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Vapor–Liquid Equilibrium Data for Binary Systems of Aniline with Acetone, Acetonitrile, Chlorobenzene, Methanol, and 1-Pentene

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Total pressure vapor–liquid equilibrium data were measured for the following five binaries containing aniline: acetone + aniline at 277.35, 313.15, 350.81, and 393.15 K; acetonitrile + aniline at 293.15, 343.15, and 393.15 K; chlorobenzene + aniline at 293.15, 343.15, and 393.15 K; methanol + aniline at 293.15, 338.15, and 385.15 K; 1-pentene + aniline at 277.35, 313.15, and 350.81 K. The P,T,x data were reduced to y, γ, and G^E values by the Mixon–Gumowski–Carpenter method. The virial equation of state truncated after the second coefficient was used to calculate the vapor-phase fugacity coefficient. The Tsonopoulos correlation was used to predict the second virial coefficients.

Introduction

The systems covered in this paper were chosen to provide examples of the interactions of an amine group on a benzene ring with other molecular groups. Aniline was chosen as the aromatic amine in binary mixtures with acetone, acetonitrile, chlorobenzene, methanol, and 1-pentene. Data were measured at four temperatures for the acetone + aniline system and at three temperatures each for the other systems. A preceding paper (*1*) presented similar data for binary systems containing chlorobenzene.

Table I. Chemicals Used

component	vendor	stated purity, %
acetone	Burdick and Jackson	99.9+
acetonitrile	Burdick and Jackson	99.9+
aniline	Aldrich DuPont	99.9+
chlorobenzene	Burdick and Jackson	99.9+
methanol	Fisher Scientific	99.9
1-pentene	Phillips Petroleum	99.9+

Experimental Apparatus and Techniques

The apparatus used for this study has been described previously (*2*). Fifteen discrete cells are loaded with the two pure components and thirteen intermediate binary mixtures. The mass of each component loaded in a cell is determined by the use of an analytical balance. The cells are attached to a low-volume manifold and the contents are degassed in situ by successive freezing–evacuation–thawing cycles. When the degassing is completed, the manifold assembly is placed in a constant-temperature bath. Pressure measurements are made by opening each cell in turn to a pressure transducer used as a nulling device. The nitrogen pressure used to balance the cell vapor pressure is measured with a separate transducer that is calibrated frequently vs. a Ruska air dead weight gage. The bath temperature is measured with a platinum resistance thermometer that is calibrated vs. a local platinum resistance temperature standard using the IPTS-68 temperature scale.

The uncertainties in the temperature and the mole fractions are ±0.03 K and ±0.0005, respectively. The pressure measurement system has an uncertainty of ±(0.035% of the reading + 0.02 mmHg + 2.5 in the last digit of the five-digit readout). The pressure uncertainty ranges from 0.09 to 0.10% for the systems presented.

Chemicals Used

Table I lists the chemicals used and their stated purity. All chemicals were available in at least 99.9% purity. Activated Linde molecular sieves (either 3A or 4A) were put in the containers with the chemicals as they were received. Prior to loading in the VLE cells, the chemicals were poured into a 500-mL flask containing freshly activated sieves and then distilled through a Vigreaux column (25 mm o.d. and 470 mm long) with the first and last portions being discarded. The distilled samples were back-flushed with nitrogen and put in amber glass bottles for transfer to the loading operation.

Table II. Experimental P vs. x_1 Values for the Acetone (1) + Aniline (2) System and a Comparison with the Smooth Values

277.35 K			313.15 K			350.81 K			386.67 K		
	pressure, kPa			pressure, kPa			pressure, kPa			pressure, kPa	
x_1	exptl	smooth	x_1	exptl	smooth	x_1	exptl	smooth	x_1	exptl	smooth
0.0	0.019	0.018	0.0	0.240	0.240	0.0	2.130	2.130	0.0	10.500	10.500
0.0436	0.367	0.374	0.0437	2.170	2.170	0.0435	11.450	11.440	0.0433	36.70	36.70
0.0797	0.686	0.678	0.0798	3.640	3.650	0.0795	17.610	17.630	0.0791	54.20	54.20
0.1376	1.163	1.169	0.1375	6.050	6.070	0.1372	27.260	27.220	0.1369	81.00	81.00
0.2025	1.726	1.720	0.2024	8.990	8.960	0.2020	38.12	38.15	0.2016	110.70	110.70
0.2906	2.534	2.546	0.2905	13.220	13.230	0.2901	53.67	53.67	0.2894	151.30	151.30
0.3912	3.742	3.707	0.3912	18.590	18.610	0.3906	72.80	72.77	0.3897	199.70	199.60
0.4907	4.906	4.969	0.4904	24.370	24.390	0.4899	92.80	92.87	0.4890	249.80	250.10
0.5894	6.311	6.212	0.5892	30.63	30.57	0.5888	113.76	113.68	0.5879	301.8	301.6
0.6913	7.529	7.554	0.6911	37.16	37.18	0.6907	135.45	135.49	0.6900	355.6	355.5
0.7831	8.824	8.873	0.7830	43.17	43.19	0.7826	155.16	155.12	0.7820	404.1	404.3
0.8546	9.936	9.894	0.8545	47.80	47.77	0.8542	170.38	170.36	0.8538	442.4	442.4
0.9169	10.711	10.711	0.9169	51.63	51.66	0.9168	183.66	183.66	0.9164	475.8	475.8
0.9570	11.154	11.173	0.9571	54.10	54.08	0.9570	192.21	192.20	0.9565	497.5	497.4
1.0000	11.596	11.591	1.0000	56.56	56.57	1.0000	201.32	201.32	1.0000	521.0	521.0

