is a constant. The equation gives excellent checks for the three alcohols at 20° and 25° C. (Table III).

REFRACTIVITY INTERCEPTS

The method of plotting refractivity intercept, $n_D - d/2$, *vs.* the composition of binary solutions, suggested by Kurtz (8) and presented by Rouleau and Thompson in the preceding article, was applied to the present data as plotted in Figure 4.

Once again extremely interesting correlations resulted. The lines for all three alcohols were reasonably straight; the lines for *n*-propyl alcohol and isopropyl alcohol were coincident but methyl alcohol gave a line with a different slope.

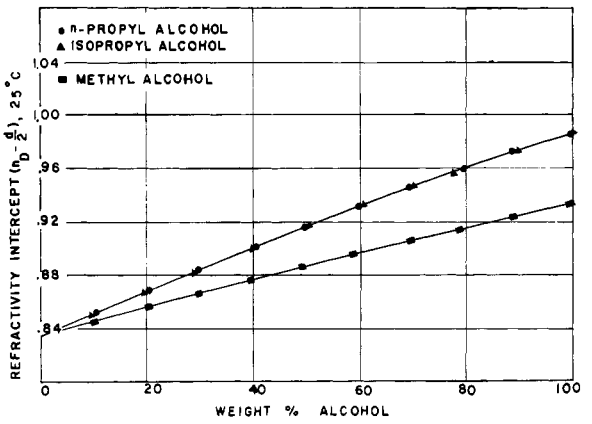

Figure 4. Refractivity intercepts for aqueous alcohol solutions at 25° C.

Table III. Applicability of Eykman Equation

Compound	Value of C_1 at 20° C.	Value of C_1 at 25° C.
n-Propyl alcohol	0.6405	0.6406
Isopropyl alcohol	0.6425	0.6424
Methyl alcohol	0.5594	0.5593

The results are very encouraging and indicate that this method of correlation might shed some light on the effect of molecular structure and association on these physical properties.

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Vapor-Liquid Equilibrium at Atmospheric Pressure for the Ternary System, Methyl Acetate–Chloroform–Benzene

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VAPOR-LIQUID EQUILIBRIUM data on the ternary methyl acetate–chloroform–benzene system were determined because available data indicated that this system was totally miscible and could be analyzed by density and refractive index measurements. This investigation also examined whether the experimental data can be well correlated by two typical methods existing in the literature, and whether ternary effects are present, since this system involves both positive and negative deviations from Raoult's law.

PURITY OF COMPOUNDS

First grade (Japanese industrial standards) chloroform was fractionated in a glass column packed with McMahon packings, and a heart cut was used for experimental work. First grade methyl acetate was purified by the procedure of Hurd and Strong (8). Special grade (Japanese industrial standards) benzene was purified by fractional crystallization repeated twice. The physical properties of the purified materials are compared with the literature values in Table I.

ANALYTICAL METHOD

The vapor and liquid compositions of the methyl acetate–chloroform–benzene mixtures can be easily determined by density and refractive index measurements. Uncertainty of ± 0.0001 in density and refractive index means an uncertainty of 0.001 in the values of mole fraction of compositions of components.

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Refractive index measurements were made using a Shimadzu Pulfrich refractometer with prism thermostated at 25° ± 0.1° C. for monochromatic light of a sodium lamp. Values were reproducible within ±0.0001.

Density determinations were made using 10-ml. pycnometers suspended in a thermostat controlled at 25° ± 0.1° C. and were reproducible within ±0.0001.

The binary mixtures were analyzed by a calibration chart of physical properties *vs.* compositions made on the known mixtures once the density or refractive index measurement was made. The compositions of binary systems determined by these two measurements did not differ by more than 0.001 mole fraction. The ternary calibration mixtures were prepared by adding benzene to nine mixtures of chloroform and methyl acetate of known composition. The densities and refractive indices of the resulting mixtures were determined. These properties of the binary and ternary mixtures are listed in Table II. The properties were plotted against mole fraction of benzene with compositions of methyl acetate on a benzene-free basis. By linear interpolation, smoothed ternary standard calibration data were obtained for isometric values of properties. These data were used to construct a ternary calibration chart as shown in Figure 1.

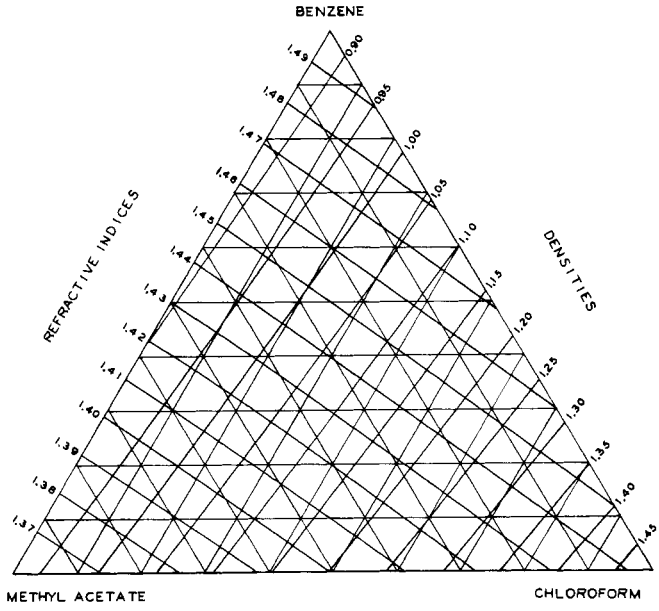

Figure 1. Lines of constant density and refractive index for the ternary system

APPARATUS

The experimental determination of vapor-liquid equilibria was carried out in a Colburn vapor-recirculating still like that of Griswold and Buford (*6*). Equilibrium temperatures were measured by a copper-constantan thermocouple which was calibrated against a standard thermometer and connected with a Yokogawa P-7 potentiometer. The precision of temperature measurements was within ±0.05° C. Since barometric pressure changed slightly, observed boiling temperatures were corrected to normal boiling points by the following equation (*15*).

$$t_c = t_o + 0.000\,12(t_o + 273.2)(760 - P)$$

t_c = corrected temperature, ° C.
t_o = observed temperature, ° C.
P = barometric pressure, mm. of mercury

VAPOR-LIQUID EQUILIBRIUM DATA

The activity coefficients of component i, γ_i, were calculated by the equation

$$\pi y_i = \gamma_i x_i P_i \qquad (1)$$

where π is the total pressure equal to 760 mm. of mercury. P_i is the vapor pressure of pure component i as the temperature of the system. The vapor pressure data for benzene were calculated using the Antoine equation given by Lange (*11*).

$$\log_{10} P_{\text{mm. Hg}} = 6.90565 - 1211.033/(t\,^\circ\text{C.} + 220.790)$$

The vapor pressure data for chloroform and methyl acetate were taken from the compilation of Timmermans (*18*).

