Isobaric Vapor-Liquid Equilibria for the Ternary System Chloroform-Methanol-Ethyl Acetate

ISAMU NAGATA[1]
Department of Chemical Engineering, Kyoto University, Kyoto, Japan

VAPOR-LIQUID equilibrium data for the ternary chloroform-methanol-ethyl acetate system and its three component binary systems at atmospheric pressure were determined as part of a continuing study of relationships for ternary systems which are prerequisite in the design of multicomponent distillation equipment. This ternary system was chosen for two reasons: to confirm whether the ternary system exhibits an azeotrope, as the binary chloroform-methanol and the methanol-ethyl acetate systems form a minimum boiling point azeotrope (*4, 10, 13*); and to examine whether ternary constants are needed in the calculation of the ternary vapor-liquid equilibria from data on the binary systems.

EXPERIMENTAL

Purity of Compounds. The compounds supplied for this work were first grade (Japanese Industrial Standards) materials. Chloroform was purified by distilling in a glass column packed with McMahon packings. Methanol was distilled in the same column. Ethyl acetate was washed with distilled water three times to remove alcohol and treated by drying over anhydrous potassium carbonate and distilled in the same column. In distillation the predistillate and residue liquids, each approximately one-sixth of the charge, were discarded, and the heart cut used for experimental work. Proper precautions minimized absorption of atmospheric moisture by methanol and ethyl acetate. The properties of the purified compounds are listed in Table I together with reliable literature values.

Analytical Method. Density and refractive index were used as means of analyses of the unknown binary and ternary mixtures. Densities were determined using 10-ml. pycnometers with graduated arms at 25° ± 0.1° C. Measurements were reproducible to within ±0.0001. Refractive indices were determined using a Shimadzu Pulfrich refractometer. Prism temperature was maintained at 25° ± 0.1° C. by circulating water from a constant temperature bath. Refractive index determinations were accurate to ±0.0001 unit. Table II shows the analytical data for binary and ternary systems. The ternary mixtures were prepared by adding methanol to selected mixtures of chloroform and ethyl acetate. The values of densities and refractive indices of these mixtures were plotted against the molal fraction of methanol with the molal fraction of chloroform on a methanol-free basis as a parameter. From these diagrams the standard ternary data were obtained for the lines of constant properties by interpolation, and a ternary calibration chart was prepared (Figure 1). To analyze each unknown ternary mixture, from a knowledge of the density and refractive index of the mixture, the compositions of vapor and liquid phases of the mixture were determined by linear interpolation on this chart. The accuracy of the ternary compositions obtained from this chart was to be ±0.002 mole fraction.

Apparatus. Experimental data were obtained by the use of a Colburn still described by Griswold and Buford (*5*). A copper-constantan thermocouple calibrated against a standard thermometer and a Yokogawa P-7 potentiometer were used to measure equilibrium temperature to within ±0.05° C. The barometric pressure was recorded after each run: the observed temperatures were corrected to 760 mm. of mercury by the following equation (*15*):

$$t_c = t_o + 0.00012(t_o + 273.2)(760 - P)$$

where

t_c = corrected temperature, ° C.
t_0 = observed temperature, ° C.
P = barometric pressure prevailing during experimental run, mm. Hg

Pressure effect on $x - y$ data was negligible because the deviation of atmospheric pressure recorded in this work from 760 mm. of mercury is small (maximum deviations of +3 and −8 mm.).

VAPOR-LIQUID EQUILIBRIA AND THERMODYNAMIC TESTING

Binary Systems. Table III shows vapor and liquid compositions, equilibrium temperatures, and activity coefficients calculated by the following equation

$$\pi y_i = \gamma_i x_i p_i^0 \qquad (1)$$

Vapor pressure data for methanol were calculated using the Antoine equation presented by Lange (*11*).

$$\log_{10} p_{\text{mm. Hg}} = 7.87863 - 1473.11/(t° \text{ C.} + 230)$$

Vapor pressure data for chloroform and ethyl acetate were obtained from the compilation of Timmermans (*19*).

Thermodynamic consistency of binary systems can be

[1] Present address, Kanazawa University, Kanazawa, Japan.

Table I. Physical Properties of Pure Compounds

Compound	Boiling Point, ° C.		Density, 25/4		Refractive Index, D/25° C.	
	Exptl.	Lit.	Exptl.	Lit.	Exptl.	Lit.
Chloroform	61.2	61.26 (*9*)	1.4802	1.4787 (*9*)	1.4433	1.4430 (*9*)
		61.152(*19*)		1.4807 (*3*)		1.4433 (*3*)
Ethyl acetate	77.1	77.1 (*13*)	0.8946	0.89462(*13*)	1.3697	1.36984 (*13*)
		77.114(*20*)		0.89455(*20*)		1.36979 (*20*)
Methanol	64.7	64.5 (*13*)	0.7867	0.78682(*13*)	1.3265	1.32668 (*13*)
		64.509(*20*)		0.78675 (*20*)		1.32663 (*20*)

tested by the area condition proposed by Redlich and Kister (*17*) and Herington (*7*).

$$\int_0^1 \log \frac{\gamma_1}{\gamma_2}\, dx_1 = 0 \qquad (2)$$

This equation is exactly valid for isothermal conditions only. It may be applied, however, even at isobaric conditions where the boiling range is about 10° C. in nonazeotropic organic systems, and more than this in azeotropic. The activity coefficients of binaries were well correlated by