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Table III. Experimental P vs. x_1 Values for the Acetonitrile (1) + Aniline (2) System and a Comparison with the Smooth Values

293.15 K			343.15 K			393.15 K		
	pressure, kPa			pressure, kPa			pressure, kPa	
x_1	exptl	smooth	x_1	exptl	smooth	x_1	exptl	smooth
0.0	0.054	0.054	0.0	1.42	1.42	0.0	13.2	13.2
0.0452	0.401	0.401	0.0452	4.10	4.09	0.0450	24.9	24.8
0.0809	0.702	0.702	0.0809	6.34	6.37	0.0807	34.2	34.2
0.1378	1.213	1.212	0.1378	10.14	10.13	0.1376	49.6	49.7
0.2007	1.809	1.811	0.2008	14.46	14.45	0.2004	67.4	67.4
0.2869	2.677	2.674	0.2870	20.59	20.61	0.2864	92.4	92.4
0.3862	3.716	3.717	0.3862	27.94	27.92	0.3858	121.7	121.7
0.4890	4.819	4.817	0.4891	35.49	35.51	0.4884	151.8	151.8
0.5874	5.792	5.794	0.5874	42.48	42.46	0.5869	180.2	180.3
0.6874	6.713	6.710	0.6874	49.17	49.19	0.6870	208.6	208.5
0.7810	7.519	7.522	0.7810	55.29	55.28	0.7807	234.2	234.2
0.8531	8.123	8.122	0.8531	59.90	59.89	0.8529	254.2	254.2
0.9154	8.634	8.630	0.9154	63.86	63.88	0.9152	272.0	272.0
0.9558	8.968	8.972	0.9559	66.53	66.52	0.9558	283.9	283.9
1.0000	9.375	9.374	1.0000	69.59	69.59	1.0000	297.7	297.7

Table IV. Experimental P vs. x_1 Values for the Chlorobenzene (1) + Aniline (2) System and a Comparison with the Smooth Values

293.15 K			343.15 K			393.15 K		
	pressure, kPa			pressure, kPa			pressure, kPa	
x_1	exptl	smooth	x_1	exptl	smooth	x_1	exptl	smooth
0.0	0.043	0.042	0.0	1.417	1.417	0.0	13.26	13.26
0.0413	0.163	0.163	0.0413	2.461	2.459	0.0412	17.96	17.95
0.0816	0.265	0.266	0.0816	3.344	3.348	0.0815	21.90	21.92
0.1383	0.388	0.387	0.1383	4.441	4.438	0.1382	26.92	26.91
0.2066	0.505	0.506	0.2066	5.554	5.555	0.2065	32.22	32.21
0.2979	0.631	0.631	0.2979	6.813	6.815	0.2977	38.45	38.46
0.3956	0.735	0.735	0.3956	7.940	7.938	0.3954	44.28	44.26
0.4928	0.820	0.820	0.4928	8.891	8.893	0.4925	49.29	49.31
0.5924	0.898	0.898	0.5924	9.797	9.796	0.5922	54.18	54.16
0.6956	0.973	0.973	0.6956	10.684	10.683	0.6954	58.96	58.97
0.7860	1.040	1.040	0.7856	11.436	11.439	0.7857	63.06	63.06
0.8545	1.092	1.093	0.8545	12.037	12.036	0.8545	66.21	66.21
0.9155	1.145	1.144	0.9155	12.599	12.595	0.9155	69.07	69.07
0.9547	1.179	1.180	0.9547	12.961	12.965	0.9547	70.91	70.92
1.0000	1.226	1.226	1.0000	13.399	13.398	1.0000	73.02	73.02

Table V. Experimental P vs. x_1 Values for the Methanol (1) + Aniline (2) System and a Comparison with the Smooth Values

293.15 K			338.15 K			385.15 K		
	pressure, kPa			pressure, kPa			pressure, kPa	
x_1	exptl	smooth	x_1	exptl	smooth	x_1	exptl	smooth
0.0	0.062	0.062	0.0	1.10	1.10	0.0	9.8	9.8
0.0418	1.231	1.229	0.0418	9.64	9.63	0.0412	45.2	45.3
0.0829	2.197	2.199	0.0829	17.02	17.04	0.0822	77.2	77.0
0.1418	3.389	3.393	0.1417	26.42	26.43	0.1406	118.9	119.0
0.2129	4.622	4.612	0.2129	36.34	36.30	0.2118	165.8	165.7
0.3036	5.932	5.934	0.3037	46.99	47.04	0.3024	218.2	218.3
0.3919	7.025	7.028	0.3919	55.92	55.91	0.3907	263.4	263.3
0.4948	8.113	8.122	0.4948	64.84	64.82	0.4936	309.5	309.5
0.5958	9.078	9.070	0.5960	72.57	72.59	0.5949	350.3	350.3
0.6988	9.991	9.983	0.6988	79.88	79.88	0.6980	388.5	388.5
0.7853	10.761	10.761	0.7853	85.88	85.86	0.7848	419.7	419.5
0.8606	11.480	11.485	0.8606	91.26	91.28	0.8602	447.3	447.5
0.9185	12.084	12.089	0.9185	95.80	95.80	0.9183	470.8	470.9
0.9584	12.537	12.538	0.9584	99.30	99.28	0.9583	488.5	488.5
1.0000	13.044	13.040	1.0000	103.35	103.36	1.0000	508.9	508.9

Table VI. Experimental P vs. x_1 Values for the 1-Pentene (1) + Aniline (2) System and a Comparison with the Smooth Values

