Vapor-Liquid Equilibria: 2,3-Dimethylbutane–Methanol and 2,3-Dimethylbutane–Methanol–Chloroform Systems

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Vapor-liquid equilibrium data have been measured in a vapor circulating (modified Colburn) still at 760 mm. of Hg for the 2,3-dimethylbutane–methanol system, which shows a minimum-boiling azeotrope at 0.39 mole fraction of methanol and 44.5° C., and for the 2,3-dimethylbutane–methanol–chloroform system, for which no ternary azeotrope was found at atmospheric pressure. The ternary data were analyzed and compared with equilibrium data predictions, utilizing a modified form of the Wilson equation.

THE VAPOR-LIQUID equilibrium data were determined as part of an over-all research program whose purpose is to develop experimentally nonideal multicomponent system data, to supply information concerning extremely nonideal systems, and to serve as a basis for testing predictive methods. The ternary system described here is composed of three binary systems, each forming a minimum-boiling azeotrope. However, no ternary azeotrope was found, probably because of the differences in the three binary azeotropic temperatures.

EXPERIMENTAL

Materials. The methanol, chloroform, and 2,3-dimethylbutane used in this work had a guaranteed purity of at least 99 mole %. A GC-2 chromatographic analysis on all three materials indicated that each had a purity in excess of 99.8 mole %. Table I gives some of the experimental and literature properties of these materials.

Procedure. The equilibrium still used to obtain vapor-liquid equilibrium data is the same modified Colburn still described by Hanson and Van Winkle (*3*) and used by Garrett and Van Winkle (*2*). This still has three separate heating units for the equilibrium chamber instead of one, to allow for a closer approach to adiabatic conditions. The pressure in the equilibrium chamber was maintained at 760 ± 0.1 mm. of Hg by using nitrogen to pressure the still. Pressure was indicated by means of a mercury manometer and read by a cathetometer. The nitrogen used for pressure control passed through a volume of tubing in a constant-temperature oil bath to minimize fluctuations in pressure with ambient temperature fluctuations.

Copper-constantan thermocouples were used to detect adiabatic conditions in the equilibrium cell and the temperatures of the vapor and liquid phases in the cell. The thermocouples measuring the liquid and vapor phase temperatures were calibrated using a National Bureau of Standards calibrated platinum resistance thermometer. A curve fit was obtained through the calibration points to give a calibration table to read intermediate temperatures.

The initial stage in determining each equilibrium point involved measuring out each pure component with a syringe, to yield a final liquid composition at some prearranged spacing over the composition range. Since methanol is quite hygroscopic, the reagents were handled in a nitrogen-filled dry-box. The sample was heated to obtain a circulating vapor, and the amount of heat to the equilibrium cell adjusted until the temperatures of the liquid and vapor phases were within 0.1° C. of each other for at least 45 minutes. At this time, the liquid and vapor samples were removed and placed in serum bottles for refrigeration until analysis.

Analysis. The liquid and vapor samples were analyzed with a Beckman GC-2 chromatograph, using a 6-foot 10% Carbowax 20*M* column, and a Model SR-72180, 1-mv., full-span Sargent recorder equipped with a disc integrator. All liquid and vapor samples were analyzed in conjunction with a control sample of known composition to eliminate errors due to different sensitivities of the GC-2 to different components. The control sample

Table I. Physical Properties of the Materials

	2,3-Dimethylbutane	Methanol	Chloroform
Molecular weight	86.17	32.04	119.39
Boiling point, 760 mm. Hg, ° C.			
Experimental	58.15	64.59	61.19
Literature	57.99 (*1*)	64.7 (*5*)	61.2 (*10*)
Antoine constants (*4*)			
A	6.80983	7.87863	6.90328
B	1127.187	1473.11	1163.0
C	228.9	230.0	227.4
Refractive index	n_D^{25}	n_D^{25}	n_D^{25}
Experimental	1.3724	1.3289	1.4430
Literature	1.3723 (*1*)	1.3288 (*5*)	1.4429 (*1*)

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was prepared after the approximate composition of each component in the unknown sample had been determined. The composition of the control sample was accurately determined by weighing the volume of each component used in making up the control sample. All weight measurements were performed on a Mettler H 10 TW balance. The known control sample was analyzed on the GC-2 immediately after analyzing the unknown sample. The counts of the known sample were used to determine the sensitivity of the GC-2 to each component. These sensitivities and the counts of the unknown samples were used to determine the concentration of the unknown samples.