Binary Systems. The correct form of the Gibbs-Duhem equation for isobaric binary systems was derived by Ibl and Dodge (*9*) to be

$$x_1 \frac{d\ln\gamma_1}{dx_1} + x_2 \frac{d\ln\gamma_2}{dx_1} = -\frac{\Delta H}{RT^2}\left(\frac{dT}{dx_1}\right)_p \qquad (2)$$

where ΔH is the integral heat of mixing per mole. Hence, the usual area condition was modified by Chao (*3*) to be

$$\int_2^1 \ln\frac{\gamma_1}{\gamma_2}\,dx_1 = \int_2^1 \frac{\Delta H}{RT^2}\left(\frac{dT}{dx_1}\right)_p dx_1 = a \qquad (3)$$

The value of a is not zero for systems showing a wide boiling point range and considerable heat of solution. However, in an azeotropic system a tends to vanish, since the sign of the slope $(dT/dx_1)_p$ changes as the composition goes through the azeotropic point.

At constant pressure the excess free energy may be expressed as the same functional form of equation originally developed by Redlich and Kister (*4*).

$$G^E = RTx_1x_2[B + C(x_1 - x_2) + D(x_1 - x_2)^2 + \ldots] \qquad (4)$$

Since the experimental evaluation of $(\Delta H/RT^2)(dT/dx_1)_p$ is difficult, Chao (*3*) included the effect of $(\Delta H/RT^2)(dT/dx_1)_p$ in the empirical equation for the ratio of activity coefficients as a series function of compositions. He proposed the following modified Redlich and Kister equation, allowing the requirements of Equation 3

$$\ln\gamma_1/\gamma_2 = a + b(x_2 - x_1) + c(6x_1x_2 - 1) + d(x_2 - x_1)(1 - 8x_1x_2) + \ldots \qquad (5)$$

Combination of Equations 4 and 5 gives the activity coefficients of the individual components. Thus,

$$\ln\gamma_1 = x_1x_2[B + C(x_1 - x_2) + D(x_1 - x_2)^2 + \ldots] + x_2[a + b(x_2 - x_1) + c(6x_1x_2 - 1) + d(x_2 - x_1)(1 - 8x_1x_2) + \ldots] \qquad (6a)$$

$$\ln\gamma_2 = x_1x_2[B + C(x_1 - x_2) + D(x_1 - x_2)^2 + \ldots] - x_1[a + b(x_2 - x_1) + c(6x_1x_2 - 1) + d(x_2 - x_1)(1 - 8x_1x_2) + \ldots] \qquad (6b)$$

The coefficients a, b, c, d, B, C, and D, if terms above d and D are neglected, must satisfy the following relation, because the value of $(\Delta H/RT^2)(dT/dx_1)_p$ becomes zero at the limiting concentrations ($x_1 \to 1$ and $x_2 \to 1$) (*14*).

$$\begin{cases} -a + (B - b) - (C - c) + (D - d) = 0 \\ -a - (B - b) - (C - c) - (D - d) = 0 \end{cases} \qquad (7)$$

As shown in Table III, the component binary systems involve a, b, c, B, and C. So Equation 7 is solved as

Table I. Physical Properties of Pure Compounds Used

Compound	Boiling Point, °C. Exptl.	Boiling Point, °C. Lit.	Density, 25/4 Exptl.	Density, 25/4 Lit.	Refractive Index, D/25 Exptl.	Refractive Index, D/25 Lit.
Methyl acetate	56.8	56.8(2)	0.9273	0.9273(*18*)	1.3589	
					1.3615(D/20)	1.3614(2)
Chloroform	61.2	61.26(*10*)	1.4802	1.4787(*10*)	1.4433	1.4430(*10*)
		61.152(*18*)		1.4807(*1*)		1.4433(*1*)
Benzene	80.1	80.1(*4*)	0.8739	0.8736(*4*)	1.4979	
				0.8738(*18*)		1.4980(*4*)

