Vapor-Liquid Equilibria of the Ternary System Acetone–Chloroform–2,3-Dimethylbutane

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Vapor-liquid equilibrium data at 760 mm. of Hg were determined in a modified Colburn still for the ternary system acetone–chloroform–2,3-dimethylbutane. This system is comprised of two binary minimum-boiling homogeneous azeotropes and one maximum-boiling homogeneous azeotrope. The data were correlated by means of the two-parameter Wilson equation.

KNOWLEDGE of multicomponent vapor-liquid equilibrium data is important in the design of distillation equipment. The purpose of this study was to determine the vapor-liquid equilibria for the non-ideal ternary system acetone–chloroform–2,3-dimethylbutane at 760 mm. of Hg, and to compare the experimental results with ternary data predicted from available binary data, using a suitable correlating equation.

EXPERIMENTAL

Materials. All three chemicals as received had a guaranteed purity of at least 99 mole %. No further purification was considered necessary. The essential properties of the materials are shown in Table I.

Procedure. The equilibrium data were obtained in a modified Colburn still (*7*), as described by Hollenshead and Van Winkle (*4*) and others (*3, 11*). The modified Colburn still used here (Figure 1) was the same as that described by Hollenshead and Van Winkle, with certain changes in the arrangement of the heating coils. The heating system for the still was the one developed by Hanson and Van Winkle (*2*) and used by Humphrey and Van Winkle (*6*). Nitrogen was used to maintain the pressure of the system at 760 mm. of Hg. An oil bath was kept at approximately 29.4° C., using a Sargent Thermonitor with two heaters. A volume of tubing in the oil bath, kept at a constant temperature, was necessary to minimize fluctuations in pressure with ambient temperature fluctuations (Figure 2).

The copper-constantan thermocouples were calibrated, using four points of data; these temperatures were indirectly referenced from a National Bureau of Standards-calibrated platinum resistance thermometer. A third-order curve was fitted through these four points, and a calibration table was used to read intermediate temperatures.

The procedure for obtaining vapor-liquid equilibrium samples consisted of measuring out each pure component with a syringe to obtain the desired concentration range and minimize exposure to air, transferring the cold, prepared sample to the still, and boiling the sample with recirculation. Adjustments were made to maintain 760 mm. of Hg ±0.1 mm. and the temperatures of liquid and vapor within 0.1° C. of each other. After eliminating fluctuations, and thus achieving steady state conditions, the still was operated for an additional 45 minutes to 1 hour to insure equilibrium. The liquid and vapor samples were then taken in serum bottles for refrigeration until analysis.

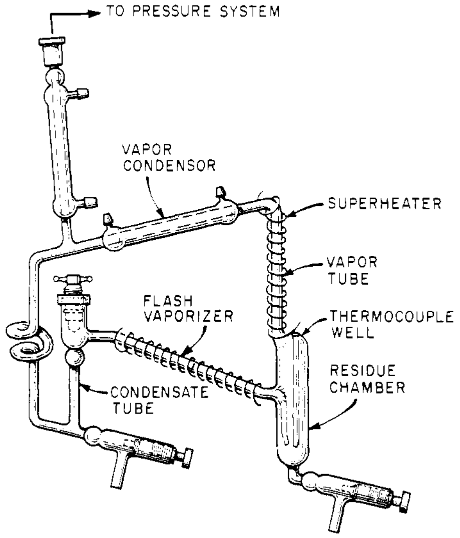

Figure 1. Modified Colburn equilibrium still

Table I. Physical Properties of the Materials

Properties	Acetone	Chloroform	2,3-Dimethylbutane
Molecular weight	58.08	119.39	86.17
Boiling point, ° C. (760 mm. of Hg)			
Literature	56.20 (*13*)	61.2 (*12*)	57.99 (*1*)
Experimental	56.15	61.15	58.15
Refractive index, n_D^{25}			
Literature	1.35609 (*13*)	1.44293 (*1*)	1.37231 (*1*)
Experimental	1.35640	1.44304	1.37244
Chromatographic analysis, purity	99.98%	99.92%	99.97%
Antoine constants (*5*)			
A	7.02447	6.90328	6.80983
B	1161.0	1163.0	1127.187
C	224.	227.4	228.900