Table II. Data for Analysis of the System Chloroform-Methanol-Ethyl Acetate

x_1[a]	x_2[b]	d_4^{25}	n_D^{25}	x_1	x_2	d_4^{25}	n_D^{25}	x_1	x_2	d_4^{25}	n_D^{25}
0.882	0.118	1.4357	1.4361	0.749	0	1.3113	1.4221	0.420	0	1.1119	1.3968
0.761	0.239	1.3864	1.4277	0.624	0.167	1.2663	1.4141	0.409	0.025	1.1080	1.3962
0.662	0.338	1.3398	1.4198	0.534	0.287	1.2286	1.4069	0.375	0.106	1.0960	1.3936
0.606	0.394	1.3114	1.4149	0.463	0.382	1.1936	1.4005	0.334	0.204	1.0886	1.3901
0.518	0.482	1.2606	1.4064	0.395	0.473	1.1555	1.3932	0.297	0.292	1.0613	1.3865
0.413	0.587	1.1940	1.3948	0.311	0.585	1.1018	1.3837	0.247	0.411	1.0352	1.3808
0.342	0.658	1.1424	1.3858	0.252	0.664	1.0585	1.3758	0.192	0.544	1.0002	1.3728
0.255	0.745	1.0705	1.3736	0.188	0.749	1.0044	1.3659	0.161	0.617	0.9768	1.3678
0.218	0.782	1.0376	1.3678	0.160	0.787	0.9757	1.3604	0.112	0.733	0.9320	1.3581
0.154	0.846	0.9716	1.3570	0.100	0.867	0.9148	1.3491	0.044	0.896	0.8532	1.3410
0.090	0.910	0.9010	1.3455	0.052	0.930	0.8585	1.3391				
								0.359	0	1.0779	1.3918
0	0.067	0.8918	1.3687	0.663	0	1.2564	1.4152	0.330	0.081	1.0672	1.3902
0	0.199	0.8850	1.3680	0.619	0.070	1.2404	1.4122	0.289	0.195	1.0502	1.3865
0	0.263	0.8814	1.3645	0.590	0.113	1.2302	1.4101	0.267	0.257	1.0401	1.3842
0	0.336	0.8765	1.3627	0.481	0.276	1.1854	1.4019	0.199	0.446	1.0026	1.3758
0	0.477	0.8661	1.3585	0.428	0.356	1.1604	1.3972	0.196	0.454	1.0011	1.3753
0	0.589	0.8555	1.3542	0.340	0.488	1.1123	1.3880	0.145	0.597	0.9641	1.3669
0	0.669	0.8467	1.3505	0.246	0.630	1.0491	1.3759	0.088	0.755	0.9115	1.3547
0	0.777	0.8319	1.3446	0.124	0.813	0.9417	1.3551	0.038	0.896	0.8484	1.3404
0	0.859	0.8181	1.3391	0.104	0.843	0.9201	1.3512				
0	0.921	0.8058	1.3340	0.071	0.893	0.8827	1.3443	0.235	0	1.0118	1.3843
								0.213	0.090	1.0028	1.3823
0.919	0	1.4246	1.4360	0.585	0	1.2096	1.4090	0.196	0.165	0.9944	1.3800
0.728	0.208	1.3481	1.4235	0.548	0.064	1.1956	1.4065	0.184	0.215	0.9885	1.3785
0.668	0.273	1.3235	1.4190	0.538	0.082	1.1922	1.4057	0.178	0.238	0.9854	1.3778
0.570	0.380	1.2759	1.4107	0.491	0.162	1.1743	1.4024	0.154	0.345	0.9710	1.3743
0.475	0.483	1.2233	1.4016	0.422	0.280	1.1447	1.3967	0.136	0.419	0.9594	1.3712
0.399	0.566	1.1757	1.3924	0.329	0.435	1.0986	1.3877	0.112	0.521	0.9408	1.3664
0.302	0.671	1.1023	1.3825	0.299	0.490	1.0799	1.3839	0.100	0.573	0.9303	1.3636
0.114	0.876	0.9306	1.3505	0.215	0.640	1.0224	1.3725	0.065	0.721	0.8944	1.3542
				0.185	0.684	0.9985	1.3677	0.059	0.747	0.8872	1.3522
0.903	0	1.4135	1.4345	0.153	0.738	0.9704	1.3622				
0.764	0.154	1.3598	1.4259	0.118	0.798	0.9370	1.3557	0.155	0	0.9701	1.3792
0.628	0.304	1.3013	1.4157					0.141	0.086	0.9630	1.3773
0.533	0.410	1.2518	1.4075	0.498	0	1.1568	1.4025	0.132	0.150	0.9576	1.3757
0.393	0.565	1.1697	1.3926	0.471	0.052	1.1476	1.4008	0.103	0.331	0.9394	1.3705
0.302	0.665	1.1039	1.3812	0.452	0.091	1.1405	1.3994	0.080	0.484	0.9191	1.3649
0.169	0.812	0.9867	1.3608	0.408	1.178	1.1240	1.3961	0.064	0.585	0.9023	1.3560
0.101	0.888	0.9145	1.3480	0.324	0.355	1.0841	1.3877	0.059	0.617	0.8967	1.3583
				0.289	0.419	1.0670	1.3842	0.042	0.728	0.8737	1.3517
				0.214	0.569	1.0188	1.3745	0.023	0.847	0.8416	1.3424
				0.196	0.605	1.0058	1.3718	0.017	0.891	0.8286	1.3385
				0.138	0.723	0.9570	1.3617				
				0.125	0.749	0.9447	1.3590				
				0.048	0.904	0.8547	1.3408				

[a] Mole fraction of chloroform.
[b] Mole fraction of methanol.

Table III. Vapor-Liquid Equilibrium Data for Three Binary Systems

Chloroform-Methanol					Chloroform-Ethyl Acetate					Methanol-Ethyl Acetate				
t, ° C.	x_1[a]	y_1	γ_1	γ_2	t, ° C.	x_1[a]	y_1	γ_1	γ_2	t, ° C.	x_1[b]	y_1	γ_1	γ_2
63.0	0.040	0.102	2.403	1.000	77.5	0.071	0.064	0.543	0.995	74.4	0.028	0.120	3.020	1.002
62.0	0.065	0.154	2.305	1.008	77.6	0.110	0.102	0.557	0.993	74.0	0.037	0.133	2.533	0.997
60.9	0.095	0.215	2.280	1.010	77.7	0.140	0.134	0.573	0.987	71.5	0.073	0.220	2.329	1.016
59.3	0.146	0.304	2.211	1.011	77.8	0.174	0.171	0.587	0.981	69.3	0.123	0.310	2.115	1.028
57.8	0.196	0.378	2.150	1.022	77.8	0.223	0.227	0.608	0.973	66.4	0.211	0.420	1.867	1.086
57.0	0.230	0.420	2.099	1.028	77.5	0.259	0.270	0.626	0.973	66.0	0.236	0.442	1.784	1.076
55.9	0.287	0.472	1.958	1.057	77.3	0.301	0.323	0.648	0.962	65.8	0.239	0.440	1.767	1.092
55.3	0.332	0.507	1.861	1.081	76.8	0.365	0.408	0.686	0.942	65.3	0.265	0.468	1.729	1.094
54.7	0.383	0.540	1.749	1.119	76.0	0.448	0.522	0.734	0.897	64.0	0.352	0.526	1.539	1.157
54.3	0.425	0.564	1.673	1.158	75.1	0.504	0.596	0.765	0.869	63.7	0.408	0.558	1.425	1.193
54.0	0.459	0.580	1.610	1.200	74.7	0.528	0.628	0.779	0.852	63.6	0.440	0.573	1.363	1.222
53.8	0.520	0.607	1.498	1.276	73.5	0.581	0.700	0.820	0.806	63.1	0.533	0.620	1.221	1.363
53.7	0.557	0.619	1.433	1.347	71.8	0.650	0.780	0.874	0.751	62.9	0.585	0.647	1.189	1.432
53.5	0.628	0.643	1.325	1.515	70.4	0.704	0.839	0.886	0.683	62.4	0.664	0.687	1.135	1.560
53.5	0.636	0.646	1.317	1.535	68.9	0.751	0.879	0.914	0.644	62.4	0.708	0.711	1.102	1.658
53.5	0.667	0.655	1.273	1.636	67.7	0.790	0.910	0.934	0.593	62.4	0.748	0.737	1.081	1.748
53.7	0.753	0.684	1.169	2.003	65.6	0.856	0.950	0.960	0.519	62.4	0.793	0.768	1.062	1.877
53.9	0.797	0.701	1.124	2.281	63.7	0.922	0.978	0.977	0.451	62.5	0.822	0.790	1.050	1.969
54.4	0.855	0.730	1.058	2.831						62.8	0.883	0.842	1.030	2.230
55.2	0.904	0.768	1.038	3.553						64.0	0.961	0.934	1.001	2.667
56.3	0.937	0.812	1.020	4.191										
57.9	0.970	0.875	1.004	5.479										