277.35 K			313.15 K			350.81 K		
	pressure, kPa			pressure, kPa			pressure, kPa	
x_1	exptl	smooth[a]	x_1	exptl	smooth	x_1	exptl	smooth
0.0	0.019		0.0	0.243	0.243	0.0	2.146	2.152
0.0359	13.865		0.0372	37.20	37.20	0.0367	79.52	79.47
0.0691	22.477		0.0712	61.73	61.71	0.0703	135.87	135.99
0.1423	31.83		0.2778	116.58	116.50	0.2731	288.1	288.3
0.2754	35.32		0.3236	119.43	119.43	0.3287	303.7	303.7
0.3762	35.33		0.3784	121.53	121.62	0.3766	313.1	312.9
0.4737	35.31		0.4755	123.41	123.41	0.4710	326.1	326.0
0.5797	35.35		0.5813	124.57	124.53	0.5797	336.5	336.7
0.6852	35.35		0.6864	125.78	125.74	0.6845	346.2	346.1
0.7739	35.37		0.7746	127.33	127.38	0.7730	356.3	356.2
0.8462	35.47		0.8467	129.81	129.91	0.8456	368.3	368.4
0.9089	35.89		0.9092	133.55	133.52	0.9086	383.0	383.3
0.9544	36.65		0.9545	137.34	137.22	0.9542	396.9	396.6
1.0000	37.82		1.0000	141.97	142.04	1.0000	412.2	412.3

[a] These values were not computed since the liquid is heterogeneous at this temperature.

Table VII. Calculated Data for the Acetone (1) + Aniline (2) System at 277.35 K

	pressure, kPa		combined correctn terms			activity coeffs		
x_1	exptl	calcd	1	2	y_1	1	2	G^E, J/mol
0.0	0.018	0.018	0.9858	1.0000	0.0	0.7114	1.0000	0.0
0.1000	0.826	0.826	0.9868	1.0030	0.9799	0.7075	0.9996	−80.62
0.2000	1.703	1.703	0.9879	1.0063	0.9914	0.7371	0.9919	−155.66
0.3000	2.693	2.693	0.9891	1.0100	0.9953	0.7790	0.9736	−215.94
0.4000	3.793	3.793	0.9904	1.0141	0.9972	0.8234	0.9448	−257.80
0.5000	5.008	5.008	0.9919	1.0187	0.9983	0.8693	0.9035	−278.50
0.6000	6.331	6.331	0.9935	1.0238	0.9990	0.9149	0.8485	−274.61
0.7000	7.722	7.722	0.9952	1.0291	0.9994	0.9553	0.7827	−243.26
0.8000	9.136	9.137	0.9970	1.0346	0.9997	0.9876	0.7079	−182.38
0.9000	10.488	10.488	0.9986	1.0399	0.9999	1.0062	0.6377	−90.95
1.0000	11.596	11.596	1.0000	1.0442	1.0000	1.0000	1.0118	0.0

Table VIII. Calculated Data for the Acetone (1) + Aniline (2) System at 313.15 K

	pressure, kPa		combined correctn terms			activity coeffs		
x_1	exptl	calcd	1	2	y_1	1	2	G^E, J/mol
0.0	0.241	0.241	0.9630	1.0000	0.0	0.8680	1.0000	0.0
0.1000	4.482	4.482	0.9658	1.0078	0.9510	0.7801	1.0040	−55.21
0.2000	8.845	8.845	0.9686	1.0157	0.9778	0.7892	1.0013	−120.52
0.3000	13.715	13.715	0.9717	1.0247	0.9875	0.8213	0.9878	−176.10
0.4000	19.104	19.104	0.9752	1.0348	0.9924	0.8592	0.9639	−215.38
0.5000	24.976	24.976	0.9790	1.0459	0.9953	0.8978	0.9298	−235.16
0.6000	31.260	31.260	0.9831	1.0581	0.9971	0.9341	0.8856	−232.93
0.7000	37.767	37.767	0.9874	1.0710	0.9983	0.9643	0.8349	−207.26
0.8000	44.286	44.286	0.9917	1.0841	0.9991	0.9858	0.7814	−158.18
0.9000	50.623	50.623	0.9960	1.0971	0.9996	0.9980	0.7293	−86.98
1.0000	56.569	56.569	1.0000	1.1095	1.0000	1.0000	0.7418	0.0

Table IX. Calculated Data for the Acetone (1) + Aniline (2) System at 350.81 K

	pressure, kPa		combined correctn terms			activity coeffs		
x_1	exptl	calcd	1	2	y_1	1	2	G^E, J/mol
0.0	2.135	2.135	0.9217	1.0000	0.0	1.3614	1.0000	0.0
0.1000	21.034	21.034	0.9290	1.0193	0.9057	1.0186	1.0126	38.16
0.2000	37.811	37.810	0.9352	1.0365	0.9521	0.9560	1.0228	26.45
0.3000	55.483	55.481	0.9418	1.0552	0.9709	0.9469	1.0256	3.86
0.4000	74.624	74.622	0.9491	1.0759	0.9812	0.9580	1.0189	−17.29
0.5000	94.966	94.963	0.9569	1.0987	0.9876	0.9736	1.0054	−31.12
0.6000	116.071	116.067	0.9652	1.1232	0.9918	0.9874	0.9883	−35.90
0.7000	137.478	137.473	0.9737	1.1490	0.9948	0.9966	0.9716	−32.10
0.8000	158.827	158.823	0.9823	1.1757	0.9970	1.0008	0.9598	−22.02
0.9000	180.096	180.093	0.9911	1.2034	0.9986	1.0015	0.9568	−8.92
1.0000	201.322	201.321	1.0000	1.2321	1.0000	1.0000	1.0236	0.0

