and these data are included in Tables I and II. Osmotic coefficients of the four salts are presented graphically in Figure 1.

Literature Cited

(1) Esval, O. E.; Tyree, S. Y. *J. Phys. Chem.* **1962**, *66*, 940.
(2) Bonner, O. D. *J. Chem. Soc., Faraday Trans. 1* **1981**, *77*, 2515.
(3) Bonner, O. D. *J. Chem. Eng. Data* **1981**, *26*, 148.
(4) Bonner, O. D. *J. Chem. Thermodyn.* **1979**, *11*, 559.
(5) Robinson, R. A.; Sinclair, D. A. *J. Am. Chem. Soc.* **1934**, *56*, 1830.
(6) Robinson, R. A.; Stokes, R. H. "Electrolyte Solutions", 2nd ed.; Butterworths: London, 1959; pp 483, 492.

Received for review May 13, 1981. Accepted November 2, 1981.

Vapor–Liquid Equilibrium with Association in Both Phases. Multicomponent Systems Containing Acetic Acid

Henryk Sawistowski* and Peter A. Pilavakis[†]

Department of Chemical Engineering and Chemical Technology, Imperial College, London SW7, England

The vapor–liquid equilibrium behavior of the quaternary system methyl acetate–methanol–water–acetic acid was modeled by using the Margules equation in combination with Marek's method for the association of acetic acid. The constants in the Margules equation were obtained from existing or experimentally determined equilibrium composition of the constituent binary and ternary mixtures. The final equation was experimentally verified on the quaternary system in the presence and the absence of the catalyst.

Introduction

Chemical reaction with simultaneous distillation in a column is an operation of particular interest. The practical evaluation of such a process requires the formulation of a model which describes the complete operation of the column (*1*). For this purpose, data on the vapor–liquid equilibria of the multicomponent system must be available.

The usual equations used in process calculations for the determination of vapor–liquid equilibrium data are the Wohl, Margules, Van Laar, Wilson, and lately the NRTL equations. Sabylin and Aristovich (*2*) concluded that the best predictions for multicomponent systems were given by the Wilson equation, while the Wohl equation produced the worst results. The NRTL equation is superior to the Wilson equation since it can also describe systems with immiscible components. Simulation of the vapor–liquid equilibria of systems that contain associating components is, however, difficult. Owing to the complexity of the system under investigation, Sabylin and Aristovich's conclusions do not necessarily apply, and also simulation cannot be established alone by these relationships.

In the past a model was developed by Marek and Standart (*3*) and used by Marek (*4*) to correlate data of acetic acid mixtures. Jenkins and Gibson-Robinson (*5, 6*) developed a new model based on that of Marek and Standart, but they also took into account a concentration-dependent factor for the association of acetic acid in the liquid phase. These models only require the calculation of adjustable parameters as those for the integrated form of the Gibbs–Duhem equation which correlate activity coefficients to component mole fractions. They also use correction-factor expressions to include the effect of association of acetic acid.

In the present work the model developed by Marek and Standart was used (*3, 4*). The model is applied to the quaternary system of acetic acid with water, methanol, and methyl acetate. It is, however, established that alcohols in solution (*7*) as well as water alone and in mixture associate to form dimers and polymers (*8*). This model assumes that only acetic acid forms dimers or higher polymers and does not take into account the association behavior of the other components but only of acetic acid. In the case of systems containing acetic acid and methanol, there is a further complication that the components react to form methyl acetate, although very slowly in the absence of the catalyst. The vapor–liquid equilibrium data for these systems were therefore obtained in a flow still in order to minimize this complication. This does not, however, exclude the possibility that acetic acid does not reach the monomer–dimer equilibrium mixture. Having described the complications, we studied the use of this model for these systems.

Data Sets Examined

The following vapor–liquid equilibrium data at 760 mmHg must be known: (a) methyl acetate–methanol, (b) methyl acetate–water, (c) methyl acetate–acetic acid, (d) methanol–water, (e) methanol–acetic acid, (f) water–acetic acid, (g) methyl acetate–methanol–water, (h) methyl acetate–methanol–acetic acid, (i) methyl acetate–water–acetic acid, (j) methanol–water–acetic acid, and (k) methyl acetate–methanol–water–acetic acid. Existing data for systems given in the literature were considered to be correct and therefore were not repeated. System a has already been investigated by Teshima et al. (*9*), Crawford et al. (*10*), Bushmakin and Kish (*11*), and Bredig and Bayer (*12*). Complete data for system b have been presented only by Teshima et al. (*9*). Similarly, system d has been investigated by Fastovskij and Petrovskij (*13*), Bennett (*14*), Bredig and Bayer (*15*), Dunlop (*16*), Huges and Maloney (*17*), Ramalho et al. (*18*), and many others; system (f) by Rivenc (*19*), Brown and Ewald (*20*), Garwin and Hutchinson (*21*), Othmer et al. (*22*), and others; and finally system g by Crawford et al. (*10*), Kogan (*23*), and Teshima et al. (*9*). Data for system e have been given in the literature by Rius et al. (*24*) at pressures of ~706 mmHg and had to be repeated at atmospheric pressure. System f (water–acetic acid) has been presented by Rivenc (*19*) in weight fraction in the liquid and vapor phases. To convert it into molar fraction, we used a constant weight of monomeric acetic acid. Systems c, e, and h–k were not available and had to be experimentally determined. All of the experimentally determined vapor–liquid equilibrium data are contained in Tables I–VI.

Thermodynamic relations are used extensively for the interpolation and extrapolation of experimental data for systems with two and more components. The commonly used expressions are valid only for an ideal, or slightly nonideal, behavior of the vapor phase, but they fail completely for substances with highly

[†] 83, Rue des Floralies, 1200-Brussels, Belgium.

0021-9568/82/1727-0064$01.25/0

Table I. Vapor-Liquid Equilibrium Data for the Methyl Acetate-Acetic Acid System

Experimental					Calculated			
x_1	x_2	y_1	y_2	t, °C	y_1	y_2	dy_1	dy_2
.021	.979	.072	.928	115.75	.064	.936	.008	-.008
.022	.978	.069	.931	115.75	.069	.931	.000	.000
.022	.978	.072	.928	115.00	.069	.931	.003	-.003
.087	.913	.285	.715	106.70	.282	.718	.003	-.003
.082	.918	.285	.715	106.50	.268	.732	.018	-.018
.108	.892	.345	.655	104.40	.348	.652	-.003	.003
.116	.884	.402	.598	102.50	.372	.628	.030	-.030
.117	.883	.397	.603	102.00	.375	.625	.022	-.022
.118	.882	.380	.620	103.60	.378	.622	.002	-.002
.143	.857	.447	.553	98.40	.447	.553	.000	.000
.144	.856	.460	.540	100.50	.449	.551	.011	-.011
.146	.854	.447	.553	100.30	.455	.545	-.008	.008
.154	.846	.470	.530	99.50	.475	.525	-.005	.005
.159	.841	.483	.517	98.10	.486	.514	-.003	.003
.166	.834	.503	.497	96.75	.503	.497	-.001	.001
.163	.837	.496	.504	96.30	.496	.504	.000	.000
.170	.830	.514	.486	98.00	.513	.487	.000	.000
.171	.829	.480	.520	98.60	.516	.484	-.036	.036
.173	.827	.535	.465	95.50	.520	.480	.015	-.015
.203	.797	.595	.405	95.50	.584	.416	.012	-.012
.216	.783	.626	.374	94.70	.609	.391	.016	-.016
.215	.785	.622	.378	93.50	.606	.394	.017	-.017
.273	.727	.680	.320	88.50	.696	.304	-.016	.016
.385	.615	.812	.188	80.00	.808	.192	.003	-.003
.412	.588	.853	.147	78.80	.826	.174	.027	-.027
.420	.580	.849	.151	77.70	.831	.169	.018	-.018
.492	.508	.876	.124	76.60	.867	.133	.009	-.009
.500	.500	.885	.115	74.00	.870	.130	.015	-.015
.581	.419	.928	.072	70.25	.896	.104	.032	-.032
.719	.281	.969	.031	64.60	.924	.076	.045	-.045
.819	.181	.999	.001	62.00	.943	.057	.056	-.056
.900	.100	.997	.003	59.40	.965	.035	.032	-.032
.950	.050	.999	.001	58.30	.984	.016	.015	-.015