[a] Mole fraction of chloroform.
[b] Mole fraction of methanol.

using two typical equations satisfying Equation 2; that is, the three-suffix Margules equations modified by Wohl (*21*, *22*) and the three-constant van Laar equations recently modified by Black (*1*) instead of the two constants found in the ordinary two-suffix van Laar equations. They are expressed as

$$\log \gamma_i = x_j^2[(A_{ij} + 2x_i(A_{ji} - A_{ij})]$$

Margules (3)

$$\log \gamma_j = x_i^2[(A_{ji} + 2x_j(A_{ij} - A_{ji})]$$

$$\log \gamma_i = \frac{B_{ij}}{\left[1 + \frac{B_{ij}x_i}{B_{ji}x_j}\right]^2} + E_i \qquad (3)$$

Modified van Laar

$$\log \gamma_j = \frac{B_{ji}}{\left[1 + \frac{B_{ji}x_j}{B_{ij}x_i}\right]^2} + E_j \qquad (4)$$

$$E_i = c_{ij}x_j(x_i - x_j)[3(x_i - x_j)(1 - x_i) + 2x_j] \qquad (5)$$

Subscripts of c are interchangeable, as $c_{ij} = c_{ji}$. The calculated activity coefficients are presented in Figure 2. Calculated values of activity coefficients of the chloroform-ethyl acetate system in the dilute ethyl acetate region deviate slightly from the experimental data. This is due to the fact that, when binary van Laar constants are used for ternary system, they must satisfy the so-called van Laar restriction

$$\frac{B_{13}}{B_{31}} = \frac{B_{12}}{B_{21}} \times \frac{B_{23}}{B_{32}} \qquad (6)$$

Vapor-liquid equilibrium data on the chloroform-methanol system were reported by Bushmakin and Kish in 1957 (*4*) and by Lang in 1950 (*10*); his data is $x - y$ relation only. The present data are in close agreement with these previous data. Data on the chloroform-ethyl acetate system are not reported in the literature. This system was referred to as a nonazeotrope in Horsley's Azeotropic Data (*8*). The present investigation shows that this system forms a maximum boiling-point azeotrope. Experimental data on the methanol-ethyl acetate system were reported by Murti and Van Winkle and 1958 (*13*). Present data agree fairly well, although values for y are slightly higher than the author's results in the ethyl acetate-rich region. Binary constants of two equations are listed in Table IV.

Ternary System. To check the thermodynamic consistency of ternary (multicomponent) vapor-liquid equilibrium data, the analytical is preferable to the graphical method because the latter must be based on smoothed data, not providing a point-by-point test. Since the binary data were well correlated with the Margules and the modified van Laar equations, these equations were also used to examine internal consistency of the ternary data.

The ternary three-suffix Margules equation for $\log \gamma_1$ is given by

$$\log \gamma_1 = x_2^2[A_{12} + 2x_1(A_{21} - A_{12})] + x_3^2[A_{13} + 2x_1(A_{31} - A_{13})] + x_2x_3[\tfrac{1}{2}(A_{21} + A_{12} + A_{31} + A_{13} - A_{23} - A_{32}) + x_1(A_{21} - A_{12} + A_{31} - A_{13}) + (x_2 - x_3)(A_{23} - A_{32}) - (1 - 2x_1)C^*] \qquad (7)$$

Similarly $\log \gamma_2$ and $\log \gamma_3$ are expressed by cyclic permutation of the subscripts (*21*, *22*).

The multicomponent modified van Laar equations are derived from the following Q function.

$$Q = G^E/2.3RT = \sum_i x_i \log \gamma_i \qquad (8)$$

$$Q = 0.5q \sum_{ij} H_{ij}z_iz_j + Q_e - \tfrac{1}{6}q \sum_{\substack{ijk \\ \neq}} H_{ijk}z_iz_jz_k \qquad (9)$$

H_{ij} and H_{ijk} are molecular interaction coefficients defined by

$$H_{ij} = B_{ij}/q_i, \qquad H_{ijk} = C_{ijk}/q_i \qquad (10)$$

Q_e is an additive correction function empirically proposed by Black (*1*).

$$Q_e = 0.5 \sum_{RM \neq} [(X_R - X_M)^2 \sum c_{rm}x_rx_m] \qquad (11)$$

Since the molecular interaction coefficients are independent of the order of the subscripts, the following relations are obtained.

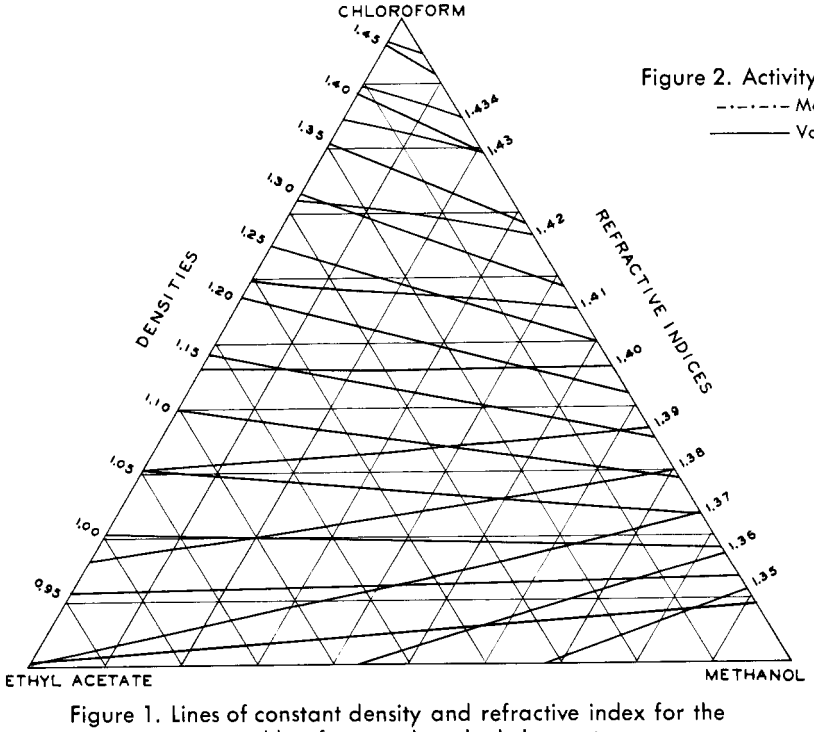

Figure 1. Lines of constant density and refractive index for the system chloroform-methanol-ethyl acetate

