J. Chem. Eng. Data 1980, 25, 163-170

(3) Kirk-Othmer, "Encyclopedia of Chemical Technology", 2nd ed., 1963, pp 734-40.
(4) Flatt, R., Burkhardt, G., *Helv. Chim. Acta*, **27**, 1605 (1944).
(5) "Official Methods of Analysis", 10th ed., Association of Official Agricultural Chemists, Washington, D.C., 1965, p 23. Shall, E. D., *Anal. Chem.*, **29**, 1044 (1957).
(6) Merrill, L., *J. Phys. Chem. Ref. Data* **6**, 1205 (1977).

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Vapor–Liquid Equilibrium for the Binary Systems Propionitrile + Ethylbenzene and Acetonitrile + Ethyl Acetate, + Ethyl Alcohol, and + Toluene

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Total pressure vapor-liquid equilibrium data were measured for the following four binaries: ethyl acetate + acetonitrile at 313.15, 353.15, and 393.15 K; ethyl alcohol + acetonitrile at 293.15, 343.15, and 393.15 K; acetonitrile + toluene at 293.15, 343.15, and 393.15 K; propionitrile + ethylbenzene at 313.15, 353.15, and 393.15 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. For comparison purposes, the data for the acetonitrile + toluene system were also reduced by the Barker method using a four-suffix Margules equation.

Introduction

The selection of the systems covered in this paper was based on the group interaction parameter grid of the UNIFAC correlation scheme outlined by Fredenslund et al. (*1*). The aim was to fill in places in the grid where either sparse or no data were available. Data were measured at three temperatures for each of the four systems. Maher and Smith (*2*, *3*) have reported similar data previously for binary systems containing chlorobenzene and aniline.

Experimental Apparatus and Techniques

The apparatus used for this study has been described previously (*4*). 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 differential pressure transducer used as a nulling device. The nitrogen pressure used to balance the cell vapor pressure is measured by using a separate transducer that is calibrated frequently vs. a dead weight gauge. 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.

Table I. Chemicals Used

component	vendor	stated purity, %
acetonitrile	Burdick and Jackson	99.9+
ethyl acetate	Burdick and Jackson	99.9
ethyl alcohol	U.S. Industrial Chemicals	200 proof
ethylbenzene	El Paso Products Co.	99.96
propionitrile	Aldrich	99.0
toluene	Burdick and Jackson	99.9

The uncertainties in the measured temperatures and mole fractions are ±0.03 K and ±0.0005, respectively. The estimated uncertainties for the three reported variables (P, T, and x) due to resolution limits in the instrumentation were summed to give an expression for the total effect on the reported vapor pressures. The total possible resolution error in kPa is given by

$$\text{total possible resolution error} = 0.03\left(\frac{\partial P}{\partial T}\right)_x + 0.0005\left|\frac{\partial P}{\partial x}\right|_T + 0.00035P + 0.003 + 6.89476[(2.5)(\text{resolution for 572})]$$

where P = experimental pressure, $(\partial P/\partial T)_x$ = temperature derivative of pressure at constant composition, and $(\partial P/\partial x)_T$ = absolute value of the composition derivative of pressure at constant temperature. The first two terms provide the uncertainty in the pressure measurement due to the possible temperature and mole fraction errors. The last three terms are related to the uncertainty in the measurement of pressure with a Datametrics 572 transducer. That transducer reads out psia and the "resolution" at various pressure levels is as follows: 0.0001 below 4 psia, 0.001 below 40 psia, 0.01 below 400 psia, etc.

The error in the reported vapor pressures, as computed by the above equation, will be referred to as the "Resolution Error Band" (REB) to distinguish it from the total possible experimental error which will include other factors such as residual gas, residual water, and chemical reaction. The width of the REB is usually about ±0.1% or less of the system pressure.

Chemicals Used

Table I lists the chemicals used and their stated purity. All chemicals except propionitrile 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 being loaded in the metal cells, the chemicals were distilled over freshly activated molecular sieves through a Vigreaux column (25 mm o.d. and 470 mm long) with the first and last portions being discarded. The distilled samples were

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Table II. Comparison of the Measured Pure Component Vapor Pressures with Literature Values

		vapor pressure, kPa	
component	T, K	measd	lit.[a]
acetonitrile	293.15	9.379	9.376
	293.15	9.408	9.376
	313.15	22.766	22.737
	343.15	69.59	69.51
	343.15	69.66	69.51
	353.15	96.37	96.34
	393.15	297.8	
	393.15	297.6	
	393.15	298.1	
ethyl acetate	313.15	25.061	25.037
	353.15	111.36	111.44
	393.15	347.4	
ethyl alcohol	293.15	5.898	5.865
	343.15	72.34	72.28
	393.15	429.0	429.3
ethylbenzene	313.15	2.955	2.877
	353.15	16.909	16.771
	393.15	64.44	64.22
propionitrile	313.15	12.631	12.701
	353.15	58.55	58.79
	393.15	192.05	193.20
toluene	293.15	2.963	2.959
	343.15	27.18	27.18
	393.15	131.9	131.7

[a] The literature values given were obtained from fits of selected values. The selection process involved plotting all known literature values in residual (deviation from a simple fitting equation) form to emphasize the scatter and identify obviously erroneous points and then making repeated fits with a reliable equation to obtain smaller and smaller root-mean-square deviation values as large deviation points were eliminated.

back-flushed with nitrogen and put in amber glass bottles for transfer to the dispenser used to load the cells.