Table II. Vapor-Liquid Equilibrium Data for the Methanol-Acetic Acid System

Experimental					Calculated			
x_1	x_2	y_1	y_2	t, °C	y_1	y_2	dy_1	dy_2
.071	.929	.222	.778	110.30	.216	.784	.006	-.006
.088	.912	.275	.725	108.50	.259	.741	.016	-.016
.098	.902	.279	.721	108.20	.282	.718	-.004	.004
.112	.888	.323	.677	107.50	.315	.685	.008	-.008
.143	.857	.377	.623	105.10	.379	.621	-.002	.002
.178	.822	.441	.559	102.10	.445	.555	-.004	.004
.282	.718	.591	.409	95.80	.602	.398	-.011	.011
.305	.695	.643	.357	93.70	.632	.368	.011	-.011
.357	.643	.684	.316	91.90	.690	.310	-.006	.006
.468	.532	.797	.203	85.00	.794	.206	.002	-.002
.514	.486	.844	.156	82.70	.830	.170	.014	-.014
.600	.400	.905	.095	78.30	.885	.115	.020	-.020
.687	.313	.943	.057	74.50	.928	.072	.014	-.014
.718	.282	.945	.055	73.50	.941	.059	.004	-.004
.749	.251	.959	.041	72.10	.952	.048	.007	-.007
.797	.203	.955	.045	70.30	.967	.033	-.011	.011
.810	.190	.970	.030	70.10	.971	.029	.000	.000
.824	.176	.978	.022	69.40	.975	.025	.003	-.003
.841	.159	.980	.020	68.60	.979	.021	.001	-.001
.878	.122	.996	.004	67.40	.987	.013	.009	-.009

nonideal vapors. Since acetic acid associates (*25*, *26*), the system was considered nonideal. The vapor-phase nonidealities for acetic acid were handled by the correction factors of Marek and Standart (*3*) and of Marek (*4*), and a summary of the correlations used is presented in the Appendix. Using the Scheibel (*27*) correlation, we found that the correction factor for the nonideality in the liquid phase was ~1, and a value of 1 was therefore assumed throughout the calculation. The pure-component association constant K for the vapor phase was obtained from the work of Marek (*4*) and is as follows:

$$-\log K = 9.7535 + 0.00425t - 3166/(t + 273.2) \quad (1)$$

Note that the K is based on the vapor-phase association measurements of acetic acid by Ritter and Simons (*25*) and Johnson and Nash (*26*). This is used for the evaluation of the correction factors which are valid only for the case of association to dimers. The dimerization constant includes the effect of the higher associations and of the slight nonideality of the various kinds of acid molecules and hence also is a function of pressure.

The vapor pressures of the pure components were estimated by the Antoine equation. For acetic acid the Antoine constants for the corrected vapor pressure were taken from the work of Marek (*4*). This corrected vapor pressure was then calculated by the expression

$$\log P_{Ac}^{0} = 15.6699 - 10821.1/(t + 698.09) \quad (2)$$

It should be noted that the determined equilibrium data are not "true" equilibrium data since thermodynamic equilibrium in reacting systems also requires that the system be in chemical equilibrium, i.e., that the reaction has been completed. However, under such conditions it would not be possible to obtain a local concentration driving force in a packed column or its instantaneous value in a batch reboiler, and no procedures for column calculation could be established. For this reason the flash vaporization technique was adopted, and the determined data were correlated on a nonreacting basis. No other procedure is currently available as the relevant theory on determination of vapor-liquid equilibrium data in reacting systems does not exist.

Experimental Section

The most direct and accurate method for the determination of vapor-liquid equilibria is by experimentation in a suitable still. The traditional types of equilibrium apparatuses are, however, unsatisfactory for measurement of vapor-liquid equilibrium data of a system in which a chemical reaction is taking place, since the compositions of the phases are constantly changing. In order to avoid this difficulty, it was necessary to use a flow still. The Cathala ebulliometer (*28*) was selected for this purpose. In it the reservoirs were filled with their respective liquids and the insulating envelope was heated to a temperature around the temperature of operation. The preheater and the boiler were then filled and heated. The flows of the two phases were adjusted in such a way that the desired composition was obtained.

Heat exchangers were used to cool liquid and vapor samples in order to minimize losses by vaporization and suppress any chemical reaction. Generally within 15-20 min steady-state conditions were obtained. Two samples from each phase were then taken and analyzed chromatographically.

Tests of Apparatus. The apparatus was tested by using a strongly colored solution as a liquid feed (concentrated potassium bichromate solution acidified with sulfuric acid). The condensed vapor was completely colorless. In a second test a KCl solution was employed as a feed, and condensed vapor phase failed to give any precipitate when mixed with a solution of $AgNO_3$. This showed that the vapor was free from liquid droplets which could have been entrained. To test further the accuracy of the Cathala still, we carried out experiments for vapor-liquid equilibrium of a system which is well documented. The system methanol-water was chosen. The agreement between these results and existing literature data was good and confirmed the reliability of the still.

Materials. Distilled water was used. Methanol was of AR quality supplied by James Burrough. Methyl acetate was from BDH Chemicals. The assay (saponification) was not less than 98%. Acetic acid was glacial obtained from Hopkin and Williams with an assay of 99% minimum. Sulfuric acid (the catalyst) was of GPR quality and was supplied by Hopkin and Williams. Hydrogen (the carrier gas for the chromatograph) was pure.

Analytical Procedure. All of the liquid and condensed-vapor samples of the phases in equilibrium were analyzed by liquid-gas chromatography for methyl acetate, methanol, water, and acetic acid with a Perkin-Elmer 452 apparatus provided with a katharometer detector (thermistors). Hydrogen was used as the carrier gas at a flow rate of ~150 cm³/min and under pressure

Table III. Vapor-Liquid Equilibrium Data for the Methyl Acetate-Methanol-Acetic Acid System

Experimental							Calculated					
x_1	x_2	x_3	y_1	y_2	y_3	t, °C	y_1	y_2	y_3	dy_1	dy_2	dy_3
.3343	.0683	.5974	.7094	.1045	.1861	80.3	.7210	.0946	.1844	-.0116	.0099	.0017
.3579	.2176	.4245	.6704	.2690	.0606	70.1	.6651	.2447	.0902	.0053	.0243	-.0296
.0947	.1357	.7696	.2936	.2827	.4237	94.7	.2735	.3030	.4235	.0201	-.0203	.0002
.1662	.4521	.3817	.3937	.5468	.0595	71.3	.3859	.5345	.0795	.0078	.0123	-.0200
.0589	.5433	.3978	.1571	.7696	.0733	76.1	.1661	.7331	.1008	-.0090	.0365	-.0275
.1192	.2974	.5834	.3407	.4790	.1803	82.9	.3144	.4776	.2081	.0263	.0014	-.0278
.2872	.3406	.3722	.5679	.3950	.0371	68.5	.5592	.3710	.0697	.0087	.0240	-.0326
.0514	.1508	.7978	.1667	.3587	.4746	98.4	.1505	.3617	.4878	.0162	-.0030	-.0132
.0695	.6633	.2672	.1875	.7764	.0361	70.0	.1918	.7626	.0456	-.0043	.0138	-.0095
.1145	.3048	.5807	.3314	.4893	.1793	82.9	.3033	.4896	.2071	.0281	-.0003	-.0278
.4343	.1789	.3868	.7323	.2191	.0486	68.2	.7301	.1922	.0778	.0022	.0269	-.0292
.0504	.4819	.4677	.1415	.7510	.1075	79.4	.1439	.7135	.1426	-.0024	.0375	-.0351
.0851	.7281	.1868	.1995	.7898	.0107	65.9	.2252	.7520	.0228	-.0257	.0378	-.0121
.2974	.0684	.6342	.6913	.1045	.2042	81.3	.6833	.1026	.2142	.0080	.0019	-.0100
.0690	.0589	.8721	.2293	.1405	.6302	103.7	.2117	.1655	.6228	.0176	-.0250	.0074
.0529	.1521	.7950	.1738	.3646	.4616	98.3	.1547	.3626	.4826	.0191	.0020	-.0210
.0948	.1874	.7178	.2220	.4100	.3680	90.9	.2671	.3800	.3529	-.0451	.0300	.0151
.0870	.2386	.6744	.2583	.4483	.2934	88.9	.2426	.4524	.3050	.0157	-.0041	-.0116
.4835	.1789	.3376	.7617	.2160	.0223	65.7	.7503	.1861	.0636	.0114	.0299	-.0413
.1986	.4815	.3199	.4387	.5342	.0271	67.7	.4281	.5177	.0542	.0106	.0165	-.0271
.0884	.1564	.7552	.2830	.3402	.3768	93.7	.2540	.3410	.4050	.0290	-.0008	-.0282
.0679	.0938	.8383	.2147	.2307	.5546	100.3	.2034	.2437	.5529	.0113	-.0130	.0017
.0848	.2365	.6787	.2518	.4463	.3019	89.3	.2372	.4524	.3104	.0146	-.0061	-.0085
.0911	.8172	.0917	.2198	.7360	.0442	62.6	.2352	.7575	.0072	-.0154	-.0215	.0370
.3712	.2160	.4128	.6907	.2681	.0412	69.5	.6750	.2392	.0858	.0157	.0289	-.0446
.0718	.6378	.2904	.1870	.7741	.0389	70.6	.1971	.7499	.0530	-.0101	.0242	-.0141
.0621	.1772	.7607	.1897	.3919	.4234	95.2	.1796	.3952	.4251	.0051	-.0033	-.0017
.0255	.1474	.8271	.0886	.3519	.5595	101.5	.0744	.3735	.5521	.0142	-.0216	.0074
.0523	.0458	.9019	.1909	.1258	.6833	106.3	.1616	.1378	.7006	.0293	-.0120	-.0173
.0776	.2139	.7085	.2312	.4270	.3418	91.5	.2198	.4319	.3483	.0114	-.0049	-.0065