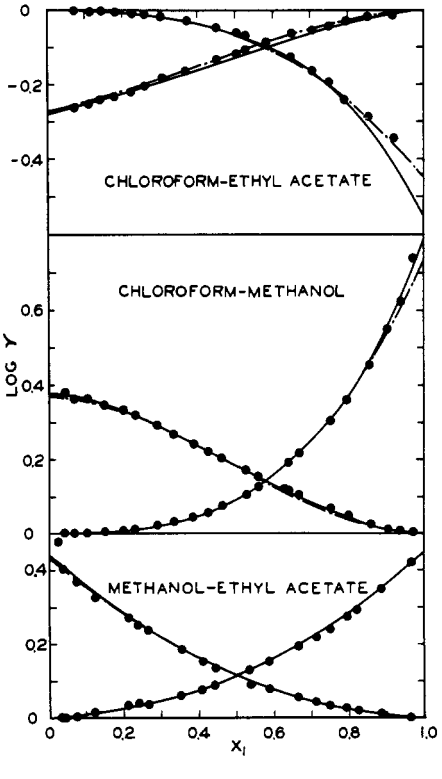

Figure 2. Activity coefficients
Margules
Van Laar

$$H_{ij} = H_{ji}, \qquad H_{ijk} = H_{ikj} = H_{jik} = H_{jki} = H_{kij} = H_{kji} \tag{12}$$

As each first term of Equation 9 is counted twice and each third term is counted six times, the coefficients are 0.5 and 1/6, respectively.

The thermodynamic relation of Equation 8 for the activity coefficient furnishes

$$\log \gamma_i = Q + \frac{\partial Q}{\partial x_i} - \sum x_j \frac{\partial Q}{\partial x_j} \tag{13}$$

Substituting Equation 9 in 13, we obtain

$$\log \gamma_i = q_i \Big[\sum_j H_{ij} z_j^2 + 0.5 \sum_{\substack{jk \\ \neq}} z_j z_k (H_{ij} + H_{ik} - H_{jk}) - 1/6 \left(3 \sum_{\substack{jk \\ \neq}} H_{ijk} z_j z_k - 2 \sum_{\substack{ijk \\ \neq}} H_{ijk} z_i z_j z_k\right) \Big] + E_{S_i} \tag{14}$$

$$E_{S_i} = \sum_R [(X_S - X_R)^2 (\sum_r c_{ir} x_r)] + 2 \sum_R [(X_S - X_R)(\sum_{sr} c_{sr} x_s x_r)] - 3/2 \sum_{\substack{RM \\ \neq}} [(X_R - X_M)^2 (\sum_{rm} c_{rm} x_r x_m)] \tag{15}$$

and similarly,

$$\log \gamma_i = [\sum_j B_{ij} R_{j2}^2 x_j^2 + 0.5 \sum_{\substack{jk \\ \neq}} x_j x_k R_{j2} R_{k2} (B_{ij} + B_{ik} - B_{jk} R_{ij})] / (\sum_j x_j R_{j2})^2 - 1/6 \Big\{ 3[\sum_{\substack{jk \\ \neq}} C_{ijk} x_j x_k R_{j2} R_{k2}] / (\sum_j x_j R_{j2})^2 - 2[\sum_{\substack{ijk \\ \neq}} C_{ijk} x_i x_j x_k R_{i2} R_{j2} R_{k2}] / (\sum_j x_j R_{j2})^3 \Big\} + E_{S_i} \tag{16}$$

Equations 14 to 16 are general expressions for the activity coefficient of component i in a multicomponent system with ternary effects. Where the ternary effects are not present, the equations reduce to the ones proposed by Black (*1*). Since the present ternary mixtures are made of components of different classes, X_S, X_R, and X_M in the E_{S_i} function reduce to values x_s, x_r, and x_m, respectively.

Apparently these equations are valid at isothermal conditions. For the application of the equations to isobaric systems, equilibrium data on the binary systems at more than two temperatures are necessary to know the quantitative effect of temperature on the activity coefficients. Sufficient data, however, are not available for the present work, so that the binary constants given in Table IV were used to correlate the ternary data. The ternary constants in the above equations were evaluated at the concentration range where the multiplier of the constant C^* or C_{123} is as large as possible. Black (*2*) has shown that vapor-liquid equilibria of a wide variety of multicomponent systems having uniformly positive deviations from ideality could be predicted from binary data alone without ternary constants. In the present ternary system including both negative and positive deviations the value of the ternary constant was 0.42 for C^* and 0.943 for C_{123}, respectively. A similar fact has been observed by Severns, Sesonske, Perry, and Pigford (*18*) in the acetone-methanol-chloroform system at 50° C. including both negative and positive deviations simultaneously.

The average deviations of the calculated activity coefficients from the experimental values are

Chloroform		Methanol		Ethyl Acetate	
M	V	M	V	M	V
0.023	0.036	0.038	0.046	0.062	0.059

M = Margules equations. V = modified van Laar equations

Equilibrium temperatures are obtained by repeated trials until the temperature is established that satisfies the relation

$$\sum_i x_i \gamma_i p_i^0 = \pi = 760 \tag{17}$$

The vapor compositions are calculated by

$$y_i = x_i \gamma_i p_i^0 / \sum_i x_i \gamma_i p_i^0 \tag{18}$$

The calculated vapor compositions and boiling temperatures using the Margules equations are compared with the observed data in Table V. The average deviation of these calculated values from the experimental results for 72 points is 0.005, 0.007, and 0.007 mole fraction for chloroform, methanol, and ethyl acetate, respectively. The calculated boiling temperatures show an average deviation of 0.3° C. from the experimental values. No serious significance is attributed to the temperature deviations between calculated and experimental, as the exact coefficient *vs.* temperature relation is not taken into consideration. Such degree of deviations is reported in many other systems. The author oncludes the ternary data do not involve serious discrepancy. No ternary azeotrope was found.