Because of the relatively low purity of the propionitrile used (stated purity was only 99%), the data for the propionitrile + ethylbenzene system may be of lower quality than for the other binaries. The vapor pressure checks shown in Table II are not as certain for the propionitrile as for the other compounds because the propionitrile is of relatively low purity and also because the vapor pressure data for propionitrile are not so well established. All the pure compound vapor pressure measurements associated with the various isotherms are shown to illustrate the reproducibility of the measurements.

Experimental Results

The raw P–x data measured for the four systems are shown in Tables III–VI. During the pressure measurements for the acetonitrile + toluene system at 293.15 K (Table V), cell 6 ($x_1 = 0.2950$) had to be excluded. On opening cell 6, it was found that the cell pressure was not steady. Since the observed behavior was erratic, the cell was closed immediately. The behavior of cell 6 was perfectly normal at the other two temperatures.

The liquid-phase mole fractions were corrected for the presence of the vapor phase and for the removal of vapor during pressure measurements as described previously (*4*). The smooth P–x values obtained from a least-squares cubic spline fit of the data are also shown in Tables III–VI.

The Mixon et al. (*5*) 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

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

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

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 (*6*). The calculated results are shown in Tables VII–XVIII. In the tables that show the calculated results, the "combined correction term" refers to the following grouping of terms.

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

Note the excellent agreement between the experimental and calculated pressure in Tables VII–XVIII. The Mixon et al. method will converge to any set of input pressure values; hence the small differences reflect the differences between the experimental and smoothed (spline fit) values in Tables III–VI.

Discussion of Results

Of the four systems studied in this work, the propionitrile + ethylbenzene system was the only one that did not exhibit azeotropic behavior. All four systems showed only positive deviation from Raoult's law.

The deviation pressure plot is shown in Figure 1 for the ethyl acetate + acetonitrile system. The deviation pressure, denoted here as P_D, is defined as

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

Table III. Experimental P vs. x_1 Values for the Ethyl Acetate (1) + Acetonitrile (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	22.766	22.770	0.0	96.37	96.39	0.0	297.8	297.8
0.0425	23.432	23.419	0.0425	99.47	99.40	0.0425	307.0	306.8
0.0814	23.932	23.941	0.0815	101.79	101.84	0.0814	314.0	314.1
0.1388	24.589	24.597	0.1389	104.89	104.93	0.1388	323.4	323.4
0.2135	25.284	25.271	0.2135	108.23	108.17	0.2134	333.4	333.3
0.3014	25.852	25.855	0.3014	111.07	111.07	0.3013	342.3	342.3
0.4017	26.308	26.315	0.4018	113.43	113.49	0.4016	349.8	349.9
0.5004	26.594	26.586	0.5004	115.15	115.10	0.5003	355.4	355.3
0.5960	26.690	26.691	0.5960	115.98	115.99	0.5959	358.5	358.5
0.6997	26.612	26.621	0.6996	116.23	116.23	0.6996	359.7	359.7
0.7874	26.415	26.399	0.7873	115.78	115.79	0.7874	358.8	358.8
0.8548	26.114	26.117	0.8547	114.97	114.96	0.8548	356.7	356.7
0.9127	25.762	25.787	0.9127	113.81	113.82	0.9127	353.8	353.9
0.9524	25.524	25.499	0.9527	112.81	112.81	0.9525	351.4	351.3
1.0000	25.061	25.067	1.0000	111.36	111.36	1.0000	347.4	347.4

Table IV. Experimental P vs. x_1 Values for the Ethyl Alcohol (1) + Acetonitrile (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	9.379	9.379	0.0	69.59	69.59	0.0	297.6	297.6
0.0434	9.971	9.971	0.0434	74.57	74.57	0.0433	318.9	318.9
0.0878	10.368	10.367	0.0878	78.55	78.56	0.0876	337.4	337.4
0.1473	10.694	10.695	0.1472	82.67	82.67	0.1469	359.2	359.2
0.2157	10.888	10.886	0.2156	86.11	86.08	0.2152	380.4	380.5
0.3113	10.978	10.979	0.3100	89.11	89.15	0.3102	403.8	403.6
0.4121	10.934	10.934	0.4120	90.97	90.95	0.4116	421.8	421.8
0.5127	10.793	10.793	0.5126	91.67	91.67	0.5122	435.1	435.1
0.6104	10.554	10.554	0.6103	91.45	91.43	0.6100	444.0	443.9
0.7060	10.185	10.186	0.7059	90.15	90.18	0.7057	448.6	448.7
0.7988	9.599	9.596	0.7987	87.70	87.69	0.7986	449.4	449.4
0.8634	8.942	8.945	0.8633	84.95	84.91	0.8633	447.1	447.0
0.9154	8.192	8.190	0.9152	81.52	81.57	0.9152	442.7	442.8
0.9580	7.263	7.263	0.9579	77.73	77.71	0.9579	437.1	437.1
1.0000	5.898	5.898	1.0000	72.34	72.34	1.0000	429.0	429.0