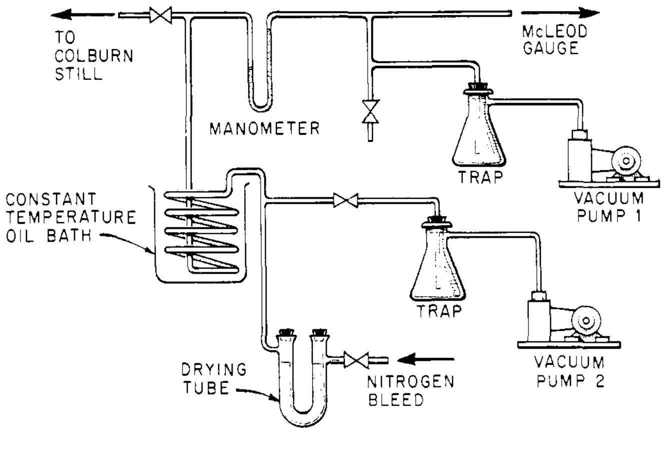

Figure 2. Pressure system

Analysis. The samples were analyzed with a Beckman GC-2 chromatograph and a Model SR-72180, 1-mv. full-span Sargent recorder equipped with a Disc integrator. The same analytical column used to check the purity of the materials was used for analysis of samples.

The composition of each sample, both liquid and vapor, was first determined approximately. Once the relative composition of each component had been determined, a corresponding amount of each component was placed in a serum bottle and weighed on a Mettler H10TW balance. Thus, for each unknown sample there was a known sample of approximately the same composition. Each sample of known composition was injected into the GC-2, and the corresponding sample of unknown composition was analyzed immediately afterwards. After correcting for integrator drift, the counts for known and unknown samples and the grams of each component in the known sample were used to calculate the mole fractions of both the samples and also the relative sensitivity of the GC-2 to each of the components. This method gave a control sample for each unknown sample and virtually eliminated errors due to different sensitivities of the GC-2 to different components.

The limits of error in these experimental data were estimated as follows: temperature, ±0.1° C.; pressure, ±0.2 mm. of Hg; composition, ±0.003 mole fraction.

Table IIa. Binary Data

Binary	P, Mm. of Hg	T, ° C.	x_A	y_A	γ_A	γ_D
Acetone (*A*)-DMB(*D*)	760.05	48.8	0.875	0.701	1.036	3.213
	760.05	45.8	0.424	0.488	1.667	1.328
Chloroform (*C*)-DMB(*D*)			x_C	y_C	γ_C	γ_D
	760.07	56.7	0.653	0.592	1.070	1.222
	759.96	56.1	0.399	0.403	1.214	1.055

RESULTS AND CORRELATION OF DATA

The derivation of the Wilson equation, which was used in correlating the data for this study, is presented by Orye and Prausnitz (*10*). This study used the Wilson equation, but vapor phase ideality was assumed. The activity coefficients of the components were calculated from the experimental data by Equation 1, neglecting the very small vapor phase nonideality effects.

$$\gamma_i = \frac{y_i P_T}{x_i P_i} \tag{1}$$

P_i, the vapor pressure, was calculated from the Antoine constants (Table I) of the respective components, using Equation 2.

$$\log_{10} P_i = A_i - \frac{B_i}{t + C_i} \tag{2}$$

Binary. The two DMB binaries were investigated by McConnell and Van Winkle (*9*), and the acetone-chloroform binary data were reported by Karr (*8*). Two binary points were determined experimentally for each of the DMB binaries, both as a check and a reference. These points, and the corresponding experimental activity coefficients, are shown in Table IIa. Table IIb shows the two Wilson equation parameters, $(\lambda_{ij} - \lambda_{ii})$ and $(\lambda_{ji} - \lambda_{jj})$, calculated from the binary data in Table IIa. The differences in these parameters make a negligible difference in the predicted vapor-liquid values because of the form of the Wilson equation. In the equation, the parameters are in exponential form, and thus it takes a relatively great change in the parameters in the following equations to make a significant change in the predicted values.

