Multicomponent Vapor-Liquid Equilibria in Systems of Mixed Positive and Negative Deviations

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Vapor-liquid equilibrium data at atmospheric pressure are reported for the methanol-benzene and methyl acetate–benzene binary systems. In addition, multicomponent data at 1-atm. pressure for the chloroform–methanol–methyl acetate ternary, the benzene–chloroform–methanol–methyl acetate quaternary, and the benzene–chloroform–methanol–methyl acetate–acetone quinary are reported. The Wilson equation correlates the multicomponent data, using only the composite binary parameters.

RECENT investigations (*8, 14, 16*) have compared the relative merits of two-parameter equations in the general area of correlating binary, liquid phase activity coefficients and calculating ternary, liquid phase activity coefficients. Because of the lack of experimental data, it has not been possible to assay the accuracy of two-parameter equations in systems containing more than three components. Weber *et al.* (*2, 9, 17*) have reported data on a quaternary system composed of component binary systems which evidence only positive deviations from ideality. The data reported here, evidencing both positive and negative deviations from ideality, establish a broader base for evaluating the multicomponent predictive accuracy of two-parameter models.

EXPERIMENTAL

Materials. All materials used in this work were certified ACS reagent grade solvents obtained from Fisher Scientific Co. Initial analysis in a Beckman GC-2A gas chromatograph showed trace impurity concentrations which could be reduced substantially by batch distillation. The benzene, chloroform, methanol, and methyl acetate were each subjected to a batch distillation at atmospheric pressure in a 30-plate, 1-inch, Oldershaw column. In a typical batch, 900 ml. were charged, and the still was operated at total reflux for 15 minutes. After establishing a reflux ratio of 20 to 1, the first 50- to 100-ml. overhead were discarded. A 600- to 700-ml. heart cut was recovered overhead, and the remaining reboiler contents were discarded. The heart cut was used for the experimental work. The acetone was used without additional purification. Gas chromatograms indicate that the purity of all materials was in excess of 99.9 mole % after distillation. Table I compares the normal boiling points and refractive indices of the purified materials, as measured in this laboratory, with literature values. Owing to the extreme hygroscopic properties of several of the compounds, an attempt was made to minimize water contamination by storing and handling the purified materials in a nitrogen-purged dry box.

Apparatus and Procedure. The vapor-liquid equilibrium data reported here were taken in a vapor-circulating, modified Colburn still (*18*). Temperature measurements were made with copper-constantan thermocouples in conjunction with a Universal Type K-3 potentiometer. The calibration technique yielded temperature measurements which are accurate to ±0.02° C. System pressure was measured with a mercury manometer made from ¾-inch glass tubing. The differential height was read with a Griffin & George precision cathetometer, and the readings were corrected for ambient temperature and local acceleration of gravity effects. During an experimental run, the system was closed to the atmosphere. Pressure was controlled by periodically bleeding nitrogen into the system. System pressure could be controlled and measured with an accuracy of 760.00 ± 0.10 mm. of Hg.

The methanol-benzene binary samples were analyzed with a Bausch & Lomb precision refractometer. Refractive index data of Ocón and Espantoso (*15*) were checked with the five samples shown in Table II. Since no point deviated more than ±0.002 mole fraction from the smoothed data of Ocón and Espantoso, their data were used for the analysis.

The methyl acetate–benzene binary samples and the multicomponent samples were analyzed with a Beckman GC-2A gas chromatograph equipped with a Sargent Model SR, 1-mv. recorder. A Porapak Type Q column under isothermal operation yielded excellent separations for the binary, ternary, and quaternary samples. The analysis for these data

Table I. Comparison of Properties

Compound	Normal Boiling Point, ° C. Exptl.	Normal Boiling Point, ° C. Lit.	Refractive Index, $\eta_{20° C.}$ Exptl.	Refractive Index, $\eta_{20° C.}$ Lit.
Benzene	80.10	80.10 (*4*)	1.50097	1.50112 (*4*)
Chloroform	61.20	61.22 (*3*)	1.44581	1.4461 (*3*)
Methanol	64.58	64.57 (*3*)	1.3288	1.3289 (*3*)
Methyl Acetate	56.89	56.80 (*3*)	1.36126	1.3614 (*3*)
Acetone	56.15	56.20 (*5*)	1.35854	1.35880 (*5*)

Table II. Methanol (1)–Benzene (2) Refractive Index Data

x_1	Refractive Index, $\eta_{20° C.}$
0.068	1.49504
0.132	1.48945
0.279	1.47455
0.520	1.44299
0.803	1.38753

Table III. Methanol (1)–Benzene (2) Binary Data
(Pressure = 760 Mm. of Hg)

x_1	y_1	t, ° C.	γ_1	γ_2
0.026	0.267	70.67	8.238	1.016
0.050	0.371	66.44	7.003	1.029
0.088	0.457	62.87	5.642	1.046
0.164	0.526	60.20	3.880	1.093
0.333	0.559	58.64	2.164	1.347
0.549	0.595	58.02	1.433	1.871
0.699	0.633	58.10	1.194	2.533
0.782	0.665	58.47	1.104	3.150
0.898	0.760	59.90	1.036	4.585
0.973	0.907	62.71	1.019	6.083

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[1] Present address: Ethyl Corp., Baton Rouge, La.