Table II. Data for Analysis of the System Methyl Acetate–Chloroform–Benzene

Methyl Acetate	Benzene	Density	Refractive Index	Methyl Acetate	Benzene	Density	Refractive Index
0.923	0.077	0.9218	1.3698	0.267	0.588	0.9675	1.4538
0.872	0.128	0.9181	1.3769	0.201	0.690	0.9429	1.4647
0.798	0.202	0.9131	1.3879	0.133	0.795	0.9198	1.4760
0.714	0.286	0.9081	1.3997	0.051	0.921	0.8913	1.4896
0.647	0.353	0.9041	1.4094	0.550	0	1.1753	1.3964
0.547	0.453	0.8986	1.4236	0.504	0.084	1.1465	1.4052
0.448	0.552	0.8920	1.4372	0.483	0.122	1.1329	1.4091
0.343	0.657	0.8881	1.4517	0.418	0.240	1.0952	1.4216
0.298	0.702	0.8861	1.4578	0.346	0.376	1.0519	1.4355
0.190	0.810	0.8814	1.4723	0.287	0.478	1.0205	1.4461
0	0.832	0.9669	1.4891	0.233	0.576	0.9915	1.4560
0	0.770	1.0016	1.4857	0.171	0.689	0.9586	1.4677
0	0.679	1.0538	1.4806	0.125	0.773	0.9352	1.4758
0	0.572	1.1164	1.4748	0.065	0.882	0.9057	1.4867
0	0.480	1.1719	1.4696				
0	0.366	1.2419	1.4636	0.460	0	1.2256	1.4042
0	0.267	1.3040	1.4581	0.424	0.078	1.1949	1.4116
0	0.165	1.3695	1.4525	0.378	0.179	1.1554	1.4215
0	0.083	1.4240	1.4481	0.331	0.280	1.1173	1.4312
0.898	0	0.9826	1.3674	0.283	0.384	1.0797	1.4409
0.827	0.078	0.9729	1.3779	0.238	0.483	1.0453	1.4503
0.752	0.192	0.9583	1.3933	0.197	0.572	1.0133	1.4587
0.644	0.283	0.9473	1.4054	0.144	0.688	0.9744	1.4694
0.554	0.383	0.9358	1.4188	0.102	0.778	0.9445	1.4779
0.478	0.468	0.9262	1.4302	0.049	0.893	0.9079	1.4885
0.380	0.577	0.9148	1.4442	0.352	0	1.2855	1.4136
0.283	0.685	0.9035	1.4581	0.324	0.079	1.2489	1.4204
0.175	0.805	0.8918	1.4735	0.284	0.193	1.1976	1.4301
0.068	0.925	0.8810	1.4886	0.249	0.292	1.1538	1.4387
0.803	0	1.0355	1.3752	0.220	0.376	1.1183	1.4460
0.753	0.062	1.0240	1.3828	0.188	0.466	1.0804	1.4537
0.658	0.180	1.0019	1.3981	0.151	0.572	1.0367	1.4626
0.582	0.275	0.9851	1.4099	0.114	0.675	0.9964	1.4714
0.508	0.367	0.9693	1.4211	0.079	0.774	0.9579	1.4795
0.416	0.483	0.9503	1.4357	0.034	0.903	0.9097	1.4905
0.333	0.586	0.9344	1.4482	0.233	0	1.3518	1.4237
0.253	0.685	0.9191	1.4603	0.216	0.075	1.3119	1.4296
0.175	0.783	0.9046	1.4721	0.190	0.184	1.2545	1.4378
0.058	0.927	0.8842	1.4895	0.169	0.275	1.2076	1.4447
0.754	0	1.0629	1.3792	0.133	0.431	1.1307	1.4564
0.680	0.098	1.0423	1.3906	0.123	0.473	1.1107	1.4595
0.586	0.188	1.0223	1.4022	0.086	0.630	1.0368	1.4712
0.549	0.271	1.0054	1.4123	0.072	0.691	1.0091	1.4756
0.466	0.382	0.9834	1.4256	0.046	0.802	0.9591	1.4838
0.395	0.476	0.9650	1.4372	0.022	0.907	0.9137	1.4917
0.320	0.575	0.9468	1.4489	0.121	0	1.4140	1.4333
0.240	0.681	0.9274	1.4615	0.110	0.086	1.3629	1.4389
0.157	0.792	0.9084	1.4715	0.097	0.193	1.2990	1.4460
0.076	0.899	0.8903	1.4867	0.087	0.277	1.2510	1.4515
0.648	0	1.1209	1.3878	0.077	0.366	1.2014	1.4572
0.582	0.102	1.0925	1.3994	0.063	0.478	1.1398	1.4644
0.533	0.178	1.0714	1.4080	0.051	0.576	1.0867	1.4708
0.460	0.291	1.0412	1.4210	0.038	0.689	1.0286	1.4780
0.402	0.380	1.0184	1.4307	0.027	0.775	0.9843	1.4837
0.341	0.474	0.9947	1.4412	0.012	0.905	0.9265	1.4920

Table III. Constants Used in Expressing Activity Coefficients

System	a_{ij}	b_{ij}	c_{ij}	B_{ij}	C_{ij}
Methyl acetate(1)–chloroform(2)	0	−0.2735	0.0409	−0.2735	0.0409
Chloroform(2)–benzene(3)	0	−0.0955	0.0143	−0.0955	0.0143
Benzene(3)–methyl acetate(1)	0.0308	0.1245	0.0183	0.1245	−0.0125

$$\begin{cases} B = b \\ C = c - a \end{cases} \quad (8)$$

In the actual numerical calculation logarithms were based on 10.

The vapor-liquid equilibrium data for the methyl acetate–chloroform system forming a maximum boiling azeotrope were reported by Bushmakin and Kish (*2*) in 1957. The present data obtained here are in close agreement with theirs. The chloroform-benzene system was determined by Reinders and de Minjer (*17*) in 1940. The *x-y* data agree well with their data, but the boiling point data are slightly lower than their data (a maximum deviation of 0.5° C.). This system shows small negative deviations from ideality. The end values of activity coefficients used are the same as those determined by Edwards, Hashmall, Gilmont, and Othmer (*5*).

The data on the methyl acetate–benzene system are not reported in the existing literature. This system indicates positive deviations from ideal solution.

The experimental data are listed in Tables IV, V, and VI for the three binaries.

Ternary System. An extension of Equation 2 to the ternary system under isobaric conditions gives

$$x_1 d\ln \gamma_1 + x_2 d\ln \gamma_2 + x_3 d\ln \gamma_3 = -\frac{\Delta H}{RT^2}\, dT \quad (9)$$

The excess free energy G^E_{123} for the ternary system is expressed as follows,

$$G^E_{123} = G^E_{12} + G^E_{23} + G^E_{31} + RTx_1x_2x_3[B + C_1(x_2 - x_3) + C_2(x_3 - x_1) + C_2(x_1 - x_2) + \dots] \quad (10)$$

where the first three terms on the right side represent contributions by the individual binaries, and the last term represents ternary effects. Equation 4 gives G^E's for binaries.