Table V. Experimental P vs. x_1 Values for the Acetonitrile (1) + Toluene (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	2.963	2.963	0.0	27.18	27.18	0.0	131.9	131.9
0.0457	4.295	4.296	0.0458	35.66	35.66	0.0396	158.6	158.6
0.0836	5.088	5.086	0.0837	40.82	40.83	0.0832	178.4	178.4
0.1418	6.011	6.012	0.1418	46.84	46.83	0.1414	201.6	201.7
0.2087	6.793	6.793	0.2089	52.13	52.15	0.2081	222.6	222.5
0.3944	8.145	8.142	0.2935	57.11	57.07	0.2952	243.2	243.3
0.4889	8.563	8.568	0.3945	61.14	61.20	0.3939	261.1	261.2
0.5983	8.952	8.947	0.4890	64.29	64.24	0.4884	274.5	274.4
0.6951	9.219	9.222	0.5984	67.07	67.06	0.5980	286.4	286.4
0.7810	9.409	9.410	0.6952	68.93	68.97	0.6950	294.6	294.7
0.8533	9.523	9.518	0.7810	70.18	70.18	0.7810	300.0	300.0
0.9187	9.561	9.567	0.8533	70.88	70.84	0.8533	302.8	302.7
0.9577	9.558	9.555	0.9187	70.98	71.01	0.9187	303.0	303.1
1.0000	9.409	9.409	0.9577	70.70	70.69	0.9577	301.9	301.8
			1.0000	69.66	69.66	1.0000	298.1	298.1

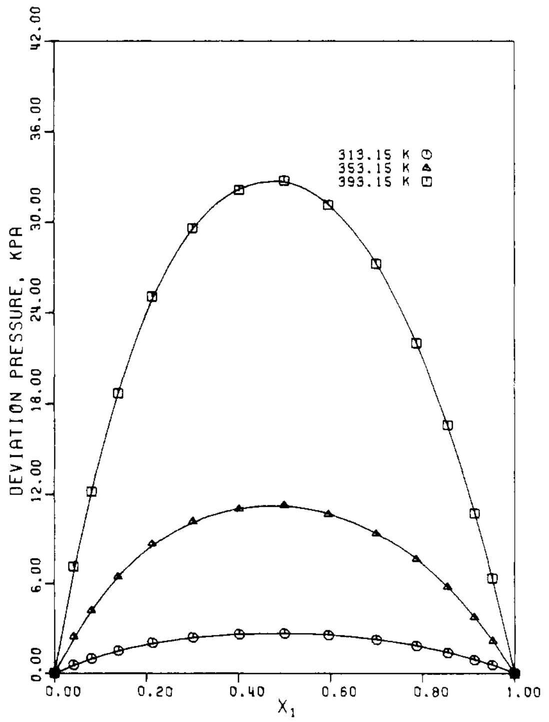

Figure 1. Deviation from Raoult's law for the ethyl acetate (1) + acetonitrile (2) system at 313.15, 353.15, and 393.15 K.

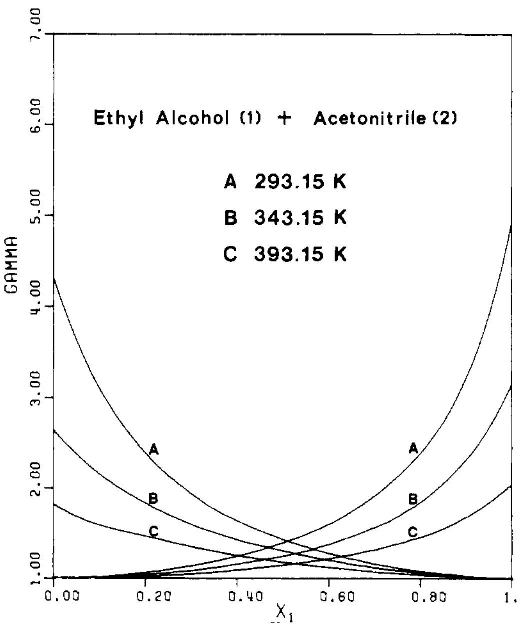

Figure 2. Activity coefficients for the ethyl alcohol (1) + acetonitrile (2) system at 293.15, 343.15, and 393.15 K.

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

Table VI. Experimental P vs. x_1 Values for the Propionitrile (1) + Ethylbenzene (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	2.955	2.955	0.0	16.91	16.91	0.0	64.44	64.44
0.0431	4.193	4.195	0.0432	22.02	22.04	0.0430	79.12	79.14
0.0825	5.057	5.052	0.0826	25.79	25.74	0.0824	90.29	90.23
0.1400	6.056	6.065	0.1402	30.03	30.10	0.1399	103.32	103.43
0.2068	7.012	7.007	0.2071	34.18	34.12	0.2065	115.80	115.69
0.2934	7.994	7.984	0.2937	38.42	38.40	0.2922	128.84	128.87
0.3931	8.851	8.869	0.3933	42.34	42.41	0.3929	141.69	141.77
0.4949	9.616	9.614	0.4951	45.84	45.84	0.4862	151.99	151.89
0.5964	10.298	10.289	0.5966	48.93	48.88	0.5964	162.33	162.39
0.6979	10.922	10.920	0.6980	51.65	51.64	0.6978	171.08	171.02
0.7855	11.427	11.433	0.7856	53.79	53.84	0.7854	177.81	177.87
0.8609	11.851	11.856	0.8610	55.63	55.63	0.8609	183.48	183.41
0.9191	12.180	12.177	0.9191	56.93	56.92	0.9191	187.26	187.34
0.9581	12.396	12.390	0.9581	57.76	57.74	0.9581	189.79	189.74
1.0000	12.630	12.617	1.0000	58.55	58.57	1.0000	192.05	192.06