$$\Lambda_{ji} = \frac{v_i}{v_j} \exp\left[-(\lambda_{ji} - \lambda_{jj})/RT\right] \tag{3a}$$

$$\Lambda_{ij} = \frac{v_j}{v_i} \exp\left[-(\lambda_{ij} - \lambda_{ii})/RT\right] \tag{3b}$$

Sometimes the quantity Λ_{ij} or Λ_{ji}, as defined in Equations 3a and 3b, is called the Wilson parameter. However, in this paper, "the Wilson parameter" refers to $(\lambda_{ij} - \lambda_{ii})$ and/or $(\lambda_{ji} - \lambda_{jj})$.

Ternary. The ternary system may best be described visually by referring to Figures 3 and 4. The figures represent the liquid and vapor surfaces drawn so that the vapor surface is in its normal position in Figure 3, but in Figure 4 it has been separated from the liquid surface in an "exploded" view. In the normal arrangement, the two surfaces would meet only at six points: at each of the three corners of the illustration, and each of the three azeotropes, as shown by points *A*, *B*, and *C*, where $x_i = y_i$. The liquid surface appears as a modified amphitheater, which has a slight *S*-curvature in one portion.

Table IIb. Wilson Parameters for the Binary Systems[a]

	Acetone (*A*)-Chloroform (*C*)-DMB (*D*)			
	Based on McConnell's Binaries[b]		Based on Table IIa	
Binary	$\lambda_{ij} - \lambda_{ii}$	$\lambda_{ji} - \lambda_{jj}$	$\lambda_{ij} - \lambda_{ii}$	$\lambda_{ji} - \lambda_{jj}$
Acetone-Chloroform (*A*, *C*)	−72.20	−332.23	. . .	. . .
Acetone-DMB (*A*, *D*)	996.65	297.36	1007.26	302.70 (from $x_A = 0.424$)
Chloroform-DMB (*C*, *D*)	213.88	223.69	210.31	213.54 (from $x_A = 0.399$)

[a] Cal. per gram-mole. [b] Based on binary data from Karr (*8*).

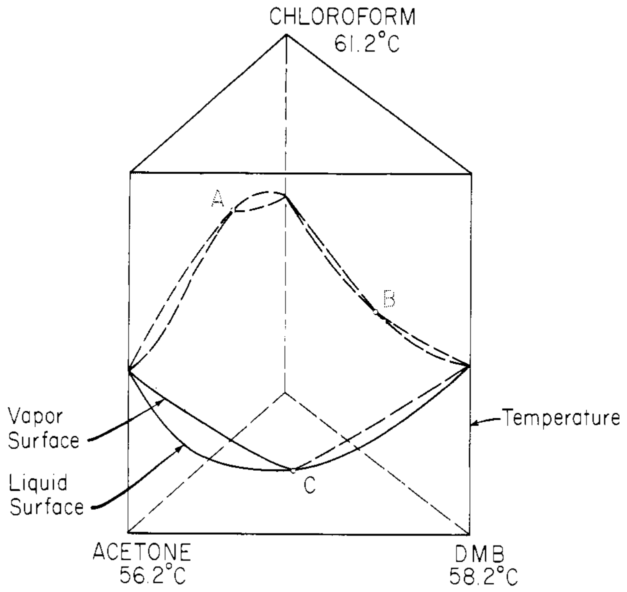

Figure 3. Vapor-liquid surfaces (normal view)
A. Maximum azeotrope, 64.5° C.
B. Minimum azeotrope, 55.5° C.
C. Minimum azeotrope, 44.8° C.