Table IV. Vapor-Liquid Equilibrium Data for the Methyl Acetate-Water-Acetic Acid System

Experimental							Calculated					
x_1	x_2	x_3	y_1	y_2	y_3	t, °C	y_1	y_2	y_3	dy_1	dy_2	dy_3
.2356	.6172	.1472	.8159	.1787	.0054	65.5	.7781	.2038	.0181	.0378	-.0251	-.0127
.0185	.6854	.2961	.1942	.6401	.1657	96.2	.2046	.6228	.1727	-.0104	.0173	-.0070
.1847	.6620	.1533	.7967	.1896	.0137	67.6	.7529	.2251	.0221	.0438	-.0355	-.0084
.2734	.4194	.3072	.7524	.2040	.0436	71.8	.7505	.1891	.0603	.0019	.0149	-.0167
.1302	.6730	.1968	.7040	.2685	.0275	72.7	.6826	.2755	.0418	.0214	-.0070	-.0143
.2479	.6091	.1430	.8256	.1680	.0064	65.0	.7834	.1997	.0170	.0422	-.0317	-.0106
.0088	.6805	.3107	.0922	.7127	.1951	99.6	.1046	.6915	.2039	-.0124	.0212	-.0088
.0522	.1718	.7760	.2113	.2454	.5433	103.4	.1954	.2476	.5570	.0159	-.0022	-.0137
.1494	.7280	.1226	.7833	.2106	.0061	67.5	.7437	.2388	.0176	.0396	-.0282	-.0115
.3901	.2331	.3768	.8256	.1300	.0444	71.7	.8054	.1149	.0797	.0202	.0151	-.0353
.0196	.6289	.3515	.1751	.6221	.2028	97.6	.1872	.5992	.2136	-.0121	.0229	-.0108
.0252	.6447	.3301	.2380	.5856	.1764	95.2	.2399	.5733	.1868	-.0019	.0123	-.0104
.2851	.4129	.3020	.7768	.1923	.0309	71.9	.7581	.1841	.0578	.0187	.0082	-.0269
.4332	.2315	.3353	.8310	.1309	.0381	69.3	.8253	.1093	.0654	.0057	.0216	-.0273
.0035	.8127	.1838	.0710	.8097	.1193	99.1	.0652	.8203	.1145	.0058	-.0106	.0048
.0048	.8194	.1758	.0679	.8234	.1087	99.2	.0896	.8045	.1059	-.0217	.0189	.0028
.0537	.1597	.7866	.2165	.2335	.5500	103.3	.1980	.2338	.5682	.0185	-.0003	-.0182
.0112	.6754	.3134	.1289	.6807	.1904	98.6	.1286	.6708	.2006	.0003	.0099	-.0102
.6322	.0555	.3123	.9174	.0423	.0403	66.0	.9007	.0268	.0726	.0167	.0155	-.0323
.0127	.6950	.2923	.1479	.6811	.1710	97.7	.1516	.6677	.1807	-.0037	.0134	-.0097
.2445	.4098	.3457	.7574	.2065	.0361	73.4	.7215	.2002	.0783	.0359	.0063	-.0422
.0262	.2584	.7154	.1155	.3523	.5322	105.1	.1132	.3569	.5299	.0023	-.0046	.0023
.0327	.4702	.4971	.1982	.5050	.2968	98.8	.2059	.4867	.3075	-.0077	.0183	-.0107
.0329	.4662	.5009	.1989	.5037	.2974	98.6	.2053	.4841	.3106	-.0064	.0196	-.0132
.0015	.9083	.0902	.0467	.8918	.0615	98.9	.0394	.9127	.0479	.0073	-.0209	.0136
.0008	.9637	.0355	.0478	.9281	.0241	98.8	.0256	.9593	.0151	.0222	-.0312	.0090
.5913	.0598	.3489	.9087	.0462	.0451	67.8	.8912	.0288	.0800	.0175	.0174	-.0349
.2684	.4199	.3117	.7371	.2119	.0510	71.9	.7464	.1910	.0626	-.0093	.0209	-.0116
.0190	.6003	.3807	.1404	.6285	.2311	99.2	.1701	.5917	.2382	-.0297	.0368	-.0071
.2447	.4793	.2760	.7330	.2339	.0331	70.6	.7420	.2057	.0523	-.0090	.0282	-.0192
.1779	.5172	.3049	.7339	.2331	.0330	75.9	.6793	.2476	.0731	.0546	-.0145	-.0401
.0172	.6035	.3793	.1359	.6325	.2316	99.4	.1570	.6023	.2407	-.0211	.0302	-.0091
.6061	.1174	.2765	.9082	.0758	.0160	64.5	.8857	.0564	.0579	.0225	.0194	-.0419
.0009	.9624	.0367	.0515	.9243	.0242	98.7	.0287	.9557	.0156	.0228	-.0314	.0086
.1166	.7554	.1280	.7153	.2707	.0140	69.8	.7079	.2702	.0219	.0074	.0005	-.0079
.1327	.6367	.2306	.6863	.2786	.0351	75.1	.6659	.2804	.0537	.0204	-.0018	-.0186
.1278	.6346	.2376	.6829	.2782	.0389	76.0	.6550	.2873	.0577	.0279	-.0091	-.0188
.5844	.1222	.2934	.8943	.0778	.0279	65.8	.8808	.0584	.0608	.0135	.0194	-.0329
.0904	.6681	.2415	.6095	.3367	.0538	80.25	.5838	.3442	.0720	.0257	-.0075	-.0182

of 1.72 bar at the entrance of the packed column. The sample (1 mm^3) was passed through a 2-m length $^3/_{16}$-in. diameter Poropak-Q column maintained at 150 °C.

The accuracy of the method was assessed by analyzing chromatographically the composition of standard test mixtures. The mean deviation between the analyzed and known component concentrations was found to be 0.5 wt %. Additional details of the analytical and operational procedure are given in ref *29*.

