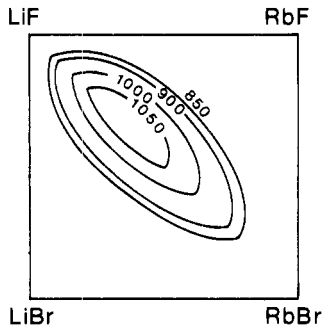

Figure 6. LL isotherms as calculated by means of the CIS theory.

along with the temperatures of the corresponding eutectics and of the LL equilibrium limits. The stratification lens (dashed) impinges on the LiF crystallization field and occupies 41.5% of the composition square. The main axis of the lens coincides with the stable diagonal. Along this axis PCT is constant at 834 ± 1 °C.

Figure 5 reports the projections of the interpolated LL isotherms at 850, 900, 950, 1000, and 1030 °C. The upper critical solution point of the system is at x_{LiF} = 0.76 and 1050 °C. The SL isotherms at 500, 600, 700, and 800 °C are also reported. Moreover, the figure brings into evidence the four invariant points presented by the system with the following coordinates: eutectic E_1 at t = 240 °C and x_{LiF} = 0.04, x_{LiBr} = 0.58, x_{RbBr} = 0.38; eutectic E_2 at t = 436 °C and x_{LiF} = 0.14, x_{RbF} = 0.55, x_{RbBr} = 0.31; peritectic P_3 at t = 268 °C and x_{LiF} = 0.04, x_{LiBr} = 0.55, x_{RbBr} = 0.41; peritectic P_4 at t = 467 °C and x_{LiF} = 0.39_5, x_{RbF} = 0.57, x_{RbBr} = 0.03_5. The general topology of the system agrees with the triangulation rules.

Discussion

In order to extend the test of the conformal ionic solution (CIS) theory (*7*) carried out in ref 2, we made attempts to predict the LL equilibria in the present system. The required data (see ref 2) are the standard Gibbs free energy change for the metathetical reaction, $\Delta G°$, the four binary mixture interaction parameters k, and the coordination number Z. Literature (*3*) reports the following values (in cal mol^{-1}): $\Delta G° = 23400 - 3.4T$, k(LiBr + LiF) = −900, k(LiBr + RbBr) = −4300, k(LiF + RbF) = −3200. Calculations carried out by using this set of data with k(RbBr + RbF) = 0 and Z = 6 led to the following results: the system presents the demixing phenomenon but the MG is too large and its symmetry is incorrect. A sensitive improvement can be reached by taking into account a possible temperature dependence of the k values; this is in agreement with the findings for the system K,Li/Br,F (*6*).

An analysis of the experimental data on the phase diagrams of the four binaries, assuming that k varies only with temperature, gives the following results: k(LiBr + LiF) = −3160 + 3.7T; k(RbBr + RbF) = −1250; k(LiBr + RbBr) = −7400 + 3.7T; k(LiF + RbF) = −3200.

This new set of data, with $\Delta G° = 19700 - 3.4T$ and Z = 6, provides the prediction shown in Figure 6; the topology of the system compares well with the experimental one, but still the agreement is not quantitative. The reservations on the CIS theory reported in ref 2 seem to be confirmed by the present results.

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

Patrick J. Maher and Buford D. Smith*

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

Total pressure vapor–liquid equilibrium data were measured for the following six binaries containing chlorobenzene: acetone + chlorobenzene at 313.15, 353.00, and 386.66 K; acetonitrile + chlorobenzene at 293.15, 343.15, and 393.15 K; ethyl acetate + chlorobenzene at 313.15, 353.15, and 393.15; chlorobenzene + ethylbenzene at 293.15 K; methanol + chlorobenzene at 293.15, 338.15, and 385.15 K; 1-pentene + chlorobenzene at 280.00, 320.00, and 360.00 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 coefficients. The Tsonopoulos correlation was used to predict the second virial coefficients.

Introduction

The data reported were measured as part of an ongoing effort to expand the experimental vapor–liquid equilibrium (VLE) data base for a general correlation of mixture properties. Systems were chosen to provide examples of the interactions of a

Table I. Chemicals Used

component	vendor	stated purity, %
acetone	Burdick and Jackson	99.9+
acetonitrile	Burdick and Jackson	99.9+
chlorobenzene	Burdick and Jackson	99.9+
ethyl acetate	Burdick and Jackson	99.9+
ethylbenzene	Phillips Petroleum	99.944
methanol	Fisher Scientific	99.9
1-pentene	Phillips Petroleum	99.9+

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

313.15 K			353.00 K			386.66 K		
	pressure, kPa			pressure, kPa			pressure, kPa	
x_1	exptl	smooth	x_1	exptl	smooth	x_1	exptl	smooth
0.0	3.563	3.564	0.0	19.602	19.599	0.0	60.33	60.33
0.0424	7.077	7.068	0.0427	31.32	31.35	0.0425	86.58	86.59
0.0811	9.923	9.939	0.0816	41.59	41.54	0.0812	109.83	109.80
0.1384	13.759	13.760	0.1391	55.47	55.49	0.1384	141.66	141.67
0.2046	17.780	17.756	0.2056	70.26	70.30	0.2048	175.71	175.74
0.2906	22.608	22.626	0.2916	88.09	88.05	0.2906	216.96	216.95
0.4872	32.65	32.67	0.4901	124.95	124.94	0.4887	304.1	304.1
0.5854	37.19	37.16	0.5882	141.90	141.95	0.5870	344.7	344.8
0.6913	41.83	41.86	0.6920	159.68	159.64	0.6912	387.4	387.4
0.7852	46.13	46.12	0.7858	175.70	175.69	0.7851	426.0	425.9
0.8559	49.44	49.43	0.8563	188.02	188.03	0.8558	455.7	455.7
0.9136	52.23	52.22	0.9138	198.38	198.41	0.9135	481.0	481.0
0.9556	54.31	54.32	0.9557	206.26	206.23	0.9556	500.1	500.1
1.0000	56.60	56.60	1.0000	214.82	214.83	1.0000	521.1	521.1

Table III. Experimental P vs. x_1 Values for the Acetonitrile (1) + Chlorobenzene (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	1.229	1.228	0.0	13.42	13.42	0.0	73.0	73.0
0.0433	2.470	2.474	0.0433	21.01	21.01	0.0430	99.1	99.1
0.0798	3.298	3.291	0.0798	26.17	26.17	0.0795	118.0	118.0
0.1407	4.340	4.348	0.1408	33.11	33.12	0.1403	144.2	144.2
0.2074	5.209	5.203	0.2076	39.08	39.04	0.2070	167.3	167.3
0.2929	6.038	6.040	0.2929	44.96	44.98	0.2922	191.6	191.6
0.3913	6.756	6.760	0.3915	50.24	50.29	0.3907	214.1	214.2
0.4914	7.331	7.321	0.4914	54.69	54.61	0.4908	233.0	232.9
0.5875	7.745	7.754	0.5876	58.02	58.05	0.5871	248.0	248.0
0.6915	8.164	8.160	0.6916	61.23	61.24	0.6913	262.0	262.1
0.7823	8.503	8.504	0.7823	63.80	63.80	0.7821	273.4	273.4
0.8580	8.796	8.796	0.8580	65.94	65.92	0.8579	282.7	282.6
0.9180	9.034	9.036	0.9180	67.61	67.63	0.9179	289.7	289.8
0.9583	9.203	9.201	0.9583	68.69	68.68	0.9583	294.1	294.0
1.0000	9.374	9.375	1.0000	69.60	69.60	1.0000	297.5	297.5

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

313.15 K			353.15 K			393.15 K		
	pressure, kPa			pressure, kPa			pressure, kPa	
x_1	exptl	smooth	x_1	exptl	smooth	x_1	exptl	smooth
0.0	3.585	3.588	0.0	19.741	19.753	0.0	73.02	73.02
0.0295	4.282	4.274	0.0295	22.790	22.749	0.0294	81.90	81.90
0.0514	4.774	4.776	0.0515	24.949	24.951	0.0513	88.38	88.37
0.0898	5.639	5.643	0.0900	28.72	28.74	0.0897	99.54	99.57
0.1835	7.721	7.717	0.1837	37.74	37.72	0.1833	126.24	126.19
0.2791	9.802	9.807	0.2794	46.61	46.63	0.2789	152.59	152.65
0.3901	12.207	12.202	0.3905	56.78	56.76	0.3898	182.75	182.70
0.4958	14.446	14.452	0.4962	66.27	66.27	0.4954	210.90	210.93
0.6031	16.712	16.709	0.6035	75.88	75.88	0.6032	239.52	239.51
0.6092	16.836	16.837	0.6095	76.40	76.41	0.6088	241.01	240.99
0.8162	21.180	21.181	0.8164	94.86	94.85	0.8160	296.2	296.2
0.9073	23.106	23.105	0.9074	102.95	102.95	0.9072	321.2	321.1
0.9459	23.921	23.924	0.9460	106.40	106.44	0.9458	331.8	331.8
0.9712	24.463	24.462	0.9712	108.79	108.74	0.9711	338.9	338.9
1.0000	25.073	25.078	1.0000	111.38	111.40	1.0000	347.2	347.1

chlorine atom on a benzene ring with other molecular groups.

Experimental Apparatus and Techniques

The apparatus used for this study has been described previously (*3*). Fifteen discrete cells are loaded with the two pure components and 13 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

Table V. Experimental P vs. x_1 Values for the Chlorobenzene (1) + Ethylbenzene (2) System at 293.15 K and a Comparison with the Smooth Values

	pressure, kPa	
x_1	exptl	smooth
0.0	0.966	0.966
0.0446	0.978	0.978
0.0649	0.983	0.983
0.1751	*a*	*a*
0.2123	1.020	1.021
0.3001	*a*	*a*
0.4045	1.071	1.071
0.5032	1.094	1.096
0.5989	1.122	1.121
0.6998	1.149	1.147
0.7905	1.171	1.171
0.8595	1.191	1.189
0.9183	1.202	1.204
0.9574	1.215	1.214
1.0000	1.225	1.225

[a] Glass cells were used for this system and the two cells at x_1 = 0.1751 and 0.3001 were broken during the experiment.

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).

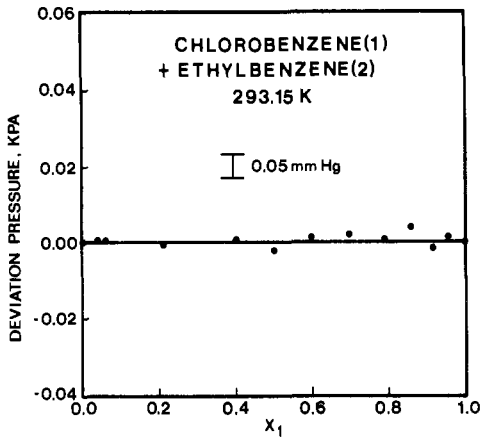

Figure 1. Deviation from Raoult's law for the chlorobenzene (1) + ethylbenzene (2) system at 293.15 K.