Algebraic Method. Algebraic methods are useful for engineering. The Prahl-type equation not only involves additional terms to improve the precise representation of binary and ternary experimental $x - y$ data, but also represents equilibrium temperature-composition relationship (*6, 12, 14, 16*). A five-constant equation for a binary system is expressed by

$$\frac{y_i}{y_j} = \frac{x_i}{x_j} \left(\frac{x_i + x_j a_{ij} + x_i x_j d_{ij}}{x_j b_{ij} + x_i c_{ij} + x_i x_i e_{ij}} \right) \tag{19}$$

The boiling points of the binary system are calculated by

$$T_m = T y_{ii} + T_{ij}(y_{ij} + y_{ji}) + T_j y_{jj} \tag{20}$$

where variable y_{ij} is defined as

$$y_{ij} = y_i \frac{x_j a_{ij} + x_i x_j d_{ij}}{x_i + x_j a_{ij} + x_i x_j d_{ij}} \tag{21}$$

and other y values are defined elsewhere (*14*). Values of a_{ij}, c_{ij}, d_{ij}, e_{ij}, and T_{ij} determined so as to agree with the experimental data are listed in Table VI. If the ternary system does not deviate much from the condition

$$b_{12} \cdot b_{23} \cdot b_{31} = 1 \tag{22}$$

the ternary vapor compositions are calculated by the following equation developed by Lu, Li, and Ting (*12*) and suggested as a three-index equation by Hála (*6*)

Table IV. Margules and Modified van Laar Constants for Three Binary Systems

System	Margules		Modified van Laar		
	A_{12}	A_{21}	B_{12}	B_{21}	c_{12}
Chloroform-ethyl acetate	−0.27	−0.45	−0.280	−0.566	0
Chloroform-methanol	0.37	0.73	0.42	0.83	−0.04
Methanol-ethyl acetate	0.43	0.45	0.44	0.45	0

Table V. Ternary Vapor-Liquid Equilibrium Data for the Chloroform-Methanol-Ethyl Acetate System

Liquid Compn.			Obsd. Vapor Compn.			Calcd. Vapor Compn.[a]			Calcd. Vapor Compn.[b]		
x_1^e	x_2^f	x_3^g	y_1	y_2	y_3	y_1	y_2	y_3	y_1	y_2	y_3
0.075	0.077	0.848	0.057	0.238	0.705	0.060	0.234	0.706	0.062	0.225	0.713
0.082	0.246	0.672	0.060	0.470	0.470	0.060	0.463	0.477	0.071	0.441	0.488
0.147	0.303	0.550	0.118	0.494	0.388	0.119	0.504	0.377	0.135	0.475	0.390
0.122	0.539	0.339	0.122	0.618	0.260	0.124	0.605	0.271	0.136	0.587	0.277
0.123	0.445	0.432	0.108	0.574	0.318	0.110	0.585	0.305	0.124	0.550	0.326
0.079	0.347	0.574	0.059	0.513	0.428	0.060	0.534	0.406	0.072	0.509	0.419
0.060	0.470	0.470	0.050	0.585	0.365	0.050	0.598	0.352	0.060	0.574	0.366
0.058	0.634	0.308	0.064	0.667	0.269	0.063	0.671	0.266	0.068	0.648	0.284
0.048	0.569	0.385	0.045	0.640	0.315	0.045	0.641	0.314	0.052	0.622	0.326
0.046	0.651	0.303	0.051	0.681	0.268	0.050	0.688	0.262	0.054	0.671	0.275
0.040	0.861	0.099	0.076	0.814	0.110	0.073	0.806	0.121	0.066	0.803	0.131
0.104	0.645	0.251	0.126	0.665	0.209	0.126	0.666	0.208	0.128	0.650	0.222
0.101	0.657	0.242	0.118	0.673	0.209	0.124	0.673	0.203	0.127	0.656	0.217
0.063	0.725	0.212	0.083	0.713	0.204	0.084	0.713	0.203	0.085	0.698	0.217
0.086	0.738	0.176	0.118	0.718	0.164	0.124	0.709	0.167	0.117	0.706	0.177
0.087	0.575	0.338	0.087	0.644	0.269	0.090	0.642	0.268	0.100	0.617	0.283
0.070	0.792	0.138	0.111	0.750	0.139	0.111	0.745	0.144	0.102	0.744	0.154
0.250	0.241	0.509	0.218	0.442	0.340	0.219	0.459	0.322	0.252	0.421	0.327
0.219	0.360	0.421	0.197	0.548	0.255	0.202	0.535	0.263	0.217	0.521	0.262
0.190	0.432	0.378	0.180	0.580	0.240	0.184	0.570	0.246	0.201	0.542	0.257
0.136	0.678	0.186	0.178	0.663	0.159	0.186	0.661	0.153	0.187	0.640	0.173
0.120	0.637	0.243	0.144	0.655	0.201	0.148	0.658	0.194	0.152	0.634	0.214
0.314	0.122	0.564	0.281	0.316	0.403	0.288	0.327	0.385	0.282	0.341	0.377
0.222	0.383	0.395	0.204	0.544	0.252	0.210	0.545	0.245	0.229	0.517	0.254