Standard procedures for deriving thermodynamic relations allow one to obtain expressions of activity coefficients and their ratios. The difficulties with the $(\Delta H/RT^2) \times (\partial T/\partial x)_p$ term are circumvented by modifying the constants as done with the binary system (*4*). The author suggests the following equation

$$\ln \gamma_1/\gamma_2 = a_{12} - b_{12}(x_1 - x_2) + c_{12}[2x_1x_2 - (x_1 - x_2)^2] + \dots + x_3\{b_{31} - b_{23} - c_{23}(2x_2 - x_3) + c_{31}(x_3 - 2x_1) - b((x_1 - x_2) - c_1[x_1(2x_2 - x_3) + x_2(x_3 - x_2)] - c_2[x_1(2x_2 - x_1)] + x_3(x_1 - x_2)] + c_3[2x_1x_2 - (x_1 - x_2)^2] + \dots\} \quad (11)$$

This equation including a_{12} term on the right side is different from that in the original article by Chao and Hougen (*4*). This comes from thermodynamic principle that the ternary equations must be consistent with component binary equations. At zero value of x_3 Equation 11 reduces to Equation 5. The similar expressions for $\ln \gamma_2/\gamma_3$ and $\ln \gamma_3/\gamma_1$ are obtained by cyclic permutation of the subscripts in the order of 1, 2, 3, 1. Combining these equations for the ratio of activity coefficients and Equation 10 gives expression of activity coefficients of the individual components, thus

$$\ln \gamma_1 = a_{12}x_2 - a_{31}x_3 + (G^E_{123}/RT) + [x_2(x_2 + x_3) - x_1x_2][b_{12} + c_{12}(x_1 - x_2) + \dots] - 2x_2x_3[b_{23} + c_{23}(x_2 - x_3) + \dots] + [(x_3 - x_1)(x_2 + x_3) + x_1x_2][b_{31} + c_{31}(x_3 - x_1) + \dots] + [x_1x_2(x_2 + x_3) + x_1x_2^2](c_{12} + \dots) + [x_2x_3(x_2 + x_3) - 2x_2^2x_3](c_{23} + \dots) + [-2x_3x_1(x_2 + x_3) + x_1x_2x_3](c_{31} + \dots) + [(x_2 + x_3)(x_2x_3 - x_1x_2) - x_2(x_1x_3 - x_1x_2)][b + c_1(x_2 - x_3) + c_2(x_3 - x_1) + c_3(x_1 - x_2) + \dots] + x_1x_2x_3[(x_2 + x_3)(c_1 - 2c_2 + c_3) - x_2(2c_1 - c_2 - c_3) + \dots] \quad (12)$$

Similarly $\ln\gamma_2$ and $\ln\gamma_3$ are obtained by cyclic advancement of the subscripts.

The ternary vapor-liquid equilibrium data could be predicted from the binary constants only by neglecting the ternary constants in the modified Redlich and Kister equations. The ternary vapor-liquid equilibrium data are listed in Table VII and compared with calculated values. The average deviation between observed and calculated vapor compositions is 0.005, 0.006, and 0.007 for methyl acetate, chloroform, and benzene, respectively. The average

Table IV. Experimental Vapor-Liquid Equilibrium Data for Methyl Acetate(1)–Chloroform(2)

Temp., °C.	Mole Fraction of Methyl Acetate		Activity Coeff.	
	Liquid	Vapor	Methyl acetate	Chloroform
58.1	0.920	0.953	0.992	0.650
59.2	0.851	0.907	0.983	0.665
60.3	0.782	0.854	0.971	0.688
61.4	0.706	0.791	0.961	0.705
62.4	0.640	0.719	0.932	0.750
63.2	0.563	0.631	0.905	0.790
63.7	0.532	0.592	0.884	0.803
64.2	0.463	0.502	0.847	0.840
64.7	0.406	0.425	0.804	0.864
64.7	0.335	0.327	0.750	0.903
64.6	0.263	0.236	0.692	0.925
64.2	0.224	0.191	0.666	0.944
63.7	0.171	0.130	0.604	0.967
63.5	0.159	0.117	0.599	0.971
62.2	0.064	0.040	0.532	0.992

Table V. Experimental Vapor-Liquid Equilibrium Data for Methyl Acetate(1)–Benzene(3)

Temp., °C.	Mole Fraction of Methyl Acetate		Activity Coeff.	
	Liquid	Vapor	Methyl acetate	Benzene
57.9	0.895	0.933	1.006	1.335
58.4	0.863	0.914	1.004	1.290
60.1	0.735	0.832	1.013	1.226
61.8	0.620	0.749	1.022	1.203
63.8	0.505	0.665	1.043	1.151
66.8	0.362	0.545	1.084	1.095
67.5	0.338	0.528	1.095	1.069
71.0	0.212	0.387	1.147	1.039
71.8	0.189	0.356	1.155	1.033
73.5	0.139	0.282	1.181	1.026
75.9	0.076	0.175	1.244	1.018
76.9	0.055	0.133	1.267	1.025

Table VI. Experimental Vapor-Liquid Equilibrium Data for Chloroform(2)–Benzene(3)

Temp., °C.	Mole Fraction of Chloroform		Activity Coefficients	
	Liquid	Vapor	Chloroform	Benzene
62.6	0.934	0.968	0.990	0.861
64.1	0.853	0.922	0.983	0.893
65.4	0.783	0.875	0.976	0.927
67.0	0.700	0.814	0.965	0.945
68.3	0.637	0.762	0.952	0.957
69.7	0.570	0.702	0.938	0.966
70.8	0.517	0.652	0.928	0.968
71.6	0.467	0.601	0.924	0.980
72.2	0.443	0.570	0.909	0.991
73.3	0.388	0.508	0.894	0.996
74.4	0.333	0.443	0.879	0.999
74.7	0.318	0.429	0.883	0.992
75.7	0.266	0.361	0.870	0.983
76.2	0.229	0.316	0.864	0.997
76.9	0.193	0.270	0.857	0.999
77.9	0.133	0.190	0.851	1.000
78.4	0.116	0.167	0.844	0.993
79.0	0.068	0.100	0.847	0.999
79.2	0.060	0.089	0.849	0.997

Table VII. Ternary Vapor-Liquid Equilibrium Data for Methly Acetate(1)–Chloroform(2)–Benzene(3)