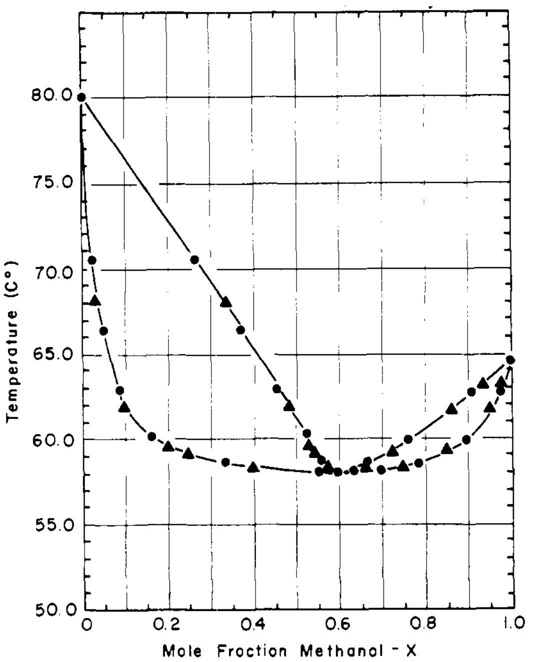

Figure 1. Methanol–benzene t-x diagram

● Data of this investigation

▲ Smoothed data of Ocón and Espantoso (15)

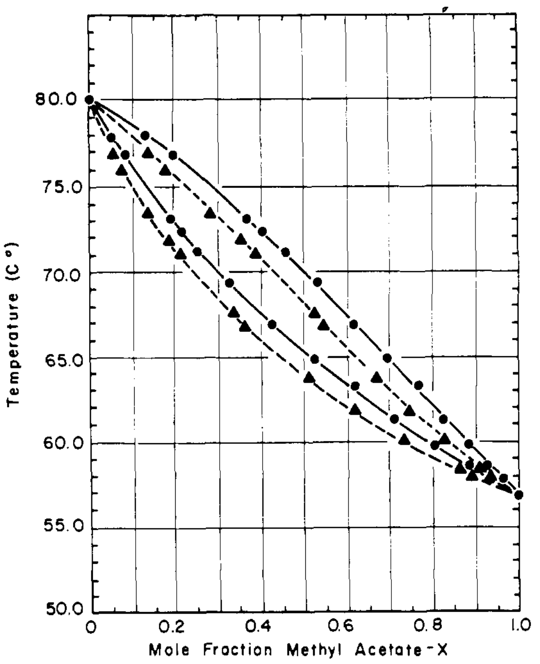

Figure 2. Methyl acetate–benzene t-x diagram

● Data of this investigation

▲ Data of Nagata (11)

are accurate to ±0.002 mole fraction. Under isothermal conditions, it was impossible to obtain complete separation of the acetone and methyl acetate peaks for the quinary analysis. A Thermotrac temperature programmer eliminated all but 4% of the peak area overlap. Analysis of known quinary samples indicated the accuracy using the temperature program was ±0.004 mole fraction.

Data. The methanol-benzene system data at 1 atm. have been reported several times (*7*, *15*, *19*), but no two sets of data are in good agreement. Therefore, the system was rerun in this laboratory. The resulting data are shown in Table III. Figure 1 shows that the data taken here give excellent agreement with the smoothed data of Ocón and Espantoso (*15*). No attempt was made to locate the azeotrope accurately.

The methyl acetate-benzene system at 1 atm. has been run by Nagata (*11*). The data in Table IV were taken because Nagata's data could not be correlated well with any two-parameter equation. Although the two sets of data show relatively good agreement on a y-x diagram, Figure 2 shows an obvious temperature discrepancy. The temperature measurements in this work were repeatedly checked. The discrepancy possibly results from an oversight by Nagata in correction of the experimental bubble-point temperatures to 760 mm. of Hg. Nagata's experimental technique requires such corrections because the equilibrium still was left open to the atmosphere during the experimental runs.

Table IV. Methyl Acetate (1)–Benzene (2) Binary Data

(Pressure = 760 Mm. of Hg)

x_1	y_1	t° C.	γ_1	γ_2
0.052	0.130	77.81	1.270	0.985
0.084	0.193	76.76	1.204	0.977
0.192	0.369	73.12	1.129	0.972
0.214	0.403	72.40	1.129	0.969
0.255	0.456	71.17	1.112	0.970
0.328	0.532	69.28	1.074	0.983
0.427	0.620	66.87	1.038	1.015
0.522	0.697	64.81	1.020	1.041
0.616	0.767	63.03	1.010	1.060
0.711	0.827	61.31	0.999	1.111
0.806	0.885	59.75	0.994	1.166
0.887	0.929	58.58	0.988	1.286
0.939	0.962	57.78	0.994	1.304

The chloroform–methanol–methyl acetate system has been studied by Bushmakin and Kish (*3*). They reported a ternary azeotrope of the saddle point type. However, they did not report the equilibrium y-x data. Thus, ternary data were run in this investigation and are included in Table V. Figure 3 displays the data in a triangular tie line diagram. The composition of the experimental run close to the reported azeotrope should not be construed as the exact azeotropic composition. It is sufficiently close, however, to confirm the reported azeotropic composition and temperature.

The benzene–chloroform–methanol–methyl acetate quaternary data have not been reported previously. The system, possessing both positive and negative deviations from ideality, is characterized by three minimum-boiling binary azeotropes, one maximum-boiling binary azeotrope, and a ternary saddle point azeotrope. Since there is no acceptable manner for evaluating consistency of four-component constant-pressure data, the first three runs shown in Table VI represent an attempt to check reproducibility of one datum point. Compositions and temperatures differ from their respective means within the experimental errors reported earlier.

A three-dimensional tetrahedron may be used to represent the quaternary composition range. In a manner completely analogous to isothermal contours of a ternary system in a two-dimensional triangular diagram, surfaces of constant temperature may be constructed inside the tetrahedron. For any arbitrarily selected temperature within the system boiling range, two surfaces may be drawn—i.e., a liquid or bubble-point surface and a vapor or dew-point surface. Such quaternary surfaces should not be confused with the liquid and vapor surfaces often shown in a three-dimensional triangular T-x diagram for ternary systems. The

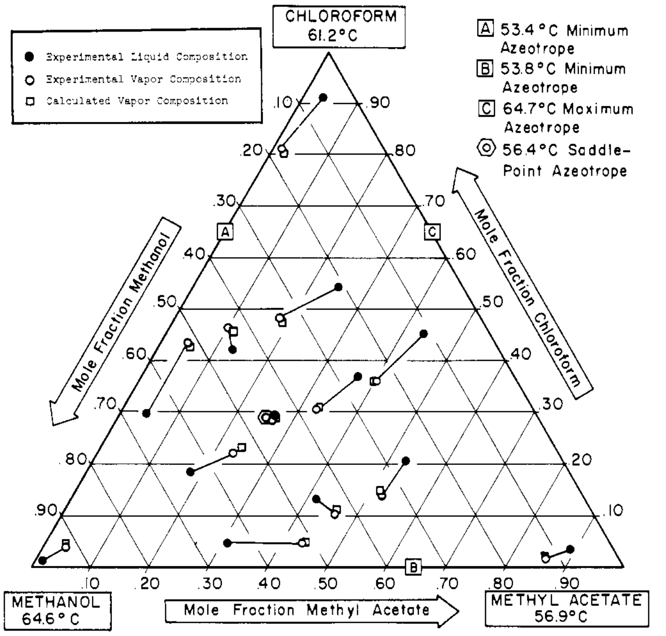

Figure 3. Chloroform–methanol–methyl acetate tie line diagram

surfaces which appear in such triangular diagrams are the locus of all equilibrium temperatures in the system, whereas the particular surfaces in the tetrahedron represent only one temperature, arbitrarily chosen.