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

Table VI. Experimental P vs. x_1 Values for the Methanol (1) + Chlorobenzene (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	1.208	1.208	0.0	10.927	10.927	0.0	57.60	57.60
0.0393	7.917	7.917	0.0395	44.79	44.79	0.0387	151.50	151.60
0.0866	9.499	9.499	0.0870	63.98	63.96	0.0854	232.70	232.50
0.1429	10.215	10.213	0.1432	73.79	73.87	0.1407	296.1	296.3
0.2059	10.633	10.640	0.2062	79.68	79.55	0.2044	341.7	341.7
0.2989	10.985	10.970	0.2990	84.58	84.68	0.2970	381.5	381.2
0.3967	11.245	11.262	0.3968	87.87	87.89	0.3950	408.2	408.4
0.4943	11.538	11.534	0.4943	90.32	90.29	0.4928	427.5	427.7
0.5951	11.771	11.769	0.5951	92.67	92.58	0.5940	443.9	443.5
0.6949	12.027	12.018	0.6948	94.93	94.98	0.6942	458.2	458.1
0.7867	12.304	12.314	0.7868	97.28	97.38	0.7864	472.4	472.6
0.8602	12.572	12.582	0.8602	99.37	99.40	0.8600	484.2	484.6
0.9171	12.799	12.794	0.9171	101.17	101.03	0.9171	494.1	493.9
0.9575	12.959	12.940	0.9576	102.34	102.22	0.9575	500.9	500.4
1.0000	13.075	13.086	1.0000	103.20	103.50	1.0000	506.7	507.0

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

280.00 K			320.00 K			360.00 K		
	pressure, kPa			pressure, kPa			pressure, kPa	
x_1	exptl	smooth	x_1	exptl	smooth	x_1	exptl	smooth
0.0	0.537	0.528	0.0	4.942	4.945	0.0	25.067	24.914
0.0262	2.388	2.392	0.0263	11.921	11.889	0.0261	43.15	43.27
0.0496	3.948	3.973	0.0496	17.726	17.787	0.0494	58.69	59.04
0.0848	6.225	6.214	0.0856	26.528	26.480	0.0846	82.16	81.82
0.1676	10.953	10.932	0.1687	44.79	44.83	0.1677	131.40	131.30
0.2659	15.750	15.754	0.2667	63.98	63.91	0.2668	183.84	184.08
0.3671	20.013	20.038	0.3680	81.26	81.34	0.3661	232.21	232.14
0.4766	24.121	24.116	0.4774	98.35	98.31	0.4758	281.7	281.7
0.5783	27.61	27.58	0.5793	113.05	113.04	0.5770	325.1	325.0
0.6995	31.54	31.54	0.7002	129.92	129.94	0.6979	374.9	375.3
0.7943	34.62	34.65	0.7949	143.33	143.31	0.7933	416.2	415.9
0.8934	38.08	38.07	0.8938	158.17	158.18	0.8928	461.1	461.2
0.9387	39.76	39.74	0.9389	165.46	165.46	0.9383	483.1	483.2
1.0000	42.12	42.13	1.0000	175.67	175.70	1.0000	514.7	514.7

Table VIII. Calculated Data for the Acetone (1) + Chlorobenzene (2) System at 313.15 K. The Tsonopoulos Correlation Was Used to Obtain the Virial Coefficients

	pressure, kPa		combined correctn terms			activity coeffs		excess
x_1	exptl	calcd	1	2	y_1	1	2	G, J/mol
0.0	3.564	3.564	0.9651	1.0000	0.0	1.6640	1.0000	0.0
0.0250	5.680	5.680	0.9665	1.0027	0.3864	1.6049	1.0005	31.95
0.0500	7.654	7.655	0.9677	1.0053	0.5546	1.5501	1.0018	61.52
0.0750	9.505	9.505	0.9689	1.0077	0.6491	1.5002	1.0040	88.78
0.1000	11.249	11.249	0.9701	1.0100	0.7101	1.4549	1.0069	113.80
0.1250	12.904	12.904	0.9711	1.0121	0.7529	1.4141	1.0106	136.70
0.1500	14.485	14.485	0.9721	1.0142	0.7848	1.3774	1.0148	157.54
0.1750	16.007	16.008	0.9731	1.0162	0.8097	1.3449	1.0195	176.47
0.2000	17.487	17.487	0.9741	1.0181	0.8300	1.3163	1.0245	193.60
0.2250	18.937	18.938	0.9750	1.0200	0.8468	1.2916	1.0298	209.09
0.2500	20.363	20.363	0.9759	1.0219	0.8612	1.2699	1.0352	223.09
0.2750	21.764	21.765	0.9769	1.0238	0.8735	1.2504	1.0409	235.70
0.3000	23.141	23.141	0.9778	1.0256	0.8843	1.2326	1.0470	246.96
0.3250	24.492	24.493	0.9786	1.0274	0.8937	1.2160	1.0534	256.95
0.3500	25.820	25.820	0.9795	1.0292	0.9021	1.2005	1.0603	265.65
0.3750	27.122	27.123	0.9803	1.0310	0.9096	1.1857	1.0678	273.11
0.4000	28.400	28.401	0.9812	1.0327	0.9164	1.1716	1.0759	279.29
0.4250	29.654	29.655	0.9820	1.0344	0.9225	1.1581	1.0847	284.20
0.4500	30.883	30.884	0.9828	1.0360	0.9281	1.1451	1.0943	287.81
0.4750	32.088	32.089	0.9836	1.0377	0.9332	1.1324	1.1049	290.10
0.5000	33.268	33.269	0.9844	1.0393	0.9379	1.1201	1.1164	291.01
0.5250	34.426	34.427	0.9851	1.0408	0.9422	1.1081	1.1291	290.52
0.5500	35.565	35.566	0.9859	1.0424	0.9463	1.0967	1.1428	288.57
0.5750	36.691	36.692	0.9866	1.0440	0.9501	1.0857	1.1577	285.16
0.6000	37.806	37.807	0.9874	1.0455	0.9537	1.0754	1.1735	280.22
0.6250	38.915	38.916	0.9881	1.0470	0.9572	1.0657	1.1904	273.79
0.6500	40.023	40.023	0.9889	1.0485	0.9605	1.0568	1.2082	265.82
0.6750	41.132	41.132	0.9896	1.0501	0.9637	1.0485	1.2269	256.35
0.7000	42.247	42.247	0.9903	1.0516	0.9668	1.0411	1.2464	245.36
0.7250	43.371	43.371	0.9911	1.0532	0.9699	1.0344	1.2665	232.92
0.7500	44.505	44.505	0.9918	1.0548	0.9728	1.0284	1.2873	219.00
0.7750	45.649	45.649	0.9926	1.0564	0.9757	1.0230	1.3091	203.68
0.8000	46.805	46.805	0.9934	1.0580	0.9785	1.0183	1.3317	186.91
0.8250	47.973	47.973	0.9942	1.0596	0.9813	1.0141	1.3554	168.75
0.8500	49.153	49.154	0.9950	1.0613	0.9841	1.0106	1.3804	149.14
0.8750	50.348	50.348	0.9958	1.0630	0.9868	1.0075	1.4072	128.15
0.9000	51.558	51.558	0.9966	1.0647	0.9894	1.0049	1.4356	105.64
0.9250	52.786	52.786	0.9974	1.0664	0.9921	1.0029	1.4666	81.72
0.9500	54.033	54.033	0.9983	1.0682	0.9947	1.0014	1.4996	56.16
0.9750	55.303	55.303	0.9991	1.0700	0.9973	1.0004	1.5401	29.14
1.0000	56.597	56.597	1.0000	1.0719	1.0000	1.0000	1.5906	0.0

Table IX. Calculated Data for the Acetone (1) + Chlorobenzene (2) System at 353.00 K. The Tsonopoulos Correlation Was Used to Obtain the Virial Coefficients

	pressure, kPa		combined correctn terms			activity coeffs		
x_1	exptl	calcd	1	2	y_1	1	2	excess G, J/mol
0.0	19.599	19.599	0.9249	1.0000	0.0	1.4932	1.0000	0.0
0.0250	26.542	26.542	0.9275	1.0051	0.2762	1.4718	1.0002	28.88
0.0500	33.305	33.305	0.9300	1.0102	0.4348	1.4498	1.0008	56.69
0.0750	39.849	39.849	0.9323	1.0150	0.5373	1.4254	1.0019	83.28
0.1000	46.139	46.138	0.9346	1.0198	0.6087	1.3986	1.0038	108.42
0.1250	52.180	52.179	0.9368	1.0243	0.6612	1.3715	1.0063	131.96
0.1500	58.001	58.000	0.9390	1.0288	0.7017	1.3451	1.0094	153.85
0.1750	63.631	63.629	0.9411	1.0331	0.7341	1.3202	1.0131	174.10
0.2000	69.098	69.096	0.9431	1.0373	0.7606	1.2970	1.0172	192.72
0.2250	74.428	74.426	0.9450	1.0414	0.7828	1.2755	1.0218	209.75
0.2500	79.636	79.634	0.9470	1.0455	0.8018	1.2555	1.0268	225.25
0.2750	84.729	84.727	0.9489	1.0495	0.8183	1.2368	1.0323	239.25
0.3000	89.716	89.713	0.9508	1.0534	0.8327	1.2192	1.0383	251.77
0.3250	94.603	94.600	0.9526	1.0573	0.8455	1.2026	1.0448	262.82
0.3500	99.399	99.395	0.9544	1.0611	0.8570	1.1870	1.0518	272.42
0.3750	104.110	104.106	0.9562	1.0649	0.8673	1.1721	1.0594	280.56
0.4000	108.745	108.741	0.9579	1.0687	0.8766	1.1580	1.0675	287.26
0.4250	113.312	113.308	0.9597	1.0724	0.8852	1.1447	1.0762	292.51
0.4500	117.817	117.813	0.9614	1.0761	0.8931	1.1321	1.0855	296.32
0.4750	122.270	122.265	0.9631	1.0797	0.9005	1.1202	1.0954	298.69
0.5000	126.677	126.672	0.9648	1.0834	0.9073	1.1090	1.1059	299.61
0.5250	131.044	131.040	0.9665	1.0870	0.9137	1.0984	1.1172	299.09
0.5500	135.379	135.374	0.9682	1.0907	0.9198	1.0885	1.1291	297.13
0.5750	139.686	139.681	0.9698	1.0943	0.9255	1.0791	1.1417	293.72
0.6000	143.971	143.966	0.9715	1.0979	0.9309	1.0703	1.1551	288.85

Table IX (*Continued*)

	pressure, kPa		combined correctn terms			activity coeffs		
x_1	exptl	calcd	1	2	y_1	1	2	excess G, J/mol
0.6250	148.239	148.234	0.9732	1.1015	0.9361	1.0620	1.1694	282.52
0.6500	152.497	152.492	0.9749	1.1052	0.9411	1.0542	1.1845	274.72
0.6750	156.749	156.745	0.9765	1.1089	0.9459	1.0470	1.2006	265.42
0.7000	161.002	160.997	0.9782	1.1125	0.9505	1.0403	1.2178	254.63
0.7250	165.261	165.256	0.9799	1.1163	0.9550	1.0341	1.2360	242.31
0.7500	169.534	169.529	0.9816	1.1200	0.9594	1.0283	1.2555	228.45
0.7750	173.828	173.824	0.9833	1.1238	0.9636	1.0231	1.2762	213.02
0.8000	178.151	178.147	0.9851	1.1276	0.9678	1.0184	1.2982	196.02
0.8250	182.510	182.506	0.9868	1.1315	0.9719	1.0142	1.3217	177.39
0.8500	186.912	186.909	0.9886	1.1354	0.9759	1.0105	1.3469	157.15
0.8750	191.366	191.363	0.9904	1.1395	0.9800	1.0073	1.3738	135.22
0.9000	195.882	195.880	0.9922	1.1435	0.9840	1.0047	1.4027	111.62
0.9250	200.474	200.472	0.9941	1.1477	0.9879	1.0026	1.4332	86.25
0.9500	205.153	205.152	0.9960	1.1520	0.9919	1.0011	1.4656	59.18
0.9750	209.934	209.932	0.9980	1.1565	0.9960	1.0002	1.4971	30.31
1.0000	214.827	214.826	1.0000	1.1610	1.0000	1.0000	1.5265	0.0