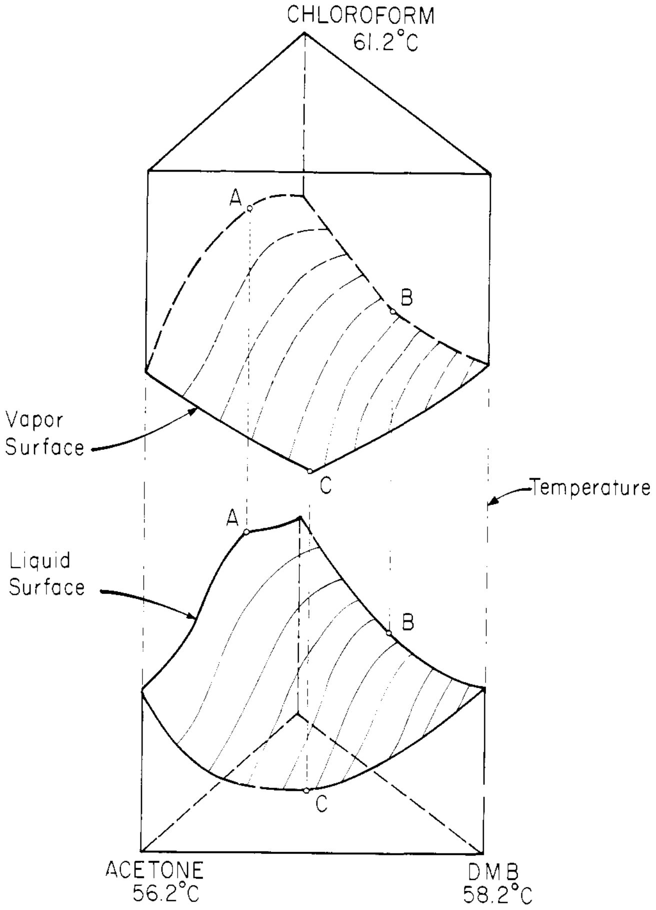

Figure 4. Vapor-liquid surfaces (exploded view)
A. Maximum azeotrope, 64.5° C.
B. Minimum azeotrope, 55.5° C.
C. Minimum azeotrope, 44.8° C.

The vapor surface is similar, but has a slight trough between points *B* and *C*. Another means of illustrating the curvature of the surfaces is given in Figures 5 and 6: These represent the liquid and vapor surfaces through the use of (isobaric) isotherms. Figure 6 indicates the slight trough in the vapor between the points *B* and *C*.

These topographical drawings should be considered only as a semi-quantitative aid in visualizing the surfaces because the temperatures (shown in Figure 7 and tabulated in Table III) do not provide enough points to draw the isotherms with accuracy. To provide additional "data points," temperature-composition points predicted by the Wilson equation have been used as a guide for the regions between the experimental points. Upon examination of Table III, one can see that the Wilson model temperature predictions were usually low by about 0.6° C. Allowances were made in construction of these topographical figures by using a "zone method."