Figures 4, 5, and 6 show the liquid and vapor surfaces for the atmospheric, benzene-chloroform-methanol-methyl acetate system at 56.4° C. (temperature of ternary saddle point azeotrope), 57.0° C., and 65.0° C. In Figure 4, the liquid and vapor surfaces touch only at a point in the base ternary—i.e., the saddle point azeotrope. The 57.0° C. surfaces shown in Figure 5 do not touch at any point in the diagram. The addition of a minute quantity of benzene breaks the saddle point azeotrope—i.e., "lifts" the liquid surface from the vapor surface. Figure 6 shows the liquid-vapor surfaces at 65.0° C. The increased separation indicates high volatility of the lower-boiling components with respect to benzene. The diagrams clearly show that no quaternary azeotropes exist. Such diagrams may be an aid in visualizing distillation paths. For example, a feed composition within the envelope on the right in Figure 4 could only produce overhead compositions within the same envelope.

The literature contains little, if any, five-component vapor-liquid equilibrium data on systems possessing highly

Table V. Chloroform–Methanol–Methyl Acetate Ternary Data
(Pressure = 760 Mm. of Hg)

	Experimental Values				Calculated Values		
Component	t, ° C.	x	y	γ	t, ° C.	y	γ
Chloroform	57.20	0.913	0.813	1.032	57.58	0.808	1.012
Methanol		0.051	0.172	4.521		0.175	4.583
Methyl acetate		0.035	0.015	0.425		0.017	0.476
Chloroform	55.70	0.034	0.017	0.609	55.69	0.018	0.634
Methanol		0.074	0.125	2.423		0.124	2.422
Methyl acetate		0.892	0.858	1.004		0.858	1.004
Chloroform	63.15	0.016	0.040	2.484	63.33	0.043	2.548
Methanol		0.972	0.921	1.008		0.920	1.001
Methyl acetate		0.012	0.039	2.605		0.037	2.487
Chloroform	55.89	0.299	0.436	1.765	56.24	0.427	1.709
Methanol		0.654	0.517	1.128		0.518	1.114
Methyl acetate		0.046	0.047	1.052		0.055	1.232
Chloroform	59.03	0.451	0.360	0.872	58.47	0.359	0.886
Methanol		0.111	0.239	2.707		0.243	2.816
Methyl acetate		0.438	0.401	0.850		0.397	0.859
Chloroform	55.53	0.048	0.047	1.187	55.76	0.052	1.326
Methanol		0.644	0.520	1.171		0.511	1.139
Methyl acetate		0.308	0.433	1.477		0.437	1.477
Chloroform	56.83	0.184	0.221	1.408	56.58	0.233	1.499
Methanol		0.637	0.549	1.183		0.528	1.152
Methyl acetate		0.178	0.230	1.293		0.239	1.356
Chloroform	55.68	0.422	0.465	1.343	55.65	0.457	1.321
Methanol		0.449	0.435	1.397		0.430	1.382
Methyl acetate		0.129	0.100	0.807		0.113	0.919
Chloroform	55.34	0.133	0.104	0.962	55.30	0.115	1.063
Methanol		0.452	0.435	1.406		0.425	1.377
Methyl acetate		0.414	0.461	1.175		0.460	1.176
Chloroform	56.39	0.297	0.288	1.158	56.02	0.294	1.193
Methanol		0.440	0.450	1.429		0.439	1.418
Methyl acetate		0.263	0.262	1.014		0.267	1.046
Chloroform	55.92	0.208	0.142	0.829	55.73	0.151	0.881
Methanol		0.264	0.335	1.814		0.336	1.831
Methyl acetate		0.529	0.522	1.023		0.513	1.011
Chloroform	57.03	0.545	0.484	1.036	56.65	0.479	1.036
Methanol		0.210	0.340	2.205		0.336	2.213
Methyl acetate		0.245	0.176	0.715		0.186	0.764
Chloroform	56.98	0.371	0.305	0.958	56.48	0.310	0.992
Methanol		0.262	0.365	1.906		0.360	1.916
Methyl acetate		0.367	0.330	0.897		0.330	0.913

$\Delta T_{av} = \pm 0.27°$ C.
$S_t = 0.33°$ C.

$\Delta Y_{av} = \pm 0.006$
Stand. Dev. = S_y
Chloroform 0.007
Methanol 0.008
Methyl acetate 0.007

Table VI. Benzene–Chloroform–Methanol–Methyl Acetate Quaternary Data

(Pressure = 760 Mm. of Hg)