Table X. Calculated Data for the Acetone (1) + Aniline (2) System at 386.67 K

x_1	pressure, kPa		combined correctn terms		y_1	activity coeffs		G^E, J/mol
	exptl	calcd	1	2		1	2	
0.0	10.452	10.452	0.8645	1.0000	0.0	1.6320	1.0000	0.0
0.1000	63.947	63.947	0.8779	1.0355	0.8457	1.1823	1.0133	92.18
0.2000	109.941	109.941	0.8889	1.0665	0.9167	1.0880	1.0273	123.58
0.3000	156.305	156.305	0.9003	1.0993	0.9466	1.0515	1.0387	133.83
0.4000	204.706	204.707	0.9124	1.1353	0.9636	1.0375	1.0459	133.83
0.5000	255.763	255.764	0.9255	1.1754	0.9748	1.0342	1.0485	130.16
0.6000	307.980	307.983	0.9393	1.2189	0.9826	1.0307	1.0529	124.65
0.7000	360.775	360.778	0.9536	1.2658	0.9883	1.0253	1.0635	115.57
0.8000	413.816	413.818	0.9685	1.3161	0.9928	1.0178	1.0878	99.48
0.9000	467.037	467.037	0.9839	1.3701	0.9965	1.0088	1.1462	69.31
1.0000	520.998	520.996	1.0000	1.4290	1.0000	1.0000	1.5496	0.0

Table XI. Calculated Data for the Acetonitrile (1) + Aniline (2) System at 293.15 K

x_1	pressure, kPa		combined correctn terms		y_1	activity coeffs		G^E, J/mol
	exptl	calcd	1	2		1	2	
0.0	0.054	0.054	0.9742	1.0000	0.0	0.7937	1.0000	0.0
0.1000	0.869	0.869	0.9764	1.0039	0.9437	0.8961	0.9942	−39.47
0.2000	1.804	1.804	0.9789	1.0084	0.9761	0.9597	0.9826	−54.36
0.3000	2.809	2.809	0.9816	1.0133	0.9867	1.0040	0.9680	−52.50
0.4000	3.866	3.866	0.9846	1.0185	0.9918	1.0386	0.9506	−37.15
0.5000	4.931	4.931	0.9875	1.0238	0.9947	1.0598	0.9356	−10.37
0.6000	5.913	5.913	0.9902	1.0287	0.9964	1.0579	0.9383	20.31
0.7000	6.822	6.822	0.9928	1.0333	0.9976	1.0447	0.9612	45.71
0.8000	7.682	7.682	0.9952	1.0377	0.9985	1.0279	1.0106	58.77
0.9000	8.504	8.504	0.9975	1.0419	0.9993	1.0097	1.1239	49.65
1.0000	9.374	9.374	1.0000	1.0464	1.0000	1.0000	1.3710	0.0

Table XII. Calculated Data for the Acetonitrile (1) + Aniline (2) System at 343.15 K

x_1	pressure, kPa		combined correctn terms		y_1	activity coeffs		G^E, J/mol
	exptl	calcd	1	2		1	2	
0.0	1.421	1.421	0.9277	1.0000	0.0	0.8798	1.0000	0.0
0.1000	7.614	7.614	0.9334	1.0109	0.8309	0.9740	0.9956	−18.94
0.2000	14.394	14.394	0.9402	1.0236	0.9200	1.0120	0.9891	−18.29
0.3000	21.557	21.557	0.9475	1.0374	0.9530	1.0386	0.9807	−6.62
0.4000	28.944	28.944	0.9552	1.0520	0.9699	1.0557	0.9722	13.61
0.5000	36.301	36.300	0.9630	1.0669	0.9798	1.0614	0.9683	39.07
0.6000	43.323	43.321	0.9706	1.0815	0.9861	1.0542	0.9769	63.66
0.7000	50.022	50.020	0.9779	1.0958	0.9906	1.0402	1.0021	80.45
0.8000	56.494	56.492	0.9851	1.1100	0.9941	1.0240	1.0513	82.76
0.9000	62.893	62.891	0.9923	1.1244	0.9971	1.0090	1.1474	62.18
1.0000	69.590	69.590	1.0000	1.1399	1.0000	1.0000	1.3884	0.0

Table XIII. Calculated Data for the Acetonitrile (1) + Aniline (2) System at 393.15 K

x_1	pressure, kPa		combined correctn terms		y_1	activity coeffs		G^E, J/mol
	exptl	calcd	1	2		1	2	
0.0	13.249	13.249	0.8570	1.0000	0.0	1.0415	1.000	0.0
0.1000	39.404	49.403	0.8672	1.0217	0.6910	1.0547	0.9993	15.30
0.2000	67.270	67.270	0.8795	1.0473	0.8356	1.0735	0.9961	36.24
0.3000	96.419	96.419	0.8929	1.0755	0.8973	1.0849	0.9928	63.39
0.4000	125.861	125.862	0.9070	1.1056	0.9306	1.0845	0.9932	92.68
0.5000	155.178	155.180	0.9214	1.1372	0.9515	1.0765	0.9995	119.60
0.6000	184.036	184.038	0.9362	1.1702	0.9658	1.0628	1.0155	139.70
0.7000	212.101	212.104	0.9511	1.2041	0.9763	1.0448	1.0491	147.29
0.8000	239.534	239.535	0.9661	1.2394	0.9848	1.0251	1.1118	134.20
0.9000	267.589	267.589	0.9821	1.2778	0.9923	1.0090	1.2199	91.41
1.0000	297.715	297.714	1.0000	1.3222	1.0000	1.0000	1.4692	0.0