Table VII. Calculated Data for the Ethyl Acetate (1) + Acetonitrile (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	22.770	22.770	0.9968	1.0000	0.0	1.5347	1.0000	0.0
0.1	24.168	24.168	0.9982	1.0027	0.1460	1.4098	1.0045	100.01
0.2	25.162	25.162	0.9992	1.0045	0.2591	1.3016	1.0188	176.08
0.3	25.847	25.846	0.9999	1.0057	0.3536	1.2155	1.0422	227.78
0.4	26.309	26.308	1.0004	1.0065	0.4396	1.1528	1.0722	257.08
0.5	26.585	26.584	1.0008	1.0069	0.5213	1.1049	1.1101	265.80
0.6	26.692	26.691	1.0010	1.0069	0.6022	1.0677	1.1577	254.83
0.7	26.621	26.620	1.0010	1.0066	0.6847	1.0377	1.2207	223.14
0.8	26.353	26.353	1.0009	1.0059	0.7750	1.0175	1.2945	170.55
0.9	25.868	25.868	1.0006	1.0047	0.8771	1.0051	1.3893	97.58
1.0	25.067	25.067	1.0000	1.0028	1.0000	1.0000	1.5345	0.0

Table VIII. Calculated Data for the Ethyl Acetate (1) + Acetonitrile (2) System at 353.15 K

	pressure, kPa		combined correctn terms			activity coeffs		
x_1	exptl	calcd	1	2	y_1	1	2	G^E, J/mol
0.0	96.389	96.388	0.9894	1.0000	0.0	1.4920	1.0000	0.0
0.1	102.901	102.900	0.9932	1.0064	0.1479	1.3761	1.0043	105.10
0.2	107.642	107.640	0.9960	1.0110	0.2628	1.2753	1.0179	184.49
0.3	111.026	111.022	0.9981	1.0142	0.3591	1.1959	1.0398	237.85
0.4	113.455	113.451	0.9997	1.0164	0.4471	1.1393	1.0672	267.79
0.5	115.093	115.089	1.0009	1.0176	0.5306	1.0961	1.1015	276.59
0.6	116.017	116.014	1.0016	1.0182	0.6131	1.0630	1.1436	265.17
0.7	116.231	116.228	1.0020	1.0179	0.6971	1.0375	1.1963	233.52
0.8	115.672	115.670	1.0019	1.0168	0.7847	1.0171	1.2704	180.44
0.9	114.104	114.103	1.0013	1.0145	0.8829	1.0040	1.3669	102.30
1.0	111.344	111.343	1.0000	1.0109	1.0000	1.0000	1.4771	0.0

Table IX. Calculated Data for the Ethyl Acetate (1) + Acetonitrile (2) System at 393.15 K

	pressure, kPa		combined correctn terms			activity coeffs		
x_1	exptl	calcd	1	2	y_1	1	2	G^E, J/mol
0.0	297.833	297.832	0.9763	1.0000	0.0	1.4244	1.0000	0.0
0.1	317.322	317.326	0.9841	1.0118	0.1418	1.3161	1.0041	101.95
0.2	331.703	331.712	0.9901	1.0204	0.2554	1.2316	1.0159	177.46
0.3	342.227	342.240	0.9946	1.0265	0.3529	1.1653	1.0348	228.22
0.4	349.820	349.835	0.9981	1.0307	0.4426	1.1165	1.0587	255.96
0.5	355.240	355.254	1.0007	1.0333	0.5299	1.0831	1.0853	264.22
0.6	358.584	358.595	1.0025	1.0345	0.6150	1.0554	1.1203	254.31
0.7	359.739	359.747	1.0035	1.0341	0.6999	1.0320	1.1683	224.52
0.8	358.480	358.485	1.0034	1.0321	0.7890	1.0144	1.2301	172.74
0.9	354.559	354.560	1.0024	1.0283	0.8874	1.0041	1.3031	98.60
1.0	347.361	347.360	1.0000	1.0222	1.0000	1.0000	1.4187	0.0

The ethyl alcohol + acetonitrile system was a particularly interesting one in the sense that, over the range of temperatures studied, the vapor pressure curves cross each other. The P_D–x values for this system looked very similar to those of the ethyl acetate + acetonitrile system. The activity coefficients for the ethyl alcohol + acetonitrile system are shown in Figure 2.

The P–x plot for the acetonitrile + toluene system at 393.15 K is shown in Figure 3. In Figure 3, the points represent the pressures measured experimentally and the curve represents a cubic spline fit of the data; the knot points used in making the

Table X. Calculated Data for the Ethyl Alcohol (1) + Acetonitrile (2) System at 293.15 K

	pressure, kPa		combined correctn terms			activity coeffs		
x_1	exptl	calcd	1	2	y_1	1	2	G^E, J/mol
0.0	9.379	9.379	1.0038	1.0000	0.0	4.3220	1.0000	0.0
0.1	10.450	10.450	1.0055	1.0030	0.1758	3.0980	1.0173	313.19
0.2	10.855	10.855	1.0062	1.0041	0.2606	2.3829	1.0653	546.63
0.3	10.976	10.976	1.0065	1.0044	0.3147	1.9393	1.1406	708.80
0.4	10.945	10.945	1.0065	1.0043	0.3554	1.6380	1.2483	805.48
0.5	10.816	10.816	1.0064	1.0039	0.3914	1.4262	1.3983	841.16
0.6	10.585	10.584	1.0061	1.0032	0.4277	1.2712	1.6096	814.97
0.7	10.215	10.215	1.0057	1.0021	0.4701	1.1565	1.9196	724.89
0.8	9.586	9.585	1.0049	1.0003	0.5318	1.0751	2.3919	566.25
0.9	8.447	8.447	1.0034	0.9970	0.6442	1.0216	3.2140	331.37
1.0	5.898	5.898	1.0000	0.9896	1.0000	1.0000	4.9255	0.0