	Experimental Values				Calculated Values		
Component	t, ° C.	x_i	y_i	γ	t, ° C.	y_i	γ
Benzene	56.90	0.196	0.153	1.692	56.53	0.151	1.689
Chloroform		0.211	0.184	1.023		0.190	1.068
Methanol		0.390	0.463	1.625		0.456	1.626
Methyl acetate		0.203	0.200	0.987		0.203	1.017
Benzene	56.89	0.194	0.152	1.693	56.52	0.149	1.692
Chloroform		0.211	0.185	1.031		0.190	1.067
Methanol		0.391	0.462	1.621		0.455	1.621
Methyl acetate		0.205	0.201	0.983		0.206	1.017
Benzene	56.85	0.195	0.152	1.695	56.53	0.149	1.683
Chloroform		0.215	0.186	1.017		0.194	1.066
Methanol		0.387	0.460	1.631		0.454	1.634
Methyl acetate		0.203	0.202	0.996		0.203	1.012
Benzene	56.66	0.089	0.048	1.183	56.75	0.047	1.158
Chloroform		0.660	0.597	1.066		0.579	1.032
Methanol		0.151	0.296	2.716		0.311	2.836
Methyl acetate		0.100	0.059	0.595		0.063	0.635
Benzene	59.09	0.045	0.094	4.201	59.08	0.099	4.405
Chloroform		0.052	0.090	1.890		0.095	1.985
Methanol		0.852	0.709	1.043		0.699	1.028
Methyl acetate		0.052	0.107	1.923		0.107	1.917
Benzene	56.05	0.093	0.059	1.427	55.96	0.060	1.443
Chloroform		0.100	0.056	0.680		0.061	0.734
Methanol		0.160	0.257	2.276		0.253	2.250
Methyl acetate		0.647	0.627	0.999		0.627	1.001
Benzene	60.79	0.678	0.397	1.106	60.57	0.385	1.080
Chloroform		0.104	0.083	0.817		0.087	0.870
Methanol		0.122	0.413	3.968		0.419	4.058
Methyl acetate		0.096	0.107	0.975		0.109	0.996
Benzene	58.02	0.446	0.286	1.337	57.79	0.277	1.303
Chloroform		0.184	0.156	0.957		0.160	0.987
Methanol		0.282	0.476	2.209		0.477	2.236
Methyl acetate		0.088	0.082	0.892		0.086	0.951
Benzene	59.66	0.480	0.287	1.176	59.19	0.276	1.149
Chloroform		0.191	0.149	0.836		0.153	0.871
Methanol		0.144	0.375	3.177		0.383	3.314
Methyl acetate		0.184	0.189	0.930		0.188	0.945
Benzene	57.70	0.442	0.291	1.389	57.46	0.282	1.355
Chloroform		0.091	0.070	0.872		0.074	0.941
Methanol		0.301	0.467	2.055		0.472	2.101
Methyl acetate		0.165	0.172	1.010		0.172	1.020
Benzene	56.62	0.085	0.057	1.470	56.31	0.059	1.540
Chloroform		0.442	0.414	1.106		0.407	1.099
Methanol		0.302	0.401	1.840		0.396	1.843
Methyl acetate		0.170	0.128	0.758		0.138	0.826
Benzene	59.03	0.178	0.103	1.166	58.50	0.103	1.180
Chloroform		0.519	0.455	0.957		0.445	0.953
Methanol		0.120	0.298	3.111		0.305	3.262
Methyl acetate		0.183	0.143	0.729		0.147	0.760
Benzene	56.54	0.159	0.102	1.406	56.41	0.103	1.432
Chloroform		0.441	0.410	1.101		0.409	1.104
Methanol		0.301	0.419	1.938		0.409	1.901
Methyl acetate		0.100	0.070	0.707		0.078	0.798
Benzene	57.30	0.056	0.083	3.149	57.12	0.083	3.205
Chloroform		0.121	0.157	1.499		0.167	1.601
Methanol		0.708	0.590	1.124		0.577	1.106
Methyl acetate		0.115	0.170	1.459		0.173	1.495
Benzene	57.18	0.110	0.152	2.955	57.08	0.154	3.016
Chloroform		0.064	0.097	1.428		0.083	1.516
Methanol		0.708	0.593	1.135		0.583	1.119
Methyl acetate		0.118	0.176	1.479		0.180	1.517
Benzene	57.40	0.119	0.157	2.820	57.24	0.160	2.884
Chloroform		0.123	0.161	1.514		0.167	1.574
Methanol		0.695	0.594	1.147		0.581	1.130
Methyl acetate		0.063	0.087	1.354		0.091	1.432
Benzene	56.06	0.082	0.062	1.682	55.80	0.062	1.716
Chloroform		0.175	0.124	0.855		0.133	0.922
Methanol		0.315	0.384	1.726		0.381	1.733
Methyl acetate		0.428	0.430	1.036		0.424	1.030
Benzene	55.74	0.163	0.115	1.601	55.65	0.117	1.631
Chloroform		0.091	0.060	0.804		0.066	0.882
Methanol		0.323	0.392	1.743		0.389	1.739

(*Continued on page 314*)

Table VI. Benzene–Chloroform–Methanol–Methyl Acetate Quaternary Data (*Continued*)

(Pressure = 760 Mm. of Hg)

	Experimental Values				Calculated Values		
Component	t, ° C.	x_i	y_i	γ	t, ° C.	y_i	γ
Methyl acetate		0.423	0.433	1.067		0.428	1.057
Benzene	57.52	0.169	0.109	1.370	57.11	0.108	1.375
Chloroform		0.198	0.132	0.763		0.138	0.813
Methanol		0.172	0.304	2.369		0.306	2.419
Methyl acetate		0.462	0.455	0.964		0.447	0.961
Benzene	75.39	0.924	0.803	1.007	75.16	0.793	1.002
Chloroform		0.036	0.046	0.839		0.047	0.866
Methanol		0.007	0.080	8.198		0.090	8.659
Methyl acetate		0.033	0.071	1.184		0.070	1.174
Benzene	66.25	0.492	0.311	0.990	65.87	0.307	0.990
Chloroform		0.456	0.492	0.936		0.488	0.939
Methanol		0.023	0.165	6.640		0.171	7.133
Methyl acetate		0.029	0.033	0.813		0.034	0.852
Benzene	57.74	0.288	0.327	2.385	57.83	0.324	2.363
Chloroform		0.025	0.028	1.318		0.031	1.407
Methanol		0.664	0.613	1.222		0.611	1.214
Methyl acetate		0.023	0.032	1.344		0.034	1.412
Benzene	61.06	0.456	0.271	1.114	60.91	0.267	1.102
Chloroform		0.053	0.035	0.671		0.037	1.722
Methanol		0.054	0.174	3.688		0.180	3.873
Methyl acetate		0.437	0.520	1.032		0.516	1.028
Benzene	55.89	0.035	0.022	1.394	55.87	0.022	1.408
Chloroform		0.049	0.025	0.612		0.026	0.654
Methanol		0.091	0.153	2.394		0.154	2.421
Methyl acetate		0.825	0.800	1.006		0.798	1.003
Benzene	56.40	0.032	0.029	2.002	56.05	0.031	2.139
Chloroform		0.253	0.243	1.142		0.250	1.189
Methanol		0.460	0.463	1.406		0.451	1.393
Methyl acetate		0.255	0.266	1.060		0.268	1.083
Benzene	61.09	0.029	0.020	1.273	60.38	0.020	1.305
Chloroform		0.470	0.392	0.852		0.385	0.855
Methanol		0.057	0.144	2.934		0.164	3.429
Methyl acetate		0.445	0.444	0.864		0.431	0.859
Benzene	57.14	0.325	0.263	1.738	56.98	0.257	1.709
Chloroform		0.089	0.081	1.054		0.084	1.096
Methanol		0.456	0.513	1.526		0.514	1.538
Methyl acetate		0.130	0.143	1.096		0.146	1.120
Benzene	55.80	0.020	0.028	3.084	55.99	0.029	3.244
Chloroform		0.027	0.028	1.295		0.031	1.383
Methanol		0.681	0.548	1.154		0.533	1.113
Methyl acetate		0.272	0.396	1.512		0.407	1.546
Benzene	63.07	0.311	0.203	1.140	62.54	0.197	1.127
Chloroform		0.330	0.280	0.814		0.280	0.827
Methanol		0.042	0.154	3.950		0.168	4.360
Methyl acetate		0.318	0.362	0.924		0.355	0.920