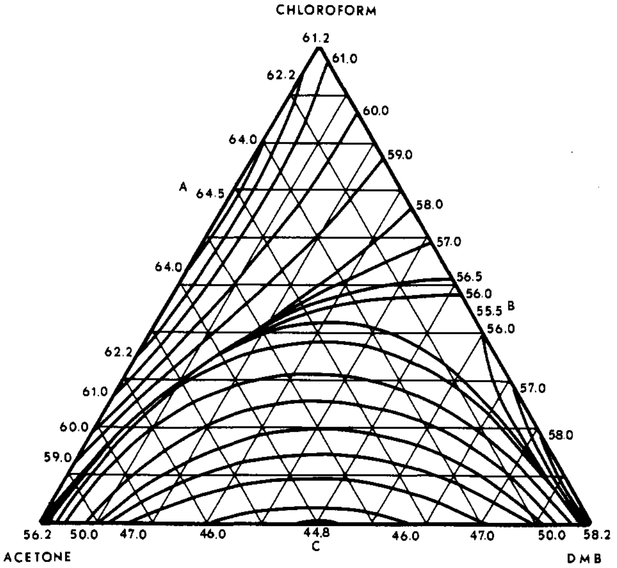

Figure 5. Isothermal lines of the liquid surface

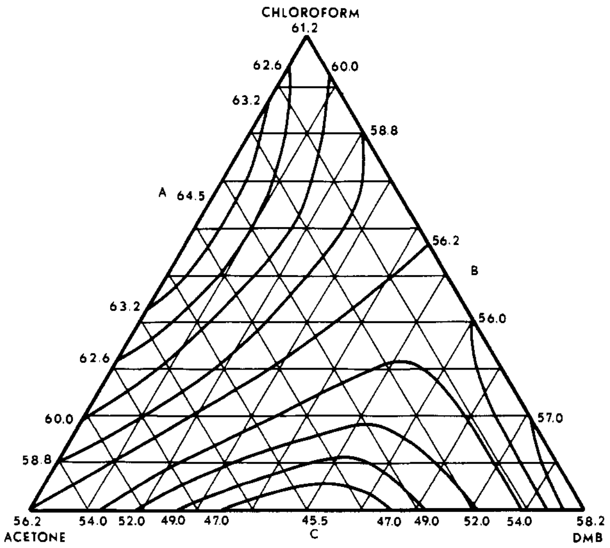

Figure 6. Isothermal lines of the vapor surface

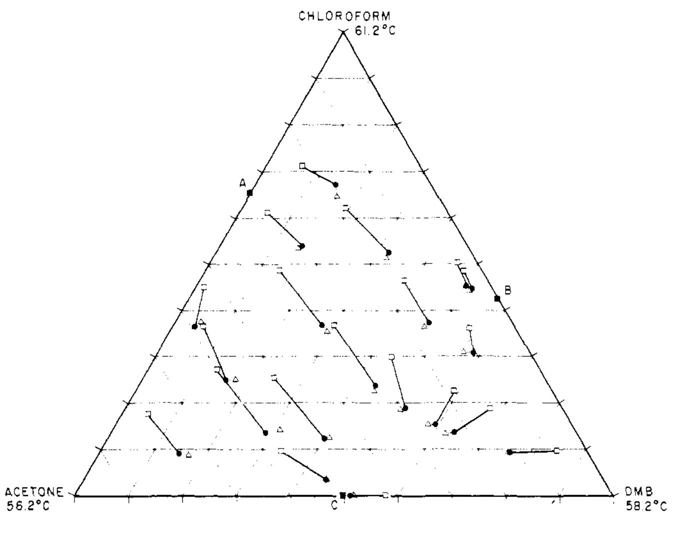

Figure 7. Experimental and theoretical values of equilibrium data

☐ Liquid composition	A. Maximum azeotrope, 64.5° C.
△ Vapor composition	B. Minimum azeotrope, 55.5° C.
● Wilson equation vapor composition prediction	C. Minimum azeotrope, 44.8° C.

Figure 7 serves several purposes; it graphically locates, in an over-all scheme, each experimental point. This provides an indication of the relative location of the experimental points upon which the exploded view and topographic drawings are based. It shows visually the relative agreement of the experimental and predicted vapor composition data. The agreement is fairly good in most cases (generally within 0.6° C. and 0.02 mole fraction of vapor composition) if the areas of high acetone-chloroform concentration are excluded.

CONCLUSIONS

The results of this study show that there is no ternary azeotrope for the system acetone–chloroform–2,3-dimethylbutane at 760 mm. of Hg. The maximum-boiling azeotrope of acetone-chloroform provides a steep "hill" on one side of the liquid temperature-composition surface, and this tends to eliminate the possibility of a minimum or ternary azeotrope within the center part of the liquid surface. Also, the results show that the Wilson equation predicts ternary data (for this system, which is quite nonideal) within 0.6° C. and 0.02 mole fraction.