Results and Discussion

In the present work initially the Wilson and the NRTL equations were tested. In the NRTL equation τ_{ij} and τ_{ji} were ad-

Table V. Vapor-Liquid Equilibrium Data for the Methanol-Water-Acetic Acid System

Experimental							Calculated					
x_1	x_2	x_3	y_1	y_2	y_3	t, °C	y_1	y_2	y_3	dy_1	dy_2	dy_3
.1148	.6056	.2796	.3442	.5361	.1197	93.4	.3506	.5204	.1290	-.0064	.0157	-.0093
.0344	.6787	.2869	.1312	.7030	.1658	99.6	.1312	.6903	.1785	.0000	.0127	-.0127
.3555	.5899	.0546	.7039	.2682	.0279	79.0	.7040	.2899	.0061	-.0001	-.0217	.0218
.0178	.9141	.0681	.0544	.8985	.0471	98.3	.1042	.8653	.0305	-.0498	.0332	.0166
.3362	.5591	.1047	.7079	.2790	.0131	80.6	.6855	.2990	.0155	.0224	-.0200	-.0024
.1724	.8097	.0179	.5984	.3991	.0025	84.1	.5418	.4557	.0025	.0566	-.0566	.0000
.3795	.5258	.0947	.7237	.2608	.0155	79.4	.7177	.2695	.0127	.0060	-.0087	.0028
.1641	.7961	.0398	.5407	.4492	.0101	85.3	.5224	.4706	.0070	.0183	-.0214	.0031
.4069	.5223	.0708	.7530	.2394	.0076	78.6	.7368	.2555	.0077	.0162	-.0161	-.0001
.0264	.3894	.5842	.0776	.5010	.4214	104.6	.0781	.4895	.4324	-.0005	.0115	-.0110
.1268	.5316	.3416	.3741	.4867	.1392	94.3	.3599	.4739	.1661	.0142	.0128	-.0269
.1482	.8090	.0428	.5304	.4587	.0109	85.5	.4966	.4952	.0082	.0338	-.0365	.0027
.0321	.4019	.5660	.0796	.5083	.4121	104.3	.0949	.4937	.4114	-.0153	.0146	.0007
.0399	.6684	.2917	.1515	.6897	.1588	98.9	.1486	.6732	.1782	.0029	.0165	-.0194
.0361	.6818	.2821	.1475	.6972	.1553	99.3	.1378	.6888	.1735	.0097	.0084	-.0182
.4386	.4855	.0759	.7765	.2157	.0078	77.4	.7563	.2357	.0080	.0202	-.0200	-.0002
.1632	.8165	.0203	.5716	.4235	.0049	84.9	.5280	.4690	.0030	.0436	-.0455	.0019
.1913	.7880	.0207	.6263	.3697	.0040	83.3	.5654	.4319	.0028	.0609	-.0622	.0012
.0214	.9098	.0688	.1316	.8273	.0411	97.7	.1225	.8475	.0301	.0091	-.0202	.0110
.4177	.4968	.0855	.7376	.2506	.0118	78.5	.7433	.2465	.0102	-.0057	.0041	.0016
.0467	.6815	.2718	.1786	.6782	.1432	98.3	.1745	.6669	.1585	.0041	.0113	-.0153
.3395	.5184	.1421	.6892	.2676	.0432	81.4	.6841	.2904	.0255	.0051	-.0228	.0177
.2225	.5762	.2013	.5558	.3869	.0573	87.8	.5534	.3891	.0575	.0024	-.0022	-.0002
.3387	.5617	.0996	.7632	.2305	.0063	80.6	.6880	.2977	.0142	.0752	-.0672	-.0079
.3985	.5217	.0798	.7500	.2411	.0089	78.7	.7314	.2595	.0092	.0186	-.0184	-.0003
.0702	.5801	.3497	.2190	.5949	.1861	97.9	.2256	.5718	.2026	-.0066	.0231	-.0165
.0889	.6060	.3051	.2865	.5717	.1418	95.7	.2839	.5574	.1587	.0026	.0143	-.0169
.3583	.5865	.0552	.7309	.2634	.0057	78.6	.7060	.2881	.0059	.0249	-.0247	-.0002

justable parameters. The third parameter, α_{ij}, was estimated according to both Renon's and Prausnitz's rules as well as calculated as a third adjustable parameter. From this fit only poor agreement between the experimental and predicted y values was obtained. This was also the case obtained by Jenkins and Gibson-Robinson when they tried to correlate data containing acetic acid with the Wilson and NRTL equations (*5*).

Since acetic acid associates in the vapor and liquid phases, Marek's method for association of acetic acid had to be used in combination with one of the usual equations.

Best results for the binary systems were obtained when Marek's method was used in combination with the Margules or NRTL equations (in the case of the NRTL equation when all three parameters were determined). The predictions for the ternary and quaternary systems with the NRTL equation were, however, not as good as those obtained with the Margules (third-order) equation. This is explained since the Margules equation is a higher form of the integrated Gibbs-Duhem equation and contains ternary determined constants to correlate the complex system. For this reason the Margules equation was finally used. The most precise of the available methods to calculate the constants in the Margules equation is from the known equilibrium compositions of the vapor and the liquid (*30*). This was therefore adopted for the present work. Data fits were computed for all systems. For the calculation of the binary and ternary constants, a computer program with a routine based on Powell's work (*31*) was used to minimize the sum of squares of the deviations of the vapor-phase mole fractions (*25*). For the quaternary system the quaternary Margules equation as expressed by Marek (*32*) was used, and no constants needed to be determined. Calculated y values as well as deviations in the y values for all experimentally determined vapor-liquid equilibrium data are contained in Tables I-VI. The references used for the experimental points, the values calculated for the binary (A_{12}, A_{21}) and ternary (C) Margules constants, as well as the values of the root mean square deviations (rmsds) for the binary, ternary , and quaternary fits are as follows: methyl acetate-methanol (*9*), A_{12} = 0.4416, A_{21} = 0.4335, rmsd = 0.005; methyl acetate-water (*9*), A_{12} = 1.0045, A_{21} = 0.6764, rmsd = 0.023; methyl acetate-acetic acid (Table I), A_{12} = -0.1026, A_{21} = 0.6118, rmsd = 0.020; methanol-water (*13*), A_{12} = 0.3444, A_{21} = 0.2268, rmsd = 0.005; methanol-acetic acid (Table II), A_{12} = -0.0305, A_{21} = 0.0098, rmsd = 0.009; water-acetic acid (*9*), A_{12} = 0.2569, A_{21} = 0.2940, rmsd = 0.010; methyl acetate-methanol-water (*10*), C = -0.1201, rmsd = 0.035; methyl acetate-methanol-acetic acid (Table III), C = -0.12, rmsd = 0.020; methyl acetate-water-acetic acid (Table IV), C = -0.0953, rmsd = 0.021; methanol-water-acetic acid (Table V), C = 0.3546, rmsd = 0.024; methyl acetate-methanol-water-acetic acid (Table VI), rmsd = 0.023. In figures 1-6 all binary data points are plotted for the more volatile component showing x vs. y values as well as x vs. deviation in the y values. Experimental results proved to be in good agreement with predicted vapor compositions for the binary, ternary, and quaternary systems. Some binary systems were highly nonideal. Thus, methyl

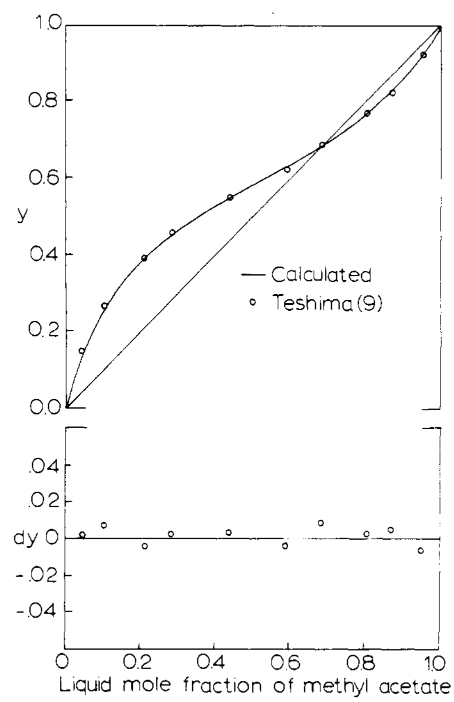

Figure 1. Plots of liquid vs. vapor and liquid vs. deviation in vapor composition for the methyl acetate-methanol system.