$\Delta T_{av} = \pm 0.25°$ C.
$S_t = 0.31°$ C.

$\Delta y_{av} = \pm 0.005$
Stand. Dev. = S_{y_i}
Benzene 0.005
Chloroform 0.006
Methanol 0.009
Methyl acetate 0.005

Table VII. Benzene–Chloroform–Methanol–Methyl Acetate–Acetone Quinary Data

(Pressure = 760 Mm. of Hg)

	Experimental Values				Calculated Values		
Component	t, ° C.	x_i	y_i	γ	t, ° C.	y_i	γ
Benzene	57.26	0.161	0.126	1.675	56.80	0.122	1.649
Chloroform		0.175	0.137	0.907		0.142	0.950
Methanol		0.322	0.391	1.640		0.397	1.698
Methyl acetate		0.162	0.175	1.067		0.170	1.056
Acetone		0.179	0.170	0.914		0.169	0.922
Benzene	66.79	0.842	0.585	1.068	66.56	0.555	1.019
Chloroform		0.044	0.042	0.829		0.043	0.833
Methanol		0.042	0.251	5.514		0.284	6.299
Methyl acetate		0.035	0.051	1.023		0.052	1.084
Acetone		0.037	0.071	1.341		0.066	1.277

(*Continued on page 315*)

Table VII. Benzene–Chloroform–Methanol–Methyl Acetate–Acetone Quinary Data (*Continued*)

(Pressure = 760 Mm. of Hg)

	Experimental Values				Calculated Values		
Component	t, ° C.	x_i	y_i	γ	t, ° C.	y_i	γ
Benzene	58.00	0.036	0.018	1.053	58.17	0.017	0.995
Chloroform		0.822	0.756	1.037		0.738	1.008
Methanol		0.063	0.180	3.747		0.199	4.116
Methyl acetate		0.037	0.019	0.482		0.021	0.550
Acetone		0.042	0.028	0.626		0.024	0.542
Benzene	61.66	0.015	0.043	5.137	61.60	0.046	5.631
Chloroform		0.018	0.039	2.162		0.041	2.310
Methanol		0.931	0.826	1.003		0.827	1.006
Methyl acetate		0.021	0.045	1.806		0.057	2.297
Acetone		0.015	0.047	2.630		0.029	1.628
Benzene	59.35	0.205	0.139	1.342	58.85	0.132	1.301
Chloroform		0.235	0.168	0.772		0.171	0.796
Methanol		0.118	0.237	2.485		0.247	2.651
Methyl acetate		0.219	0.227	0.951		0.227	0.968
Acetone		0.222	0.229	0.927		0.223	0.920
Benzene	56.63	0.198	0.152	1.679	56.36	0.152	1.702
Chloroform		0.070	0.050	0.839		0.054	0.913
Methanol		0.359	0.404	1.559		0.405	1.579
Methyl acetate		0.174	0.197	1.140		0.192	1.127
Acetone		0.199	0.198	0.982		0.197	0.984
Benzene	57.48	0.061	0.045	1.563	56.95	0.044	1.561
Chloroform		0.230	0.163	0.814		0.169	0.861
Methanol		0.219	0.300	1.830		0.307	1.916
Methyl acetate		0.224	0.236	1.030		0.229	1.021
Acetone		0.265	0.256	0.925		0.251	0.922
Benzene	56.79	0.051	0.044	1.902	56.27	0.044	1.915
Chloroform		0.264	0.241	1.075		0.244	1.102
Methanol		0.397	0.436	1.512		0.426	1.510
Methyl acetate		0.229	0.228	1.000		0.233	1.041
Acetone		0.059	0.050	0.825		0.053	0.896
Benzene	57.94	0.141	0.102	1.510	57.27	0.100	1.523
Chloroform		0.298	0.246	0.934		0.250	0.972
Methanol		0.265	0.379	1.878		0.379	1.928
Methyl acetate		0.141	0.136	0.931		0.136	0.953
Acetone		0.154	0.136	0.832		0.135	0.842
Benzene	56.45	0.055	0.037	1.479	56.37	0.033	1.346
Chloroform		0.074	0.040	0.648		0.040	0.636
Methanol		0.077	0.109	1.966		0.121	2.201
Methyl acetate		0.385	0.397	1.048		0.392	1.037
Acetone		0.409	0.417	1.010		0.414	1.007
Benzene	57.42	0.094	0.060	1.362	57.21	0.058	1.315
Chloroform		0.109	0.062	0.654		0.063	0.674
Methanol		0.076	0.131	2.306		0.143	2.553
Methyl acetate		0.567	0.580	1.005		0.574	1.001
Acetone		0.155	0.167	1.036		0.162	1.008
Benzene	57.72	0.088	0.060	1.422	57.45	0.057	1.376
Chloroform		0.103	0.058	0.644		0.058	0.648
Methanol		0.072	0.100	1.834		0.117	2.171
Methyl acetate		0.150	0.168	1.092		0.162	1.061
Acetone		0.588	0.615	0.993		0.606	0.987
Benzene	60.51	0.299	0.192	1.226	59.69	0.184	1.209
Chloroform		0.319	0.261	0.850		0.259	0.868
Methanol		0.117	0.280	2.828		0.298	3.110
Methyl acetate		0.130	0.132	0.898		0.129	0.901
Acetone		0.135	0.135	0.867		0.130	0.857
Benzene	59.09	0.304	0.192	1.264	58.66	0.185	1.238
Chloroform		0.146	0.097	0.723		0.101	0.765
Methanol		0.119	0.243	2.569		0.263	2.818
Methyl acetate		0.304	0.331	1.007		0.318	0.985
Acetone		0.127	0.138	0.982		0.133	0.960
Benzene	59.10	0.125	0.084	1.345	58.42	0.082	1.342
Chloroform		0.309	0.230	0.810		0.232	0.837
Methanol		0.128	0.246	2.397		0.260	2.623
Methyl acetate		0.304	0.308	0.939		0.299	0.932
Acetone		0.133	0.132	0.899		0.127	0.884