Table XIV. Calculated Data for the Chlorobenzene (1) + Aniline (2) System at 293.15 K

	pressure, kPa		combined correctn terms			activity coeffs		G^E,
x_1	exptl	calcd	1	2	y_1	1	2	J/mol
0.0	0.042	0.042	0.9978	1.0000	0.0	2.6030	1.0000	0.0
0.1000	0.308	0.308	0.9983	1.0009	0.8746	2.1998	1.0090	211.75
0.2000	0.496	0.496	0.9986	1.0015	0.9288	1.8801	1.0374	379.28
0.3000	0.633	0.633	0.9989	1.0019	0.9489	1.6363	1.0865	501.67
0.4000	0.739	0.739	0.9991	1.0023	0.9599	1.4482	1.1604	578.63
0.5000	0.826	0.826	0.9993	1.0026	0.9674	1.3050	1.2636	609.58
0.6000	0.904	0.904	0.9994	1.0028	0.9735	1.1968	1.4048	594.12
0.7000	0.977	0.977	0.9995	1.0030	0.9790	1.1151	1.6026	530.70
0.8000	1.050	1.050	0.9997	1.0033	0.9846	1.0552	1.8930	415.84
0.9000	1.130	1.130	0.9998	1.0035	0.9911	1.0160	2.3519	243.16
1.0000	1.226	1.226	1.0000	1.0038	1.0000	1.0000	3.3383	0.0

Table XV. Calculated Data for the Chlorobenzene (1) + Aniline (2) System at 343.15 K

	pressure, kPa		combined correctn terms			activity coeffs		G^E,
x_1	exptl	calcd	1	2	y_1	1	2	J/mol
0.0	1.417	1.417	0.9899	1.0000	0.0	2.1454	1.0000	0.0
0.1000	3.721	3.721	0.9919	1.0030	0.6533	1.8290	1.0083	193.37
0.2000	5.453	5.453	0.9933	1.0053	0.7844	1.6071	1.0314	341.31
0.3000	6.842	6.841	0.9945	1.0071	0.8439	1.4444	1.0687	447.42
0.4000	7.984	7.984	0.9955	1.0086	0.8793	1.3160	1.1237	513.06
0.5000	8.960	8.961	0.9963	1.0098	0.9041	1.2139	1.2005	537.16
0.6000	9.863	9.863	0.9970	1.0110	0.9245	1.1376	1.2995	519.74
0.7000	10.720	10.721	0.9978	1.0121	0.9425	1.0798	1.4321	460.75
0.8000	11.561	11.561	0.9985	1.0132	0.9598	1.0369	1.6181	357.29
0.9000	12.450	12.450	0.9992	1.0143	0.9785	1.0111	1.8661	206.27
1.0000	13.398	13.398	1.0000	1.0155	1.0000	1.0000	2.4717	0.0

Table XVI. Calculated Data for the Chlorobenzene (1) + Aniline (2) System at 393.15 K

	pressure, kPa		combined correctn terms			activity coeffs		G^E,
x_1	exptl	calcd	1	2	y_1	1	2	J/mol
0.0	13.249	13.249	0.8656	1.0000	0.0	1.0310	1.0000	0.0
0.1000	39.404	39.403	0.8767	1.0179	0.6922	1.0451	0.9992	12.17
0.2000	67.270	67.270	0.8885	1.0373	0.8372	1.0645	0.9960	30.28
0.3000	96.419	96.418	0.9012	1.0583	0.8990	1.0768	0.9923	54.95
0.4000	125.861	125.860	0.9144	1.0804	0.9323	1.0776	0.9922	82.22
0.5000	155.178	155.174	0.9279	1.1033	0.9530	1.0706	0.9976	107.66
0.6000	184.036	184.029	0.9416	1.1268	0.9672	1.0582	1.0123	126.96
0.7000	212.101	212.093	0.9554	1.1506	0.9775	1.0413	1.0437	134.63
0.8000	239.534	239.526	0.9692	1.1749	0.9857	1.0228	1.1025	122.79
0.9000	267.589	267.584	0.9838	1.2009	0.9929	1.0079	1.2017	83.16
1.0000	297.715	297.714	1.0000	1.2303	1.0000	1.0000	1.3920	0.0

Table XVII. Calculated Data for the Methanol (1) + Aniline (2) System at 293.15 K

	pressure, kPa		combined correctn terms			activity coeffs		G^E,
x_1	exptl	calcd	1	2	y_1	1	2	J/mol
0.0	0.062	0.062	0.9863	1.0000	0.0	2.3919	1.0000	0.0
0.1000	2.565	2.565	0.9888	1.0129	0.9777	1.9450	1.0103	184.73
0.2000	4.405	4.405	0.9908	1.0226	0.9880	1.6847	1.0360	323.25
0.3000	5.887	5.887	0.9923	1.0305	0.9918	1.5043	1.0757	423.13
0.4000	7.121	7.121	0.9937	1.0371	0.9938	1.3656	1.1333	486.81
0.5000	8.172	8.172	0.9948	1.0428	0.9952	1.2540	1.2154	513.53
0.6000	9.107	9.107	0.9958	1.0479	0.9962	1.1646	1.3306	501.32
0.7000	9.993	9.993	0.9967	1.0528	0.9971	1.0953	1.4915	447.69
0.8000	10.899	10.899	0.9977	1.0578	0.9979	1.0452	1.7174	349.81
0.9000	11.892	11.892	0.9988	1.0634	0.9989	1.0135	2.0470	204.05
1.0000	13.038	13.038	1.0000	1.0698	1.0000	1.0000	2.8457	0.0