Liquid Compn.			Observed Vapor Compn.			Calcd. Vapor[a] Compn.			Calcd. Vapor[b] Compn.			Temp., °C.			Obsd. Activity Coeff.			Calcd. Activity Coeff.		
												Obs.	Calcd.							
x_1	x_2	x_3	y_1	y_2	y_3	y_1	y_2	y_3	y_1	y_2	y_3		c	b	γ_1	γ_2	γ_3	γ_1	γ_2	γ_3
0.078	0.844	0.078	0.056	0.899	0.045	0.059	0.893	0.048	0.059	0.899	0.042	63.9	64.0	63.5	0.566	0.974	0.977	0.601	0.986	0.919
0.090	0.756	0.154	0.078	0.829	0.093	0.080	0.823	0.097	0.078	0.832	0.090	65.1	65.4	65.0	0.658	0.966	0.981	0.660	0.973	0.946
0.093	0.655	0.252	0.092	0.729	0.179	0.097	0.735	0.168	0.094	0.748	0.158	67.2	67.1	66.7	0.701	0.917	1.078	0.728	0.955	0.965
0.073	0.647	0.280	0.071	0.744	0.185	0.077	0.738	0.185	0.075	0.750	0.175	67.3	67.4	67.1	0.687	0.944	1.077	0.732	0.959	0.952
0.060	0.595	0.345	0.068	0.693	0.239	0.069	0.698	0.233	0.063	0.698	0.239	68.5	68.4	67.7	0.770	0.879	1.004	0.735	0.952	0.953
0.069	0.546	0.385	0.081	0.644	0.275	0.084	0.646	0.270	0.083	0.657	0.260	69.1	69.1	68.9	0.782	0.911	1.015	0.806	0.938	0.965
0.057	0.450	0.493	0.079	0.542	0.379	0.080	0.555	0.365	0.080	0.562	0.358	70.9	70.8	70.8	0.873	0.885	1.029	0.881	0.919	0.974
0.075	0.381	0.544	0.108	0.461	0.431	0.112	0.469	0.419	0.105	0.478	0.417	71.8	71.5	72.0	0.882	0.865	1.031	0.932	0.891	0.990
0.069	0.312	0.619	0.108	0.385	0.507	0.112	0.394	0.494	0.115	0.394	0.491	72.9	72.6	72.9	0.928	0.852	1.029	0.990	0.871	0.995
0.056	0.264	0.680	0.102	0.332	0.566	0.097	0.344	0.559	0.095	0.342	0.563	73.8	73.7	74.2	1.050	0.845	1.015	0.968	0.860	0.995
0.052	0.206	0.742	0.095	0.263	0.642	0.097	0.274	0.629	0.088	0.271	0.641	74.9	74.6	75.5	1.016	0.824	1.019	0.924	0.840	1.000
0.045	0.136	0.819	0.103	0.175	0.722	0.091	0.186	0.723	0.075	0.180	0.745	75.7	75.8	76.8	1.243	0.818	1.012	0.874	0.814	1.007
0.045	0.063	0.892	0.103	0.081	0.816	0.097	0.088	0.815	0.074	0.083	0.843	76.6	76.6	78.1	1.175	0.796	1.020	0.832	0.781	1.006
0.154	0.760	0.086	0.133	0.815	0.052	0.138	0.805	0.057	0.132	0.817	0.051	64.8	65.0	64.2	0.640	0.923	0.959	0.672	0.974	0.997
0.125	0.692	0.183	0.119	0.760	0.121	0.123	0.755	0.122	0.117	0.771	0.112	66.3	66.2	65.3	0.695	0.931	1.032	0.708	0.974	0.982
0.148	0.646	0.206	0.149	0.712	0.139	0.156	0.701	0.143	0.148	0.722	0.130	66.7	66.7	65.7	0.725	0.923	1.040	0.742	0.965	1.003
0.153	0.576	0.271	0.170	0.638	0.192	0.175	0.630	0.195	0.166	0.653	0.181	67.4	67.3	66.5	0.782	0.906	1.066	0.788	0.955	1.034
0.132	0.532	0.336	0.163	0.602	0.235	0.160	0.597	0.243	0.154	0.621	0.225	68.7	68.5	67.5	0.833	0.888	1.007	0.817	0.954	1.003
0.121	0.466	0.413	0.156	0.535	0.309	0.159	0.534	0.307	0.154	0.561	0.285	69.9	69.6	68.5	0.837	0.869	1.035	0.863	0.953	1.003
0.136	0.379	0.485	0.186	0.443	0.371	0.194	0.432	0.374	0.191	0.457	0.352	70.6	70.2	69.5	0.870	0.867	1.034	0.924	0.925	1.017
0.139	0.331	0.530	0.205	0.377	0.418	0.207	0.378	0.415	0.206	0.400	0.394	70.9	70.7	70.1	0.929	0.837	1.056	0.957	0.907	1.021