Table X. Calculated Data for the Acetone (1) + Chlorobenzene (2) System at 386.66 K. The Tsonopoulos Correlation Was Used to Obtain the Virial Coefficients

	pressure, kPa		combined correctn terms			activity coeffs		
x_1	exptl	calcd	1	2	y_1	1	2	excess G, J/mol
0.0	60.327	60.327	0.8764	1.0000	0.0	1.4507	1.0000	0.0
0.0250	75.821	75.821	0.8802	1.0080	0.2180	1.4413	1.0001	29.64
0.0500	91.171	91.171	0.8840	1.0159	0.3611	1.4294	1.0004	58.75
0.0750	106.160	106.159	0.8876	1.0237	0.4612	1.4112	1.0013	87.00
0.1000	120.591	120.589	0.8912	1.0313	0.5343	1.3873	1.0030	113.90
0.1250	134.448	134.446	0.8946	1.0387	0.5900	1.3612	1.0054	139.14
0.1500	147.808	147.805	0.8979	1.0459	0.6341	1.3353	1.0085	162.60
0.1750	160.749	160.746	0.9011	1.0530	0.6700	1.3107	1.0122	184.27
0.2000	173.349	173.345	0.9042	1.0599	0.7001	1.2878	1.0163	204.15
0.2250	185.680	185.675	0.9073	1.0667	0.7258	1.2668	1.0208	222.33
0.2500	197.773	197.768	0.9104	1.0735	0.7481	1.2475	1.0257	238.86
0.2750	209.645	209.638	0.9134	1.0802	0.7676	1.2295	1.0310	253.79
0.3000	221.307	221.300	0.9164	1.0869	0.7850	1.2126	1.0368	267.16
0.3250	232.776	232.768	0.9193	1.0936	0.8005	1.1967	1.0430	278.97
0.3500	244.065	244.055	0.9223	1.1002	0.8145	1.1817	1.0497	289.26
0.3750	255.188	255.177	0.9252	1.1067	0.8272	1.1675	1.0569	298.01
0.4000	266.159	266.148	0.9280	1.1133	0.8388	1.1541	1.0647	305.26
0.4250	276.994	276.981	0.9309	1.1198	0.8495	1.1414	1.0730	310.98
0.4500	287.706	287.692	0.9337	1.1263	0.8595	1.1293	1.0819	315.18
0.4750	298.309	298.294	0.9365	1.1328	0.8687	1.1179	1.0914	317.86
0.5000	308.817	308.802	0.9393	1.1394	0.8774	1.1071	1.1016	319.03
0.5250	319.245	319.228	0.9421	1.1459	0.8856	1.0968	1.1124	318.66
0.5500	329.603	329.585	0.9450	1.1524	0.8933	1.0871	1.1239	316.76
0.5750	339.903	339.885	0.9478	1.1590	0.9007	1.0780	1.1362	313.31
0.6000	350.158	350.140	0.9506	1.1656	0.9077	1.0694	1.1493	308.30
0.6250	360.379	360.360	0.9534	1.1723	0.9144	1.0612	1.1633	301.71
0.6500	370.578	370.559	0.9562	1.1790	0.9209	1.0536	1.1782	293.54
0.6750	380.767	380.747	0.9590	1.1858	0.9271	1.0464	1.1941	283.75
0.7000	390.958	390.938	0.9619	1.1926	0.9331	1.0397	1.2111	272.32
0.7250	401.166	401.146	0.9648	1.1995	0.9390	1.0334	1.2293	259.21
0.7500	411.414	411.396	0.9677	1.2066	0.9448	1.0277	1.2488	244.42
0.7750	421.725	421.708	0.9706	1.2137	0.9504	1.0224	1.2695	227.89
0.8000	432.121	432.105	0.9736	1.2210	0.9560	1.0177	1.2914	209.64
0.8250	442.625	442.610	0.9767	1.2284	0.9615	1.0135	1.3147	189.60
0.8500	453.259	453.246	0.9798	1.2360	0.9670	1.0099	1.3394	167.81
0.8750	464.046	464.035	0.9829	1.2437	0.9724	1.0068	1.3653	144.22
0.9000	475.010	475.001	0.9862	1.2517	0.9779	1.0043	1.3926	118.85
0.9250	486.175	486.167	0.9895	1.2600	0.9833	1.0023	1.4208	91.67
0.9500	497.563	497.557	0.9929	1.2684	0.9888	1.0010	1.4503	62.77
0.9750	509.199	509.195	0.9964	1.2772	0.9944	1.0002	1.4780	32.07
1.0000	521.106	521.104	1.0000	1.2863	1.0000	1.0000	1.5031	0.0

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.

Experimental Results

The raw $P-x$ data measured for the six systems are in Tables II–VII. The liquid-phase mole fractions were corrected for the presence of the vapor phase and the removal of vapor during pressure measurement as described previously (*3*). Also shown are the smooth $P-x$ values obtained from a least-squares cubic spline fit of the data.

The Mixon et al. (*1*) 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

Table XI. Calculated Data for the Acetonitrile (1) + Chlorobenzene (2) System at 393.15 K. The Tsonopoulos Correlation Was Used to Obtain the Virial Coefficients

	pressure, kPa		combined correctn terms			activity coeffs		
x_1	exptl	calcd	1	2	y_1	1	2	excess G, J/mol
0.0	1.233	1.233	0.9787	1.0000	0.0	3.5910	1.0000	0.0
0.0250	1.977	1.977	0.9802	1.0017	0.3903	3.3589	1.0008	75.84
0.0500	2.627	2.627	0.9817	1.0035	0.5510	3.1457	1.0034	147.55
0.0750	3.194	3.194	0.9832	1.0051	0.6382	2.9484	1.0078	215.09
0.1000	3.686	3.686	0.9844	1.0066	0.6927	2.7668	1.0139	278.38
0.1250	4.115	4.115	0.9856	1.0079	0.7299	2.6006	1.0219	337.43
0.1500	4.490	4.490	0.9866	1.0090	0.7570	2.4498	1.0317	392.22
0.1750	4.821	4.821	0.9875	1.0100	0.7776	2.3142	1.0431	442.82
0.2000	5.118	5.118	0.9883	1.0110	0.7942	2.1937	1.0561	489.32
0.2250	5.391	5.391	0.9890	1.0118	0.8080	2.0880	1.0702	531.90
0.2500	5.644	5.644	0.9897	1.0126	0.8198	1.9947	1.0855	570.77
0.2750	5.878	5.878	0.9903	1.0134	0.8301	1.9109	1.1022	606.05
0.3000	6.095	6.094	0.9909	1.0141	0.8390	1.8348	1.1205	637.83
0.3250	6.295	6.295	0.9915	1.0147	0.8470	1.7650	1.1404	666.15
0.3500	6.482	6.482	0.9920	1.0153	0.8541	1.7007	1.1621	691.06
0.3750	6.655	6.655	0.9925	1.0159	0.8605	1.6412	1.1859	712.56
0.4000	6.816	6.816	0.9929	1.0164	0.8663	1.5859	1.2119	730.66
0.4250	6.967	6.967	0.9933	1.0169	0.8716	1.5344	1.2403	745.34
0.4500	7.109	7.108	0.9937	1.0174	0.8766	1.4864	1.2714	756.59
0.4750	7.241	7.241	0.9941	1.0178	0.8812	1.4414	1.3054	764.37
0.5000	7.366	7.366	0.9944	1.0182	0.8855	1.3993	1.3428	768.66
0.5250	7.484	7.484	0.9947	1.0186	0.8897	1.3599	1.3838	769.40
0.5500	7.595	7.595	0.9951	1.0190	0.8936	1.3229	1.4289	766.54
0.5750	7.702	7.702	0.9953	1.0194	0.8974	1.2883	1.4785	760.01
0.6000	7.804	7.805	0.9956	1.0197	0.9012	1.2559	1.5331	749.76
0.6250	7.904	7.904	0.9959	1.0201	0.9049	1.2257	1.5933	735.70
0.6500	8.000	8.001	0.9962	1.0204	0.9086	1.1975	1.6597	717.79
0.6750	8.096	8.096	0.9964	1.0208	0.9124	1.1715	1.7329	695.93
0.7000	8.190	8.191	0.9967	1.0211	0.9163	1.1475	1.8138	670.07
0.7250	8.285	8.285	0.9970	1.0214	0.9204	1.1254	1.9032	640.13
0.7500	8.380	8.380	0.9972	1.0218	0.9247	1.1052	2.0027	606.05
0.7750	8.476	8.476	0.9975	1.0222	0.9293	1.0868	2.1140	567.69
0.8000	8.571	8.572	0.9978	1.0225	0.9341	1.0700	2.2398	524.96
0.8250	8.668	8.668	0.9980	1.0229	0.9393	1.0548	2.3830	477.66
0.8500	8.765	8.765	0.9983	1.0233	0.9450	1.0412	2.5477	425.64
0.8750	8.864	8.864	0.9986	1.0237	0.9512	1.0293	2.7388	368.62
0.9000	8.963	8.963	0.9988	1.0242	0.9582	1.0191	2.9636	306.37
0.9250	9.064	9.064	0.9991	1.0247	0.9662	1.0108	3.2288	238.53
0.9500	9.166	9.166	0.9994	1.0252	0.9756	1.0046	3.5430	164.84
0.9750	9.270	9.270	0.9997	1.0257	0.9868	1.0010	3.8716	84.93
1.0000	9.375	9.375	1.0000	1.0263	1.0000	1.0000	4.1997	0.0

Table XII. Calculated Data for the Acetonitrile (1) + Chlorobenzene (2) System at 343.15 K. The Tsonopoulos Correlation Was Used to Obtain the Virial Coefficients

	pressure, kPa		combined correctn terms			activity coeffs		
x_1	exptl	calcd	1	2	y_1	1	2	excess G, J/mol
0.0	13.421	13.421	0.9439	1.0000	0.0	3.1894	1.0000	0.0
0.0250	18.036	18.036	0.9473	1.0044	0.2706	2.9610	1.0009	80.04
0.0500	22.033	22.032	0.9507	1.0087	0.4141	2.7576	1.0037	154.72
0.0750	25.537	25.536	0.9539	1.0128	0.5037	2.5831	1.0080	224.22
0.1000	28.667	28.667	0.9569	1.0165	0.5658	2.4355	1.0137	288.95
0.1250	31.486	31.485	0.9596	1.0200	0.6117	2.3069	1.0207	349.25
0.1500	34.030	34.029	0.9621	1.0232	0.6470	2.1920	1.0290	405.27
0.1750	36.337	36.336	0.9645	1.0261	0.6752	2.0886	1.0387	457.13
0.2000	38.444	38.442	0.9666	1.0289	0.6984	1.9953	1.0497	504.92
0.2250	40.385	40.384	0.9686	1.0314	0.7179	1.9114	1.0619	548.76
0.2500	42.184	42.182	0.9704	1.0338	0.7347	1.8354	1.0754	588.76
0.2750	43.852	43.850	0.9722	1.0360	0.7494	1.7660	1.0903	625.01
0.3000	45.403	45.401	0.9738	1.0382	0.7623	1.7021	1.1066	657.56
0.3250	46.848	46.846	0.9753	1.0401	0.7738	1.6432	1.1245	686.44
0.3500	48.200	48.199	0.9767	1.0420	0.7843	1.5887	1.1439	711.67
0.3750	49.473	49.472	0.9781	1.0438	0.7938	1.5384	1.1651	733.29
0.4000	50.679	50.678	0.9794	1.0455	0.8026	1.4919	1.1879	751.32
0.4250	51.826	51.825	0.9806	1.0472	0.8109	1.4489	1.2126	765.79
0.4500	52.918	52.918	0.9818	1.0488	0.8187	1.4090	1.2392	776.72
0.4750	53.958	53.958	0.9829	1.0503	0.8261	1.3717	1.2681	784.10
0.5000	54.948	54.949	0.9840	1.0517	0.8331	1.3369	1.2996	787.93
0.5250	55.892	55.893	0.9850	1.0532	0.8398	1.3041	1.3339	788.14
0.5500	56.791	56.793	0.9859	1.0545	0.8462	1.2733	1.3715	784.70
0.5750	57.649	57.651	0.9869	1.0558	0.8524	1.2442	1.4128	777.54
0.6000	58.469	58.472	0.9878	1.0571	0.8584	1.2168	1.4584	766.57