Table XVIII. Calculated Data for the Methanol (1) + Aniline (2) System at 338.15 K

	pressure, kPa		combined correctn terms			activity coeffs		G^E,
x_1	exptl	calcd	1	2	y_1	1	2	J/mol
0.0	1.103	1.103	0.9619	1.0000	0.0	2.2028	1.0000	0.0
0.1000	19.899	19.899	0.9685	1.0323	0.9481	1.8846	1.0080	198.23
0.2000	34.613	34.613	0.9739	1.0588	0.9722	1.6715	1.0294	354.12
0.3000	46.635	46.635	0.9784	1.0812	0.9809	1.5079	1.0654	471.10
0.4000	56.661	56.661	0.9821	1.1003	0.9856	1.3753	1.1196	549.03
0.5000	65.241	65.241	0.9854	1.1170	0.9887	1.2667	1.1978	586.05
0.6000	72.885	72.884	0.9883	1.1323	0.9910	1.1785	1.3085	579.55
0.7000	79.966	79.965	0.9910	1.1466	0.9930	1.1075	1.4695	525.69
0.8000	86.891	86.890	0.9936	1.1610	0.9949	1.0522	1.7157	418.07
0.9000	94.304	94.303	0.9965	1.1766	0.9971	1.0144	2.1187	247.22
1.0000	103.357	103.357	1.0000	1.1960	1.0000	1.0000	2.7742	0.0

Table XIX. Calculated Data for the Methanol (1) + Aniline (2) System at 385.15 K

	pressure, kPa		combined correctn terms			activity coeffs		G^E,
x_1	exptl	calcd	1	2	y_1	1	2	J/mol
0.0	9.779	9.779	0.9125	1.0000	0.0	1.9811	1.0000	0.0
0.1000	90.188	90.187	0.9259	1.0607	0.8958	1.7145	1.0070	192.73
0.2000	158.331	158.331	0.9372	1.1158	0.9436	1.5661	1.0231	345.86
0.3000	217.032	217.031	0.9472	1.1666	0.9613	1.4427	1.0516	464.92
0.4000	267.725	267.722	0.9560	1.2130	0.9709	1.3357	1.0963	547.45
0.5000	312.233	312.229	0.9638	1.2559	0.9771	1.2440	1.1622	590.31
0.6000	352.281	352.275	0.9710	1.2963	0.9819	1.1667	1.2575	589.70
0.7000	389.261	389.253	0.9777	1.3352	0.9859	1.1019	1.3992	540.25
0.8000	425.004	424.997	0.9842	1.3744	0.9898	1.0498	1.6204	433.51
0.9000	463.252	463.248	0.9914	1.4179	0.9941	1.0142	1.9751	258.62
1.0000	508.906	508.904	1.0000	1.4720	1.0000	1.0000	2.6118	0.0

Table XX. Calculated Data for the 1-Pentene (1) + Aniline (2) System at 313.15 K

	pressure, kPa		combined correction terms			activity coeffs		G^E,
x_1	exptl	calcd	1	2	y_1	1	2	J/mol
0.0	0.243	0.243	0.9471	1.0000	0.0	8.8291	1.0000	0.0
0.1000	77.281	77.281	0.9753	1.0994	0.9968	5.5606	1.0235	501.23
0.2000	107.363	107.363	0.9866	1.1420	0.9977	3.8217	1.0932	883.80
0.3000	118.066	118.067	0.9907	1.1578	0.9980	2.7909	1.2136	1154.45
0.4000	122.185	122.185	0.9923	1.1640	0.9981	2.1630	1.3918	1319.86
0.5000	123.689	123.688	0.9929	1.1662	0.9981	1.7507	1.6545	1384.49
0.6000	124.722	124.721	0.9933	1.1678	0.9981	1.4706	2.0479	1349.00
0.7000	125.932	125.930	0.9938	1.1696	0.9982	1.2722	2.6831	1209.66
0.8000	128.108	128.107	0.9946	1.1729	0.9983	1.1316	3.8209	955.49
0.9000	132.887	132.886	0.9964	1.1801	0.9987	1.0418	6.1370	568.38
1.0000	142.044	142.043	1.0000	1.1937	1.0000	1.0000	18.0766	0.0

Table XXI. Calculated Data for the 1-Pentene (1) + Aniline (2) System at 350.81 K

	pressure, kPa		combined correction terms			activity coeffs		G^E,
x_1	exptl	calcd	1	2	y_1	1	2	J/mol
0.0	2.152	2.152	0.8929	1.0000	0.0	6.3181	1.0000	0.0
0.1000	174.463	174.463	0.9359	1.1371	0.9871	4.4636	1.0193	486.54
0.2000	255.554	255.556	0.9569	1.2112	0.9912	3.2106	1.0796	859.20
0.3000	296.564	296.565	0.9678	1.2515	0.9925	2.4590	1.1799	1125.03
0.4000	316.637	316.634	0.9733	1.2720	0.9931	1.9592	1.3332	1287.94
0.5000	329.190	329.182	0.9767	1.2851	0.9935	1.6244	1.5541	1350.48
0.6000	338.467	338.453	0.9793	1.2948	0.9938	1.3887	1.8829	1312.91
0.7000	347.592	347.578	0.9818	1.3045	0.9942	1.2197	2.3975	1170.65
0.8000	360.189	360.176	0.9853	1.3180	0.9949	1.1028	3.2471	915.32
0.9000	380.985	380.975	0.9911	1.3403	0.9964	1.0323	4.7284	536.66
1.0000	412.254	412.252	1.0000	1.3740	1.0000	1.0000	11.2009	0.0

Experimental Results

The raw P–x data measured for the five systems are in Tables II–VI. The liquid-phase mole fractions were corrected for the presence of the vapor phase as described previously (*2*). Also shown are the smooth P–x values obtained from a least-squares cubic spline fit of the data.