0.202	0.597	0.201	0.242	0.619	0.139	0.233	0.633	0.134	0.258	0.583	0.159
0.180	0.651	0.169	0.240	0.639	0.121	0.248	0.631	0.121	0.245	0.608	0.147
0.097	0.822	0.081	0.178	0.748	0.074	0.176	0.742	0.082	0.168	0.729	0.103
0.416	0.071	0.513	0.409	0.235	0.356	0.419	0.233	0.348	0.394	0.254	0.352
0.364	0.207	0.429	0.329	0.414	0.257	0.340	0.421	0.239	0.351	0.412	0.237
0.289	0.482	0.229	0.322	0.553	0.125	0.331	0.546	0.123	0.332	0.520	0.148
0.347	0.300	0.353	0.329	0.489	0.182	0.337	0.480	0.183	0.347	0.458	0.195
0.223	0.659	0.118	0.319	0.603	0.078	0.326	0.598	0.076	0.316	0.583	0.101
0.384	0.314	0.302	0.376	0.475	0.149	0.384	0.473	0.143	0.388	0.452	0.160
0.345	0.465	0.190	0.388	0.526	0.086	0.398	0.514	0.088	0.394	0.492	0.114
0.338	0.504	0.158	0.398	0.531	0.071	0.409	0.517	0.074	0.402	0.499	0.099
0.327	0.579	0.094	0.433	0.509	0.058	0.440	0.516	0.044	0.426	0.509	0.065
0.265	0.660	0.075	0.401	0.558	0.041	0.401	0.565	0.034	0.380	0.551	0.069
0.486	0.211	0.303	0.463	0.412	0.125	0.472	0.399	0.129	0.467	0.391	0.142
0.507	0.191	0.302	0.485	0.380	0.135	0.489	0.383	0.128	0.484	0.377	0.139
0.470	0.285	0.243	0.467	0.426	0.107	0.469	0.435	0.096	0.466	0.419	0.115
0.419	0.407	0.174	0.470	0.478	0.052	0.457	0.477	0.066	0.453	0.455	0.092
0.597	0.077	0.326	0.603	0.242	0.155	0.609	0.239	0.152	0.585	0.263	0.152
0.527	0.219	0.254	0.509	0.393	0.098	0.512	0.396	0.092	0.504	0.384	0.112
0.499	0.338	0.163	0.515	0.437	0.048	0.515	0.431	0.054	0.508	0.417	0.075
0.492	0.363	0.145	0.512	0.449	0.039	0.519	0.434	0.047	0.510	0.421	0.069
0.434	0.486	0.080	0.529	0.448	0.023	0.520	0.452	0.028	0.506	0.449	0.045
0.397	0.518	0.085	0.488	0.475	0.037	0.494	0.469	0.037	0.481	0.468	0.051
0.588	0.183	0.229	0.570	0.361	0.069	0.563	0.358	0.079	0.551	0.355	0.094
0.653	0.082	0.265	0.652	0.247	0.101	0.652	0.243	0.105	0.626	0.265	0.109
0.608	0.234	0.158	0.584	0.371	0.045	0.581	0.374	0.045	0.572	0.367	0.061
0.599	0.351	0.090	0.580	0.402	0.018	0.574	0.402	0.024	0.565	0.397	0.038
0.680	0.200	0.120	0.634	0.347	0.019	0.630	0.341	0.029	0.620	0.338	0.042
0.824	0.102	0.074	0.736	0.248	0.016	0.738	0.247	0.015	0.722	0.258	0.020
0.195	0.174	0.631	0.158	0.386	0.456	0.162	0.401	0.437	0.181	0.396	0.423
0.208	0.745	0.047	0.353	0.622	0.025	0.359	0.616	0.025	0.340	0.608	0.052
0.115	0.179	0.706	0.088	0.382	0.530	0.088	0.398	0.514	0.104	0.393	0.503
0.170	0.072	0.758	0.144	0.241	0.615	0.145	0.227	0.628	0.162	0.239	0.599
0.482	0.067	0.451	0.481	0.235	0.284	0.494	0.226	0.280	0.473	0.265	0.262
0.290	0.644	0.066	0.426	0.540	0.034	0.428	0.538	0.034	0.405	0.527	0.068
0.206	0.740	0.054	0.345	0.617	0.038	0.349	0.613	0.038	0.330	0.603	0.067
0.470	0.071	0.459	0.468	0.235	0.297	0.481	0.233	0.286	0.472	0.260	0.268
0.540	0.075	0.385	0.542	0.244	0.214	0.554	0.239	0.207	0.536	0.264	0.200
0.454	0.325	0.221	0.464	0.440	0.096	0.464	0.450	0.086	0.472	0.418	0.110
0.731	0.077	0.192	0.704	0.230	0.066	0.713	0.225	0.062	0.711	0.219	0.070
0.566	0.342	0.092	0.584	0.391	0.025	0.577	0.399	0.024	0.598	0.361	0.041
0.246	0.197	0.557	0.206	0.420	0.374	0.212	0.421	0.367	0.234	0.413	0.353
0.033	0.861	0.106	0.058	0.809	0.133	0.055	0.812	0.133	0.058	0.801	0.141
0.030	0.898	0.072	0.057	0.838	0.105	0.059	0.844	0.097	0.053	0.840	0.107
0.076	0.328	0.596	0.059	0.506	0.435	0.056	0.528	0.416	0.070	0.512	0.418
0.329	0.639	0.032	0.468	0.517	0.015	0.483	0.503	0.014	0.458	0.518	0.024
0.309	0.260	0.431	0.280	0.471	0.249	0.285	0.467	0.248	0.301	0.451	0.248
0.203	0.739	0.058	0.340	0.615	0.045	0.343	0.618	0.039	0.318	0.626	0.056