Accuracy. The limits of errors in the experimental data were estimated as follows: composition, ±0.005 mole fraction; pressure, ±0.02 mm. of Hg; temperature, ±0.1° C.

EXPERIMENTAL RESULTS

The relationship between the composition of component i in the liquid phase and the composition of component i in the vapor phase can be expressed as

$$\gamma_{iv} y_i f_{iv} = \gamma_{il} x_i f_{il} \qquad (1)$$

γ_{iv} and γ_{il} are the corrections for nonideality of component i in the vapor and liquid solution, f_{iv} is the pure component fugacity at the system pressure (P_T), and f_{il} is the pure component fugacity at the total pressure (P_T). The vapor solution correction (γ_{iv}) is normally one at low pressures, and f_{iv} is normally expressed in terms of a fugacity coefficient $(\gamma_i = f_{iv}/P_T)$. At atmospheric conditions, f_{iv} approaches P_T, and f_{il} approaches P_i. Therefore, Equation 1 can be closely approximated by

$$y_i P_T = \gamma_{il} x_i P_i \qquad (2)$$

γ_{il} was predicted by the Wilson equation as presented by Orye and Prausnitz (*8*), and the vapor pressures were calculated from the Antoine constants (Table I) of the respective components.

To compare the experimental results of the 2,3-dimethylbutane–methanol–chloroform ternary with results based on ternary activity coefficients predicted by the Wilson equation, experimental vapor-liquid equilibrium data were required for the following binary systems: 2,3-dimethylbutane–chloroform (*2, 6*), methanol-chloroform (*7*), and 2,3-dimethylbutane–methanol.

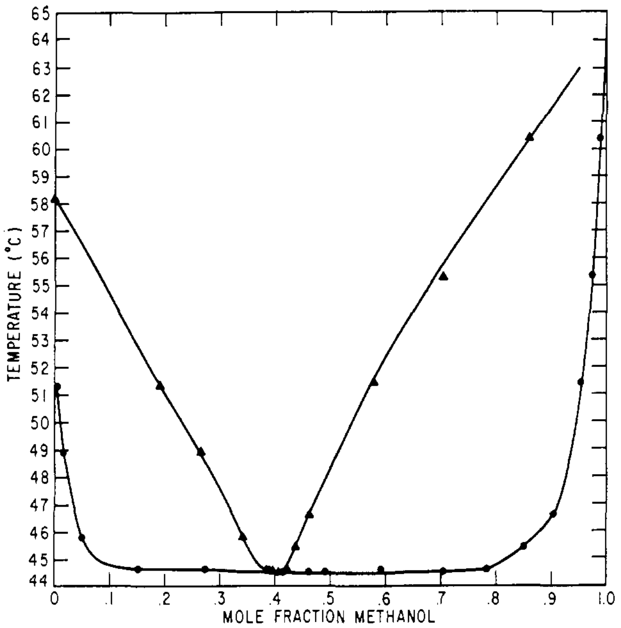

Figure 1. *T-x-y* diagram for the 2,3-dimethylbutane–methanol system

▲ Vapor mole fraction

● Liquid mole fraction

2,3-Dimethylbutane–Methanol Binary System. Data for the 2,3-dimethylbutane–methanol system were not available, and were run jointly by Willock (*11*) and this author. The experimental binary data are listed in Table II.

Figures 1 and 2 show the *T-x-y* diagram and the plot of activity coefficients, respectively, for the dimethylbutane-methanol system. Figure 1 strongly indicates that this binary approaches immiscibility at 760 mm. of Hg because of the small change in equilibrium temperature over a wide range of liquid compositions. At about 24.5° C., approximately 20° C. below the azeotrope temperature, liquid-liquid separation was encountered. At 44.5° C. the Wilson equation (*12*), using Equation 2, fit the activity coefficient–composition relations quite well, using the constants derived from the experimental data as shown in Figure 2. Thermodynamic evaluation (*9*) of the Wilson equation indicates that "it is not suitable for mixtures of partially miscible liquids." It appears that for the above system it is applicable to within around 20° C. of the immiscibility temperature.