Table XII (*Continued*)

	pressure, kPa		combined correctn terms			activity coeffs		
x_1	exptl	calcd	1	2	y_1	1	2	excess G, J/mol
0.6250	59.255	59.258	0.9886	1.0583	0.8644	1.1910	1.5087	751.71
0.6500	60.013	60.016	0.9894	1.0596	0.8703	1.1668	1.5643	732.84
0.6750	60.748	60.751	0.9902	1.0607	0.8762	1.1441	1.6257	709.88
0.7000	61.466	61.469	0.9910	1.0619	0.8822	1.1231	1.6936	682.72
0.7250	62.173	62.176	0.9918	1.0631	0.8884	1.1037	1.7683	651.28
0.7500	62.874	62.877	0.9926	1.0643	0.8949	1.0860	1.8506	615.47
0.7750	63.576	63.579	0.9933	1.0656	0.9018	1.0700	1.9406	575.24
0.8000	64.284	64.286	0.9941	1.0669	0.9092	1.0559	2.0385	530.55
0.8250	64.997	64.999	0.9949	1.0682	0.9172	1.0436	2.1451	481.40
0.8500	65.712	65.715	0.9957	1.0696	0.9259	1.0329	2.2616	427.76
0.8750	66.428	66.430	0.9965	1.0711	0.9354	1.0239	2.3897	369.60
0.9000	67.133	67.135	0.9972	1.0726	0.9456	1.0163	2.5350	306.85
0.9250	67.816	67.818	0.9980	1.0741	0.9568	1.0099	2.7080	239.21
0.9500	68.464	68.465	0.9987	1.0757	0.9691	1.0048	2.9287	166.15
0.9750	69.063	69.063	0.9994	1.0774	0.9832	1.0012	3.2090	86.60
1.0000	69.600	69.600	1.0000	1.0791	1.0000	1.0000	3.5377	0.0

Table XIII. Calculated Data for the Acetonitrile (1) + Chlorobenzene (2) System at 393.15 K. The Tsonopoulos Correlation Was Used to Obtain the Virial Coefficients

	pressure, kPa		combined correctn terms			activity coeffs		
x_1	exptl	calcd	1	2	y_1	1	2	excess G, J/mol
0.0	73.052	73.051	0.8912	1.0000	0.0	2.6778	1.0000	0.0
0.0250	88.757	88.757	0.8968	1.0081	0.1904	2.5341	1.0007	78.21
0.0500	102.961	102.959	0.9023	1.0162	0.3131	2.4020	1.0028	151.86
0.0750	115.824	115.822	0.9077	1.0239	0.3989	2.2812	1.0062	220.98
0.1000	127.507	127.505	0.9128	1.0312	0.4624	2.1712	1.0110	285.63
0.1250	138.149	138.147	0.9175	1.0381	0.5115	2.0708	1.0171	345.90
0.1500	147.879	147.878	0.9220	1.0445	0.5507	1.9792	1.0244	401.83
0.1750	156.829	156.828	0.9262	1.0506	0.5829	1.8959	1.0330	453.53
0.2000	165.126	165.126	0.9301	1.0564	0.6101	1.8205	1.0427	501.07
0.2250	172.897	172.897	0.9338	1.0619	0.6337	1.7527	1.0534	544.61
0.2500	180.204	180.204	0.9374	1.0672	0.6544	1.6914	1.0652	584.28
0.2750	187.080	187.080	0.9408	1.0722	0.6727	1.6351	1.0781	620.18
0.3000	193.555	193.554	0.9440	1.0771	0.6892	1.5833	1.0922	652.36
0.3250	199.660	199.659	0.9471	1.0817	0.7041	1.5351	1.1076	680.87
0.3500	205.426	205.424	0.9500	1.0862	0.7177	1.4903	1.1245	705.71
0.3750	210.885	210.882	0.9528	1.0905	0.7302	1.4486	1.1428	726.91
0.4000	216.066	216.062	0.9555	1.0946	0.7418	1.4096	1.1627	744.46
0.4250	220.995	220.990	0.9581	1.0986	0.7527	1.3731	1.1842	758.38
0.4500	225.690	225.682	0.9605	1.1024	0.7630	1.3390	1.2077	768.65
0.4750	230.164	230.156	0.9629	1.1061	0.7727	1.3070	1.2331	775.26
0.5000	234.437	234.427	0.9651	1.1097	0.7820	1.2769	1.2607	778.16
0.5250	238.522	238.512	0.9673	1.1132	0.7909	1.2486	1.2908	777.33
0.5500	242.438	242.426	0.9694	1.1167	0.7996	1.2220	1.3235	772.72
0.5750	246.199	246.187	0.9714	1.1200	0.8080	1.1970	1.3591	764.29
0.6000	249.823	249.810	0.9734	1.1233	0.8163	1.1736	1.3979	751.96
0.6250	253.324	253.311	0.9753	1.1265	0.8245	1.1517	1.4402	735.70
0.6500	256.716	256.704	0.9771	1.1297	0.8328	1.1313	1.4862	715.43
0.6750	260.014	260.002	0.9789	1.1328	0.8411	1.1124	1.5363	691.11
0.7000	263.232	263.221	0.9807	1.1360	0.8495	1.0949	1.5909	662.66
0.7250	266.384	266.374	0.9824	1.1392	0.8582	1.0788	1.6501	630.04
0.7500	269.484	269.475	0.9841	1.1424	0.8673	1.0643	1.7143	593.20
0.7750	272.546	272.538	0.9858	1.1456	0.8768	1.0513	1.7833	552.13
0.8000	275.585	275.577	0.9875	1.1490	0.8869	1.0399	1.8567	506.82
0.8250	278.614	278.607	0.9892	1.1525	0.8977	1.0302	1.9336	457.38
0.8500	281.648	281.641	0.9909	1.1561	0.9095	1.0223	2.0117	403.91
0.8750	284.695	284.688	0.9926	1.1599	0.9223	1.0162	2.0883	346.74
0.9000	287.702	287.695	0.9943	1.1638	0.9360	1.0114	2.1672	286.18
0.9250	290.578	290.571	0.9959	1.1677	0.9502	1.0074	2.2595	222.18
0.9500	293.232	293.226	0.9975	1.1716	0.9652	1.0038	2.3874	154.16
0.9750	295.572	295.568	0.9988	1.1755	0.9813	1.0011	2.5710	80.58
1.0000	297.508	297.506	1.0000	1.1794	1.0000	1.0000	2.7981	0.0

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

and

$$G^E = RT \sum_i x_i \ln \gamma_i$$

The Mixon et al. method does not assume any correlation equation for G^E and is the preferred method for reduction of total pressure VLE data when the experimental data are quite smooth. 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 (*2*).

Table XIV. Calculated Data for the Ethyl Acetate (1) + Chlorobenzene (2) System at 313.15 K. The Tsonopoulos Correlation Was Used to Obtain the Virial Coefficients

	pressure, kPa		combined correctn terms			activity coeffs		
x_1	exptl	calcd	1	2	y_1	1	2	excess G, J/mol
0.0	3.588	3.588	0.9834	1.0000	0.0	1.0923	1.0000	0.0
0.0250	4.170	4.170	0.9839	1.0008	0.1604	1.0843	1.0001	5.50
0.0500	4.744	4.744	0.9843	1.0015	0.2802	1.0768	1.0004	10.52
0.0750	5.311	5.311	0.9848	1.0022	0.3732	1.0700	1.0008	15.09
0.1000	5.872	5.872	0.9852	1.0029	0.4477	1.0639	1.0013	19.23
0.1250	6.428	6.428	0.9857	1.0036	0.5088	1.0585	1.0020	22.98
0.1500	6.980	6.980	0.9861	1.0043	0.5600	1.0538	1.0027	26.38
0.1750	7.530	7.530	0.9865	1.0050	0.6036	1.0498	1.0034	29.46
0.2000	8.079	8.079	0.9869	1.0056	0.6412	1.0465	1.0041	32.26
0.2250	8.626	8.627	0.9874	1.0063	0.6740	1.0437	1.0049	34.83
0.2500	9.173	9.173	0.9878	1.0070	0.7029	1.0411	1.0056	37.20
0.2750	9.717	9.718	0.9882	1.0077	0.7285	1.0388	1.0064	39.35
0.3000	10.260	10.261	0.9886	1.0083	0.7514	1.0365	1.0073	41.32
0.3250	10.802	10.802	0.9890	1.0090	0.7719	1.0343	1.0083	43.08
0.3500	11.341	11.341	0.9894	1.0097	0.7904	1.0322	1.0094	44.64
0.3750	11.878	11.879	0.9899	1.0103	0.8073	1.0301	1.0105	45.99
0.4000	12.414	12.415	0.9903	1.0110	0.8226	1.0281	1.0118	47.14
0.4250	12.948	12.949	0.9907	1.0117	0.8367	1.0260	1.0132	48.06
0.4500	13.481	13.481	0.9911	1.0123	0.8496	1.0241	1.0147	48.78
0.4750	14.011	14.012	0.9915	1.0130	0.8616	1.0221	1.0164	49.26
0.5000	14.540	14.541	0.9919	1.0136	0.8727	1.0202	1.0182	49.52
0.5250	15.068	15.068	0.9923	1.0143	0.8830	1.0184	1.0201	49.53
0.5500	15.594	15.595	0.9927	1.0149	0.8926	1.0166	1.0222	49.30
0.5750	16.119	16.120	0.9931	1.0156	0.9016	1.0149	1.0244	48.81
0.6000	16.644	16.645	0.9935	1.0162	0.9100	1.0132	1.0268	48.07
0.6250	17.168	17.169	0.9939	1.0169	0.9180	1.0117	1.0293	47.07
0.6500	17.692	17.693	0.9943	1.0175	0.9255	1.0102	1.0319	45.83
0.6750	18.216	18.217	0.9947	1.0182	0.9326	1.0089	1.0345	44.32
0.7000	18.740	18.741	0.9951	1.0188	0.9393	1.0077	1.0373	42.57
0.7250	19.265	19.265	0.9955	1.0195	0.9457	1.0065	1.0402	40.54
0.7500	19.789	19.790	0.9959	1.0201	0.9518	1.0055	1.0433	38.28
0.7750	20.314	20.314	0.9963	1.0208	0.9575	1.0045	1.0465	35.74
0.8000	20.840	20.840	0.9967	1.0215	0.9631	1.0037	1.0498	32.96
0.8250	21.366	21.366	0.9971	1.0221	0.9684	1.0029	1.0533	29.89
0.8500	21.893	21.893	0.9975	1.0228	0.9734	1.0022	1.0571	26.58
0.8750	22.421	22.421	0.9979	1.0234	0.9783	1.0016	1.0609	22.95
0.9000	22.950	22.950	0.9984	1.0241	0.9829	1.0011	1.0653	19.09
0.9250	23.480	23.480	0.9988	1.0248	0.9874	1.0007	1.0697	14.86
0.9500	24.011	24.011	0.9992	1.0254	0.9918	1.0004	1.0760	10.41
0.9750	24.542	24.542	0.9996	1.0261	0.9959	1.0001	1.0833	5.37
1.0000	25.078	25.078	1.0000	1.0268	1.0000	1.0000	1.0887	0.0