Table VI. Vapor-Liquid Equilibrium Data for the Methyl Acetate-Methanol-Water-Acetic Acid System

H_2SO_4	Experimental							Calculated							
W%	x_1	x_2	x_3	y_1	y_2	y_3	t, °C	y_1	y_2	y_3	y_4	dy_1	dy_2	dy_3	dy_4
0	.0912	.1947	.5280	.4471	.2863	.2404	74.20	.4521	.2972	.2215	.0291	-.0050	-.0109	.0189	-.0029
4	.2011	.6096	.1837	.4824	.4588	.0546	58.80	.4416	.4983	.0600	.0002	.0408	-.0395	-.0054	.0040
5	.0414	.0900	.8002	.4791	.1988	.3022	76.20	.4294	.2154	.3440	.0112	.0497	-.0166	-.0418	.0087
0	.0136	.0835	.7967	.2060	.2615	.4961	86.80	.1935	.2738	.5024	.0303	.0125	-.0123	-.0063	.0061
0	.1958	.6769	.0083	.3583	.5448	.0923	61.70	.3969	.5910	.0031	.0090	-.0386	-.0462	.0892	-.0044
0	.0373	.1974	.6396	.2998	.3933	.2853	77.90	.2945	.3877	.2966	.0212	.0053	.0056	-.0113	.0004
0	.0370	.1998	.6024	.2667	.3842	.3170	79.30	.2771	.3926	.2987	.0315	-.0104	-.0084	.0183	.0006
0	.1265	.0827	.5223	.5754	.1304	.2567	76.20	.5611	.1342	.2452	.0595	.0143	-.0038	.0115	-.0220
5	.1693	.2173	.5402	.6161	.1803	.1507	63.20	.5859	.2495	.1597	.0049	.0302	-.0692	-.0090	.0480
0	.0409	.0585	.7128	.4011	.1420	.4041	83.60	.3822	.1497	.4105	.0576	.0189	-.0077	-.0064	-.0048
0	.0548	.3971	.1512	.1702	.6276	.1077	80.85	.1945	.6088	.0885	.1081	-.0243	.0188	.0192	-.0136
0	.0625	.2067	.4802	.3165	.3564	.2743	79.50	.3391	.3568	.2486	.0555	-.0226	-.0004	.0257	-.0027
0	.0556	.0330	.7569	.5358	.0712	.3600	78.60	.5024	.0805	.3766	.0405	.0334	-.0093	-.0166	-.0075
2	.0237	.0441	.7474	.2354	.1507	.5276	90.35	.2803	.1380	.5107	.0709	-.0449	.0127	.0169	.0154
0	.1065	.1902	.2045	.3408	.3136	.1776	84.90	.3637	.3243	.1416	.1704	-.0229	-.0107	.0360	-.0024
0	.1049	.0618	.4971	.4776	.1161	.3153	82.10	.5028	.1132	.2844	.0997	-.0252	.0029	.0309	-.0087
0	.0570	.1686	.3855	.2562	.3355	.2848	85.80	.2824	.3247	.2610	.1319	-.0262	.0108	.0238	-.0084
0	.0277	.1827	.6579	.2382	.4099	.3280	80.45	.2452	.3969	.3327	.0253	-.0070	.0130	-.0047	-.0014
0	.1008	.0398	.7116	.6482	.0635	.2665	72.50	.6229	.0733	.2768	.0271	.0253	-.0098	-.0103	-.0053
0	.0245	.1699	.7257	.2611	.3909	.3348	78.60	.2510	.3918	.3444	.0129	.0101	-.0009	-.0096	.0003
0	.0570	.1259	.2213	.1963	.2674	.2456	94.00	.2248	.2721	.2075	.2955	-.0285	-.0047	.0381	-.0048
0	.0886	.2724	.4608	.3876	.3813	.2161	72.90	.4037	.3818	.1901	.0244	-.0161	-.0005	.0260	-.0094
2	.0196	.0525	.8030	.2409	.1909	.5145	88.00	.2708	.1745	.5140	.0407	-.0299	.0164	.0005	.0130
0	.0295	.0875	.5091	.1855	.2187	.4421	91.70	.2043	.2171	.4101	.1686	-.0188	.0016	.0320	-.0149
0	.0127	.0535	.7251	.1499	.1690	.5880	92.20	.1592	.1805	.5677	.0926	-.0093	-.0115	.0203	.0005
0	.0704	.1238	.5198	.3515	.2425	.3397	83.35	.3962	.2341	.2911	.0787	-.0447	.0084	.0486	-.0124
0	.0244	.1511	.6878	.2213	.3934	.3542	81.80	.2379	.3610	.3704	.0307	-.0166	.0324	-.0162	.0004
0	.0699	.0944	.5969	.4287	.1798	.3334	80.60	.4404	.1860	.3115	.0622	-.0117	-.0062	.0219	-.0041
0	.0605	.3742	.1431	.1813	.6150	.0974	81.25	.2094	.5829	.0863	.1215	-.0281	.0321	.0111	-.0152
4	.0197	.0696	.8426	.2341	.2620	.4725	86.30	.2887	.2254	.4702	.0158	-.0546	.0366	.0023	.0156
0	.0116	.0491	.7249	.1463	.1587	.5977	92.80	.1476	.1694	.5844	.0987	-.0013	-.0107	.0133	-.0014
0	.0267	.0810	.5135	.1692	.2090	.4565	92.80	.1894	.2065	.4261	.1780	-.0202	.0025	.0304	-.0127
0	.0713	.1216	.5194	.3756	.2321	.3222	83.40	.3997	.2299	.2913	.0792	-.0241	.0022	.0309	-.0091
2	.0317	.0531	.7279	.2954	.1714	.4618	88.15	.3312	.1493	.4551	.0644	-.0358	.0221	.0067	.0070
4	.1291	.0519	.6043	.5421	.1375	.2631	78.40	.6174	.0857	.2535	.0434	-.0753	.0518	.0096	.0139
0	.0682	.2353	.4933	.3470	.3650	.2566	76.40	.3611	.3759	.2273	.0356	-.0141	-.0109	.0293	-.0042
0	.0964	.3669	.2900	.3357	.4863	.1501	72.90	.3520	.4775	.1313	.0391	-.0163	.0088	.0188	-.0112
0	.2468	.3765	.1189	.5048	.4071	.0676	66.20	.5279	.3889	.0493	.0338	-.0231	.0182	.0183	-.0133
0	.1174	.0691	.4604	.5218	.1185	.2760	81.45	.5145	.1210	.2625	.1020	.0073	-.0025	.0135	-.0183
4	.1064	.0380	.6187	.5233	.1095	.2937	81.80	.5809	.0699	.2907	.0585	-.0576	.0396	.0030	.0150
0	.0884	.3504	.3026	.3228	.4769	.1625	74.20	.3382	.4756	.1420	.0442	-.0154	.0013	.0205	-.0064
4	.3686	.2055	.3540	.7091	.1884	.0968	60.70	.6689	.2087	.1183	.0042	.0402	-.0203	-.0215	.0015
0	.0813	.1457	.4733	.3931	.2492	.2869	80.95	.4074	.2563	.2588	.0775	-.0143	-.0071	.0281	-.0067
4	.3893	.1920	.3472	.7292	.1624	.1026	60.60	.6800	.1975	.1183	.0042	.0492	-.0351	-.0157	.0016
0	.0576	.1271	.2234	.2014	.2750	.2354	93.85	.2276	.2735	.2079	.2910	-.0262	.0015	.0275	-.0028
0	.0244	.1371	.6464	.1905	.3484	.4032	85.30	.2228	.3338	.3887	.0547	-.0323	.0146	.0145	.0032
4	.1110	.0391	.6111	.5282	.1129	.2846	81.35	.5873	.0706	.2843	.0579	-.0591	.0423	.0003	.0164
2	.0073	.0631	.7895	.1226	.2244	.5931	90.90	.1133	.2358	.5969	.0540	.0093	-.0114	-.0038	.0059
4	.1122	.0073	.3810	.5015	.0211	.2343	90.20	.4730	.0148	.3001	.2121	.0285	.0063	-.0658	.0310
0	.0096	.0389	.5608	.0714	.1145	.5942	98.60	.0832	.1204	.5596	.2368	-.0118	-.0059	.0346	-.0169
0	.1044	.1769	.6135	.5544	.2337	.2016	69.00	.5255	.2547	.2090	.0108	.0289	-.0210	-.0074	-.0005
0	.1192	.0475	.6159	.6348	.0785	.2569	74.80	.6058	.0817	.2666	.0458	.0290	-.0032	-.0097	-.0160
2	.0057	.0057	.8231	.0916	.0373	.7599	98.20	.1055	.0268	.7745	.0932	-.0139	.0105	-.0146	.0180
0	.0092	.0725	.7820	.1412	.2568	.5511	89.65	.1355	.2559	.5601	.0485	.0057	.0009	-.0090	.0024
0	.1337	.1726	.5894	.5829	.2103	.1964	67.10	.5718	.2284	.1898	.0100	.0111	-.0181	.0066	.0004
0	.1231	.0798	.5247	.5666	.1274	.2629	76.90	.5561	.1315	.2505	.0619	.0105	-.0041	.0124	-.0188
0	.1220	.0715	.4540	.5043	.1088	.2962	80.95	.5218	.1231	.2556	.0994	-.0175	-.0143	.0406	-.0087
4	.1763	.6252	.1923	.4577	.4742	.0651	59.70	.4176	.5195	.0627	.0002	.0401	-.0453	.0024	.0028
0	.0879	.1575	.4703	.4129	.2592	.2720	79.25	.4242	.2649	.2437	.0673	-.0113	-.0057	.0283	-.0114
0	.0797	.1736	.5478	.4230	.2841	.2650	76.40	.4323	.2865	.2453	.0360	-.0093	-.0024	.0197	-.0081
0	.0129	.0775	.7996	.2069	.2502	.5050	87.20	.1876	.2611	.5184	.0330	.0193	-.0109	-.0134	.0049
0	.0312	.1383	.7244	.3306	.3071	.3410	79.10	.3057	.3218	.3520	.0205	.0249	-.0147	-.0110	.0008
0	.1179	.0423	.6704	.6513	.0635	.2634	72.50	.6357	.0728	.2610	.0305	.0156	-.0093	.0024	-.0087
0	.0546	.2020	.4675	.2829	.3677	.2866	81.80	.3039	.3659	.2610	.0691	-.0210	.0018	.0256	-.0063
0	.1079	.1930	.2112	.3445	.3190	.1799	84.00	.3693	.3250	.1433	.1623	-.0248	-.0060	.0366	-.0057
0	.1022	.3976	.3249	.3306	.4852	.1460	70.75	.3726	.4767	.1302	.0205	-.0420	.0085	.0158	.0177
0	.1043	.3928	.3242	.3406	.4965	.1494	70.85	.3778	.4716	.1303	.0204	-.0372	.0249	.0191	-.0069
2	.0353	.0998	.7730	.3494	.2584	.3681	80.40	.3703	.2461	.3659	.0178	-.0209	.0123	.0022	.0063
2	.0348	.0962	.7762	.3493	.2471	.3767	80.70	.3699	.2405	.3712	.0184	-.0206	.0066	.0055	.0085
0	.0026	.0137	.8303	.0401	.0668	.7994	98.20	.0511	.0667	.7969	.0853	-.0110	.0001	.0025	.0084
0	.0082	.0646	.7892	.1266	.2352	.5816	90.40	.1255	.2375	.5853	.0518	.0011	-.0023	-.0037	.0048
5	.1303	.0454	.6273	.6715	.0552	.2290	73.00	.6344	.0750	.2526	.0380	.0371	-.0198	-.0236	.0063
0	.0480	.0469	.7731	.5413	.1121	.3255	79.20	.4687	.1177	.3812	.0324	.0726	-.0056	-.0557	-.0113
0	.0698	.1164	.5225	.3768	.2329	.3227	83.40	.3965	.2234	.2975	.0826	-.0197	.0095	.0252	-.0150