Table II. Methanol (1) –2,3-Dimethylbutane (2) Binary Data

P, Mm. Hg	T, ° C.	x_1	y_1	γ_1	γ_2
760.0	51.3	0.009	0.190	35.78	1.014
759.0	48.9	0.017	0.266	30.28	1.005
760.1	45.8	0.051	0.342	14.89	1.035
760.1	44.6	0.153	0.384	5.849	1.134
760.1	44.6	0.274	0.391	3.324	1.306
760.0	44.5	0.390	0.393	2.351	1.553
760.0^a	44.5	0.415	0.392	2.210	1.625
760.1	44.5	0.493	0.392	1.864	1.876
760.0^a	44.5	0.704	0.406	1.348	3.137
759.9^a	44.6	0.784	0.421	1.249	4.173
760.1^a	45.4	0.851	0.437	1.152	5.720
760.1^a	46.6	0.904	0.464	1.090	8.110
760.0^a	51.4	0.955	0.580	1.048	11.54
760.1^a	55.3	0.976	0.703	1.055	13.49
760.1^a	60.4	0.991	0.861	1.031	14.31

^{a} Data by Willock (*11*).

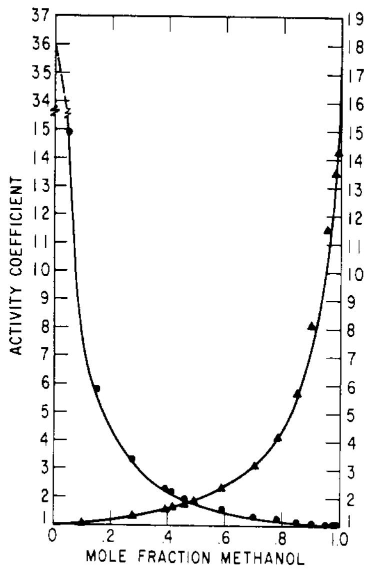

Figure 2. Activity coefficient—liquid composition curves for the 2,3-dimethylbutane—methanol system

▲ Activity coefficients of 2,3-dimethylbutane
● Activity coefficients of methanol
— Wilson fit of activity coefficients

A Redlich-Kister consistency test was performed on the activity coefficient composition data. For isobaric data, this is a necessary but insufficient criterion of consistency. The results of the test indicated that the ratio of areas was 0.92. The T-x-y data also satisfied the thermodynamic requirement that dT/dx and dt/dy be zero at the azeotrope, 0.390-0.391 mole fraction of methanol.

The Prausnitz *et al.* (9) computer program was used to obtain the Wilson parameters ($\lambda_{ij} - \lambda_{ii}$) for the three binary systems (Table III), utilizing all three sets of

Table III. Wilson Parameters for the Binary Systems

Binary Components	$\lambda_{12} - \lambda_{11}$[a]	$\lambda_{21} - \lambda_{22}$
2,3-Dimethylbutane (1)-methanol (2)	449.08	2771.85
Methanol (1)-chloroform (2)[b]	1703.68	−373.30
2,3-Dimethylbutane (1)-chloroform (2)[c]	223.69	213.88

[a] In calories per gram-mole.
[b] Based on data by Nagata (7).
[c] Based on data by McConnell (6).