0.105	0.214	0.681	0.180	0.253	0.567	0.181	0.259	0.560	0.187	0.268	0.545	73.3	72.7	72.7	1.004	0.807	1.031	1.059	0.873	1.012
0.106	0.151	0.743	0.197	0.178	0.625	0.192	0.184	0.624	0.203	0.186	0.611	73.6	73.2	73.5	1.078	0.797	1.033	1.112	0.836	1.014
0.108	0.070	0.822	0.224	0.064	0.712	0.208	0.085	0.707	0.221	0.083	0.696	74.2	73.8	74.5	1.181	0.607	1.042	1.158	0.777	1.012
0.226	0.703	0.071	0.213	0.740	0.047	0.221	0.728	0.051	0.212	0.742	0.046	65.3	65.3	64.7	0.605	0.788	0.903	0.722	0.941	1.059
0.208	0.670	0.122	0.197	0.723	0.080	0.212	0.701	0.087	0.204	0.717	0.079	65.7	65.8	65.3	0.705	0.932	1.045	0.737	0.935	1.046
0.200	0.600	0.200	0.215	0.645	0.140	0.220	0.634	0.146	0.214	0.652	0.134	66.7	66.8	66.4	0.725	0.900	1.079	0.778	0.918	1.043
0.196	0.542	0.262	0.225	0.585	0.190	0.230	0.576	0.194	0.225	0.594	0.181	67.6	67.5	67.3	0.802	0.878	1.085	0.813	0.902	1.042
0.186	0.476	0.338	0.232	0.518	0.250	0.234	0.512	0.254	0.232	0.528	0.240	68.4	68.4	68.2	0.849	0.863	1.076	0.855	0.884	1.038
0.190	0.531	0.279	0.218	0.578	0.204	0.226	0.567	0.207	0.222	0.585	0.193	67.9	68.1	67.5	0.794	0.876	1.083	0.820	0.900	1.036
0.190	0.468	0.342	0.237	0.511	0.252	0.241	0.501	0.258	0.239	0.517	0.244	68.4	68.4	68.3	0.849	0.866	1.072	0.860	0.881	1.043
0.182	0.285	0.533	0.272	0.311	0.417	0.272	0.308	0.420	0.279	0.313	0.408	70.5	70.1	70.5	0.953	0.813	1.062	0.977	0.818	1.039
0.162	0.213	0.625	0.263	0.236	0.501	0.261	0.236	0.503	0.271	0.235	0.494	71.4	71.1	71.6	1.007	0.802	1.056	1.030	0.795	1.031
0.172	0.136	0.692	0.289	0.148	0.563	0.289	0.148	0.563	0.308	0.144	0.548	71.8	71.3	71.8	1.029	0.778	1.059	1.099	0.758	1.031
0.136	0.080	0.784	0.255	0.090	0.655	0.249	0.092	0.659	0.264	0.089	0.647	73.1	72.6	73.6	1.086	0.772	1.046	1.127	0.747	1.012
0.253	0.665	0.082	0.247	0.695	0.058	0.259	0.680	0.061	0.248	0.698	0.054	65.5	65.5	64.8	0.733	0.911	1.141	0.749	0.932	1.084
0.273	0.591	0.136	0.290	0.612	0.098	0.301	0.596	0.103	0.291	0.616	0.093	66.0	65.9	65.6	0.782	0.886	1.136	0.794	0.902	1.095
0.273	0.535	0.192	0.309	0.551	0.140	0.316	0.537	0.147	0.308	0.557	0.135	66.8	66.5	66.3	0.813	0.859	1.120	0.825	0.884	1.095
0.266	0.476	0.258	0.323	0.488	0.189	0.325	0.478	0.197	0.320	0.496	0.184	67.3	67.1	67.0	0.857	0.842	1.107	0.857	0.865	1.087
0.246	0.405	0.349	0.316	0.419	0.265	0.320	0.411	0.269	0.320	0.426	0.254	68.2	68.0	68.0	0.880	0.825	1.112	0.898	0.844	1.072
0.201	0.330	0.469	0.286	0.352	0.362	0.285	0.349	0.366	0.291	0.358	0.351	69.7	69.3	69.5	0.930	0.812	1.074	0.952	0.831	1.050
0.236	0.292	0.472	0.338	0.298	0.364	0.335	0.296	0.369	0.343	0.303	0.354	69.2	68.9	69.2	0.951	0.789	1.091	0.964	0.804	1.063
0.224	0.225	0.551	0.339	0.232	0.429	0.336	0.229	0.435	0.347	0.232	0.421	69.8	69.5	70.0	0.986	0.783	1.080	1.004	0.780	1.054
0.244	0.147	0.609	0.381	0.145	0.474	0.375	0.144	0.481	0.391	0.144	0.465	69.8	70.0	69.9	1.017	0.749	1.079	1.041	0.740	1.054
0.226	0.076	0.698	0.382	0.076	0.542	0.368	0.075	0.557	0.388	0.073	0.539	70.3	69.9	70.7	1.084	0.749	1.059	1.084	0.710	1.040

