Eng. Data* **1999**, *44*, 532−538.

Renon, H.; Prausnitz, J. M. Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures. *AIChE J.* **1968**, *14*, 135−144.

Tanaka, R.; Murakami, S.; Fujishiro, R. Excess Enthalpies of Mixing of a Polar Liquid + a Nonpolar Liquid at 298.15 K. *J. Chem. Thermodyn.* **1974**, *6*, 209−218.

Vernier, P.; Raimbault, C.; Renon, H. Thermodynamic Properties of Solutions of Infinite Diluted Hydrocarbons in Polar Solvents. *J. Chim. Phys. Phys.-Chim. Biol.* **1969**, *66*, 429−436.

Wilhelm, E.; et al. Private communication, 1998.

Wilson, G. M. Vapor−Liquid Equilibrium. XI. A New Expression for the Excess Free Energy of Mixing. *J. Am. Chem. Soc.* **1964**, *86*, 127−130.

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