Table XI. Calculated Data for the Ethyl Alcohol (1) + Acetonitrile (2) System at 343.15 K

	pressure, kPa		combined correctn terms			activity coeffs		
x_1	exptl	calcd	1	2	y_1	1	2	G^E, J/mol
0.0	69.589	69.589	0.9898	1.0000	0.0	2.6346	1.0000	0.0
0.1	79.508	79.510	0.9965	1.0112	0.1952	2.1532	1.0104	245.42
0.2	85.404	85.407	1.0005	1.0175	0.3106	1.8327	1.0395	434.05
0.3	88.899	88.902	1.0031	1.0209	0.3915	1.5989	1.0878	569.77
0.4	90.800	90.803	1.0047	1.0225	0.4553	1.4219	1.1587	653.80
0.5	91.634	91.636	1.0058	1.0227	0.5153	1.2979	1.2482	688.26
0.6	91.498	91.500	1.0064	1.0218	0.5707	1.1954	1.3812	674.01
0.7	90.290	90.291	1.0064	1.0195	0.6293	1.1148	1.5727	604.58
0.8	87.646	87.646	1.0059	1.0154	0.7017	1.0565	1.8497	476.49
0.9	82.684	82.684	1.0042	1.0084	0.8032	1.0158	2.3186	280.08
1.0	72.343	72.342	1.0000	0.9943	1.0000	1.0000	3.1516	0.0

Table XII. Calculated Data for the Ethyl Alcohol (1) + Acetonitrile (2) System at 393.15 K

	pressure, kPa		combined correctn terms			activity coeffs		
x_1	exptl	calcd	1	2	y_1	1	2	G^E, J/mol
0.0	297.644	297.643	0.9453	1.0000	0.0	1.8217	1.0000	0.0
0.1	342.202	342.213	0.9606	1.0264	0.1912	1.5880	1.0066	170.52
0.2	376.100	376.116	0.9723	1.0454	0.3238	1.4598	1.0216	303.31
0.3	401.482	401.499	0.9812	1.0587	0.4230	1.3449	1.0501	402.47
0.4	420.000	420.015	0.9881	1.0674	0.5038	1.2480	1.0932	464.52
0.5	433.705	433.717	0.9936	1.0725	0.5773	1.1748	1.1486	489.71
0.6	443.213	443.221	0.9979	1.0744	0.6474	1.1172	1.2216	479.00
0.7	448.555	448.560	1.0009	1.0733	0.7174	1.0707	1.3225	430.35
0.8	449.333	449.334	1.0027	1.0685	0.7931	1.0356	1.4617	339.62
0.9	444.282	444.281	1.0028	1.0592	0.8801	1.0099	1.6897	200.59
1.0	428.995	428.993	1.0000	1.0420	1.0000	1.0000	2.0488	0.0

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

	pressure, kPa		correctn terms			activity coeffs		
x_1	exptl	calcd	1	2	y_1	1	2	G^E, J/mol
0.0	2.963	2.963	0.9761	1.0000	0.0	4.1416	1.0000	0.0
0.1	5.377	5.377	0.9859	1.0003	0.4948	2.8680	1.0185	297.01
0.2	6.704	6.704	0.9904	0.9993	0.6246	2.2467	1.0627	513.23
0.3	7.571	7.571	0.9933	0.9983	0.6909	1.8655	1.1303	664.96
0.4	8.171	8.171	0.9953	0.9975	0.7336	1.6003	1.2276	758.22
0.5	8.611	8.611	0.9968	0.9966	0.7661	1.4069	1.3640	794.37
0.6	8.952	8.952	0.9979	0.9958	0.7948	1.2631	1.5564	772.86
0.7	9.234	9.234	0.9989	0.9949	0.8246	1.1573	1.8319	691.93
0.8	9.444	9.444	0.9997	0.9937	0.8577	1.0764	2.2823	545.85
0.9	9.558	9.558	1.0002	0.9919	0.9073	1.0238	3.0160	320.68
1.0	9.409	9.409	1.0000	0.9885	1.0000	1.0000	5.2467	0.0

cubic spline fit are indicated with circles.

Comparison of Data Reduction Methods

The data for the acetonitrile + toluene system were also reduced by fitting G^E to a four-suffix Margules equation using the Barker method. The resulting expressions for γ_1 and γ_2 are given by

$$\log \gamma_1 = [a_{12} + 2(a_{21} - a_{12} - d)x_1 + 3dx_1^2]x_2^2$$

$$\log \gamma_2 = [a_{21} + 2(a_{12} - a_{21} - d)x_2 + 3dx_2^2]x_1^2$$

The results obtained are shown in Table XIX along with a comparison to the Mixon et al. results. In Figure 4, the continuous lines represent the activity coefficients obtained for the acetonitrile + toluene system using the Barker method and the dashed lines represent the Mixon et al. results. As can be seen from Figure 4, the Barker results are considerably different from those obtained by the Mixon et al. method, and this is especially true in the dilute regions.

In Table XIX, the departure of the calculated pressures from the experimental pressures is shown for both the Barker method and the Mixon et al. method. It is obvious that the Mixon et al.