0.335	0.596	0.069	0.356	0.595	0.049	0.367	0.582	0.051	0.364	0.586	0.050	65.5	65.2	66.0	0.796	0.868	1.139	0.802	0.843	1.141
0.326	0.511	0.163	0.375	0.508	0.117	0.380	0.493	0.127	0.372	0.512	0.116	66.1	66.0	65.9	0.964	0.848	1.128	0.844	0.865	1.128
0.306	0.487	0.207	0.360	0.487	0.153	0.365	0.475	0.160	0.358	0.494	0.148	66.6	66.5	66.3	0.988	0.840	1.146	0.854	0.860	1.113
0.303	0.424	0.273	0.378	0.421	0.201	0.378	0.410	0.212	0.381	0.419	0.200	67.1	66.9	67.3	1.032	0.821	1.119	0.888	0.814	1.107
0.306	0.360	0.334	0.397	0.351	0.252	0.397	0.343	0.260	0.399	0.357	0.244	67.4	67.2	67.4	0.913	0.798	1.136	0.920	0.813	1.101
0.304	0.290	0.406	0.418	0.277	0.305	0.412	0.272	0.316	0.418	0.282	0.300	67.7	67.5	67.8	0.958	0.776	1.120	0.956	0.785	1.096
0.293	0.215	0.492	0.422	0.203	0.375	0.416	0.201	0.383	0.429	0.206	0.365	68.3	68.6	69.1	0.984	0.751	1.112	0.976	0.743	1.055
0.289	0.159	0.552	0.438	0.149	0.413	0.423	0.147	0.430	0.428	0.151	0.421	68.4	68.2	69.4	1.032	0.743	1.088	0.978	0.732	1.073
0.300	0.076	0.624	0.466	0.068	0.466	0.450	0.068	0.482	0.445	0.074	0.481	68.6	68.1	70.0	1.052	0.705	1.079	0.961	0.708	1.064
0.385	0.525	0.090	0.430	0.504	0.066	0.439	0.489	0.072	0.426	0.509	0.065	65.4	65.1	64.9	0.839	0.837	1.180	0.845	0.861	1.171
0.387	0.482	0.131	0.445	0.458	0.097	0.453	0.443	0.104	0.442	0.463	0.095	65.7	65.7	65.2	0.856	0.821	1.180	0.865	0.844	1.167
0.391	0.418	0.191	0.471	0.389	0.140	0.473	0.376	0.151	0.464	0.398	0.138	65.8	65.6	65.3	0.893	0.802	1.163	0.894	0.831	1.161
0.360	0.385	0.255	0.447	0.362	0.191	0.449	0.351	0.200	0.447	0.368	0.185	66.7	66.2	66.2	0.894	0.787	1.155	0.908	0.812	1.137
0.325	0.358	0.317	0.419	0.344	0.237	0.418	0.335	0.247	0.420	0.349	0.231	67.3	66.9	67.0	0.910	0.789	1.130	0.921	0.809	1.114
0.377	0.216	0.407	0.511	0.188	0.301	0.503	0.184	0.313	0.513	0.199	0.288	66.6	66.3	66.7	0.979	0.731	1.144	0.982	0.772	1.091
0.372	0.141	0.487	0.528	0.121	0.351	0.512	0.118	0.370	0.520	0.124	0.356	66.6	66.6	67.3	1.025	0.721	1.114	0.989	0.722	1.105
0.367	0.072	0.561	0.535	0.061	0.404	0.518	0.059	0.423	0.522	0.061	0.417	66.8	66.6	68.2	1.047	0.707	1.106	0.976	0.675	1.088
0.448	0.491	0.061	0.518	0.438	0.044	0.515	0.436	0.049	0.521	0.437	0.042	64.8	64.4	63.0	0.886	0.793	1.187	0.944	0.838	1.211
0.439	0.427	0.134	0.514	0.387	0.099	0.521	0.372	0.107	0.512	0.391	0.097	65.2	64.8	64.7	0.886	0.796	1.196	0.895	0.815	1.194
0.442	0.358	0.200	0.550	0.295	0.155	0.539	0.303	0.158	0.537	0.318	0.145	65.2	64.9	64.9	0.941	0.724	1.254	0.930	0.787	1.183
0.430	0.281	0.289	0.549	0.240	0.211	0.544	0.233	0.223	0.546	0.245	0.209	65.5	65.3	65.5	0.956	0.741	1.171	0.953	0.756	1.161
0.431	0.224	0.345	0.564	0.187	0.249	0.554	0.181	0.265	0.562	0.189	0.249	65.6	65.3	65.6	0.976	0.723	1.152	0.974	0.731	1.151
0.439	0.141	0.420	0.586	0.115	0.299	0.575	0.110	0.315	0.588	0.113	0.299	65.3	65.2	65.6	1.006	0.714	1.149	1.001	0.693	1.136
0.407	0.091	0.502	0.575	0.071	0.354	0.552	0.072	0.376	0.570	0.073	0.357	65.8	65.8	66.3	1.048	0.676	1.119	1.022	0.677	1.111
0.503	0.425	0.072	0.576	0.371	0.053	0.587	0.355	0.058	0.574	0.373	0.053	64.3	63.9	63.8	0.892	0.788	1.230	0.903	0.805	1.237
0.493	0.355	0.152	0.590	0.299	0.111	0.591	0.289	0.120	0.585	0.305	0.110	64.4	64.1	64.1	0.929	0.758	1.218	0.929	0.781	1.215
0.494	0.303	0.203	0.603	0.250	0.147	0.601	0.240	0.159	0.600	0.254	0.146	64.5	64.2	64.3	0.944	0.740	1.100	0.945	0.755	1.203
0.473	0.285	0.242	0.589	0.234	0.177	0.584	0.228	0.188	0.586	0.240	0.174	64.7	64.1	64.7	0.957	0.732	1.204	0.951	0.751	1.186
0.496	0.155	0.349	0.634	0.120	0.246	0.624	0.115	0.261	0.631	0.124	0.245	64.3	64.2	64.3	0.995	0.699	1.177	0.991	0.724	1.170
0.494	0.081	0.425	0.649	0.059	0.292	0.630	0.058	0.312	0.646	0.060	0.294	64.2	64.2	64.6	1.026	0.660	1.151	1.010	0.656	1.146
0.569	0.357	0.074	0.655	0.290	0.055	0.665	0.276	0.059	0.655	0.291	0.054	63.3	62.9	63.1	0.927	0.758	1.284	0.932	0.766	1.262
0.561	0.305	0.134	0.659	0.241	0.100	0.664	0.231	0.105	0.660	0.244	0.096	63.4	63.1	63.3	0.943	0.735	1.285	0.948	0.747	1 .244
0.571	0.223	0.206	0.687	0.168	0.145	0.683	0.160	0.157	0.684	0.170	0.146	63.3	63.0	63.1	0.969	0.703	1.216	0.971	0.717	1.227
0.554	0.157	0.289	0.687	0.114	0.199	0.674	0.110	0.216	0.679	0.121	0.200	63.4	63.2	63.3	0.995	0.675	1.186	0.987	0.719	1.199
0.557	0.082	0.361	0.698	0.057	0.245	0.683	0.055	0.262	0.696	0.057	0.247	63.2	63.1	63.4	1.012	0.651	1.177	1.003	0.650	1.178
0.638	0.294	0.068	0.730	0.220	0.050	0.737	0.209	0.054	0.725	0.226	0.049	62.5	62.0	62.0	0.945	0.716	1.306	0.956	0.748	1.288
0.637	0.221	0.142	0.738	0.161	0.101	0.741	0.151	0.108	0.739	0.161	0.100	62.4	62.0	62.1	0.972	0.699	1.268	0.973	0.711	1.264
0.655	0.148	0.197	0.763	0.103	0.134	0.759	0.095	0.146	0.757	0.101	0.142	61.8	61.7	61.5	0.986	0.681	1.240	0.987	0.674	1.325
0.646	0.076	0.278	0.765	0.050	0.185	0.753	0.047	0.200	0.764	0.050	0.186	61.8	61.7	61.9	1.002	0.644	1.213	0.998	0.640	1.221
0.711	0.222	0.067	0.800	0.153	0.047	0.805	0.144	0.051	0.797	0.156	0.047	61.2	60.9	61.0	0.972	0.688	1.304	0.975	0.708	1.307
0.722	0.146	0.132	0.812	0.098	0.090	0.813	0.089	0.098	0.815	0.095	0.090	61.0	60.7	60.8	0.978	0.674	1.275	0.988	0.658	1.287
0.715	0.084	0.201	0.814	0.052	0.134	0.806	0.050	0.144	0.813	0.053	0.134	60.9	60.7	60.8	0.993	0.624	1.251	0.996	0.640	1.258
0.789	0.151	0.060	0.861	0.098	0.041	0.867	0.089	0.044	0.863	0.097	0.040	60.1	59.7	59.7	0.977	0.671	1.318	0.989	0.669	1.325
0.784	0.066	0.150	0.860	0.040	0.100	0.857	0.037	0.106	0.862	0.039	0.099	59.9	59.7	59.7	0.989	0.631	1.296	0.997	0.627	1.290
0.862	0.072	0.066	0.914	0.043	0.043	0.915	0.038	0.047	0.915	0.042	0.043	58.9	58.6	58.7	0.988	0.643	1.313	0.997	0.626	1.332
0.207	0.346	0.447	0.291	0.367	0.342	0.289	0.364	0.347	0.293	0.372	0.335	69.5	69.1	69.4	0.924	0.813	1.072	0.933	0.827	1.055