Table XV. Calculated Data for the Ethyl Acetate (1) + Chlorobenzene (2) System at 353.15 K. The Tsonopoulos Correlation Was Used to Obtain the Virial Coefficients

	pressure, kPa		combined correctn terms			activity coeffs		
x_1	exptl	calcd	1	2	y_1	1	2	excess G, J/mol
0.0	19.753	19.753	0.9571	1.0000	0.0	1.1325	1.0000	0.0
0.0250	22.295	22.295	0.9583	1.0019	0.1345	1.1237	1.0001	8.84
0.0500	24.802	24.802	0.9595	1.0037	0.2403	1.1154	1.0004	17.11
0.0750	27.275	27.276	0.9606	1.0055	0.3259	1.1076	1.0009	24.82
0.1000	29.719	29.719	0.9618	1.0073	0.3966	1.1002	1.0015	31.98
0.1250	32.135	32.136	0.9629	1.0090	0.4561	1.0932	1.0023	38.62
0.1500	34.528	34.529	0.9640	1.0108	0.5069	1.0867	1.0032	44.73
0.1750	36.900	36.901	0.9651	1.0125	0.5509	1.0807	1.0043	50.35
0.2000	39.254	39.255	0.9662	1.0142	0.5895	1.0751	1.0055	55.49
0.2250	41.593	41.594	0.9672	1.0159	0.6235	1.0699	1.0068	60.18
0.2500	43.917	43.918	0.9683	1.0176	0.6539	1.0651	1.0083	64.41
0.2750	46.227	46.228	0.9694	1.0193	0.6811	1.0605	1.0098	68.22
0.3000	48.525	48.527	0.9704	1.0210	0.7058	1.0561	1.0115	71.60
0.3250	50.812	50.814	0.9715	1.0226	0.7281	1.0520	1.0133	74.56
0.3500	53.090	53.091	0.9725	1.0243	0.7485	1.0482	1.0152	77.11
0.3750	55.358	55.360	0.9736	1.0260	0.7673	1.0445	1.0172	79.26
0.4000	57.619	57.621	0.9746	1.0276	0.7845	1.0411	1.0193	81.00
0.4250	59.874	59.875	0.9757	1.0293	0.8005	1.0378	1.0216	82.35
0.4500	62.123	62.125	0.9767	1.0310	0.8154	1.0347	1.0239	83.31
0.4750	64.369	64.370	0.9778	1.0326	0.8293	1.0319	1.0264	83.89
0.5000	66.611	66.613	0.9788	1.0343	0.8422	1.0292	1.0289	84.09
0.5250	68.852	68.854	0.9799	1.0360	0.8544	1.0267	1.0316	83.93
0.5500	71.091	71.092	0.9809	1.0376	0.8658	1.0243	1.0343	83.39
0.5750	73.328	73.330	0.9819	1.0393	0.8766	1.0221	1.0372	82.51
0.6000	75.564	75.565	0.9830	1.0410	0.8868	1.0200	1.0402	81.25
0.6250	77.797	77.799	0.9840	1.0427	0.8964	1.0181	1.0434	79.64

Table XV (*Continued*)

	pressure, kPa		combined correctn terms			activity coeffs		excess G,
x_1	exptl	calcd	1	2	y_1	1	2	J/mol
0.6500	80.029	80.031	0.9851	1.0443	0.9056	1.0162	1.0468	77.64
0.6750	82.260	82.261	0.9861	1.0460	0.9143	1.0144	1.0505	75.28
0.7000	84.489	84.490	0.9872	1.0477	0.9225	1.0127	1.0544	72.51
0.7250	86.716	86.717	0.9882	1.0494	0.9304	1.0110	1.0586	69.35
0.7500	88.941	88.943	0.9893	1.0511	0.9380	1.0095	1.0633	65.75
0.7750	91.166	91.167	0.9903	1.0528	0.9452	1.0080	1.0684	61.73
0.8000	93.388	93.389	0.9914	1.0545	0.9521	1.0065	1.0741	57.20
0.8250	95.610	95.610	0.9925	1.0562	0.9587	1.0051	1.0805	52.19
0.8500	97.831	97.832	0.9935	1.0579	0.9652	1.0038	1.0877	46.58
0.8750	100.057	100.057	0.9946	1.0596	0.9713	1.0027	1.0957	40.42
0.9000	102.291	102.291	0.9956	1.0613	0.9774	1.0017	1.1042	33.56
0.9250	104.539	104.539	0.9967	1.0631	0.9832	1.0009	1.1133	26.12
0.9500	106.803	106.803	0.9978	1.0648	0.9890	1.0004	1.1215	17.93
0.9750	109.089	109.089	0.9989	1.0666	0.9945	1.0001	1.1301	9.35
1.0000	111.385	111.384	1.0000	1.0684	1.0000	1.0000	1.1417	0.0

Table XVI. Calculated Data for the Ethyl Acetate (1) + Chlorobenzene (2) System at 393.15 K. The Tsonopoulos Correlation Was Used to Obtain the Virial Coefficients

	pressure, kPa		combined correctn terms			activity coeffs		
x_1	exptl	calcd	1	2	y_1	1	2	excess G, J/mol
0.0	73.022	73.022	0.9131	1.0000	0.0	1.1621	1.0000	0.0
0.0250	80.584	80.583	0.9155	1.0037	0.1131	1.1475	1.0002	11.75
0.0500	87.990	87.990	0.9177	1.0072	0.2054	1.1351	1.0006	22.46
0.0750	95.303	95.302	0.9199	1.0108	0.2828	1.1255	1.0011	32.37
0.1000	102.541	102.540	0.9221	1.0143	0.3487	1.1173	1.0018	41.60
0.1250	109.710	109.708	0.9243	1.0178	0.4057	1.1098	1.0027	50.20
0.1500	116.815	116.813	0.9264	1.0212	0.4554	1.1028	1.0037	58.20
0.1750	123.863	123.860	0.9286	1.0247	0.4992	1.0963	1.0048	65.60
0.2000	130.860	130.857	0.9307	1.0281	0.5382	1.0901	1.0062	72.43
0.2250	137.809	137.805	0.9328	1.0315	0.5732	1.0842	1.0076	78.70
0.2500	144.714	144.710	0.9349	1.0349	0.6047	1.0787	1.0092	84.41
0.2750	151.580	151.576	0.9370	1.0384	0.6333	1.0734	1.0110	89.58
0.3000	158.410	158.406	0.9391	1.0418	0.6595	1.0683	1.0129	94.20
0.3250	165.208	165.203	0.9412	1.0452	0.6835	1.0635	1.0150	98.28
0.3500	171.977	171.971	0.9433	1.0486	0.7056	1.0589	1.0172	101.82
0.3750	178.720	178.714	0.9454	1.0520	0.7261	1.0545	1.0196	104.84
0.4000	185.443	185.437	0.9474	1.0554	0.7451	1.0504	1.0222	107.33
0.4250	192.146	192.140	0.9495	1.0589	0.7628	1.0464	1.0249	109.29
0.4500	198.832	198.825	0.9516	1.0623	0.7794	1.0427	1.0278	110.72
0.4750	205.500	205.494	0.9537	1.0658	0.7950	1.0390	1.0309	111.64
0.5000	212.154	212.147	0.9558	1.0692	0.8097	1.0356	1.0341	112.02
0.5250	218.794	218.787	0.9579	1.0727	0.8235	1.0323	1.0377	111.87
0.5500	225.423	225.416	0.9600	1.0762	0.8366	1.0291	1.0414	111.16
0.5750	232.046	232.038	0.9621	1.0797	0.8490	1.0260	1.0453	109.92
0.6000	238.665	238.658	0.9642	1.0832	0.8609	1.0232	1.0495	108.12
0.6250	245.284	245.277	0.9663	1.0868	0.8721	1.0205	1.0539	105.77
0.6500	251.907	251.900	0.9684	1.0903	0.8829	1.0179	1.0586	102.84
0.6750	258.537	258.530	0.9706	1.0939	0.8932	1.0155	1.0635	99.36
0.7000	265.178	265.172	0.9727	1.0975	0.9031	1.0133	1.0686	95.29
0.7250	271.835	271.828	0.9749	1.1011	0.9126	1.0112	1.0740	90.67
0.7500	278.509	278.503	0.9771	1.1048	0.9218	1.0093	1.0797	85.44
0.7750	285.206	285.200	0.9793	1.1085	0.9307	1.0076	1.0856	79.66
0.8000	291.928	291.923	0.9815	1.1122	0.9392	1.0061	1.0918	73.26
0.8250	298.680	298.675	0.9837	1.1160	0.9476	1.0047	1.0983	66.31
0.8500	305.464	305.460	0.9860	1.1198	0.9556	1.0035	1.1050	58.70
0.8750	312.286	312.281	0.9882	1.1237	0.9635	1.0025	1.1123	50.56
0.9000	319.148	319.144	0.9905	1.1276	0.9711	1.0016	1.1196	41.71
0.9250	326.054	326.051	0.9929	1.1316	0.9786	1.0009	1.1280	32.36
0.9500	333.014	333.012	0.9952	1.1356	0.9859	1.0005	1.1352	22.19
0.9750	340.041	340.039	0.9976	1.1397	0.9930	1.0002	1.1456	11.71
1.0000	347.082	347.081	1.0000	1.1438	1.0000	1.0000	1.1627	0.0

The calculated results are shown in Tables VIII–XXII for all the systems except the chlorobenzene + ethylbenzene system where the activity coefficients were all less than 1.0001. In those tables, the "combined correction term" refers to the following grouping of terms.

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

Discussion of Results

The systems measured varied greatly in behavior, ranging from almost ideal solution behavior to strong positive deviation. No azeotropes were found for these six systems.

The chlorobenzene + ethylbenzene system (see Figure 1) showed essentially no departure from ideality. The deviation pressure, denoted here as P_D, is defined as

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

A plot of this nature emphasizes the scatter in the data and

Table XVII. Calculated Data for the Methanol (1) + Chlorobenzene (2) System at 293.15 K. The Tsonopoulos Correlation Was Used to Obtain the Virial Coefficients

	pressure, kPa		combined correctn terms			activity coeffs		
x_1	exptl	calcd	1	2	y_1	1	2	excess G, J/mol
0.0	1.208	1.208	0.9891	1.0000	0.0	34.3339	1.0000	0.0
0.0250	7.073	7.072	0.9939	1.0182	0.8291	18.0477	1.0082	195.63
0.0500	8.354	8.354	0.9952	1.0225	0.8559	10.9899	1.0260	351.57
0.0750	9.143	9.143	0.9960	1.0252	0.8689	8.1340	1.0460	484.61
0.1000	9.710	9.709	0.9966	1.0272	0.8772	6.5359	1.0678	601.53
0.1250	10.096	10.096	0.9970	1.0285	0.8824	5.4669	1.0921	705.40
0.1500	10.345	10.345	0.9973	1.0294	0.8857	4.6841	1.1192	797.81
0.1750	10.499	10.499	0.9974	1.0299	0.8876	4.0834	1.1493	879.86
0.2000	10.601	10.601	0.9975	1.0303	0.8890	3.6128	1.1821	952.32
0.2250	10.691	10.691	0.9976	1.0306	0.8902	3.2425	1.2170	1016.01
0.2500	10.780	10.780	0.9977	1.0309	0.8914	2.9463	1.2537	1071.74
0.2750	10.869	10.869	0.9978	1.0312	0.8926	2.7040	1.2925	1120.14
0.3000	10.956	10.956	0.9979	1.0316	0.8938	2.5018	1.3336	1161.70
0.3250	11.042	11.042	0.9980	1.0319	0.8951	2.3303	1.3773	1196.81
0.3500	11.125	11.125	0.9981	1.0322	0.8963	2.1829	1.4239	1225.79
0.3750	11.204	11.204	0.9982	1.0325	0.8975	2.0545	1.4737	1248.88
0.4000	11.280	11.280	0.9982	1.0327	0.8986	1.9415	1.5274	1266.28
0.4250	11.351	11.351	0.9983	1.0330	0.8998	1.8411	1.5854	1278.12
0.4500	11.419	11.419	0.9984	1.0332	0.9009	1.7512	1.6483	1284.50
0.4750	11.484	11.484	0.9984	1.0335	0.9020	1.6704	1.7167	1285.50
0.5000	11.546	11.546	0.9985	1.0337	0.9031	1.5973	1.7913	1281.16
0.5250	11.606	11.606	0.9986	1.0339	0.9043	1.5311	1.8729	1271.53
0.5500	11.666	11.666	0.9986	1.0342	0.9054	1.4708	1.9624	1256.60
0.5750	11.725	11.725	0.9987	1.0344	0.9067	1.4158	2.0610	1236.38
0.6000	11.785	11.785	0.9988	1.0346	0.9080	1.3655	2.1698	1210.84
0.6250	11.845	11.845	0.9988	1.0349	0.9094	1.3196	2.2905	1179.95
0.6500	11.907	11.907	0.9989	1.0351	0.9109	1.2775	2.4247	1143.64
0.6750	11.972	11.971	0.9989	1.0354	0.9126	1.2391	2.5746	1101.86
0.7000	12.039	12.039	0.9990	1.0357	0.9145	1.2040	2.7426	1054.51
0.7250	12.110	12.110	0.9991	1.0360	0.9167	1.1721	2.9318	1001.53
0.7500	12.185	12.185	0.9992	1.0363	0.9192	1.1431	3.1457	942.78
0.7750	12.264	12.264	0.9992	1.0367	0.9221	1.1169	3.3892	878.16
0.8000	12.348	12.348	0.9993	1.0371	0.9256	1.0934	3.6675	807.50
0.8250	12.437	12.437	0.9994	1.0375	0.9297	1.0725	3.9869	730.67
0.8500	12.531	12.531	0.9995	1.0380	0.9347	1.0544	4.3537	647.49
0.8750	12.631	12.631	0.9996	1.0385	0.9407	1.0390	4.7734	557.85
0.9000	12.734	12.734	0.9997	1.0391	0.9481	1.0262	5.2645	461.67
0.9250	12.835	12.835	0.9998	1.0398	0.9569	1.0157	5.8712	358.59
0.9500	12.928	12.928	0.9999	1.0405	0.9675	1.0071	6.6766	247.85
0.9750	13.011	13.010	0.9999	1.0413	0.9815	1.0017	7.6558	128.08
1.0000	13.076	13.076	1.0000	1.0422	1.0000	1.0000	8.7591	0.0