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

	pressure, kPa		combined correctn terms			activity coeffs		
x_1	exptl	calcd	1	2	y_1	1	2	G^E, J/mol
0.0	27.179	27.179	0.9358	1.0000	0.0	3.7112	1.0000	0.0
0.1	42.701	42.701	0.9599	1.0047	0.4144	2.6462	1.0174	321.95
0.2	51.530	51.530	0.9722	1.0045	0.5511	2.0962	1.0592	553.54
0.3	57.383	57.383	0.9803	1.0033	0.6261	1.7537	1.1240	714.19
0.4	61.393	61.393	0.9858	1.0018	0.6759	1.5106	1.2178	808.01
0.5	64.559	64.559	0.9903	1.0000	0.7179	1.3435	1.3400	838.81
0.6	67.098	67.098	0.9941	0.9978	0.7566	1.2218	1.5052	809.62
0.7	69.048	69.048	0.9971	0.9952	0.7950	1.1289	1.7447	718.43
0.8	70.386	70.386	0.9994	0.9917	0.8378	1.0587	2.1172	558.25
0.9	71.032	71.032	1.0010	0.9859	0.9009	1.0195	2.6277	325.26
1.0	69.665	69.664	1.0000	0.9758	1.0000	1.0000	3.9067	0.0

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

	pressure, kPa		combined correctn terms			activity coeffs		
x_1	exptl	calcd	1	2	y_1	1	2	G^E, J/mol
0.0	131.895	131.895	0.8773	1.0000	0.0	3.5555	1.0000	0.0
0.1	185.386	185.385	0.9152	1.0155	0.3370	2.2901	1.0197	328.29
0.2	220.252	220.251	0.9389	1.0208	0.4850	1.9084	1.0532	558.02
0.3	244.280	244.279	0.9554	1.0222	0.5716	1.6344	1.1087	717.99
0.4	262.117	262.116	0.9680	1.0218	0.6338	1.4394	1.1872	812.73
0.5	275.838	275.836	0.9780	1.0199	0.6844	1.2952	1.2942	844.35
0.6	286.596	286.594	0.9863	1.0166	0.7305	1.1869	1.4401	812.95
0.7	295.074	295.072	0.9933	1.0117	0.7777	1.1073	1.6389	717.61
0.8	300.884	300.882	0.9987	1.0044	0.8300	1.0487	1.9306	554.45
0.9	303.281	303.279	1.0021	0.9922	0.8996	1.0150	2.3264	319.75
1.0	298.065	298.064	1.0000	0.9716	1.0000	1.0000	3.1226	0.0

Table XVI. Calculated Data for the Propionitrile (1) + Ethylbenzene (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	2.955	2.955	0.9878	1.0000	0.0	2.9344	1.0000	0.0
0.1	5.384	5.384	0.9907	1.0036	0.4966	2.1388	1.0156	234.19
0.2	6.920	6.920	0.9926	1.0059	0.6392	1.7659	1.0499	397.61
0.3	8.049	8.049	0.9941	1.0077	0.7148	1.5292	1.1013	507.59
0.4	8.923	8.923	0.9952	1.0091	0.7647	1.3586	1.1736	569.24
0.5	9.649	9.649	0.9961	1.0103	0.8036	1.2338	1.2696	584.32
0.6	10.312	10.312	0.9970	1.0114	0.8390	1.1463	1.3889	555.38
0.7	10.932	10.932	0.9978	1.0124	0.8734	1.0835	1.5422	484.51
0.8	11.516	11.516	0.9986	1.0135	0.9088	1.0384	1.7532	370.75
0.9	12.072	12.072	0.9993	1.0145	0.9489	1.0094	2.0598	210.11
1.0	12.617	12.617	1.0000	1.0155	1.0000	1.0000	2.4260	0.0

predicted pressures are much closer to the experimental pressures than the Barker predicted pressures. Figure 5 depicts graphically how the Mixon et al. predicted pressures and the Barker predicted pressures compare with the resolution error band (REB) for the acetonitrile + toluene system at 293.15 K. It is evident from Figure 5, that the Mixon et al. method gives a better representation of the experimental data than the Barker method employing the four-suffix Margules equation. Three of the Barker predicted pressures lie outside the resolution error band whereas all the Mixon et al. predicted pressures lie well within the resolution error band. An extensive study of the Mixon et al. method and the Barker method using various types of activity coefficient correlations is being made, and the results of that study will be published in the near future.

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

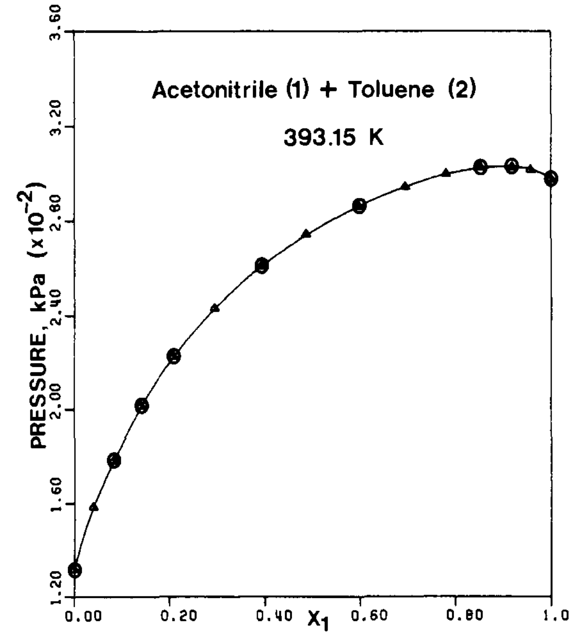

Figure 3. A plot of P vs. x_1 for the acetonitrile (1) + toluene (2) system at 393.15 K.