(*Table continued*)

[a] Margules equations. [b] Method of Lu, Li, and Ting. [c] Method of Nagata. [d] Modified van Laar equations. [e] Mole fraction of chloroform. [f] Mole fraction of methanol. [g] Mole fraction of ethyl acetate.

Table V. Ternary Vapor-Liquid Equilibrium Data for the Chloroform-Methanol-Ethyl Acetate System

Temp., ° C.			Activity Coeff. γ_1			γ_2			γ_3		
Obsd.	Calcd.[a]	Calcd.[c]	Obsd.	Calcd.[a]	Calcd.[d]	Obsd.	Calcd.[a]	Calcd.[d]	Obsd.	Calcd.[a]	Calcd.[d]
72.0	71.6	71.9	0.540	0.577	0.561	2.345	2.333	2.397	0.986	1.003	1.026
65.4	65.9	66.3	0.638	0.624	0.627	1.863	1.797	1.823	1.053	1.050	1.051
64.1	64.6	65.1	0.730	0.725	0.710	1.673	1.673	1.707	1.112	1.059	1.060
61.9	61.7	62.4	0.976	1.006	0.991	1.283	1.270	1.280	1.310	1.378	1.252
62.8	63.0	63.3	0.833	0.846	0.842	1.393	1.412	1.418	1.216	1.155	1.161
63.8	64.3	64.3	0.686	0.687	0.694	1.535	1.568	1.582	1.187	1.106	1.109
63.1	63.2	63.3	0.782	0.781	0.769	1.328	1.353	1.357	1.269	1.221	1.226
62.1	62.4	62.0	1.070	1.047	1.080	1.168	1.163	1.163	1.480	1.449	1.454
62.3	62.6	63.1	0.903	0.897	0.936	1.239	1.226	1.226	1.383	1.353	1.358
62.2	62.3	62.3	1.072	1.048	1.095	1.157	1.163	1.146	1.494	1.453	1.498
62.4	62.7	62.3	1.826	1.730	1.796	1.037	1.016	1.023	1.862	2.032	2.057
61.4	61.9	61.7	1.202	1.184	1.186	1.177	1.158	1.159	1.448	1.409	1.416
61.4	61.8	61.6	1.159	1.207	1.225	1.169	1.149	1.147	1.502	1.434	1.440
62.0	62.1	62.1	1.281	1.290	1.334	1.096	1.094	1.092	1.636	1.624	1.628
61.3	62.0	61.3	1.365	1.409	1.441	1.115	1.073	1.084	1.626	1.614	1.619
62.0	62.4	62.5	0.972	0.988	1.007	1.248	1.226	1.229	1.353	1.327	1.333
62.1	62.0	61.4	1.537	1.546	1.599	1.051	1.053	1.050	1.707	1.774	1.781
64.5	64.9	65.0	0.782	0.773	0.738	1.852	1.891	1.929	1.038	0.967	0.979
62.8	63.1	62.6	0.853	0.869	0.834	1.643	1.586	1.616	1.001	1.020	1.033
62.5	62.6	62.4	0.902	0.925	0.901	1.467	1.442	1.463	1.072	1.084	1.094
61.1	61.1	60.8	1.311	1.367	1.371	1.130	1.128	1.131	1.504	1.444	1.415
61.3	61.7	61.4	1.194	1.205	1.211	1.178	1.166	1.169	1.443	1.375	1.380
69.0	68.3	67.7	0.697	0.730	0.700	2.199	2.340	2.242	0.944	0.926	0.939
62.4	62.7	62.5	0.883	0.901	0.867	1.558	1.540	1.569	1.068	1.026	1.039
60.5	60.7	60.2	1.223	1.168	1.271	1.227	1.245	1.216	1.243	1.196	1.197
60.3	60.5	60.4	1.369	1.405	1.388	1.171	1.147	1.156	1.296	1.290	1.292
61.1	61.3	60.4	1.837	1.804	1.899	1.051	1.035	1.035	1.605	1.770	1.796
69.8	69.7	69.4	0.746	0.766	0.735	2.727	2.715	2.721	0.891	0.874	0.888
63.6	64.2	63.3	0.835	0.846	0.798	2.092	2.076	2.113	0.961	0.874	0.890
60.0	60.2	59.8	1.156	1.182	1.111	1.385	1.361	1.393	1.000	0.975	0.981
62.0	62.2	61.6	0.922	0.940	0.884	1.817	1.775	1.824	0.877	0.876	0.893
59.0	59.3	58.8	1.511	1.550	1.528	1.151	1.129	1.139	1.253	1.210	1.207
60.9	61.1	60.6	0.986	1.000	1.062	1.783	1.743	1.803	0.874	0.830	0.842
59.0	59.1	58.8	1.207	1.233	1.174	1.422	1.385	1.417	0.860	0.881	0.875
58.3	58.6	58.3	1.293	1.317	1.266	1.363	1.312	1.346	0.878	0.898	0.891
57.3	57.5	57.2	1.505	1.516	1.481	1.185	1.192	1.213	1.250	0.937	0.911
57.5	58.2	57.8	1.709	1.667	1.647	1.130	1.113	1.124	1.099	0.897	1.100
61.4	61.4	60.9	0.945	0.965	0.904	2.229	2.158	2.203	0.717	0.739	0.748
61.6	61.7	60.9	0.942	0.948	0.900	2.253	2.264	2.296	0.772	0.725	0.733
59.8	59.8	59.4	1.036	1.043	0.989	1.804	1.858	1.926	0.843	0.724	0.723
57.9	58.1	58.3	1.253	1.205	1.151	1.544	1.529	1.554	0.592	0.763	0.751
65.7	65.2	63.6	0.872	0.895	0.860	3.029	3.051	2.905	0.734	0.707	0.715
60 0	60.3	59.8	1.003	0.998	0.940	2.166	2.152	2.325	0.707	0.655	0.666
57.5	57.8	57.6	1.166	1.154	1.106	1.728	1.687	1.754	0.592	0.662	0.637
57.3	57.4	57.2	1.183	1.194	1.150	1.667	1.608	1.670	0.545	0.662	0.632
56.0	56.3	56.1	1.450	1.410	1.378	1.311	1.310	1.327	0.585	0.723	0.681
56.7	56.6	56.5	1.426	1.449	1.410	1.275	1.258	1.296	0.901	0.897	0.755
59.7	59.9	59.4	1.027	0.997	0.958	2.411	2.377	2.413	0.509	0.632	0.620
63.8	63.3	62.0	0.917	0.934	0.903	3.126	3.138	3.000	0.607	0.642	0.639
57.4	57.7	57.6	1.088	1.072	1.042	2.128	2.123	2.189	0.576	0.569	0.531
56.0	55.9	55.9	1.234	1.225	1.200	1.629	1.632	1.687	0.426	0.566	0.506
57.1	56.9	56.8	1.067	1.069	1.045	2.358	2.342	2.447	0.323	0.503	0.452
57.2	57.1	56.9	1.019	1.019	1.020	3.295	3.283	3.340	0.439	0.423	0.338
67.1	67.7	66.7	0.670	0.675	0.656	2.025	2.054	2.099	1.025	0.961	0.995
58.1	58.7	58.0	1.878	1.869	1.870	1.089	1.053	1.057	0.832	1.347	1.334
67.5	67.5	67.2	0.625	0.618	0.613	1.917	1.995	1.994	1.049	1.018	1.019
72.3	71.8	71.2	0.596	0.611	0.601	2.505	2.395	2.460	0.953	0.989	0.989
68.8	68.9	67.0	0.792	0.809	0.759	2.929	2.864	2.754	0.850	0.824	0.841
57.2	57.5	57.4	1.703	1.667	1.646	1.132	1.120	1.132	1.047	1.043	1.025
58.5	58.7	58.3	1.829	1.834	1.838	1.072	1.058	1.063	1.364	1.341	1.332
68.5	68.7	66.9	0.787	0.804	0.770	2.752	2.817	2.719	0.870	0.833	0.848
66.4	66.9	65.1	0.848	0.855	0.819	3.048	2.939	2.811	0.808	0.766	0.782
59.1	59.2	59.1	1.117	1.090	1.035	1.698	1.728	1.793	0.823	0.731	0.728
60.6	61.3	61.2	0.981	0.971	0.954	3.525	3.359	3.343	0.615	0.558	0.530
55.9	56.0	56.1	1.231	1.213	1.190	1.630	1.662	1.718	0.580	0.559	0.500
65.8	66.2	65.6	0.721	0.733	0.703	2.047	2.017	2.057	0.997	0.964	0.976
62.4	62.9	61.8	1.689	1.584	1.763	1.031	1.015	1.023	2.101	2.071	2.074
62.6	62.8	62.0	1.814	1.870	1.937	1.015	1.013	1.011	2.425	2.221	2.225
64.4	64.2	64.4	0.698	0.669	0.677	1.563	1.643	1.621	1.190	1.095	1.097
56.6	56.3	56.1	1.658	1.725	1.760	1.122	1.105	1.111	0.973	0.907	0.890
63.0	63.7	63.2	0.854	0.851	0.820	1.940	1.870	1.848	0.946	0.918	0.935
59.2	58.8	58.4	1.785	1.821	1.881	1.033	1.060	1.064	1.425	1.300	1.306

[a] Margules equations. [b] Method of Lu, Li, and Ting.
[c] Method of Nagata. [d] Modified van Laar equations.
[e] Mole fraction of chloroform. [f] Mole fraction of methanol.
[g] Mole fraction of ethyl acetate.

