Total-Pressure Vapor-Liquid Equilibrium Data for Binary Systems of Aniline with 1-Chlorobutane and Ethyl Acetate

Jagjit R. Khurma, Ol Muthu, Sarat Munjal, and Buford D. Smith*

Thermodynamics Research Laboratory, Washington University, St. Louis, Missouri 63130

Total-pressure vapor-liquid equilibrium (VLE) data are reported for the following two binary systems: 1-chlorobutane + aniline at 298.20 K, and ethyl acetate + aniline at 297.49, 348.23, and 397.89 K. The experimental *PTx* data were reduced to y_i, γ_i, and G^E values by both the Mixon–Gumowski–Carpenter and the Barker methods, but only the Mixon et al. results are reported in their entirety. Six G^E correlations were tested in the Barker data reduction. Various equations of state were used to estimate the vapor-phase fugacity coefficients.

Introduction

This is the third paper reporting total-pressure vapor–liquid equilibrium (VLE) data on binary systems containing aniline. The first paper (*1*) described in detail the apparatus and techniques used for the experimental measurements and reported data on the ethanol + aniline system. The second paper (*2*) covered aniline with acetone, acetonitrile, chlorobenzene, methanol, and 1-pentene.

The defining equation for the activity coefficient and the definition of the standard states used are given in the first paper cited (*1*).

Chemicals Used

The sources and purities of the chemicals used are listed in Table I. Activated molecular sieves (either 3A or 4A) were put into the chemical containers as they were received. Just prior to being loaded into the VLE cells, the chemicals were poured into distillation flasks and distilled through a Vigreux column (25-mm o.d. and 470 mm long). It has been found useful to distill aniline for the second time just before loading the cells. The first and last portions of the distillates were discarded. The retained portions were caught in amber bottles and back-flushed with dry nitrogen for transfer to the cell-loading operation. The stated purities of the chemicals were verified by gas–liquid chromatography at this point.

None of the compounds exhibited any degradation during the VLE measurements. The cell pressures were stable with respect to time, and all liquids were perfectly clear when removed from the cells at the end of the last isotherm.

Experimental Data

Tables II and III present the experimental *PTx* data. The "smooth" pressure values reported are from the least-squares cubic splined fits used to provide the evenly spaced values required by the finite-difference Mixon–Gumowski–Carpenter method (*3*) for reduction of *PTx* data.

Table I. Chemicals Used

component	vendor	stated purity, %
1-chlorobutane	Burdick and Jackson	99.9+
ethyl acetate	Burdick and Jackson	99.9
aniline	Aldrich Chem. Co.	99.9+%

Table II. Experimental P vs. x_1 Values for the 1-Chlorobutane (1) + Aniline (2) System

298.20 K		
	PRESSURE, KPA	
X1	EXPTL	SMOOTH
.0000	0.077	0.077
.0478	1.880	1.881
.0953	3.354	3.351
.1657	5.042	5.046
.2232	6.106	6.104
.3108	7.337	7.336
.4444	8.747	8.739
.5259	9.416	9.424
.6205	10.136	10.138
.7219	10.896	10.892
.8065	11.582	11.580
.8576	12.047	12.049
.9282	12.784	12.785
.9617	13.177	13.176
1.0000	13.657	13.657

Figures 1 and 2 show the experimental data in terms of the pressure deviation P_D from Raoult's law

$$P_D = P - [P_2' + x_1(P_1' - P_2')]$$

where P is the experimental mixture pressure and the P_i' values are the pure-component vapor pressures. The deviation pressure plot emphasizes the scatter of the P vs. x_1 data but does not show whether or not an azeotrope exists.

The point symbols in Figures 1 and 2 denote the experimental data points exactly. The curves approximate the cubic splined fits of those data points.

It was not possible to measure data for the 1-chlorobutane + aniline system at 348 and 398 K because of a chemical reaction between the two compounds. At 298.20 K, the deviation from Raoult's law was positive at all compositions. No azeotrope was formed.