Table VI (*Continued*)

H_2SO_4	Experimental							Calculated							
wt%	x_1	x_2	x_3	y_1	y_2	y_3	t, °C	y_1	y_2	y_3	y_4	dy_1	dy_2	dy_3	dy_4
0	.1418	.0493	.6005	.6424	.0727	.2585	72.50	.6400	.0786	.2427	.0388	.0024	-.0059	.0158	-.0124
2	.0124	.0516	.8125	.1508	.2102	.5823	90.60	.1922	.1899	.5735	.0444	-.0414	.0203	.0088	.0123
4	.1344	.0522	.6022	.5677	.1201	.2583	77.40	.6262	.0846	.2480	.0412	-.0585	.0355	.0103	.0127
0	.0137	.0935	.6732	.1187	.2878	.5118	90.50	.1481	.2759	.4917	.0843	-.0294	.0119	.0201	-.0026
0	.0232	.1459	.6423	.1946	.3673	.3886	84.50	.2117	.3525	.3843	.0515	-.0171	.0148	.0043	-.0020
0	.0119	.0864	.6802	.1203	.2581	.5340	91.20	.1333	.2643	.5130	.0894	-.0130	-.0062	.0210	-.0018
2	.0249	.0408	.7489	.2238	.1547	.5336	90.30	.2926	.1273	.5089	.0712	-.0688	.0274	.0247	.0167
0	.0922	.0363	.7222	.6420	.0622	.2719	73.50	.6092	.0701	.2915	.0292	.0328	-.0079	-.0196	-.0053
4	.1971	.1362	.5175	.6058	.2014	.1628	69.95	.6409	.1689	.1741	.0161	-.0351	.0325	-.0113	.0139
2	.0241	.0345	.7561	.2240	.1384	.5457	91.30	.2914	.1107	.5243	.0737	-.0674	.0277	.0214	.0182
0	.0615	.1308	.7541	.5551	.2102	.2310	69.00	.4840	.2445	.2660	.0055	.0711	-.0343	-.0350	-.0018
0	.0424	.0436	.7853	.5145	.1081	.3535	80.00	.4465	.1161	.4044	.0330	.0680	-.0080	-.0509	-.0091
4	.1752	.2805	.4766	.5257	.3202	.1480	66.60	.5537	.2994	.1428	.0040	-.0280	.0208	.0052	.0021
0	.0097	.1116	.7852	.1378	.3586	.4759	86.40	.1377	.3543	.4842	.0239	.0001	.0043	-.0083	.0038
0	.0084	.1011	.7949	.1305	.3384	.4945	87.35	.1252	.3378	.5109	.0261	.0053	.0006	-.0164	.0105
4	.0114	.0521	.8684	.1620	.2280	.5701	90.30	.2041	.2043	.5723	.0193	-.0421	.0237	-.0022	.0206
0	.1654	.6446	.0773	.3381	.5911	.0632	62.50	.3809	.5824	.0287	.0080	-.0428	.0087	.0345	-.0004
0	.1240	.0480	.6089	.6258	.0763	.2684	74.60	.6118	.0812	.2615	.0454	.0140	-.0049	.0069	-.0159
0	.0393	.2113	.5897	.2873	.3878	.2984	78.10	.2831	.4013	.2864	.0291	.0042	-.0135	.0120	-.0026
4	.1991	.0236	.4709	.6831	.0533	.1861	80.45	.6778	.0354	.2190	.0679	.0053	.0179	-.0329	.0096
4	.1775	.3063	.4359	.5201	.3443	.1256	66.20	.5385	.3209	.1354	.0053	-.0184	.0234	-.0098	.0047
4	.1721	.2954	.4609	.5224	.3286	.1422	66.50	.5420	.3134	.1402	.0044	-.0196	.0152	.0020	.0024
0	.0583	.1258	.2238	.1860	.2668	.2463	94.20	.2299	.2703	.2080	.2918	-.0439	-.0035	.0383	.0091
4	.2089	.1382	.4822	.6048	.2011	.1642	71.15	.6414	.1695	.1690	.0200	-.0366	.0316	-.0048	.0099
0	.0248	.1447	.7446	.3007	.3511	.3330	79.40	.2663	.3531	.3654	.0152	.0344	-.0020	-.0324	.0000
0	.0413	.0591	.7109	.4008	.1451	.4037	83.50	.3833	.1505	.4087	.0575	.0175	-.0054	-.0050	-.0071
0	.0183	.1305	.7416	.2362	.3445	.3944	82.50	.2118	.3509	.4125	.0248	.0244	-.0064	-.0181	.0001
4	.1379	.0520	.6062	.5700	.1242	.2561	76.90	.6345	.0833	.2439	.0383	-.0645	.0409	.0122	.0114
0	.2558	.0934	.5158	.7302	.0940	.1706	64.60	.7063	.1131	.1682	.0124	.0239	-.0191	.0024	-.0072
2	.0149	.0480	.8124	.1962	.1865	.5568	89.90	.2243	.1726	.5592	.0438	-.0281	.0139	-.0024	.0167
2	.0055	.0056	.8292	.0916	.0373	.7599	98.20	.1040	.0266	.7800	.0894	-.0124	.0107	-.0201	.0218
0	.0916	.0366	.7211	.6420	.0622	.2719	73.70	.6067	.0709	.2927	.0297	.0353	-.0087	-.0208	-.0058
0	.0697	.0946	.6081	.4313	.1820	.3346	80.40	.4460	.1862	.3105	.0573	-.0147	-.0042	.0241	-.0052
0	.1215	.3182	.4007	.4443	.3812	.1629	68.80	.4476	.3847	.1509	.0169	-.0033	-.0035	.0120	-.0053
0	.0974	.0357	.6879	.6261	.0603	.2850	74.70	.6015	.0677	.2924	.0384	.0246	-.0074	-.0074	-.0098
0	.2550	.0929	.5177	.7367	.0885	.1643	64.70	.7063	.1126	.1685	.0125	.0304	-.0241	-.0042	-.0020
0	.0934	.2811	.4459	.3938	.3820	.2027	72.30	.4091	.3846	.1824	.0238	-.0153	-.0026	.0203	-.0023
0	.0602	.1310	.7527	.5551	.2102	.2310	69.00	.4780	.2470	.2691	.0059	.0771	-.0368	-.0381	-.0022
0	.2542	.3693	.1397	.5046	.4065	.0713	66.10	.5392	.3756	.0565	.0286	-.0346	.0309	.0148	-.0110