Table III. Vapor-Liquid Equilibrium Data[a]

P, mm. of Hg	T, ° C.	Acetone (A)–Chloroform (C)–DMB (D)								
		x_A	x_C	y_A	y_C	γ_A	γ_C	γ_D	α_{AC}	α_{DC}
760.07	55.5^b	0.778	0.175	0.760^b	0.090^b	0.999^b	0.633^b	3.420^b	1.90^b	6.08^b
	55.1^c			0.743^c	0.089^c	0.990^c	0.627^c	3.843^c	1.89^c	6.96^c
760.05	52.9^b	0.263	0.296	0.291^b	0.188^b	1.241^b	0.854^b	1.393^b	1.74^b	1.86^b
	52.1^c			0.303^c	0.187^c	1.333^c	0.873^c	1.399^c	1.82^c	1.83^c
759.99	52.3^b	0.181	0.226	0.254^b	0.153^b	1.605^b	0.923^b	1.201^b	2.07^b	1.48^b
	51.6^c			0.267^c	0.156^c	1.724^c	0.965^c	1.192^c	2.13^c	1.41^c
760.06	55.7^b	0.153	0.465	0.153^b	0.372^b	1.019^b	0.976^b	1.339^b	1.25^b	1.55^b
	54.7^c			0.166^c	0.363^c	1.137^c	0.980^c	1.360^c	1.39^c	1.58^c
760.02	61.1^b	0.220	0.710	0.179^b	0.670^b	0.691^b	0.963^b	1.952^b	0.86^b	2.29^b
	60.5^c			0.186^c	0.646^c	0.730^c	0.945^c	2.209^c	0.93^c	2.64^c
760.04	54.0^b	0.331	0.364	0.328^b	0.231^b	1.069^b	0.817^b	1.645^b	1.56^b	2.28^b
	53.0^c			0.329^c	0.228^c	1.105^c	0.831^c	1.698^c	1.59^c	2.33^c
759.92	58.6^b	0.578	0.368	0.593^b	0.248^b	0.949^b	0.745^b	2.901^b	1.52^b	4.36^b
	58.1^c			0.575^c	0.248^c	0.931^c	0.756^c	3.256^c	1.48^c	4.87^c
760.00	57.9^b	0.379	0.488	0.354^b	0.367^b	0.884^b	0.852^b	2.101^b	1.24^b	2.79^b
	56.9^c			0.351^c	0.352^c	0.902^c	0.843^c	2.307^c	1.28^c	3.10^c
760.05	53.8^b	0.052	0.098	0.142^b	0.092^b	2.946^b	1.215^b	1.030^b	2.52^b	0.96^b
	53.6^c			0.148^c	0.094^c	3.101^c	1.253^c	1.024^c	2.96^c	0.93^c
760.00	56.0^b	0.037	0.485	0.039^b	0.449^b	1.057^b	1.116^b	1.141^b	1.14^b	1.16^b
	55.5^c			0.046^c	0.443^c	1.270^c	1.115^c	1.151^c	1.37^c	1.17^c
760.06	56.1^b	0.038	0.501	0.041^b	0.455^b	1.083^b	1.093^b	1.163^b	1.19^b	1.20^b
	55.6^c			0.046^c	0.454^c	1.226^c	1.106^c	1.162^c	1.33^c	1.19^c
760.05	58.2^b	0.187	0.625	0.151^b	0.527^b	0.752^b	0.946^b	1.707^b	0.96^b	2.03^b
	57.3^c			0.163^c	0.514^c	0.839^c	0.947^c	1.749^c	1.06^c	2.09^c
760.09	47.9^b	0.568	0.095	0.516^b	0.034^b	1.214^b	0.565^b	1.858^b	2.54^b	3.95^b
	47.7^c			0.514^c	0.036^c	1.217^c	0.608^c	1.864^c	2.38^c	3.52^c
760.01	52.3^b	0.137	0.183	0.229^b	0.134^b	1.902^b	0.996^b	1.127^b	2.28^b	1.28^b
	51.7^c			0.242^c	0.137^c	2.053^c	1.038^c	1.116^c	2.36^c	1.23^c
760.07	62.3^b	0.537	0.450	0.591^b	0.365^b	0.896^b	0.796^b	2.987^b	1.36^b	4.17^b
	62.1^c			0.579^c	0.370^c	0.883^c	0.810^c	3.491^c	1.31^c	4.85^c
760.06	61.7^b	0.337	0.611	0.308^b	0.538^b	0.758^b	0.881^b	2.633^b	1.04^b	3.36^b
	60.9^c			0.315^c	0.536^c	0.796^c	0.897^c	2.610^c	1.07^c	3.28^c
759.94	54.1^b	0.600	0.272	0.574^b	0.137^b	1.026^b	0.650^b	2.555^b	1.90^b	4.48^b
	53.5^c			0.547^c	0.144^c	0.997^c	0.694^c	2.781^c	1.72^c	4.57^c
760.06	52.0^b	0.502	0.251	0.475^b	0.121^b	1.095^b	0.664^b	1.990^b	1.96^b	3.39^b
	51.2^c			0.462^c	0.125^c	1.091^c	0.707^c	2.074^c	1.84^c	3.35^c
760.07	55.0^b	0.085	0.360	0.109^b	0.307^b	1.335^b	1.065^b	1.156^b	1.50^b	1.23^b
	54.3^c			0.123^c	0.308^c	1.542^c	1.089^c	1.148^c	1.70^c	1.20^c