Table XVIII. Calculated Data for the Methanol (1) + Chlorobenzene (2) System at 338.15 K. The Tsonopoulos Correlation Was Used to Obtain the Virial Coefficients

	pressure, kPa		combined correctn terms			activity coeffs		
x_1	exptl	calcd	1	2	y_1	1	2	excess G, J/mol
0.0	10.927	10.927	0.9681	1.0000	0.0	12.8131	1.0000	0.0
0.0250	35.586	35.585	0.9751	1.0274	0.6913	9.7505	1.0035	169.54
0.0500	50.264	50.262	0.9803	1.0454	0.7815	7.7430	1.0120	319.65
0.0750	60.358	60.355	0.9840	1.0581	0.8185	6.4680	1.0241	455.59
0.1000	67.119	67.117	0.9865	1.0667	0.8375	5.5050	1.0400	578.73
0.1250	71.544	71.543	0.9881	1.0725	0.8481	4.7463	1.0597	689.85
0.1500	74.628	74.626	0.9893	1.0765	0.8550	4.1543	1.0823	789.52
0.1750	77.082	77.081	0.9902	1.0798	0.8602	3.6970	1.1069	878.94
0.2000	79.103	79.102	0.9910	1.0825	0.8644	3.3333	1.1336	959.04
0.2250	80.827	80.827	0.9916	1.0848	0.8679	3.0378	1.1623	1030.56
0.2500	82.319	82.318	0.9922	1.0868	0.8709	2.7926	1.1931	1094.10
0.2750	83.606	83.606	0.9927	1.0885	0.8735	2.5849	1.2263	1150.11
0.3000	84.717	84.717	0.9931	1.0900	0.8758	2.4062	1.2622	1198.92
0.3250	85.681	85.681	0.9934	1.0914	0.8778	2.2506	1.3011	1240.80
0.3500	86.526	86.526	0.9938	1.0925	0.8795	2.1141	1.3433	1275.95
0.3750	87.280	87.280	0.9940	1.0935	0.8812	1.9934	1.3889	1304.55
0.4000	87.971	87.971	0.9943	1.0945	0.8827	1.8864	1.4382	1326.74
0.4250	88.624	88.623	0.9945	1.0954	0.8842	1.7912	1.4914	1342.68
0.4500	89.245	89.245	0.9948	1.0963	0.8856	1.7060	1.5490	1352.49
0.4750	89.843	89.842	0.9950	1.0971	0.8871	1.6293	1.6115	1356.25
0.5000	90.422	90.422	0.9952	1.0979	0.8886	1.5601	1.6795	1354.03
0.5250	90.991	90.991	0.9954	1.0987	0.8901	1.4974	1.7535	1345.88
0.5500	91.555	91.554	0.9956	1.0995	0.8917	1.4404	1.8343	1331.83
0.5750	92.120	92.119	0.9959	1.1004	0.8933	1.3886	1.9228	1311.90
0.6000	92.693	92.693	0.9961	1.1012	0.8951	1.3414	2.0199	1286.07
0.6250	93.279	93.279	0.9963	1.1020	0.8970	1.2984	2.1267	1254.35

Table XVIII (*Continued*)

	pressure, kPa		combined correctn terms			activity coeffs		excess
x_1	exptl	calcd	1	2	y_1	1	2	G, J/mol
0.6500	93.878	93.877	0.9965	1.1029	0.8991	1.2591	2.2448	1216.70
0.6750	94.489	94.489	0.9967	1.1038	0.9014	1.2232	2.3760	1173.07
0.7000	95.113	95.113	0.9970	1.1048	0.9039	1.1903	2.5228	1123.36
0.7250	95.750	95.749	0.9972	1.1058	0.9067	1.1602	2.6881	1067.47
0.7500	96.398	96.397	0.9974	1.1068	0.9098	1.1327	2.8757	1005.25
0.7750	97.058	97.057	0.9977	1.1078	0.9133	1.1076	3.0904	936.50
0.8000	97.730	97.729	0.9979	1.1089	0.9172	1.0849	3.3382	861.01
0.8250	98.413	98.413	0.9982	1.1100	0.9218	1.0643	3.6268	778.50
0.8500	99.108	99.107	0.9984	1.1112	0.9271	1.0461	3.9654	688.66
0.8750	99.814	99.813	0.9987	1.1125	0.9336	1.0303	4.3632	591.17
0.9000	100.530	100.530	0.9989	1.1139	0.9416	1.0173	4.8237	485.76
0.9250	101.257	101.257	0.9992	1.1154	0.9519	1.0076	5.3231	372.38
0.9500	101.995	101.994	0.9994	1.1172	0.9655	1.0021	5.7579	251.78
0.9750	102.743	102.742	0.9997	1.1191	0.9822	1.0003	5.9975	126.60
1.0000	103.500	103.500	1.0000	1.1212	1.0000	1.0000	6.1174	0.0

Table XIX. Calculated Data for the Methanol (1) + Chlorobenzene (2) System at 385.15 K. The Tsonopoulos Correlations Was Used to Obtain the Virial Coefficients

	pressure, kPa		combined correctn terms			activity coeffs		excess
x_1	exptl	calcd	1	2	y_1	1	2	G, J/mol
0.0	57.603	57.603	0.9223	1.0000	0.0	5.9492	1.0000	0.0
0.0250	121.507	121.506	0.9320	1.0353	0.5209	5.3571	1.0013	138.51
0.0500	174.022	174.020	0.9406	1.0662	0.6630	4.8383	1.0053	268.53
0.0750	216.984	216.981	0.9478	1.0926	0.7285	4.3859	1.0119	390.09
0.1000	252.201	252.198	0.9538	1.1151	0.7660	3.9945	1.0210	503.34
0.1250	281.034	281.031	0.9588	1.1341	0.7900	3.6535	1.0326	608.52
0.1500	304.489	304.487	0.9629	1.1499	0.8064	3.3531	1.0468	705.66
0.1750	323.557	323.558	0.9662	1.1630	0.8183	3.0883	1.0636	794.91
0.2000	339.234	339.238	0.9690	1.1740	0.8273	2.8560	1.0830	876.33
0.2250	352.457	352.463	0.9714	1.1834	0.8344	2.6540	1.1046	950.17
0.2500	363.774	363.782	0.9734	1.1915	0.8403	2.4775	1.1285	1016.68
0.2750	373.571	373.581	0.9752	1.1986	0.8453	2.3223	1.1548	1076.08
0.3000	382.232	382.244	0.9768	1.2049	0.8496	2.1858	1.1833	1128.55
0.3250	390.072	390.084	0.9782	1.2107	0.8535	2.0654	1.2142	1174.33
0.3500	397.195	397.207	0.9795	1.2160	0.8570	1.9584	1.2475	1213.61
0.3750	403.674	403.686	0.9807	1.2208	0.8602	1.8624	1.2836	1246.54
0.4000	409.579	409.591	0.9817	1.2252	0.8632	1.7758	1.3229	1273.21
0.4250	414.983	414.993	0.9827	1.2293	0.8660	1.6971	1.3657	1293.68
0.4500	419.957	419.965	0.9836	1.2331	0.8686	1.6254	1.4123	1307.99
0.4750	424.571	424.577	0.9845	1.2366	0.8711	1.5599	1.4632	1316.18
0.5000	428.896	428.902	0.9853	1.2399	0.8735	1.5000	1.5187	1318.24
0.5250	432.996	433.000	0.9860	1.2431	0.8759	1.4450	1.5795	1314.19
0.5500	436.913	436.916	0.9868	1.2461	0.8783	1.3946	1.6461	1303.99
0.5750	440.692	440.693	0.9875	1.2490	0.8807	1.3482	1.7193	1287.63
0.6000	444.375	444.375	0.9881	1.2518	0.8832	1.3055	1.7999	1265.06
0.6250	448.004	448.003	0.9888	1.2547	0.8857	1.2664	1.8887	1236.22
0.6500	451.624	451.622	0.9895	1.2575	0.8885	1.2304	1.9867	1201.06
0.6750	455.277	455.274	0.9902	1.2603	0.8914	1.1976	2.0952	1159.51
0.7000	459.005	459.002	0.9909	1.2633	0.8946	1.1677	2.2151	1111.50
0.7250	462.833	462.830	0.9916	1.2663	0.8982	1.1405	2.3481	1056.98
0.7500	466.750	466.746	0.9923	1.2693	0.9022	1.1160	2.4963	995.88
0.7750	470.737	470.734	0.9931	1.2725	0.9067	1.0938	2.6627	928.08
0.8000	474.779	474.775	0.9938	1.2756	0.9117	1.0738	2.8512	853.43
0.8250	478.857	478.855	0.9946	1.2788	0.9175	1.0560	3.0661	771.72
0.8500	482.957	482.954	0.9954	1.2821	0.9240	1.0403	3.3127	682.75
0.8750	487.059	487.057	0.9962	1.2853	0.9317	1.0268	3.5959	586.27
0.9000	491.148	491.146	0.9970	1.2884	0.9408	1.0157	3.9167	482.07
0.9250	495.207	495.205	0.9977	1.2916	0.9520	1.0074	4.2622	370.17
0.9500	499.218	499.217	0.9985	1.2946	0.9658	1.0025	4.5807	251.12
0.9750	503.165	503.163	0.9993	1.2975	0.9822	1.0004	4.8010	126.89
1.0000	507.030	507.028	1.0000	1.3004	1.0000	1.0000	4.9610	0.0

better illustrates the precision levels that can be achieved with the apparatus. An attempt was made to measure data at 353.15 K for this system, but the run had to be aborted due to the rise in the ethylbenzene vapor pressure of 0.03 kPa (0.23 mmHg) over the time period needed for the measurements.

The ethyl acetate + chlorobenzene system showed only a slight positive deviation from ideal behavior. The $P-x$ values for the 313.15 K isotherm are plotted in Figure 2 and the corresponding P_D-x values are plotted in Figure 3. Comparison of the two plots shows why the latter is preferred. Note that the ordinate in Figure 3 covers the range from 0.0 to 0.3 kPa. The curve represents the spline fit.