At 297.49 K, the ethyl acetate + aniline system deviates from Raoult's law in the negative direction from $x_1 = 0.0$ to about $x_1 = 0.92$, and in the positive direction above $x_1 = 0.92$. The deviation is negative at all compositions at 348.23 and 397.89 K and the negative deviation becomes progressively stronger as the temperature increases. It is likely that the deviation for this system is entirely positive at temperatures somewhat below 297.49 K. The system did not form an azeotrope at any of the three temperatures studied

Reduced Data

The y_i, γ_i, and G^E values selected for publication are in Tables IV and V. Those values were obtained with the Mixon et al. data reduction method. The Peng–Robinson equation of state (*4*) was used to estimate the vapor-phase fugacity coefficients. The parameters used for the Peng–Robinson equation are in Table VI.

The "experimental" pressure values tabulated in Tables IV

0021-9568/83/1728-0108$01.50/0

Table III. Experimental P vs. x_1 Values for the Ethyl Acetate (1) + Aniline (2) System

297.49 K			348.23 K			397.89 K		
	PRESSURE, KPA			PRESSURE, KPA			PRESSURE, KPA	
X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH	X1	EXPTL	SMOOTH
.0000	0.075	0.074	.0000	1.990	1.890	.0000	15.960	15.960
.0579	0.756	0.759	.0578	7.264	7.245	.0577	37.65	37.64
.0762	0.967	0.965	.0761	8.887	8.900	.0757	44.29	44.30
.1427	1.708	1.698	.1425	14.826	14.844	.1421	68.51	68.53
.2079	2.399	2.406	.2076	20.618	20.611	.2070	91.98	91.91
.2910	3.309	3.321	.2907	27.92	27.94	.2901	121.49	121.58
.3998	4.600	4.580	.3995	37.71	37.65	.3987	160.41	160.34
.4919	5.694	5.703	.4916	46.13	46.11	.4908	193.67	193.65
.6021	7.100	7.106	.6018	56.43	56.47	.6010	234.10	234.16
.6928	8.308	8.300	.6925	65.13	65.16	.6918	268.28	268.29
.7952	9.653	9.659	.7949	75.02	75.06	.7943	307.7	307.7
.8528	10.419	10.413	.8526	80.74	80.67	.8521	330.5	330.5
.9256	11.332	11.338	.9255	87.76	87.75	.9252	359.8	359.8
.9599	11.764	11.761	.9598	91.13	91.09	.9597	374.0	373.9
1.0000	12.242	12.241	1.0000	94.92	94.98	1.0000	390.5	390.6

Table IV. Calculated Data for the 1-Chlorobutane (1) + Aniline (2) System at 298.20 K

LIQUID MOLAR VOLUMES, CC/MOL: VL(1) = 105.120 VL(2) = 91.530

	TOTAL PRESSURE, KPA		MIXTURE FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		EXCESS GIBBS FUNCTION, J/MOLE
X1	EXPTL.	CALC.	1	2	Y1	1	2	
.0000	0.077	0.077	1.0000	.9999	.0000	3.0752	1.0000	0.00
.1000	3.481	3.481	.9981	.9973	.9798	2.5120	1.0108	252.36
.2000	5.707	5.707	.9970	.9956	.9887	2.0753	1.0455	450.36
.3000	7.203	7.203	.9962	.9945	.9917	1.7498	1.1067	592.07
.4000	8.319	8.319	.9956	.9936	.9933	1.5173	1.1948	678.31
.5000	9.216	9.216	.9951	.9929	.9944	1.3456	1.3183	710.57
.6000	9.987	9.987	.9947	.9923	.9954	1.2156	1.4928	687.84
.7000	10.725	10.725	.9943	.9918	.9962	1.1195	1.7401	607.92
.8000	11.524	11.524	.9939	.9912	.9972	1.0531	2.0910	468.36
.9000	12.478	12.478	.9934	.9904	.9984	1.0142	2.5882	267.20
1.0000	13.657	13.657	.9927	.9895	1.0000	1.0000	3.5469	0.00