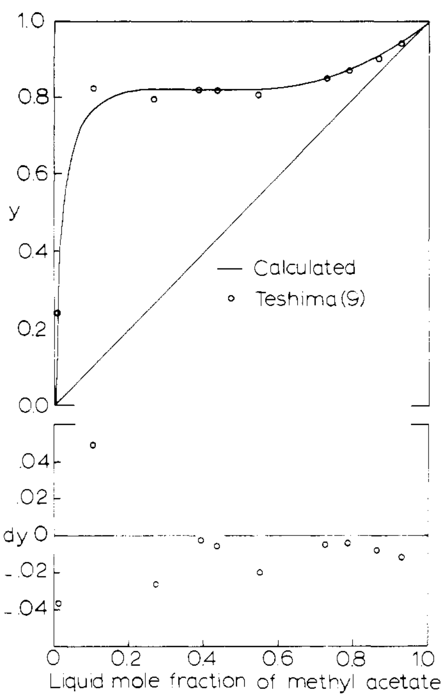

Figure 2. Plots of liquid vs. vapor and liquid vs. deviation in vapor composition for the methyl acetate–water system.

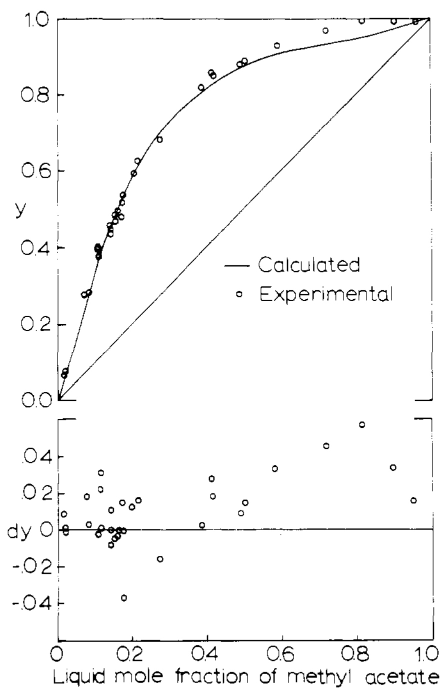

Figure 3. Plots of liquid vs. vapor and liquid vs. deviation in vapor composition for the methyl acetate–acetic acid system.

acetate–water was only partially miscible (*9*), whereas methyl acetate–methanol exhibited an azeotrope at 0.323 mole fraction of methanol and a corresponding minimum boiling point of 54 °C (*9*). System c was inaccurate for vapor mole fractions of ester higher than 0.90. It might be argued that the fit for this system could be improved by use of the Jenkins and Gibson-Robinson equation which includes a liquid-phase association factor (*5*). This is, however, unlikely since the inaccuracy occurs at the low acetic acid concentration end, and, in view of the wish to limit this study to the Marek equation, this test was outside the scope of this paper.

Since during operation of a reaction/distillation column sulfuric acid is present as a catalyst, it was necessary to investigate the quaternary system in the presence of this catalyst. It was

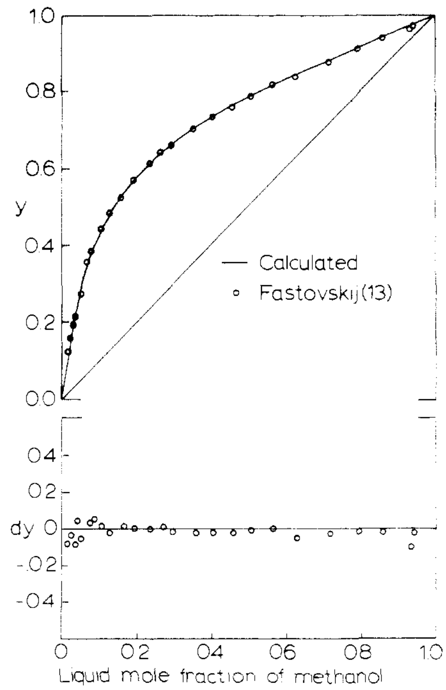

Figure 4. Plots of liquid vs. vapor and liquid vs. deviation in vapor composition for the methanol-water system.

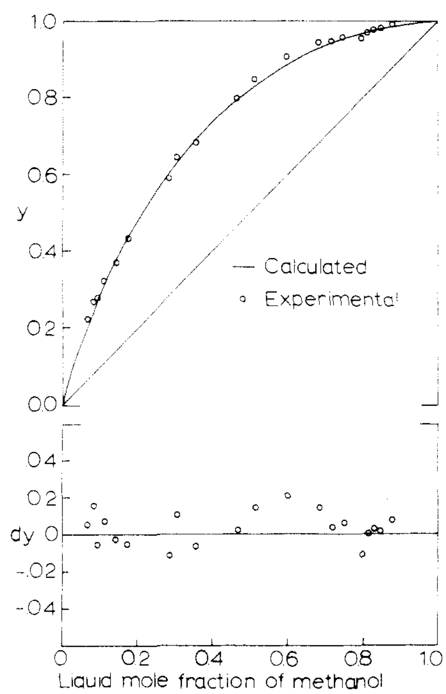

Figure 5. Plots of liquid vs. vapor and liquid vs. deviation in vapor composition for the methanol-acetic acid system.

found that the same vapor-liquid equilibrium equations were valid even when the nonvolatile catalyst was present. Teshima, et al. (*33*) expressed the influence of sulfuric acid catalyst on vapor-liquid equilibrium of the system water-acetic acid by an equation which provided further proof that the effect of the catalyst was negligible. Hirata and Komatsu (*34*) investigated the same quaternary system and presented four equations to predict the vapor-liquid equilibrium ratios as a function of temperature. Their equations were tested in the present work with known equilibrium data, and the results were found to be unsatisfactory.

Suzuki et al. (*35*) also tried to simulate the system with the Margules equation modified by Marek, but they reported that their trial failed to obtain a good relation. This is believed to be

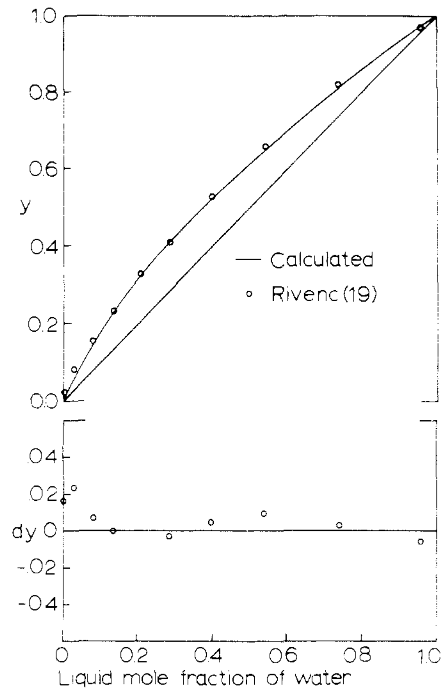

Figure 6. Plots of liquid vs. vapor and liquid vs. deviation in vapor composition for the water-acetic acid system.

due to the fact that they only used quaternary experimental data to fit their constants. They then presented an equation to calculate the activity coefficients of this quaternary system. Their equation, which consisted of 64 constants, was based on the Margules equation rearranged as a polynomial series in mole fractions of the components in the mixture. Their equation was tested with binary, ternary, and quaternary vapor-liquid equilibrium data, and the results were also found to be unsatisfactory.

Further studies of vapor-liquid relations, for quaternary systems of esterification of acetic acid with butanol and ethanol, were made by Hirata and Komatsu (*36*, *37*). They derived some relations with graphical correlation to predict vapor-liquid equilibrium ratios as a function of temperature. Their quaternary system was, however, outside the scope of this article, and their equations were not tested.

Finally, Sebastiani and Lacquaniti (*38*) have also taken into account the association of acetic acid in their equation to correlate acetic acid-water binary systems. They introduced a temperature influence on the activity coefficient and explained that this played a very important role in the thermodynamic correlation.