$\Delta t_{av} = \pm 0.39°$ C.
$S_t = 0.47°$ C.

$\Delta y_{av} = \pm 0.006$
Stand. Dev. = S_{y_i}
Benzene 0.009
Chloroform 0.006
Methanol 0.015
Methyl acetate 0.007
Acetone 0.007

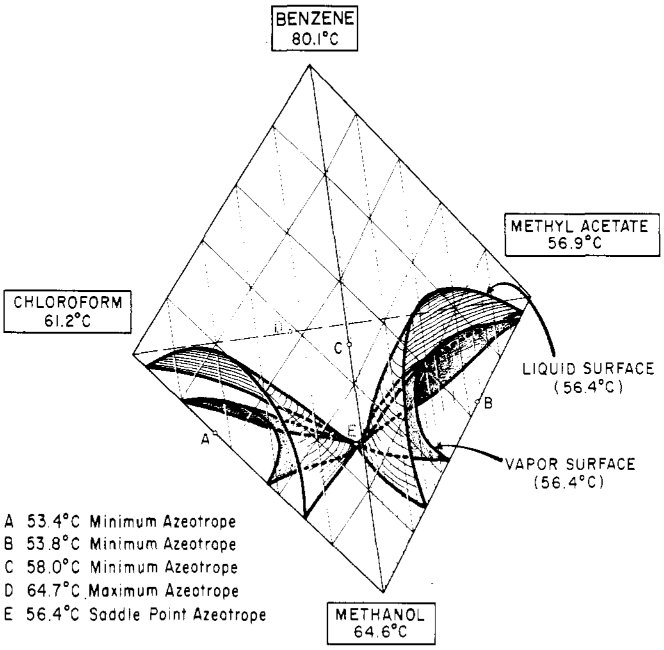

Figure 4. Quaternary 56.4° C. bubble-point and dew-point surfaces

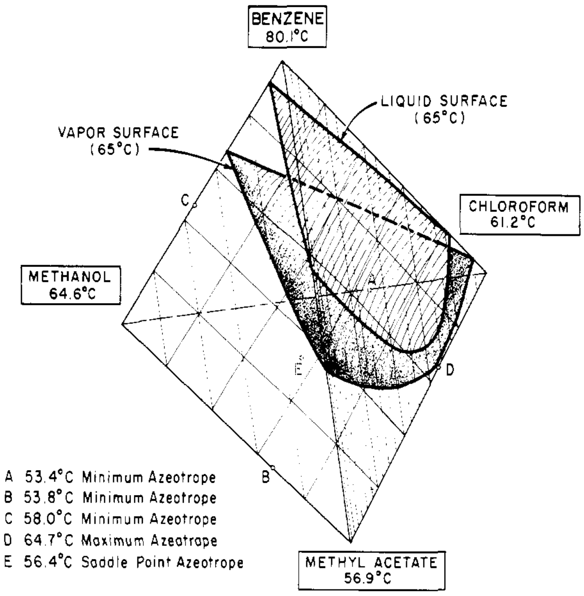

Figure 6. Quaternary 65.0° C. bubble-point and dew-point surfaces

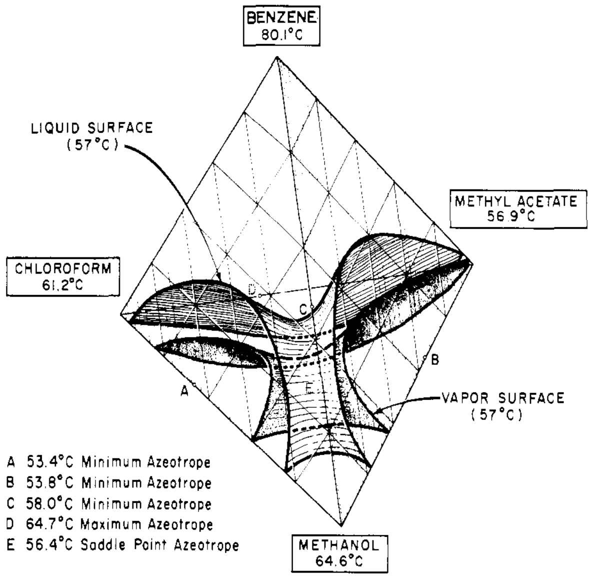

Figure 5. Quaternary 57.0° C. bubble-point and dew-point surfaces

Table VIII. Methyl Acetate Vapor Pressure Data

$T_{\text{exptl.}}$, °C.	$P_{\text{exptl.}}$, Mm. of Hg	$P_{\text{cal.}}$, Mm. of Hg	Antoine Constants
45.30	497.13	497.23	A = 6.98944
49.93	591.45	591.58	
54.25	691.95	691.90	B = 1111.04
56.90	760.04	759.83	C = 213.51
63.56	953.27	953.85	
76.60	1444.52	1444.50	

polar or hydrogen bonding components. Table VII includes limited experimental quinary data which exhibit a high degree of solution complexity.