Table VI. Primary Information

System	a_{12}	b_{12}	c_{12}	d_{12}	e_{12}	T_{12}
Chloroform-ethyl acetate	1.171	1.371	0.125	0	0	356.7
Chloroform-methanol	3.371	1.350	6.293	8.523	−3.681	325.3
Methanol-ethyl acetate	3.664	0.900	2.103	0	0	333.7

$$y_1:y_2:y_3 = \left(\frac{b_{31}}{b_{12}}\right)^{1/3} x_1\left(x_1 + x_2a_{12} + x_1x_2d_{12} + x_3\frac{c_{31}}{b_{31}} + x_1x_3\frac{e_{31}}{b_{31}} + x_2x_3\alpha_1\right)$$

$$:\left(\frac{b_{12}}{b_{23}}\right)^{1/3} x_2\left(x_2 + x_3a_{23} + x_2x_3d_{23} + x_1\frac{c_{12}}{b_{12}} + x_2x_1\frac{e_{12}}{b_{12}} + x_3x_1\alpha_2\right)$$

$$:\left(\frac{b_{23}}{b_{31}}\right)^{1/3} x_3\left(x_3 + x_1a_{31} + x_3x_1d_{31} + x_2\frac{c_{23}}{b_{23}} + x_3x_2\frac{e_{23}}{b_{23}} + x_1x_2\alpha_3\right) \quad (23)$$

α_1, α_2, and α_3 are constants to be evaluated from ternary data. The boiling points of the ternary system are calculated in accordance with the method proposed by the author (*14*).

$$T_m = \sum_i T_i y_{ii} + \sum_{ij\neq} T_{ij}y_{ij} + T_{123}(y_{123} + y_{231} + y_{312}) \quad (24)$$

where variable y_{123} is defined as

$$y_{123} = y_1 \frac{x_2x_3\alpha_1}{x_1 + x_2a_{12} + x_1x_2d_{12} + x_3\frac{c_{31}}{b_{31}} + x_1x_3\frac{e_{31}}{b_{31}} + x_2x_3\alpha_1} \quad (25)$$

y_{231} and y_{312} are similarly, defined. T_{123} is determined from ternary data in the same way done for T_{12} in the binary systems. The value of $b_{12}\cdot b_{23}\cdot b_{31}$ of the present ternary system is 0.886. The following ternary constants were used to correlate the equilibrium data.

α_1	α_2	α_3	T_{123}
1.536	1.093	0.933	375.0

That the ternary constants were necessary for the representation of vapor-liquid equilibrium data was expected from the results of the preceding thermodynamic analysis confirming the presence of ternary effect. The calculated results are given in Table V. The average deviation of the calculated boiling temperatures from the experimental values is 0.4° C. The calculated vapor compositions give average deviations of approximately two times those obtained by using the Margules equations.

ACKNOWLEDGMENT

The author thanks Fumitake Yoshida for his support and encouragement in this study; and Minoru Hirayama and Yoshio Tamaki for their part in the experimental work.

NOMENCLATURE

a_{ij}, b_{ij}, c_{ij}, d_{ij}, e_{ij} = constants of Equation 19
A_{ij}, A_{ji} = binary constants of Margules equations
B_{ij}, B_{ji} = binary constants of van Laar equations
c_{ij} = constant of Equation 5
C^* = ternary constant of Margules equations
C_{ijk} = ternary constant of van Laar equations
E_i = defined by Equation 5
G^E = excess free energy
H_{ij}, H_{ijk} = B_{ij}/q_i, C_{ijk}/q_i, molecular interaction coefficients
p_i^0 = vapor pressure of component i mm. Hg
P = barometric pressure, mm., Hg
q = $\sum_i x_iq_i$
q_i = unspecified molecular property of component i
R = gas constant
t = temperature, ° C.
T = temperature, ° K.
T_{ij}, T_{123} = constants
x_r = mole fraction of any component in class R
x_m = mole fraction of any component in class M
x_s = mole fraction of any component in particular class S
X_R = $\sum x_r$, mole fraction in class R
X_M = $\sum x_m$, mole fraction in class M
X_S = $\sum x_s$, mole fraction in class S
x_i = liquid mole fraction of component i
y_i = vapor mole fraction of component i
z_i = $x_iq_i/\sum x_iq_i$
y_{ii}, y_{ij}, y_{123}, y_{231}, y_{312} = variables
α_1, α_2, α_3 = ternary constants of Equation 23
γ = activity coefficient
π = total pressure

Subscripts

1, 2, 3, i, j, k = number of components
c = corrected
m = mixture
o = observed

LITERATURE CITED

(1) Black, C., *Ind. Eng. Chem.* **50**, 403 (1958).
(2) *Ibid.*, **51**, 211 (1959).
(3) Brown, J., Fock, W., *Australian J. Chem.* **8**, 361 (1955).
(4) Bushmakin, I.N., Kish, I.N., *Zhur. Priklad. Khim.* **30**, 200 (1957).
(5) Griswold, J., Buford, C.B., *Ind. Eng. Chem.* **41**, 2347 (1949).
(6) Hála, E., *Collection Czechoslov. Chem. Communs.* **24**, 2453 (1959).
(7) Herington, E.F.G., *J. Inst. Petrol.* **37**, 457 (1951).
(8) Horsley, L.H., *Advances in Chem. Ser.* No. **6** (1952).
(9) Karr, A.E., Bowes, W.M., Scheibel, E.G., *Ana. Chem.* **23**, 459 (1951).
(10) Lang, H., *Z. physik. Chem.* **196**, 278 (1950–1).
(11) Lange, N.A., ed., "Handbook of Chemistry," 9th ed., p. 1432, Handbook Publishers, Inc., Sandusky, Ohio, 1956.
(12) Lu, B.C.-Y., Li, J.C.M., Ting, T-W., *Ind. Eng. Chem.* **51**, 219 (1959).
(13) Murti, P.S., Van Winkle, M., J. CHEM. ENG. DATA **3**, 72 (1958).
(14) Nagata, I., *Ibid.*, **6**, 586 (1961).
(15) Perry, J.H., ed., "Chemical Engineers' Handbook," 3rd ed., p. 293, McGraw-Hill, New York, 1950.
(16) Prahl, W.H., *Ind. Eng. Chem.* **43**, 1767 (1951).
(17) Redlich, O., Kister, A.T., *Ind. Eng. Chem.* **40**, 345 (1948).
(18) Severns, W.H., Jr., Sesonske, A., Perry, R.H., Pigford, R.L., *A.I.Ch.E. Journal* **1**, 401 (1955).
(19) Timmermans, J., "Physico-chemical Constants of Pure Organic Compounds," Elsevier, New York, 1950.
(20) Weissberger, A., Proskauer, E.S., Riddick, J.A., Toops, E., Jr., "Organic Solvents," 2nd ed., Interscience, New York, 1955.
(21) Wohl, K., *Chem. Eng. Progr.* **49**, 218 (1953).
(22) Wohl, K., *Trans, Am. Inst. Chem. Engrs.* **42**, 215 (1946).

RECEIVED for review December 4, 1961. Accepted April 9, 1962.