The Mixon et al. (*3*) method was used to calculate the G^E, γ_i, and y_i values from the smooth P–x data. The equations used to calculate the γ_i and G^E values were

$$\gamma_i = \frac{y_i P \hat{\phi}_{i,P}}{x_i P_i' \hat{\phi}_{i,P_i'}} \left[\exp \frac{V_i^L(P - P_i'}{RT} \right]^{-1} \tag{1}$$

and

$$G^E = RT \sum_i x_i \ln \gamma_i \tag{2}$$

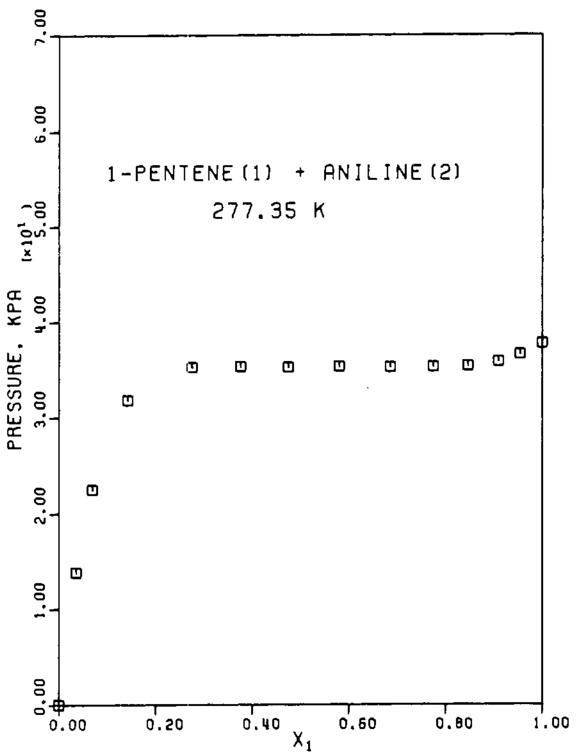

Figure 1. A plot of P vs. x_1 for the 1-pentene (1) + aniline (2) system at 277.35 K.

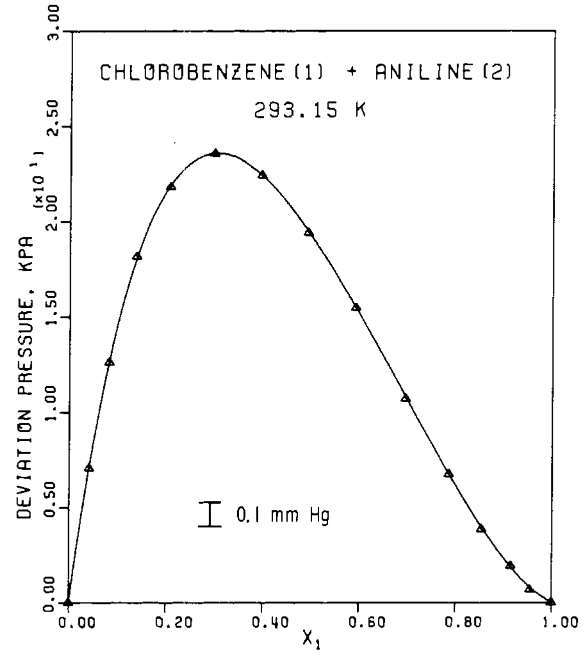

Figure 2. Deviation from Raoult's law for the chlorobenzene (1) + aniline (2) system at 293.15 K.

The standard state for each component was the pure liquid at the mixture temperature and pressure. The fugacity coefficients were predicted with the virial equation of state truncated after the second coefficient. The B_{11}, B_{12}, and B_{22} values were calculated by using the Tsonopoulos correlation (*4*). The calculated results are shown in Tables VII–XXI. In those tables, the "combined correction term" refers to the following grouping of terms.

$$\frac{\hat{\phi}_{i,P}}{\phi_{i,P_i'}}\left[\exp\frac{V_i^{L}(P-P_i')}{RT}\right]^{-1} \qquad (3)$$

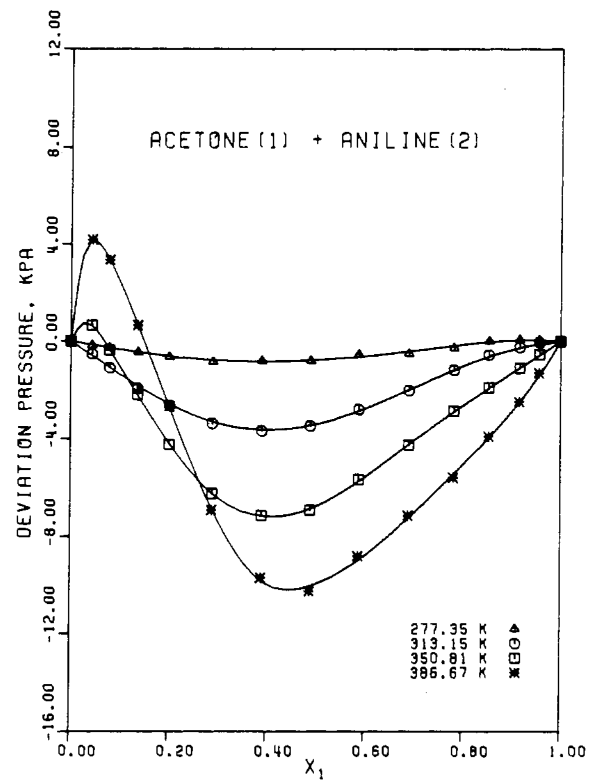

Figure 3. Deviation from Raoult's law for the acetone (1) + aniline (2) system at 277.35, 313.15, 350.81, and 386.67 K.