During the experimental work, the commonly accepted methyl acetate Antoine constants yielded vapor pressure data which deviated 10 to 20 mm. of Hg near the normal boiling point. Sufficient vapor pressure data were obtained over the range of temperatures used in this investigation to establish a better set of Antoine constants. Table VIII contains the experimental data, and the Antoine constants obtained from a non-linear regression fit of the experimental data.

CORRELATION OF DATA

Throughout this work, the liquid phase activity coefficients have been calculated from

$$\gamma_i = \frac{y_i P}{x_i P_i^s} \tag{1}$$

which neglects vapor phase nonideality. The binary activity coefficients were correlated with the Wilson equation (*20*).

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2\left[\frac{\Lambda_{12}}{(x_1 + \Lambda_{12}x_2)} - \frac{\Lambda_{21}}{(\Lambda_{21}x_1 + x_2)}\right] \tag{2}$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) - x_1\left[\frac{\Lambda_{12}}{(x_1 + \Lambda_{12}x_2)} - \frac{\Lambda_{21}}{(\Lambda_{21}x_1 + x_2)}\right] \tag{3}$$

where

$$\Lambda_{ij} = \frac{v_j}{v_i}\exp[-(\lambda_{ij} - \lambda_{ii})/RT] \tag{4}$$

The binary parameters were obtained using the regression technique of Holmes (*8*), in which the minimization function is as follows.

$$\beta = \frac{\sum_{i=1}^{n}(\gamma_{1\,\text{exptl.}} - \gamma_{1\,\text{cal.}})^2}{\sum_{i=1}^{n}(\gamma_{1\,\text{exptl.}} - 1.0)} + \frac{\sum_{i=1}^{n}(\gamma_{2\,\text{exptl.}} - \gamma_{2\,\text{cal.}})^2}{\sum_{i=1}^{n}(\gamma_{2\,\text{exptl.}} - 1.0)} \tag{5}$$

Table IX. Wilson Parameters

Components	Binary, i-j	$\lambda_{ij} - \lambda_{ii}$	$\lambda_{ij} - \lambda_{jj}$	Ref.
1. Acetone	1-2	494.92	−167.90	(*6*)
2. Benzene	1-3	−73.15	−331.10	(*10*)
3. Chloroform	1-4	−215.01	664.29	(*1*)
4. Methanol	1-5	−65.21	161.26	(*13*)
5. Methyl acetate	2-3	148.44	−208.50	(*11*)
	2-4	216.13	1679.46	[a]
	2-5	200.54	−10.17	[a]
	3-4	−372.25	1702.56	(*12*)
	3-5	−431.41	79.10	(*11*)
	4-5	845.83	−98.42	(*3*)

[a] Data of this investigation.

Table IX contains the parameters for all binary data used in this work. Multicomponent predictions resulted from bubble-point calculations in which the binary parameters in Table IX were used in conjunction with the Wilson equation written for "k" components.

$$\ln \gamma_m = 1 - \ln\left[\sum_{j=1}^{k} x_j \Lambda_{mj}\right] - \sum_{i=1}^{k} \frac{x_i \Lambda_{im}}{\sum_{j=1}^{k} x_j \Lambda_{ij}} \tag{6}$$

The average deviations of the calculated values from experimental values shown at the end of Tables V, VI, and VII were obtained from

$$\Delta y_{\text{av}} = \frac{\sum_{j=1}^{n} \sum_{i=1}^{k} \left| y_{i_{\text{exptl.}}} - y_{i_{\text{cal.}}} \right|}{nk} \tag{7}$$

$$\Delta T_{\text{av}} = \frac{\sum_{i=1}^{n} \left| T_{\text{exptl.}} - T_{\text{cal.}} \right|}{n} \tag{8}$$

RESULTS AND CONCLUSIONS

Figure 7 shows that the Wilson equation satisfactorily correlates the methanol-benzene binary data. In the methyl acetate–benzene binary system (Figure 8), the experimental benzene activity coefficient curve possesses an unusual minimum. This phenomenon cannot be attributed to vapor phase nonideality. Correcting the benzene liquid phase activity coefficients for vapor phase nonideality tends to lower rather than raise the benzene γ-x curve. The benzene vapor pressure data, as given by commonly accepted Antoine constants, have been checked and are accurately described by the accepted constants. Experimental errors are of insufficient magnitude to explain the observed minimum. The pure components were repeatedly checked for purity by measuring the refractive indices and normal boiling points, and by analyzing the components on a gas chromatograph. The duplicate measurements agreed with previous measurements within experimental error, and impurity peaks were not evident on the chromatograms. A similar, but deeper, minimum has been observed by Nagata (*13*) on the butyl acetate-benzene system. His explanation of "slight experimental error" does not seem realistic in light of his reported experimental error and the results of this investigation. As pointed out by Orye and Prausnitz (*16*), the Wilson equation cannot "reproduce maxima or minima in the activity coefficient." However, the fit is sufficiently good to yield accurate multicomponent predictions, as evidenced by the results of the calculations on the quaternary and quinary data.

Although no attempt has been made to locate accurately the reported (*3*) saddle point azeotrope, the data taken in this study on the chloroform-methanol-methyl acetate system confirm the existence and approximate composition of the reported azeotrope. Using only binary parameters, the Wilson equation fits the ternary vapor compositions with an average deviation of $\Delta y_{\text{av}} = \pm 0.006$ mole fraction. An excellent prediction of the saddle point azeotrope is shown in Figure 4. The corresponding average bubble-point temperature error was $\Delta T_{\text{av}} = \pm 0.27°$ C.