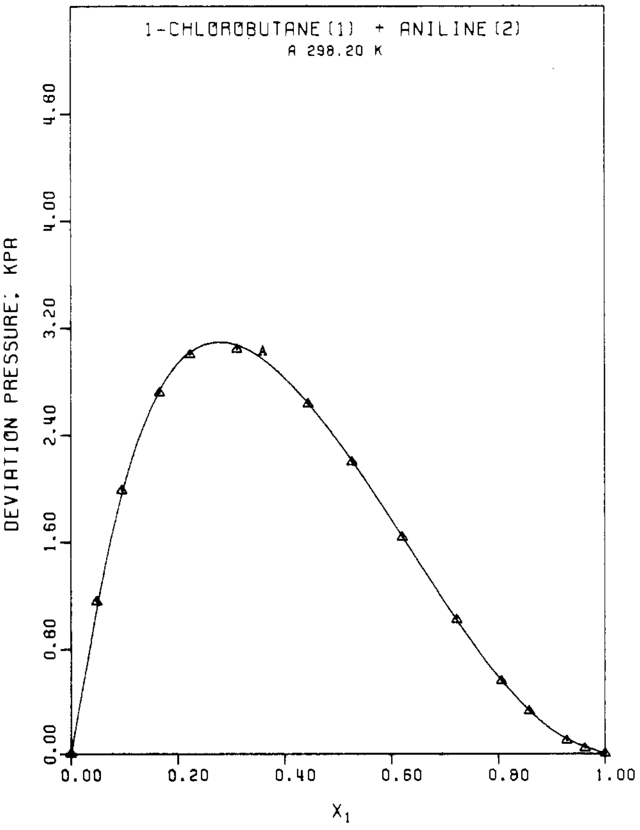

Figure 1. Deviation from Raoult's law for the 1-chlorobutane (1) + aniline (2) system.

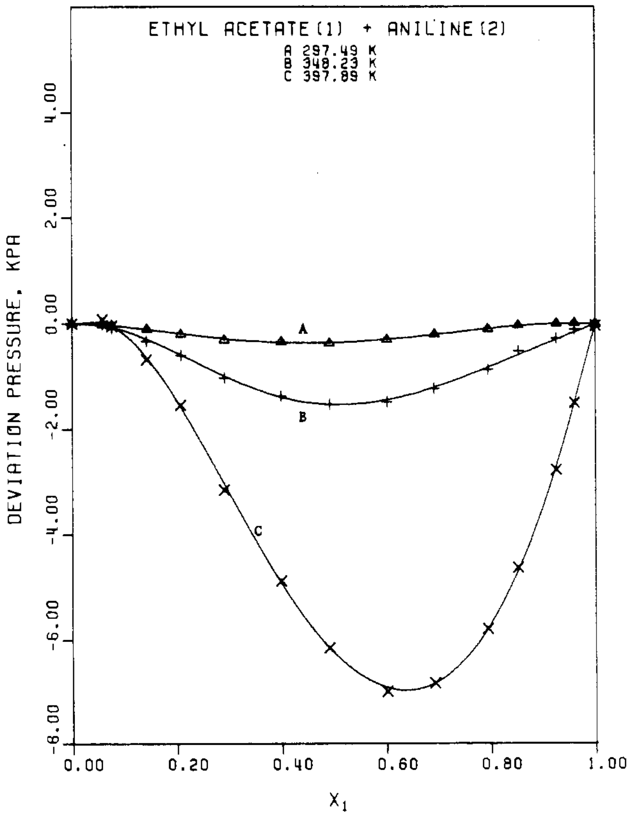

Figure 2. Deviation from Raoult's law for the ethyl acetate (1) + aniline (2) system.