Table XVII. Calculated Data for the Propionitrile (1) + Ethylbenzene (2) System at 353.15 K

x_1	pressure, kPa exptl	pressure, kPa calcd	combined correctn terms 1	combined correctn terms 2	y_1	activity coeffs 1	activity coeffs 2	G^E, J/mol
0.0	16.907	16.907	0.9715	1.0000	0.0	2.6409	1.0000	0.0
0.1	27.170	27.171	0.9781	1.0086	0.4276	2.0281	1.0134	242.81
0.2	33.734	33.735	0.9825	1.0145	0.5742	1.6832	1.0468	413.26
0.3	38.677	38.677	0.9859	1.0190	0.6587	1.4707	1.0946	525.56
0.4	42.653	42.653	0.9887	1.0227	0.7181	1.3225	1.1589	588.09
0.5	45.994	45.993	0.9910	1.0258	0.7656	1.2133	1.2434	603.68
0.6	48.974	48.974	0.9931	1.0287	0.8082	1.1342	1.3501	574.38
0.7	51.689	51.689	0.9951	1.0314	0.8494	1.0762	1.4885	501.29
0.8	54.193	54.193	0.9968	1.0340	0.8920	1.0350	1.6736	383.33
0.9	56.509	56.509	0.9985	1.0365	0.9401	1.0093	1.9325	218.01
1.0	58.567	58.567	1.0000	1.0389	1.0000	1.0000	2.3026	0.0

Table XVIII. Calculated Data for the Propionitrile (1) + Ethylbenzene (2) System at 393.15 K

x_1	pressure, kPa exptl	pressure, kPa calcd	combined correctn terms 1	combined correctn terms 2	y_1	activity coeffs 1	activity coeffs 2	G^E, J/mol
0.0	64.436	64.435	0.9456	1.0000	0.0	2.3687	1.0000	0.0
0.1	94.602	94.604	0.9576	1.0169	0.3695	1.9005	1.0114	243.39
0.2	114.586	114.587	0.9659	1.0287	0.5176	1.5985	1.0424	415.32
0.3	129.965	129.965	0.9724	1.0380	0.6088	1.4121	1.0860	527.18
0.4	142.591	142.591	0.9779	1.0459	0.6757	1.2825	1.1437	588.55
0.5	153.283	153.282	0.9825	1.0528	0.7303	1.1864	1.2187	602.71
0.6	162.715	162.715	0.9867	1.0590	0.7796	1.1156	1.3139	571.51
0.7	171.197	171.197	0.9905	1.0647	0.8274	1.0637	1.4354	495.82
0.8	178.974	178.974	0.9940	1.0701	0.8776	1.0285	1.5880	375.71
0.9	186.090	186.090	0.9972	1.0753	0.9337	1.0079	1.7819	212.01
1.0	192.063	192.062	1.0000	1.0800	1.0000	1.0000	2.0791	0.0

Table XIX. Results Obtained by Fitting the Data for the Acetonitrile (1) + Toluene (2) System to a Four-Suffix Margules Equation and a Comparison with the Mixon Results

temp, K	fitting constants for the four-suffix Margules equation a_{12}	a_{21}	d	% difference between the predicted and exptl pressures: Barker method av	Barker method max	Mixon method av	Mixon method max
293.15	0.6101	0.6669	0.2991	0.157	0.457	0.039	0.071
343.15	0.5562	0.5676	0.2065	0.099	0.299	0.043	0.102
393.15	0.4648	0.4823	0.1056	0.107	0.659	0.036	0.076

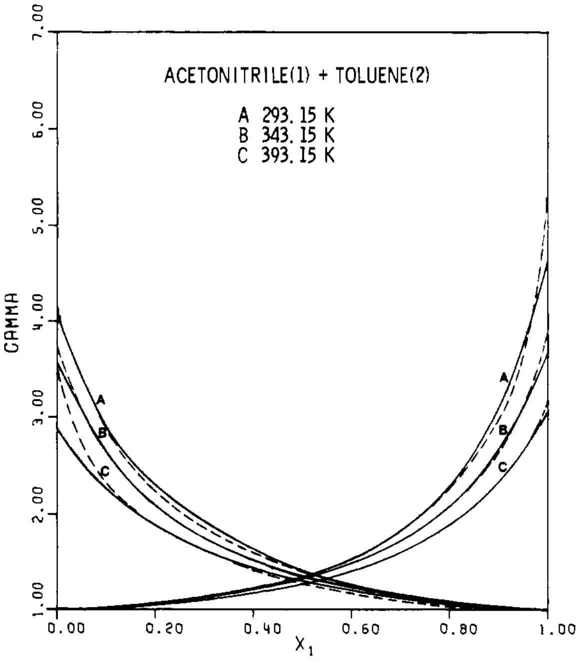

Figure 4. Comparison of the Mixon et al. and the Barker results for the acetonitrile (1) + toluene (2) system at 293.15, 343.15, and 393.15 K.