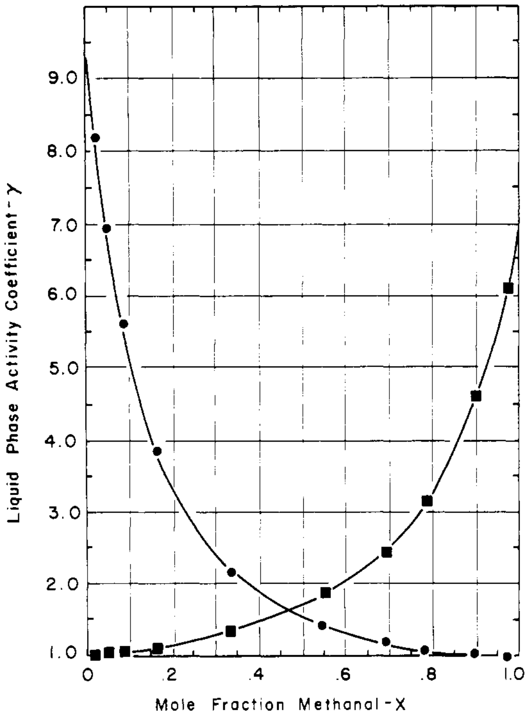

Figure 7. Methanol-benzene γ-x diagram

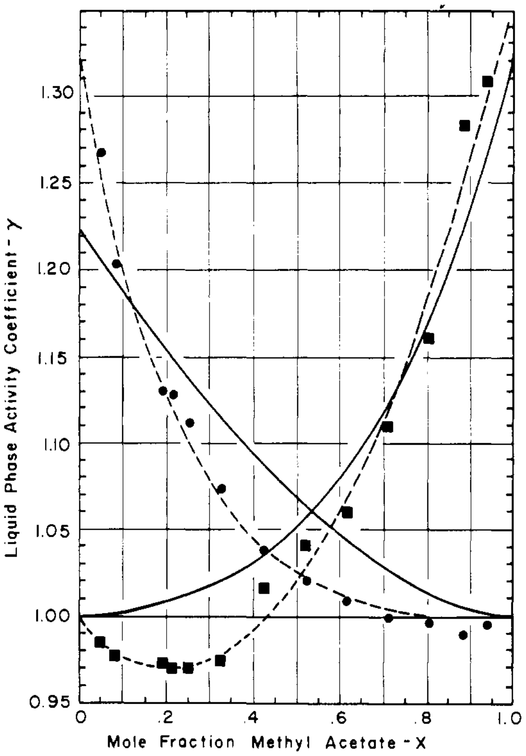

Figure 8. Methyl acetate–benzene γ-x diagram

--- Experimental Data

— Wilson equation

The benzene–chloroform–methanol–methyl acetate system at 1-atm. pressure does not contain a quaternary azeotrope. The Wilson equation predicts the quaternary vapor mole fractions and bubble-point temperatures with an average error of $\Delta y_{\text{av}} = \pm 0.005$ and $\Delta T_{\text{av}} = \pm 0.25^\circ$ C., respectively. In the benzene–chloroform–methanol–methyl acetate–acetone quinary system at 1 atm., the average calculation errors were $\Delta y_{\text{av}} = \pm 0.006$ and $\Delta T_{\text{av}} = \pm 0.39^\circ$ C.

These results indicate that the Wilson equation yields sufficient accuracy on multicomponent systems containing mixed positive and negative deviations using only binary parameters for practical application in design of separation process equipment. The average vapor composition errors are only slightly larger than the inherent analytical uncertainty. Such accuracy is obtained in spite of the assumption of vapor phase ideality. Since some components used in this work may associate in the vapor phase (i.e., chloroform-acetone), the assumption is arduously tested. The results indicate that little accuracy may be gained in systems up to 1-atm. pressure from the laborious calculations required to obtain vapor phase fugacity coefficients.

NOMENCLATURE

β = minimization function
k = number of components in the system
n = number of data points
P = pressure, mm. of Hg
P_i^s = vapor pressure of component i, mm. of Hg
R = gas constant, cal./gram mole, ° K.
T = temperature, ° K.
t = temperature, ° C.
v_i = molar volume of component i, cc./gram mole
x_i = liquid mole fraction of component i
y_i = vapor mole fraction of component i
γ_i = liquid phase activity coefficient of component i
$(\lambda_{ij} - \lambda_{ii})$ = Wilson parameters, cal./gram mole

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Received for review December 12, 1968. Accepted April 29, 1969. The authors are indebted to the National Science Foundation for financial support.

Activity of $NaNO_3$ in Molten $CdCl_2$-$NaNO_3$ Mixtures

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Freezing point depressions are reported for the system $CdCl_2$-$NaNO_3$ over the range 0 to 0.16 mole fraction of $CdCl_2$. The freezing point depression of $NaNO_3$ indicates that the dominant factor at these temperatures is the presence of the cadmium species, $CdCl_4^{2-}$, $CdCl_2$, and Cd^{2-}.

A FREEZING POINT depression study of the system $CdCl_2$-$NaNO_3$ has been reported by Van Artsdalen (*15*), and similar studies of $CdSO_4$-$LiNO_3$ and CdF_2-$LiNO_3$ have been described by Isbell *et al.* (*6*). The studies were confined to the region dilute in the cadmium salt, to a maximum concentration of about 0.10 to 0.15*m*. The maximum freezing point depression of the solvent was about 2° to 3.5° K. Assuming dilute solution behavior, the results were taken to indicate that $CdSO_4$ and $CdCl_2$ dissociate incompletely into the simple ions, and also form the complexes $Cd(SO_4)_2^{2-}$ and $CdCl_4^{2-}$, while CdF_2 dissociates completely.

The present work extends Van Artsdalen's study to higher concentrations of $CdCl_2$ for the purpose of determining if the behavior there is consistent with the concept of incomplete dissociation and complexation, or is better represented by models assuming complete dissociation. This is accomplished by calculating $NaNO_3$ activity from freezing point depressions to the eutectic composition, 0.95*m* $CdCl_2$, and comparing the experimental values with those predicted with models of energy and entropy behavior.

EXPERIMENTAL

Materials. All chemicals were reagent grade, used without further purification. The sodium nitrate was dried and stored in sealed bottles. The freezing point of the sodium nitrate, 579.2° K. [lit., 579.0° (*15*) and 579.2° K. (*7*)],