Table V. Calculated Data for the Ethyl Acetate (1) + Aniline (2) System at 297.49, 348.23, and 397.89 K

LIQUID MOLAR VOLUMES, CC/MOL: VL(1) = 98.361 VL(2) = 91.481

	TOTAL PRESSURE, KPA		MIXTURE FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		EXCESS GIBBS FUNCTION,
X1	EXPTL.	CALC.	1	2	Y1	1	2	J/MOLE
.0000	0.074	0.074	1.0000	.9999	.0000	1.0261	1.0000	0.00
.1000	1.230	1.230	.9994	.9991	.9453	0.9557	1.0032	-4.02
.2000	2.321	2.321	.9988	.9982	.9741	0.9284	1.0081	-20.82
.3000	3.422	3.422	.9982	.9974	.9846	0.9220	1.0101	-42.89
.4000	4.582	4.592	.9976	.9965	.9902	0.9306	1.0048	-64.10
.5000	5.803	5.803	.9970	.9955	.9936	0.9455	0.9916	-79.75
.6000	7.079	7.079	.9964	.9946	.9959	0.9626	0.9699	-86.84
.7000	8.396	8.396	.9957	.9936	.9975	0.9795	0.9388	-82.73
.8000	9.722	9.722	.9950	.9925	.9986	0.9928	0.9014	-65.61
.9000	11.017	11.017	.9943	.9916	.9994	1.0001	0.8652	-35.57
1.0000	12.241	12.241	.9937	.9906	1.0000	1.0000	0.9280	0.00

LIQUID MOLAR VOLUMES, CC/MOL: VL(1) = 105.860 VL(2) = 95.891

	TOTAL PRESSURE, KPA		MIXTURE FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		EXCESS GIBBS FUNCTION,
X1	EXPTL.	CALC.	1	2	Y1	1	2	J/MOLE
.0000	1.890	1.890	.9994	.9990	.0000	1.0505	1.0000	0.00
.1000	11.052	11.052	.9963	.9943	.8451	1.0149	1.0016	8.53
.2000	19.938	19.937	.9933	.9898	.9230	0.9966	1.0048	9.04
.3000	28.763	28.763	.9904	.9853	.9529	0.9863	1.0082	4.49
.4000	37.702	37.702	.9874	.9807	.9690	0.9827	1.0100	-2.91
.5000	46.890	46.889	.9843	.9761	.9792	0.9846	1.0083	-10.53
.6000	56.302	56.302	.9811	.9713	.9861	0.9887	1.0031	-16.20
.7000	65.878	65.878	.9779	.9664	.9911	0.9930	0.9949	-18.66
.8000	75.558	75.558	.9747	.9615	.9949	0.9966	0.9840	-17.14
.9000	85.278	85.279	.9715	.9566	.9977	0.9991	0.9704	-11.13
1.0000	94.979	94.979	.9682	.9517	1.0000	1.0000	0.9511	0.00

LIQUID MOLAR VOLUMES, CC/MOL: VL(1) = 115.440 VL(2) = 100.686

	TOTAL PRESSURE, KPA		MIXTURE FUGACITY COEFFICIENTS			ACTIVITY COEFFICIENTS		EXCESS GIBBS FUNCTION,
X1	EXPTL.	CALC.	1	2	Y1	1	2	J/MOLE
.0000	15.960	15.960	.9966	.9940	.0000	1.1224	1.0000	0.00
.1000	53.208	53.206	.9879	.9806	.7255	1.0843	1.0017	31.84
.2000	89.389	89.386	.9795	.9677	.8521	1.0594	1.0058	53.40
.3000	125.101	125.099	.9714	.9551	.9056	1.0405	1.0118	66.52
.4000	160.826	160.824	.9632	.9425	.9357	1.0265	1.0191	72.23
.5000	196.986	196.984	.9550	.9298	.9553	1.0168	1.0270	71.69
.6000	233.789	233.788	.9466	.9169	.9691	1.0100	1.0354	65.89
.7000	271.392	271.392	.9381	.9037	.9796	1.0054	1.0444	55.45
.8000	309.950	309.950	.9294	.8903	.9878	1.0023	1.0539	40.81
.9000	349.621	349.621	.9204	.8765	.9944	1.0006	1.0641	22.29
1.0000	390.559	390.559	.9111	.8623	1.0000	1.0000	1.0769	0.00