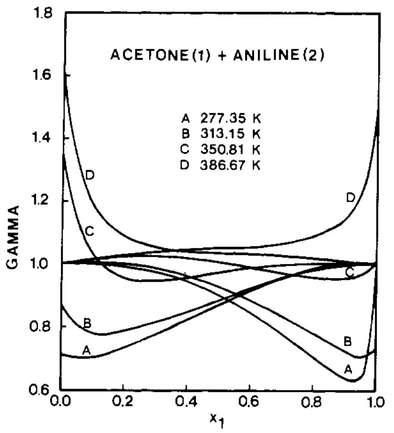

Figure 4. Activity coefficients for the acetone (1) + aniline (2) system at 277.35, 313.15, 350.81, and 386.67 K.

Discussion of Results

Although there were no azeotropes for these five systems, the 1-pentene + aniline system did have two liquid phases at 277.35 K. The P vs. x_1 plot is shown in Figure 1. The points in the two-phase region agree to within 0.057%. At the next highest temperature (313.15 K), the two-phase region disappeared.

The chlorobenzene + aniline system at 293.15 K is shown in Figure 2 and is used to illustrate the performance capabilities of the equipment. The deviation pressure, denoted here as P_D, is defined as

$$P_D = P - [P_2' + (P_1' - P_2')x_1] \qquad (4)$$

The smoothness of the data is illustrated better on this sort of plot than on a P vs. x plot.

The acetone + aniline system had both positive and negative values for P_D, as is shown in Figure 3. As the temperature

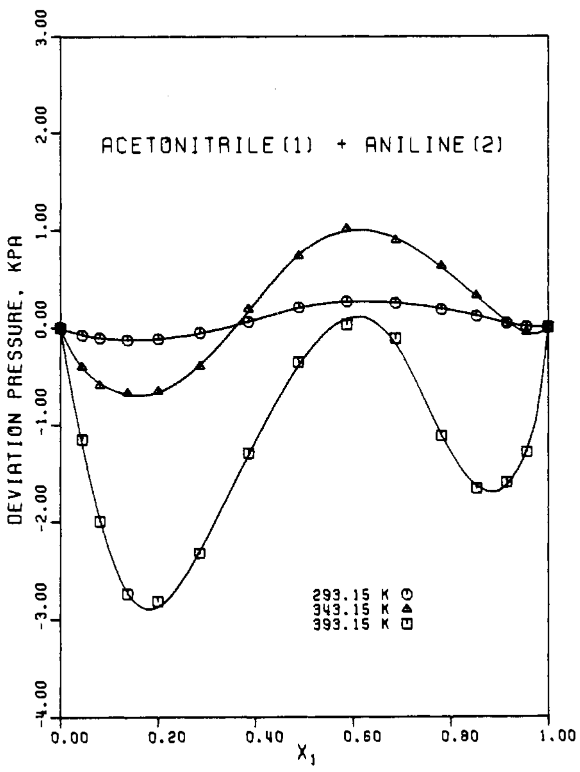

Figure 5. Deviation from Raoult's law for the acetonitrile (1) + aniline (2) system at 293.15, 343.15, and 393.15 K.

increased, the tendency was toward larger negative deviation in the region of high acetone concentration and larger positive deviation in the region of low acetone concentration. The activity coefficients for this system are shown in Figure 4. Note that γ_2^∞ goes through a minimum with respect to temperature.

Perhaps the most unusual system, on the basis of the shape of the P_D vs. x_1 curve, is acetonitrile + aniline (see Figure 5). The curves cross the Raoult law line ($P_D = 0$) at two places for all three temperatures and will apparently show only negative deviation just above the range of temperatures measured. The activity coefficients, shown in Figure 6, all cross over the $\gamma = 1.0$ line except for the γ_1 curve at 393.15 K, which appears to be "unfolding" and turning upward to form a more regularly shaped γ curve.

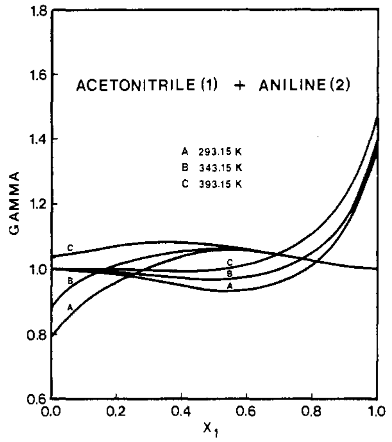

Figure 6. Activity coefficients for the acetonitrile (1) + aniline (2) system at 293.15, 343.15, and 393.15 K.

Glossary

B	second virial coefficient, cm^3 mol^{-1}
G	Gibbs function, J mol^{-1}
P	pressure, kPa
R	gas constant
T	absolute temperature, K
V	molar volume, cm^3 mol^{-1}
x	liquid-phase mole fraction
y	vapor-phase mole fraction

Greek Letters

γ	activity coefficient
ϕ	fugacity coefficient

Subscripts

1	more volatile component
2	less volatile component

Superscripts

E	excess property
L	liquid-phase property
V	vapor-phase property
^	mixture component property
′	vapor pressure

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Gas–Liquid Equilibrium in the Hydrogen + *n*-Decane System at Elevated Temperatures and Pressures

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Vapor–liquid equilibrium data for mixtures of hydrogen and *n*-decane are reported at four temperatures (189.3, 230.2, 269.8, 310.3 °C) and at pressures from 20 to 250 atm.

Introduction

There recently has been an increased interest in gas–liquid equilibrium data for mixtures of hydrogen and organic liquids due

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