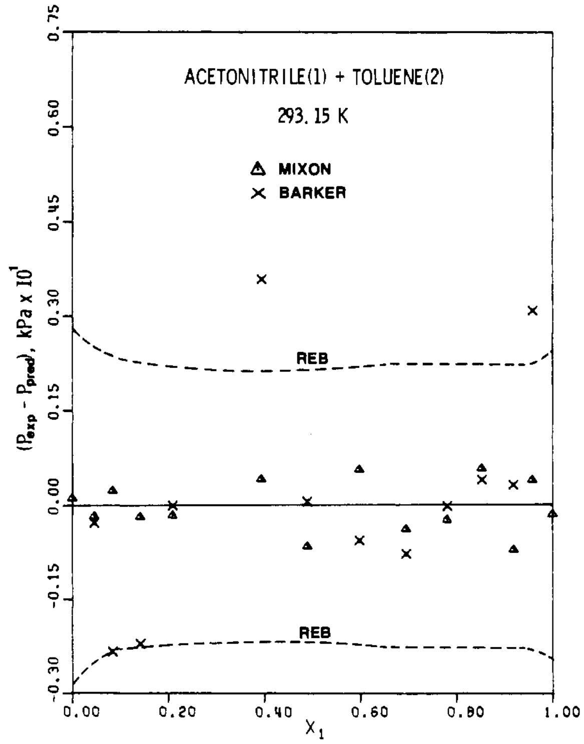

Figure 5. Comparison of the Mixon et al. and the Barker results with the resolution error band for the acetonitrile (1) + toluene (2) system at 293.15 K.

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

Literature Cited

(1) Fredenslund, A.; Gmehling, J.; Michelsen, M. L.; Rasmussen, P.; Prausnitz, J. M. *Ind. Eng. Chem. Process Des. Develop.* **1977**, *16*, 450.
(2) Maher, P.; Smith, B. D. *J. Chem. Eng. Data* **1979**, *24*, 363.
(3) Maher, P., Smith, B. D. *J. Chem. Eng. Data* **1980**, *25*, 61.
(4) Maher, P., Smith, B. D. *J. Chem. Eng. Data* **1979**, *24*, 16.
(5) Mixon, F. O., Gumowski, B., Carpenter, B. H. *Ind. Eng. Chem. Fundam.* **1965**, *4*, 455.
(6) Tsonopoulos, C. *AIChE J.* **1974**, *20*, 263.

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Solubility of Sodium Formate in Aqueous Hydroxide Solutions

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Measurements were made of the solubility of sodium formate at 21, 60, and 120 °C in aqueous solutions of sodium hydroxide. The concentration of sodium hydroxide ranges from 0 to 40% w/w. The results are combined with data of binary systems to give a semiquantitative description of the total phase diagram HCOONa–NaOH–H_2O.

Today sodium formate is industrially made by contacting gaseous carbon monoxide with a warm solution of sodium hydroxide.

We are investigating the possibility of continuously separating the product from the reacting mixture. The initial concentration of sodium hydroxide and the reaction temperature suitable to precipitate sodium formate have been investigated.

As a part of this ongoing study, it is necessary to know the solubility of sodium formate in aqueous solutions of sodium hydroxide.

Experimental Section

Weighed amounts of NaOH and HCOONa ("Carlo Erba" pure reagents) were dissolved in deionized water and stored in a 250-cm³ closed flask to prevent any evaporation; the flask was placed in an oil bath (±0.5 °C). After 6 h, no changes in concentrations could be observed. The results are based on samples taken 24 h after the preparation.

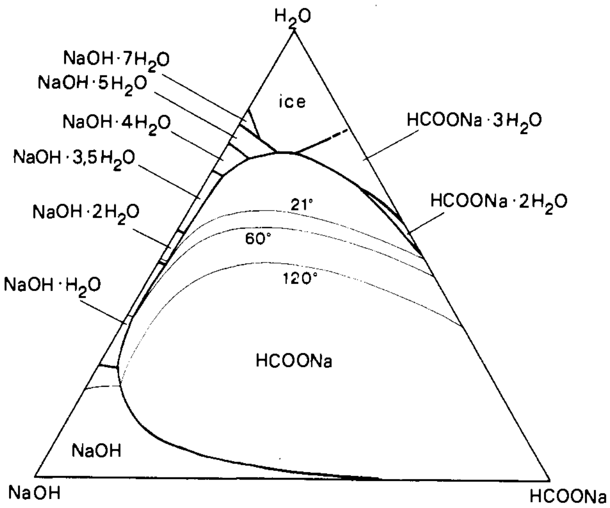

Figure 1. The phase diagram HCOONa–NaOH–H_2O (w/w).

The analysis of sodium formate was made on weighed samples of the supernatant liquid by potassium permanganate oxidation and by iodometric titration of permanganate excess. The analysis of sodium hydroxide was made by titration with newly titrated HCOOH solution (phenolphthalein indicator).

Table I. Liquid-Phase Composition (wt %) of Saturated Solutions of Sodium Formate[a]

T = 21 °C			T = 60 °C			T = 120 °C		
NaOH	HCOONa	H_2O	NaOH	HCOONa	H_2O	NaOH	HCOONa	H_2O
0.0	50.3	49.7	0.0	54.7	45.3	0.0	65.6	34.4
1.7	47.9	50.4	3.3	50.0	46.7	12.6	44.8	42.6
3.7	45.4	50.9	7.3	44.2	48.5	15.9	35.7	48.4
8.8	36.9	54.3	11.8	37.2	51.0	36.6	18.0	45.4
9.9	35.5	54.6	16.2	30.9	52.9	37.3	15.6	47.1
12.0	31.6	56.4	21.4	25.1	53.5	79.2	0.0	20.8
16.0	26.3	57.7	32.8	11.1	56.1			
18.6	22.2	59.2	40.6	5.1	54.3			
21.5	19.2	59.3	63.6	0.0	34.6			
24.1	16.0	59.9						
32.4	8.2	59.4						
35.5	5.6	58.9						
52.1	0.0	47.9						

[a] Error ±0.05.

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