and V are actually interpolated values from the cubic splined fits of the experimental P vs. x_1 values. (The fidelity with which the splined fits represent the actual experimental P values is shown in Tables II and III.) The "calculated" pressure values are from the Mixon et al. data reduction method. That method usually can be made to reproduce the input (experimental) pressure values to any desired precision.

The *PTx* data were also reduced with the Barker (*5*) method using six different G^E correlations—"absolute" Van Laar, Wilson, NRTL, modified Margules, UNIQUAC, and the five-constant Redlich–Kister equation. Usually, the five-constant Redlich–Kister equation reproduces the experimental P vs. x_1 values best but, for the ethyl acetate + aniline system, the modified Margules equation (*6*) performed equally well. The Barker fits of the experimental P values (based on the Redlich–Kister equation) are compared to the Mixon et al. fits in Table VII. It is usually difficult for the Barker method to equal the Mixon et al. pressure fits but it actually does better for the 348.23 K set of the ethyl acetate + aniline data.

The calculated activity coefficient curves are shown in Figures 3 and 4. The points are from the Mixon et al. method while the curves approximate the Barker results. The curves are actually fits by the plotting software of closely spaced Barker results fed to the program and, in some cases, there can be a noticeable difference between the input values and the actual location of the curve drawn.

The Barker results in Figures 3 and 4 are from the five-constant Redlich–Kister correlation for G^E. The agreement between the Barker and Mixon et al. activity coefficients is very good, even for the complicated ethyl acetate system. The only serious deviations between the two occur at high x_1 values for the 297.49 and 348.23 K isotherms.

Table VIII compares the pressure fits and the infinite-dilution activity coefficients from the Mixon et al. and the various Barker solutions. Note that the modified Margules (five constants) and the five-constant Redlich–Kister equations are the only ones which approach the Mixon et al. results in the accuracy of the P fits. As is usually the case, the Barker solutions which agree best with the Mixon et al. pressure fits will also agree best in the γ_i^∞ values obtained.

Even the modified Margules and Redlich–Kister Barker solutions deviate somewhat from the Mixon et al. γ_i^∞ values in Tables VIII (where the virial equation of state with the Tsonopoulos B correlation was used) and in Figure 4 (where the

Table VI. Parameters for Peng-Robinson Equation[a]

component	T_c, K	P_c, MPa	ω
aniline	699.0	5.309	0.3820
ethyl acetate	532.2	3.830	0.3630
1-chlorobutane	542.0	3.688	0.2180

[a] Binary interaction constant was set at 0.0 for all systems.

Table VII. Comparison of the Barker and Mixon et al. Pressure Fits

	max % dev in P[a]		rms for % dev[b]	
temp, K	Barker	Mixon	Barker	Mixon
Ethyl Acetate (1) + Aniline (2), Peng-Robinson				
297.49	0.902	0.556	0.361	0.259
348.23	0.244	0.260	0.089	0.103
397.89	0.199	0.078	0.077	0.034
1-Chlorobutane (1) + Aniline (2), Peng-Robinson				
298.20	0.319	0.091	0.107	0.049

[a] % dev = $100[|P_{calcd} - P_{exptl}|/P_{exptl}]$. [b] rms for % dev = $[\Sigma^n(\%\ \text{dev})^2/n]^{1/2}$.