[a] Lu, Li, and Ting's method (*12*). [b] Modified Redlich and Kister's equations. [c] Nagata's method (*13*).

difference between experimental and calculated temperatures is 0.4° C.

Algebraic Method. Another method which correlates the vapor-liquid equilibria of binary systems and can predict ternary vapor-liquid equilibria from binary data treats algebraic equations. Such as algebraic equation is expressed for binary systems as follows (*12, 16*).

$$\frac{y_i}{y_j} = \frac{x_i}{x_j}\left(\frac{x_i + x_j a_{ij}}{x_j b_{ij} + x_i c_{ij}}\right) \tag{13}$$

The boiling points of the binary systems, T_m, are calculated according to the equation recently proposed by the author (*13*).

$$T_m = T_i y_{ii} + T_j y_{jj} + T_{ij}(y_{ij} + y_{ji}) \tag{14}$$

where a_{ij}, b_{ij}, c_{ij}, and T_{ij} are constants determined from experimental data and given in Table VIII in which the value of T_{23} is not equal to the one listed in the previous article (*13*), because the present boiling point data for the chloroform-benzene system are a little lower than those of Reinders and de Minjer (*17*), y's are variables defined by the following equations

$$y_{ii} = y_i \cdot x_i/(x_i + x_i a_{ij}) \tag{15}$$

$$y_{ij} = y_i \cdot x_j a_{ij}/(x_i + x_j a_{ij}) \tag{16}$$

$$y_{jj} = y_j \cdot x_j b_{ij}/(x_j b_{ij} + x_i c_{ij}) \tag{17}$$

$$y_{ji} = y_j \cdot x_i c_{ij}/(x_j b_{ij} + x_i c_{ij}) \tag{18}$$

If a ternary system does not deviate too much from the condition,

$$b_{12} \cdot b_{23} \cdot b_{31} = 1 \tag{19}$$

the vapor compositions of the system are obtainable from binary constants using the equation recommended by Lu, Li, and Ting (*12*).

$$\begin{aligned} y_1 : y_2 : y_3 = {} & (b_{31}/b_{12})^{1/3} x_1(x_1 + x_2 a_{12} + x_3 c_{31}/b_{31}) \\ & (b_{12}/b_{23})^{1/3} x_2(x_2 + x_3 a_{23} + x_1 c_{12}/b_{12}) \\ & (b_{23}/b_{31})^{1/3} x_3(x_3 + x_1 a_{31} + x_2 c_{23}/b_{23}) \end{aligned} \tag{20}$$

Analogous equations were empirically proposed by Hála (*7*). Equation 20 is more flexible for practical use than Hála's equation, because the former may satisfy the restriction of Equation 19 approximately, but the latter must fulfil it strictly. The boiling points of the system, T_m, are calculated by using Equation 20 in the same manner as those of the binary systems.

$$\begin{aligned} T_m = {} & T_1 y_{11} + T_2 y_{22} + T_3 y_{33} + T_{12}(y_{12} + y_{21}) \\ & + T_{23}(y_{23} + y_{32}) + T_{13}(y_{13} + y_{31}) \end{aligned} \tag{21}$$

where y_{11} is given by the equation,

$$y_{11} = y_1 x_1/(x_1 + x_2 a_{12} + x_3 c_{31}/b_{31}) \tag{22}$$

and the other y's are defined similarly.

For the present ternary system $b_{12} \cdot b_{23} \cdot b_{31} = 1.259$, so the above equations are applicable. Calculated values of vapor compositions and boiling points are also given in Table VII. Average deviation of the calculated from the observed vapor compositions is 0.006 for methyl acetate, 0.008 for chloroform, and 0.008 for benzene. The average deviation of the calculated boiling temperatures from the experimental values is 0.2° C.

Conclusions. The two correlation methods give comable results on the predicted vapor compositions. The analytical equations expressing ln γ involve a lengthy trial and error method for the prediction of boiling temperatures and vapor compositions, but the algebraic method allows one to handle such problems in a straight forward manner, without involving trial calculations. The ternary predicted boiling temperatures by the latter agree better with the experimental data than those obtained by the trial error method. Apparently further investigations will be needed for making a inclusive comparison of their merits. No ternary azeotrope was found.

Table VIII. Primary Information Used for Prediction of Ternary Vapor-Liquid Equilibria

($b_{12}.b_{23}.b_{31} = 1.259$)

System	a_{ij}	b_{ij}	c_{ij}	T_{ij}
Methyl acetate(*1*)-chloroform(*2*)	0.255	0.534	0.497	348.1
Chloroform(*2*)-benzene(*3*)	0.960	0.653	0.500	347.1
Benzene(*3*)-methyl acetate(*1*)	2.271	3.610	2.744	338.7

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NOMENCLATURE

a_{12}, a_{23}, a_{31}
b_{12}, b_{23}, b_{31}
c_{12}, c_{23}, c_{31} = constants defined by Equations 13 to 22

$a, b, c, d,$
B, C, D = modified Redlich-kister binary constants defined by Equations 4 to 8

B, C_1, C_2, C_3
b, c_1, c_2, c_3 = modified Redlich-Kister ternary constants defined by Equations 10 to 12

G^E = excess free energy per mole of solution
ΔH = integral heat of mixing per mole of solution
P = barometric pressure, mm. of mercury
P_i = vapor pressure of component i, mm. of mercury
R = gas contants
t_c = corrected temperature, ° C.
t_o = observed temperature, ° C.
T = boiling temperature, ° K.
T_{12}, T_{23}, T_{13} = constants defined by Equations 14 and 21
x_i = mole fraction of liquid phase of component i
y_i = mole fraction of vapor phase of component i
γ_i = activity coefficient of component i
π = total pressure, mm. of mercury

Subscripts

1, 2, 3, i, j = components
m = mixture

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