Consistency Testing of Binaries

All six binaries fitted a binary third-order Margules equation, in combination with Marek's equations for association of acetic acid, and were therefore considered thermodynamically consistent (*39*). System b presented some deviations mainly due to its strong nonideality, but this system satisfied Herington's test of consistency. System c did not satisfy Herington's test, but this was probably due to the fact that the boiling point of the components of this sytem were widely different. Furthermore, systems a and d-f satisfied Herington's test.

Acknowledgment

We express our gratitude to ICI-Europa for permission to use its computer.

Appendix

A model was developed by Marek and Standart (*3*) and by Marek (*4*) leading to the final correlations presented here. Thus, according to Marek, for the associating component A

$$\Pi y_A Z_A = P_{Ac}{}^0 x_A \gamma_A \quad (3)$$

where

$$Z_A = \frac{[1 + 4K\Pi y_A(2 - y_A)]^{1/2}}{2K\Pi y_A(2 - y_A)} \quad (4)$$

Similarly, for the nonassociating component B

$$\Pi y_B Z_B z_B = P_B{}^0 x_B \gamma_B \quad (5)$$

where

$$Z_B = \frac{2\{1 - y_A + [1 + 4K\Pi y_A(2 - y_A)]^{1/2}\}}{(2 - y_A)\{1 + [1 + 4K\Pi y_A(2 - y_A)]^{1/2}\}} \quad (6)$$

The factors Z_A and Z_B, which express the influence of the vapor-phase association of A, may be evaluated from a knowledge of its association constant K. The factor z_B is a correction for the nonideality in the liquid phase and may be evaluated from various generalized relations, for example, from the Scheibel correlation. The corrected vapor pressure of the associating component, $P_{Ac}{}^0$, and the vapor pressure of the nonassociating component $P_B{}^0$ may be determined from the properties of the pure substances. The dependence of the activity coefficients γ_A and γ_B on the liquid-phase composition may be expressed by means of suitable equations. The usual empirical equations containing an adequate number of empirical constants may then be used for the correlation.

Glossary

A_{12}, A_{21}	constants in Margules' binary equation
C	constant in Margules' ternary equation
K	association constant
$P_{Ac}{}^0$	corrected vapor pressure of acetic acid
$P_B{}^0$	vapor pressure of nonassociating component
t	temperature, °C
x_i	mole fraction of component i in the liquid phase
y_i	mole fraction of component i in the vapor phase
Z_A	factor for the influence of the vapor-phase association of A
Z_B	factor for the influence of the vapor-phase association of B
z_B	factor for the correction of nonideality in the liquid phase
γ_i	activity coefficient of component i
Π	total pressure

Subscripts

A	associating component, i.e., acetic acid
B	nonassociating component, i.e., methyl acetate, methanol, or water
c	correction
i	component i

Literature Cited

(1) Sawistowski, H.; Pilavakis, P. A. "International Symposium on Distillation"; Institution of Chemical Engineers: London, 1979; Vol. 2, p 4.2/49.
(2) Sabylin, I. I.; Aristovich, V. Yu. *Zh. Prikl. Khim.* (*Leningrad*) **1970**, *43*, 2021.
(3) Marek, J.; Standart, G. *Collect. Czech. Chem. Commun.* **1954**, *19*, 1074.
(4) Marek, J. *Collect. Czech. Chem. Commun.* **1955**, *20*, 1490.
(5) Jenkins, J. D.; Gibson-Robinson, M. "International Symposium on Distillation"; Institution of Chemical Engineers: London, 1979; Vol. 1, p 1.1/17.
(6) Jenkins, J. D.; Gibson-Robinson, M. *Chem. Eng. Sci.* **1977**, *32*, 931.
(7) Nitta, T.; Takeuchi, S.; Katayama, T. *Chem. Eng. Sci.* **1974**, *29*, 2213.
(8) Franks, F. "Water—A Comprehensive Treatise", 1st ed.; Plenum Press: New York, 1972; Vol. 1.
(9) Teshima, T.; Hiyoshi, S.; Natsuda, H.; Monma, S.; Iwaba, S. *J. Chem. Soc. Jpn., Ind. Chem. Sect.* **1952**, *55*, 801.
(10) Crawford, A. G.; Edwards, G.; Lindsay, D. S. *J. Chem. Soc.* **1949**, 1054.
(11) Bushmakin, Y. N.; Kish, Y. N. *Zh. Prikl. Khim.* (*Leningrad*) **1957**, *30*, 200.
(12) Bredig, G.; Bayer, R. *Z. Phys. Chem., Abt. A* **1927**, *130*, 15.
(13) Fastovskij, V. G.; Petrovskij, Yu. V. *Zh. Fiz. Khim.* **1957**, *31*, 2317.
(14) Bennett, G. W. *J. Chem. Educ.* **1929**, *6*, 1544.
(15) Bredig, G.; Bayer, R. *Z. Phys. Chem., Abt. A* **1927**, *130*, 1.
(16) Dunlop, J. G. M.Ch.E. Thesis, Polytechnic Institute of Brooklyn, New York, NY, 1948.
(17) Hughes, H. E.; Maloney, J. O. *Chem. Eng. Prog.* **1952**, *48*, 192.
(18) Ramalho, R. S.; Tiller, F. M.; James, W. J.; Bunch, O. W. *Ind. Eng. Chem.* **1961**, *53*, 895.
(19) Rivenc, G. *Mem. Serv. Chim. Etat* **1953**, *38*, 311.
(20) Brown, I.; Ewald, A. H. *Aust. J. Sci. Res., Ser. A.* **1950**, *3*, 306.
(21) Garwin, L.; Hutchinson, K. E. *Ind. Eng. Chem.* **1950**, *42*, 727.
(22) Othmer, D. F.; Silvis, S. J.; Spiel, A. *Ind. Eng. Chem.* **1952**, *44*, 1864.
(23) Kogan, V. B. *Zh. Fiz. Khim.* **1955**, *29*, 1470.
(24) Rius, A.; Otero, J. L.; Macarron, A. *Chem. Eng. Sci.* **1959**, *10*, 105; errata, p 288.
(25) Ritter, H. L.; Simons, J. H. *J. Am. Chem. Soc.* **1945**, *67*, 757.
(26) Johnson, E. W.; Nash, L. K. *J. Am. Chem. Soc.* **1950**, *72*, 547.
(27) Scheibel, E. G. *Ind. Eng. Chem.* **1949**, *41*, 1076.
(28) Cathala, M. E. J. "International Symposium on Distillation"; Institution of Chemical Engineers: London, 1960; p 115.
(29) Pilavakis, P. A. Ph.D. Thesis, University of London, London, England, 1974.
(30) Hala, E.; Pick, J.; Fried, V.; Vilim, O. "Vapor Liquid Equilibrium", 2nd English ed.; Pergamon Press: Oxford, 1967; p 37.
(31) Powell, M. J. D. *Comput. J.* **1964**, *7*, 155.
(32) Marek, J. *Collect. Czech. Chem. Commun.* **1954**, *19*, 1.
(33) Teshima, T.; Hiyoshi, S.; Monma, S.; Iwaba, S. *J. Chem. Soc. Jpn. Ind. Chem. Sect.* **1952**, *55*, 492.
(34) Hirata, M.; Komatsu, H. *Kagaku Kogaku* **1967**, *31*, 1184.
(35) Suzuki, I.; Komatsu, H.; Hirata, M. *J. Chem. Eng. Jpn.* **1970**, *3*, 152.
(36) Hirata, M.; Komatsu, H. *Kagaku Kogaku* (*Abr. Ed. Engl.*) **1966**, *4*, 242; *Kagaku Kogaku* **1966**, *30*, 129.
(37) Hirata, M.; Komatsu, H. *Kagaku Kogaku* (*Abr. Ed. Engl.*) **1967**, *5*, 143; *Kagaku Kogaku* **1966**, *30*, 989.
(38) Sebastiani, E.; Lacquaniti, L. *Chem. Eng. Sci.* **1967**, *22*, 1155.
(39) Perry, J. H. "Chemical Engineer's Handbook", 4 ed.; McGraw-Hill: New York, 1963, p 13-8.

Received for review July 28, 1980. Revised manuscript received November 3, 1980. Accepted September 8, 1981. P.A.P. thanks the Greek Ministry of Coordination for awarding a NATO scholarship which enabled the work to be conducted.