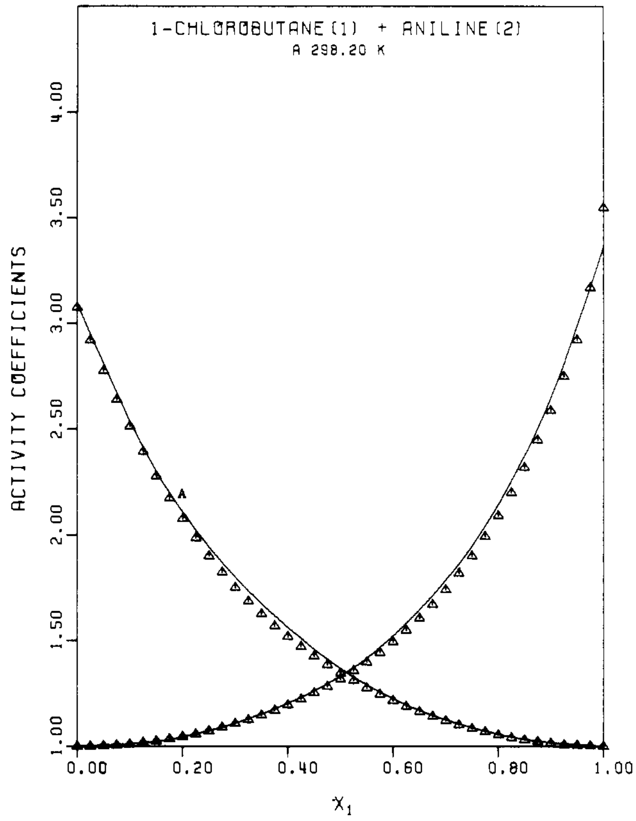

Figure 3. Activity coefficients for the 1-chlorobutane (1) + aniline (2) system. Curves are from Barker results; points are from Mixon et al. method.

Peng–Robinson equation of state was used). Note the variation in the γ_i^∞ values in Table VIII with the Barker G^E correlation used. Sometimes the Gautreaux–Coates equation (*8*, *9*) can be used to provide further evidence concerning the most probable γ_i^∞ values but for this system its component-2 values are not reasonable. Usually, when the $(dP/dx_1)_i^\infty$ values needed by the Gautreaux–Coates equation are obtained from the splined fits, its γ_i^∞ values agree well with the Mixon et al. results (which are also based on the splined fits). However, the Mixon et al. finite-difference method "reaches" the x_1 = 0.0 and x_1 = 1.0 points by a quadratic G^E extrapolation based on the G^E = 0 values at x_1 = 0.0 or x_1 = 1.0 and the two adjacent G^E points. That G^E extrapolation will, in a few cases, generate $(dP/dx_1)_i^\infty$ values which differ appreciably from the splined-fit slopes.