The system with the largest deviation from ideal behavior was methanol + chlorobenzene. The activity coefficients are shown

Table XX. Calculated Data for the 1-Pentane (1) + Chlorobenzene (2) System at 280.00 K. The Tsonopoulos Correlation Was Used to Obtain the Virial Coefficients

	pressure, kPa		combined correctn terms			activity coeffs		excess
x_1	exptl	calcd	1	2	y_1	1	2	G, J/mol
0.0	0.528	0.528	0.9767	1.0000	0.0	1.7891	1.0000	0.0
0.0250	2.309	2.309	0.9780	1.0031	0.7763	1.7399	1.0004	33.03
0.0500	3.999	3.999	0.9789	1.0057	0.8737	1.6943	1.0014	64.42
0.0750	5.606	5.605	0.9798	1.0082	0.9119	1.6511	1.0031	94.25
0.1000	7.135	7.134	0.9807	1.0106	0.9323	1.6100	1.0055	122.43
0.1250	8.593	8.593	0.9815	1.0128	0.9451	1.5712	1.0087	149.04
0.1500	9.986	9.986	0.9822	1.0150	0.9538	1.5345	1.0124	174.01
0.1750	11.322	11.322	0.9829	1.0171	0.9602	1.5001	1.0169	197.45
0.2000	12.604	12.604	0.9836	1.0191	0.9651	1.4677	1.0221	219.26
0.2250	13.837	13.837	0.9843	1.0210	0.9690	1.4369	1.0279	239.57
0.2500	15.023	15.022	0.9850	1.0229	0.9721	1.4077	1.0345	258.25
0.2750	16.165	16.164	0.9856	1.0247	0.9747	1.3798	1.0419	275.42
0.3000	17.265	17.265	0.9862	1.0264	0.9769	1.3532	1.0501	290.95
0.3250	18.327	18.327	0.9868	1.0281	0.9788	1.3277	1.0593	304.93
0.3500	19.354	19.354	0.9873	1.0297	0.9805	1.3034	1.0692	317.24
0.3750	20.349	20.349	0.9879	1.0313	0.9819	1.2802	1.0802	327.99
0.4000	21.313	21.314	0.9884	1.0329	0.9832	1.2581	1.0922	337.01
0.4250	22.252	22.252	0.9889	1.0343	0.9844	1.2371	1.1053	344.45
0.4500	23.166	23.166	0.9894	1.0358	0.9855	1.2170	1.1193	350.13
0.4750	24.059	24.060	0.9899	1.0372	0.9864	1.1981	1.1346	354.19
0.5000	24.935	24.935	0.9904	1.0386	0.9873	1.1801	1.1510	356.46
0.5250	25.794	25.795	0.9909	1.0400	0.9882	1.1630	1.1688	357.09
0.5500	26.640	26.641	0.9914	1.0414	0.9890	1.1470	1.1878	355.88
0.5750	27.474	27.476	0.9918	1.0427	0.9897	1.1318	1.2084	353.01
0.6000	28.300	28.301	0.9923	1.0441	0.9904	1.1175	1.2304	348.26
0.6250	29.118	29.119	0.9927	1.0454	0.9911	1.1041	1.2543	341.81
0.6500	29.932	29.933	0.9932	1.0467	0.9917	1.0915	1.2797	333.41
0.6750	30.742	30.744	0.9936	1.0480	0.9924	1.0797	1.3074	323.28
0.7000	31.553	31.554	0.9941	1.0493	0.9930	1.0687	1.3369	311.13
0.7250	32.365	32.366	0.9945	1.0506	0.9935	1.0586	1.3691	297.23
0.7500	33.181	33.183	0.9950	1.0520	0.9941	1.0493	1.4034	281.20
0.7750	34.005	34.006	0.9955	1.0533	0.9947	1.0407	1.4410	263.37
0.8000	34.837	34.838	0.9959	1.0546	0.9953	1.0330	1.4811	243.32
0.8250	35.681	35.682	0.9964	1.0560	0.9958	1.0260	1.5255	221.43
0.8500	36.540	36.541	0.9969	1.0574	0.9964	1.0199	1.5728	197.15
0.8750	37.415	37.416	0.9974	1.0589	0.9970	1.0146	1.6264	171.01
0.9000	38.309	38.310	0.9979	1.0603	0.9975	1.0100	1.6836	142.22
0.9250	39.226	39.226	0.9984	1.0618	0.9981	1.0063	1.7526	111.54
0.9500	40.166	40.166	0.9989	1.0634	0.9987	1.0034	1.8267	77.64
0.9750	41.133	41.134	0.9994	1.0649	0.9993	1.0013	1.9509	41.80
1.0000	42.130	42.130	1.0000	1.0666	1.0000	1.0000	2.1582	0.0

Table XXI. Calculated Data for the 1-Pentane (1) + Chlorobenzene (2) System at 320.00 K. The Tsonopoulos Correlation Was Used to Obtain the Virial Coefficients

	pressure, kPa		combined correctn terms			activity coeffs		
x_1	exptl	calcd	1	2	y_1	1	2	excess G, J/mol
0.0	4.945	4.945	0.9393	1.0000	0.0	1.6584	1.0000	0.0
0.0250	11.553	11.553	0.9424	1.0064	0.5798	1.6183	1.0003	32.82
0.0500	17.886	17.886	0.9448	1.0119	0.7339	1.5815	1.0012	64.00
0.0750	23.971	23.971	0.9469	1.0171	0.8054	1.5472	1.0027	93.65
0.1000	29.824	29.824	0.9489	1.0221	0.8467	1.5147	1.0047	121.71
0.1250	35.460	35.460	0.9508	1.0269	0.8738	1.4837	1.0073	148.26
0.1500	40.891	40.891	0.9527	1.0316	0.8928	1.4541	1.0106	173.22
0.1750	46.132	46.131	0.9544	1.0361	0.9070	1.4258	1.0145	196.67
0.2000	51.194	51.194	0.9562	1.0405	0.9181	1.3988	1.0189	218.50
0.2250	56.089	56.089	0.9578	1.0447	0.9269	1.3730	1.0241	238.82
0.2500	60.826	60.825	0.9594	1.0489	0.9341	1.3482	1.0299	257.51
0.2750	65.414	65.413	0.9610	1.0529	0.9402	1.3245	1.0364	274.65
0.3000	69.863	69.862	0.9625	1.0568	0.9453	1.3017	1.0437	290.13
0.3250	74.184	74.182	0.9640	1.0606	0.9498	1.2800	1.0517	304.04
0.3500	78.385	78.384	0.9655	1.0644	0.9537	1.2591	1.0606	316.25
0.3750	82.477	82.476	0.9669	1.0681	0.9572	1.2392	1.0702	326.87
0.4000	86.470	86.469	0.9683	1.0717	0.9603	1.2202	1.0808	335.75
0.4250	90.373	90.371	0.9696	1.0752	0.9630	1.2021	1.0922	343.01
0.4500	94.196	94.194	0.9709	1.0787	0.9656	1.1848	1.1045	348.50
0.4750	97.949	97.947	0.9722	1.0821	0.9679	1.1684	1.1179	352.34
0.5000	101.642	101.640	0.9735	1.0855	0.9701	1.1529	1.1321	354.38
0.5250	105.281	105.279	0.9748	1.0888	0.9721	1.1382	1.1476	354.76
0.5500	108.876	108.874	0.9761	1.0921	0.9740	1.1243	1.1640	353.29
0.5750	112.433	112.431	0.9773	1.0954	0.9758	1.1112	1.1818	350.14
0.6000	115.960	115.957	0.9786	1.0987	0.9775	1.0988	1.2008	345.09
0.6250	119.464	119.461	0.9798	1.1020	0.9791	1.0871	1.2213	338.33

Table XXI (*Continued*)

	pressure, kPa		combined correctn terms			activity coeffs		
x_1	exptl	calcd	1	2	y_1	1	2	excess G, J/mol
0.6500	122.953	122.951	0.9810	1.1053	0.9807	1.0762	1.2431	329.61
0.6750	126.434	126.432	0.9823	1.1085	0.9821	1.0660	1.2667	319.14
0.7000	129.915	129.913	0.9835	1.1118	0.9836	1.0564	1.2919	306.66
0.7250	133.405	133.403	0.9847	1.1151	0.9850	1.0476	1.3193	292.37
0.7500	136.915	136.913	0.9860	1.1185	0.9864	1.0394	1.3484	275.97
0.7750	140.459	140.457	0.9872	1.1219	0.9877	1.0320	1.3799	257.75
0.8000	144.051	144.049	0.9885	1.1253	0.9891	1.0254	1.4130	237.33
0.8250	147.704	147.702	0.9898	1.1288	0.9904	1.0196	1.4486	215.10
0.8500	151.431	151.429	0.9912	1.1324	0.9918	1.0145	1.4855	190.60
0.8750	155.246	155.244	0.9926	1.1361	0.9931	1.0104	1.5252	164.37
0.9000	159.162	159.161	0.9940	1.1399	0.9945	1.0070	1.5646	135.82
0.9250	163.182	163.181	0.9954	1.1438	0.9958	1.0044	1.6085	105.75
0.9500	167.287	167.286	0.9969	1.1479	0.9972	1.0025	1.6531	73.18
0.9750	171.457	171.456	0.9984	1.1520	0.9986	1.0010	1.7351	39.22
1.0000	175.699	175.698	1.0000	1.1562	1.0000	1.0000	1.8759	0.0

Table XXII. Calculated Data for the 1-Pentene (1) + Chlorobenzene (2) System at 360.00 K. The Tsonopoulos Correlation Was Used to Obtain the Virial Coefficients

	pressure, kPa		combined correctn terms			activity coeffs		
x_1	exptl	calcd	1	2	y_1	1	2	excess G, J/mol
0.0	24.914	24.914	0.8787	1.0000	0.0	1.6162	1.0000	0.0
0.0250	42.512	42.512	0.8840	1.0109	0.4222	1.5781	1.0003	35.02
0.0500	59.434	59.433	0.8883	1.0205	0.5931	1.5422	1.0012	68.24
0.0750	75.721	75.721	0.8922	1.0296	0.6858	1.5079	1.0027	99.67
0.1000	91.418	91.418	0.8959	1.0383	0.7441	1.4754	1.0048	129.30
0.1250	106.568	106.567	0.8994	1.0467	0.7843	1.4445	1.0075	157.16
0.1500	121.212	121.210	0.9028	1.0550	0.8137	1.4152	1.0108	183.22
0.1750	135.394	135.393	0.9060	1.0630	0.8363	1.3875	1.0147	207.53
0.2000	149.153	149.151	0.9092	1.0709	0.8542	1.3613	1.0191	230.06
0.2250	162.521	162.519	0.9123	1.0786	0.8688	1.3365	1.0242	250.85
0.2500	175.529	175.527	0.9153	1.0861	0.8809	1.3129	1.0299	269.88
0.2750	188.209	188.206	0.9183	1.0936	0.8912	1.2906	1.0362	287.19
0.3000	200.592	200.588	0.9212	1.1009	0.9002	1.2695	1.0431	302.74
0.3250	212.709	212.705	0.9240	1.1082	0.9079	1.2495	1.0507	316.59
0.3500	224.592	224.587	0.9268	1.1154	0.9148	1.2307	1.0588	328.68
0.3750	236.272	236.266	0.9296	1.1225	0.9210	1.2129	1.0676	339.09
0.4000	247.772	247.765	0.9323	1.1296	0.9266	1.1961	1.0771	347.77
0.4250	259.103	259.095	0.9351	1.1366	0.9317	1.1803	1.0872	354.78
0.4500	270.277	270.268	0.9377	1.1436	0.9363	1.1652	1.0981	360.06
0.4750	281.303	281.294	0.9404	1.1506	0.9406	1.1509	1.1099	363.66
0.5000	292.194	292.184	0.9430	1.1576	0.9446	1.1373	1.1225	365.50
0.5250	302.959	302.948	0.9457	1.1645	0.9483	1.1244	1.1361	365.63
0.5500	313.608	313.597	0.9483	1.1714	0.9518	1.1120	1.1508	363.95
0.5750	324.154	324.142	0.9509	1.1783	0.9551	1.1002	1.1667	360.50
0.6000	334.609	334.596	0.9535	1.1852	0.9582	1.0890	1.1839	355.17
0.6250	345.001	344.989	0.9560	1.1921	0.9612	1.0783	1.2025	347.99
0.6500	355.365	355.353	0.9586	1.1991	0.9640	1.0682	1.2224	338.85
0.6750	365.734	365.722	0.9612	1.2061	0.9668	1.0589	1.2439	327.81
0.7000	376.141	376.129	0.9638	1.2132	0.9695	1.0501	1.2667	314.75
0.7250	386.620	386.608	0.9665	1.2204	0.9721	1.0421	1.2910	299.76
0.7500	397.204	397.192	0.9692	1.2277	0.9747	1.0348	1.3167	282.70
0.7750	407.927	407.916	0.9719	1.2352	0.9772	1.0282	1.3440	263.70
0.8000	418.821	418.810	0.9747	1.2429	0.9797	1.0224	1.3726	242.62
0.8250	429.915	429.905	0.9776	1.2508	0.9822	1.0173	1.4028	219.62
0.8500	441.228	441.219	0.9805	1.2589	0.9847	1.0129	1.4344	194.53
0.8750	452.776	452.769	0.9836	1.2673	0.9872	1.0092	1.4682	167.55
0.9000	464.578	464.572	0.9867	1.2759	0.9897	1.0061	1.5036	138.42
0.9250	476.650	476.645	0.9898	1.2848	0.9922	1.0036	1.5429	107.42
0.9500	489.010	489.006	0.9931	1.2940	0.9948	1.0018	1.5844	74.07
0.9750	501.675	501.672	0.9965	1.3036	0.9973	1.0006	1.6413	38.82
1.0000	514.663	514.661	1.0000	1.3134	1.0000	1.0000	1.7204	0.0