[a] In mole fractions. [b] Experimental data. [c] Predicted by the Wilson Equation.

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NOMENCLATURE

A, B, C = Antoine constants
DMB = 2,3-dimethylbutane
mm. = millimeters
P = pressure, in mm. of Hg
R = gas constant
T = temperature, absolute
t = temperature, ° C.
x_{i_c} = calculated mole fraction of component i in the liquid phase
x_{i_e} = experimental mole fraction of component i in the liquid phase
y_{i_c} = calculated mole fraction of component i in the vapor phase
y_{i_e} = experimental fraction of component i in the vapor phase
α_{ij} = relative volatility of component i to component j
$(\lambda_{ij} - \lambda_{ii})$, $(\lambda_{ji} - \lambda_{jj})$ = empirically determined Wilson parameter energy terms (for constant pressure data here) related to the cohesive energy density, and appearing in the Wilson equation, Equations 3; cal. per gram-mole
$\Lambda_{ij}, \Lambda_{ji}$ = dimensionless expression in Wilson equation, defined in Equations 3
γ = activity coefficient

Subscripts

A = acetone
c = calculated
C = chloroform
D = 2,3-dimethylbutane
e = experimental
i, j, k = components i, j, k

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Vapor-Liquid Equilibrium of the System 2-Propanol–Water–1,2,3-Propanetriol at 760 Mm. of Hg

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The vapor-liquid equilibrium data of the ternary system 2-propanol–water–1,2,3-propanetriol for 1,2,3-propanetriol contents of 10, 20, 30, 40, and 50 wt. % have been reported. A diagram containing lines of constant value of specific gravity d_{25}^{25} and refractive index n_D^{25} has also been reported.

VAPOR-LIQUID equilibrium data of the ternary system 2-propanol-water-1,2,3-propanetriol have been determined by means of an Othmer still (*4*). The samples were analyzed by determination of refractive index and specific gravity. These data were not published for the ternary system or for the binary system, 2-propanol-1,2,3-propanetriol. Consequently, they are published in the present paper, and a diagram containing lines of constant value of specific gravity and refractive index is also added.

EXPERIMENTAL

Purity of Materials. The purification of 2-propanol was carried out by rectification through a glass column 3 cm. in diameter and 2 meters high, containing packings of 3 mm. in stainless steel wire, under high reflux.

The purification of 1,2,3-propanetriol was carried out by distillation at reduced pressure of about 10 mm. of Hg through a well-insulated 1-meter-high Vigreux column.

A large quantity of starting material was used and many fractions were sampled. Only the fractions of which the specific gravity and the refractive index remain constant were kept. The physical properties of the materials used in the present work are listed and compared with critically chosen values from literature in Table I.

Table I. Physical Properties of Materials

Materials	Specific Gravity, d_4^{25}		Refractive Index, n_D^{25}	
	Exptl.	Lit. (*6*)	Exptl.	Lit. (*6*)
1,2,3-propanetriol	1.2581	1.25822[a]	1.4732	1.47352
2-Propanol	0.7808	0.78095	1.3749	1.3747

[a] Interpolated.