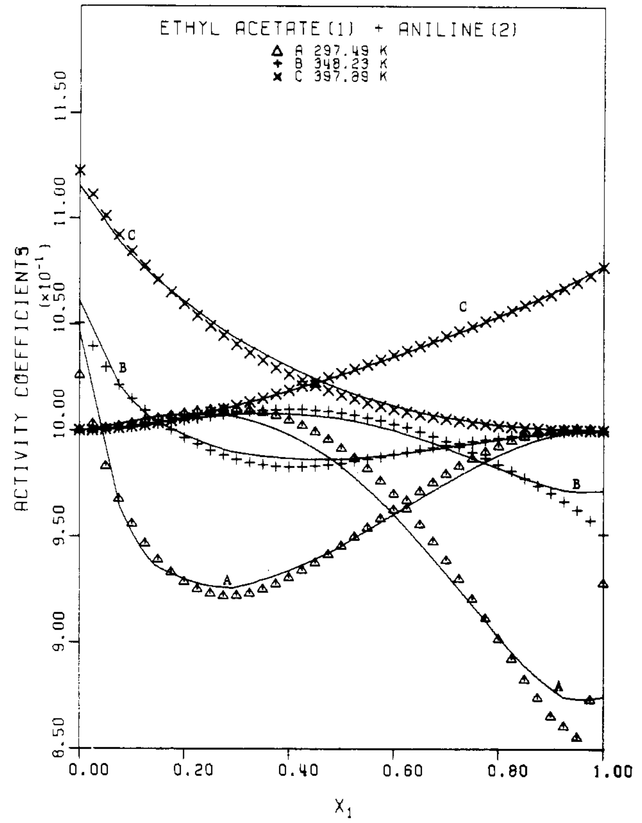

Figure 4. Activity coefficients for the ethyl acetate (1) + aniline (2) system. Curves are from Barker results; points are from Mixon et al. method. The X10^{-1} multiplier means that decimal must be moved one place to the left in ordinate scale values.

The Gautreaux–Coates values obtained from the x_1x_2/P_D plots are equally unreasonable. (The x_1x_2/P_D plots extrapolate better at x_1 = 1.0 than do the P_D/x_1x_2 plots in this instance.) In both cases, the Gautreaux–Coates method fails to give useful values at 297.49 and 348.23 K because of some scatter in the measured P or x_1 values at x_1 = 0.925 and 0.960. That scatter is not apparent in Figure 2 but does become apparent on the more sensitive x_1x_2/P_D plot. Because of the shapes of the P vs. x_1 isotherms and the very small departures from Raoult's law in that region, those two points must be known with extreme accuracy if the γ_2^∞ values calculated with the Gautreaux–Coates equations are to be accurate.

Except for the Van Laar value at 297.49 K, the Barker values in Table VIII agree reasonably well with the Mixon et al. values for γ_2^∞. The Barker results are less sensitive to the positions of the experimental P values near x_1 = 0.0 and 1.0 because the G^E correlation constants are based on all the P points across the entire composition range. The Mixon et al. results are much more sensitive than the Barker method to the extreme x_1 points but the splined fits and the quadratic extrapolation of the G^E curve to the end points do tend to smooth the data somewhat. For this system, that smoothing action probably brings the calculated results closer to the truth, but in general it can obscure the true behavior of the activity coefficients at the very low and very high x_1 values.

The uncertainty concerning the true values of the γ_1^∞ and γ_2^∞ values is increased by the effect of the equation of state used. A close comparison between the γ_2^∞ values in Table VIII (Redlich–Kister solution) and Figure 4 shows appreciable differences between the values obtained with the virial and

Table VIII. Effect of Calculation Method on γ_i^∞ Values for the Ethyl Acetate (1) + Aniline (2) System[a]

	accuracy of P fits, max % dev/rmsd			calcd γ_i^∞ values					
				component 1			component 2		
calculation method	297.49 K	348.23 K	397.89 K	297.49 K	348.23 K	397.89 K	297.49 K	348.23 K	397.89 K
Mixon et al.	0.6/0.3	0.3/0.1	0.1/0.0	1.030	1.057	1.129	0.943	0.982	1.113
Barker:									
absolute Van Laar	3.1/1.6	0.7/0.2	0.3/0.1	0.942	1.048	1.116	2.982	0.967	1.087
Wilson	4.9/1.6	0.6/0.2	0.3/0.1	1.276	1.083	1.116	0.870	0.975	1.087
NRTL	1.5/0.5	0.3/0.1	0.6/0.2	1.060	1.062	1.109	0.843	0.970	1.088
modified Margules	0.8/0.3	0.3/0.1	0.1/0.0	1.040	1.055	1.126	0.898	1.079	1.116
UNIQUAC	7.0/2.2	2.1/0.8	0.3/0.2	1.322	1.155	1.145	0.886	0.994	1.097
Redlich-Kister, five constants	0.9/0.4	0.3/0.1	0.1/0.0	1.051	1.070	1.129	0.885	0.994	1.104
Gautreaux-Coates:									
splined fits				1.025	1.058	1.129	8.046	1.208	1.244
x_1x_2/P_D plots				0.983	1.074	1.125	9.666	1.819	1.336

[a] Virial equation, Tsonopoulos correlation (*7*).