in Figure 4, with a γ_1^∞ value of 34.3 at 293.15 K.

Interesting behavior was exhibited by the acetone + chlorobenzene, ethyl acetate + chlorobenzene, and 1-pentene + chlorobenzene systems. At the lowest temperature, these systems showed only positive deviations ($P_D > 0$) for the entire composition range. As the temperature increased, the tendency was to show stronger positive deviations at low values of x_1 while at the same time moving to negative deviations at the other end of the composition range. At the highest temperature, all three systems showed negative deviations at high x_1 values. This behavior is illustrated with the acetone + chlorobenzene system in Figure 5.

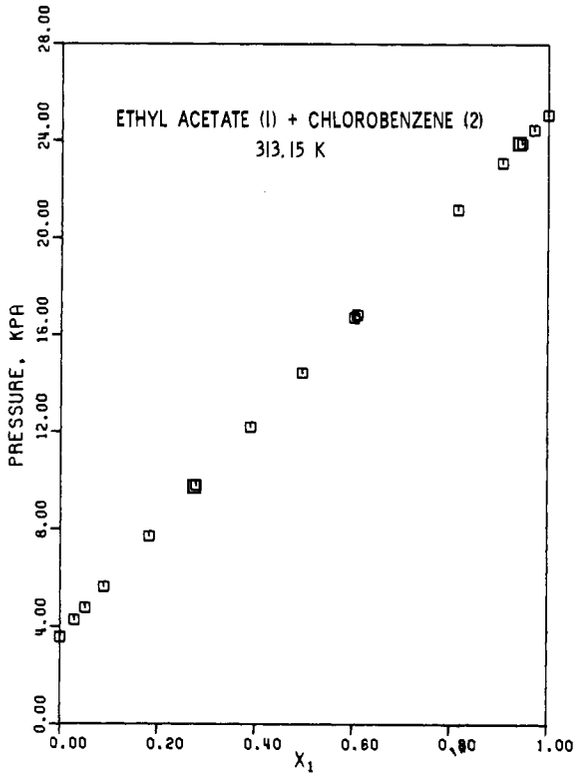

Figure 2. A plot of P vs. x_1 for the ethyl acetate (1) + chlorobenzene (2) system at 313.15 K.

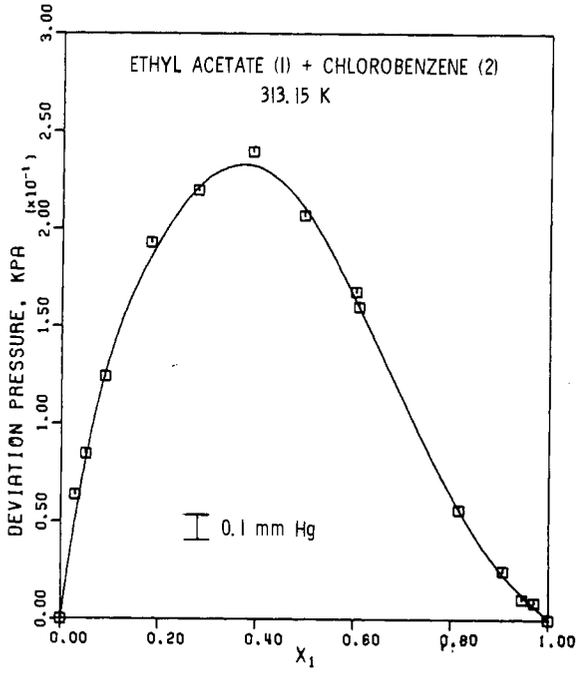

Figure 3. Deviation from Raoult's law for the ethyl acetate (1) + chlorobenzene (2) system at 313.15 K.

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

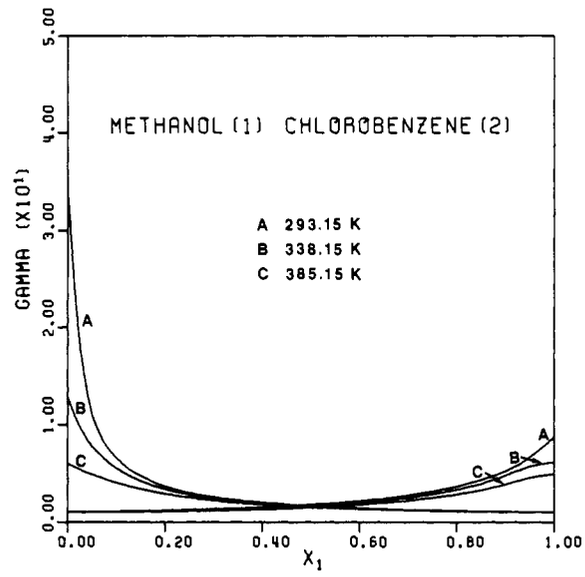

Figure 4. Activity coefficients for the methanol (1) + chlorobenzene (2) system at 293.15, 338.15, and 385.15 K.

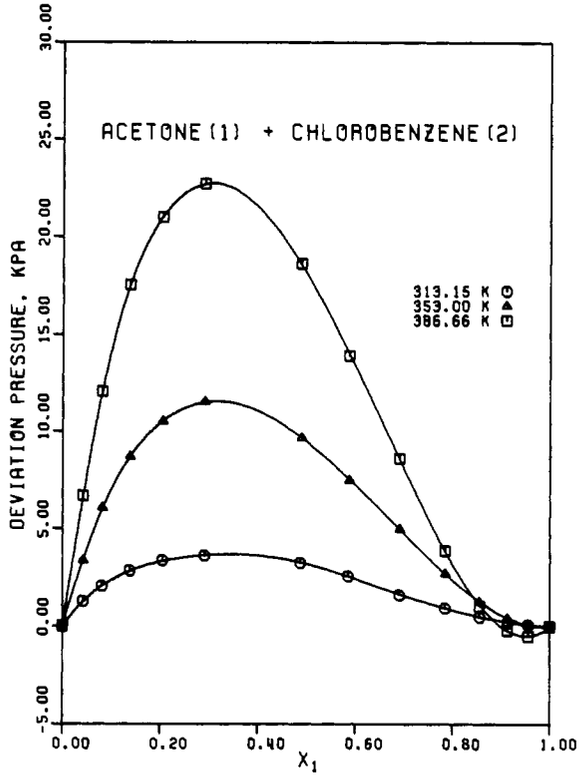

Figure 5. Deviation from Raoult's law for the acetone (1) + chlorobenzene (2) system at 313.15, 353.00, and 386.66 K.

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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NEW COMPOUNDS

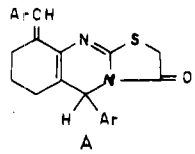
Reactions with (Arylmethylene)cycloalkanones. 2.† Synthesis of 10-(Arylmethylene)hexahydrocyclohepteno[1,2-*d*]-thiazolo[3,2-*a*]pyrimidin-3-one Derivatives of Probable Anticancer Activity

Mohamed I. Ali, Mohamed A.-F. El-Kasherf, Abou El-Fotooh, G. Hammam,* and Salah A. Khallaf

Department of Chemistry, Faculty of Science, University of Cairo, Giza, Arab Republic of Egypt, and National Research Centre, Dokki, Giza, Arab Republic of Egypt

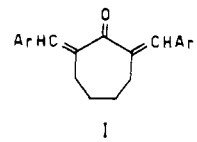
Cyclohepteno[1,2-*d*]pyrimidine-2-thiones (II) were prepared by heating 2,7-bis(arylmethylene)cycloheptanones with thiourea in ethanolic potassium hydroxide. Compounds II reacted with chloroacetic acid to yield the title compounds III. The 2,10-bis(arylmethylene) derivatives (VI) were prepared.

In part 1 (*1*) of this series 2,6-bis(arylmethylene)cyclohexanones were condensed with thiourea and then with chloroacetic acid to give (arylmethylene)thiazolo[2,3-*b*]-quinazolin-3-one derivatives (A) (*1*).

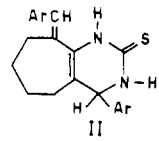


A

The previous sequence of reactions was applied to the cycloheptanone series. When 2,7-bis(arylmethylene)cycloheptanones were heated with thiourea in ethanolic potassium hydroxide, they yielded 4-aryl-9*H*-9-arylmethylene-1,2,3,4,5,-6,7,8-octahydrocyclohepteno[1,2-*d*]pyrimidine-2-thione (II) (cf. ref 2 and references cited therein). The cyclohepteno[1,2-*d*]pyrimidine-2-thiones (II) were reacted with chloroacetic acid,

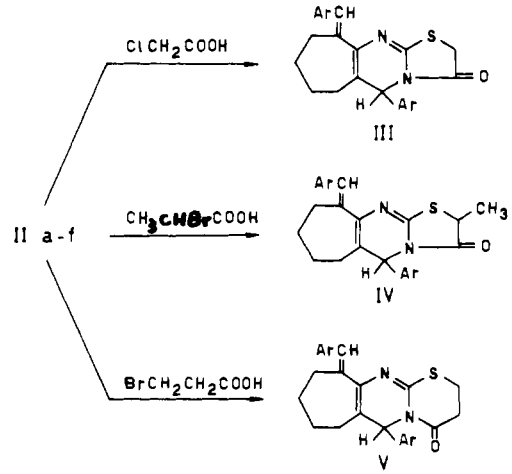


I



II

2-bromopropanoic acid, and 3-bromopropanoic acid in acetic acid–acetic anhydride, in the presence of anhydrous sodium acetate to give respectively 5-aryl-10-(arylmethylene)-2,3,6,-7,8,9-hexahydro-5*H*,10*H*-cyclohepteno[1,2-*d*]thiazolo[3,2-*a*]pyrimidin-3-ones (III), their 2-methyl derivatives (IV), and 6-aryl-11-(arylmethylene)-2,3,6,7,8,9,10-heptahydro-4*H*,6*H*,-11*H*-cyclohepteno[1,2-*d*]pyrimidino[2,1-*b*]1,3-thiazin-4-one (V).



III IV V

†For part 1, see ref 1.
* To whom correspondence should be addressed at the National Research Centre, Dokki.

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