Table IX. Effect of Equation of State Choice on γ_i^∞ Values Obtained with the Mixon et al. Method for Ethyl Acetate (1) + Aniline (2) at 397.89 K

	γ_i^∞	
eq of state used	1	2
ideal gas	1.0306	0.7003
virial through B_{ij}:		
Tsonopoulous (*7*)	1.1286	1.1127
Hayden-O'Connell (*10*)	1.1452	1.2045
Redlich-Kwong:		
Lu modification (*11*)	1.1094	1.0162
Peng-Robinson (*4*)	1.1224	1.0769

Peng–Robinson (*4*) equations of state. Table IX compares several equations of state. It should be remembered in making these comparisons that the system pressure is very low at the aniline end (see the x_1 = 0.0 values in Table III). At the ethyl acetate end (x_1 = 1.0) at 397.89 K, the pressure is still only 390.5 kPa but that is high enough to bring out the differences between the various equations of state shown in Table IX. At 390.5 kPa, the virial equation of state truncated after the second coefficient should work well but the results depend upon the correlation used to predict the B_{ii} and B_{ij} values. Pure-component data evaluation work done in the Laboratory has shown that for ketones and alcohols the Tsonopoulos correlation (*7*) will more closely approximate the reliable experimental B_{ii} values for more compounds than does the Hayden–O'Connell correlation (*10*). Even when the Hayden–O'Connell correlation works best for a ketone or an alcohol, the Tsonopoulos values are also quite close but the reverse is not always true. Also, on the basis of limited experience with comparisons such as the one shown in Table IX, our tendency now is to trust the Tsonopoulos results more.

The Peng–Robinson equation (*4*) is convenient to use because, unlike the various modifications to the Redlich–Kwong equations such as that due to Lu (*11*), only the acentric factor is needed beyond the critical temperature and pressure values. Also, as in the case of the ethyl acetate + aniline system covered in this paper, the Peng–Robinson results tend to fall in the middle of the various equations tested. The values reported in Tables IV and V are based on the Peng–Robinson equation, while the comparisons shown in Table VIII are based on the virial equation and the Tsonopoulos correlation.

Registry No. Aniline, 62-53-3; ethyl acetate, 141-78-6; 1-chlorobutane, 109-69-3.

Literature Cited

(1) Maher, P. J.; Smith, B. D. *J. Chem. Eng. Data* **1979**, *24*, 16.
(2) Maher, P. J.; Smith, B. D. *J. Chem. Eng. Data* **1980**, *25*, 61.
(3) Mixon, F. O.; Gumowski, B.; Carpenter, B. H. *Ind. Eng. Chem. Fundam.* **1965**, *4*, 455.
(4) Peng, D.-Y.; Robinson, D. B. *Ind. Eng. Chem. Fundam.* **1976**, *4*, 455.
(5) Barker, J. A. *Aust. J. Chem.* **1953**, *6*, 207.
(6) Abbott, M. M.; Van Ness, H. C. *AIChE J.* **1975**, *21*, 62.
(7) Tsonopoulos, C. *AIChE J.* **1974**, *20*, 263.
(8) Gautreaux, M. F.; Coates, J. *AIChE J.* **1955**, *1*, 496.
(9) Maher, P. J.; Smith, B. D. *Ind. Eng. Chem. Fundam.* **1979**, *18*, 354.
(10) Hayden, J. G.; O'Connell, J. P. *Ind. Eng. Chem. Process Des. Dev.* **1975**, *14*, 209.
(11) Haman, S. E. M.; Chung, W. K.; Elshayal, I. M.; Lu, B. C. Y. *Ind. Eng. Chem. Process Des. Dev.* **1977**, *16*, 51.

Received for review July 22, 1982. Accepted September 24, 1982. We gratefully acknowledge the financial support received from the National Science Foundation Grant CPE-80000534 and from the Industrial Participants in the Thermodynamics Research Laboratory.