Table IV. 2,3-Dimethylbutane (1)—Methanol (2)—Chloroform (3) Ternary Data

P, Mm. Hg	T_e[a], ° C. T_c[b], ° C.	x_{1e}	x_{2e}	y_{1e} y_{1c}	y_{2e} y_{2c}	γ_{1e} γ_{1c}	γ_{2e} γ_{2c}	γ_{3e} γ_{3c}	α_{12e} α_{12c}	α_{32e} α_{32c}
760.0	49.4	0.093	0.637	0.303	0.391	4.304	1.156	1.737	5.30	1.85
	49.2			0.315	0.390	4.509	1.161	1.662	5.34	1.79
760.0	46.0	0.395	0.397	0.482	0.348	1.809	1.915	1.406	1.39	0.93
	46.0			0.489	0.340	1.838	1.874	1.403	1.44	0.96
760.0	51.2	0.052	0.824	0.333	0.492	7.977	1.040	2.044	10.72	2.36
	51.4			0.323	0.497	7.689	1.040	2.048	10.32	2.41
760.1	47.4	0.256	0.376	0.370	0.323	2.025	1.750	1.364	1.68	0.97
	47.4			0.381	0.320	2.105	1.748	1.320	1.75	0.96
760.1	46.9	0.380	0.282	0.425	0.318	1.604	2.366	1.276	0.99	0.68
	46.8			0.426	0.315	1.617	2.351	1.270	1.00	0.69
759.9	52.0	0.038	0.683	0.181	0.441	5.776	1.085	1.898	7.37	2.10
	52.2			0.190	0.448	6.034	1.096	1.780	7.63	1.98
760.0	49.6	0.135	0.359	0.243	0.325	2.365	1.688	1.300	1.99	0.94
	49.4			0.258	0.315	2.529	1.649	1.276	2.18	0.96
760.0	48.4	0.167	0.419	0.303	0.329	2.468	1.541	1.413	2.30	1.12
	48.4			0.318	0.326	2.602	1.527	1.349	2.45	1.11
760.0	50.0	0.067	0.740	0.308	0.443	5.994	1.096	1.937	7.80	2.16
	50.2			0.315	0.441	6.033	1.080	1.860	7.88	2.13
760.0	46.3	0.747	0.090	0.552	0.321	1.084	7.714	1.327	0.21	0.22
	46.1			0.553	0.321	1.094	7.759	1.313	0.21	0.22
760.0	49.8	0.930	0.015	0.172	0.234	1.000	28.09	1.465	0.05	0.06
	49.9			0.720	0.228	1.006	27.92	1.424	0.05	0.06
760.0	49.3	0.349	0.094	0.343	0.253	1.304	5.091	1.117	0.37	0.29
	49.2			0.348	0.248	1.328	5.020	1.060	0.38	0.28
760.1	51.4	0.193	0.082	0.237	0.226	1.519	4.773	1.060	0.45	0.27
	51.4			0.241	0.220	1.545	4.630	1.048	0.47	0.28
760.0	51.2	0.088	0.236	0.157	0.317	2.217	2.334	1.119	1.33	0.58
	51.3			0.163	0.289	2.300	2.118	1.146	1.51	0.66
760.0	53.3	0.102	0.068	0.146	0.222	1.662	5.197	1.020	0.45	0.23
	53.5			0.153	0.199	1.737	4.630	1.024	0.51	0.27
760.1	49.6	0.528	0.039	0.449	0.217	1.116	10.51	1.174	0.16	0.14
	49.6			0.451	0.211	1.121	10.09	1.171	0.16	0.14
759.9	45.3	0.335	0.586	0.555	0.380	2.518	1.464	1.441	2.56	1.27
	45.4			0.555	0.372	2.504	1.423	1.618	2.61	1.46
760.0	46.6	0.578	0.153	0.487	0.313	1.228	4.352	1.259	0.41	0.36
	46.4			0.485	0.314	1.229	4.408	1.257	0.41	0.36
760.0	46.7	0.206	0.597	0.448	0.380	3.146	1.347	1.468	3.44	1.37
	46.7			0.449	0.363	3.153	1.286	1.591	3.58	1.58
760.0	48.4	0.288	0.223	0.335	0.298	1.592	2.627	1.196	0.88	0.56
	48.2			0.345	0.291	1.649	2.589	1.177	0.92	0.57
760.0	45.3	0.537	0.350	0.549	0.362	1.556	2.339	1.396	0.99	0.76
	45.4			0.553	0.355	1.561	2.277	1.429	1.02	0.81

[a] The subscript e represents experimental data.
[b] The subscript c represents predictions using the Wilson equation.

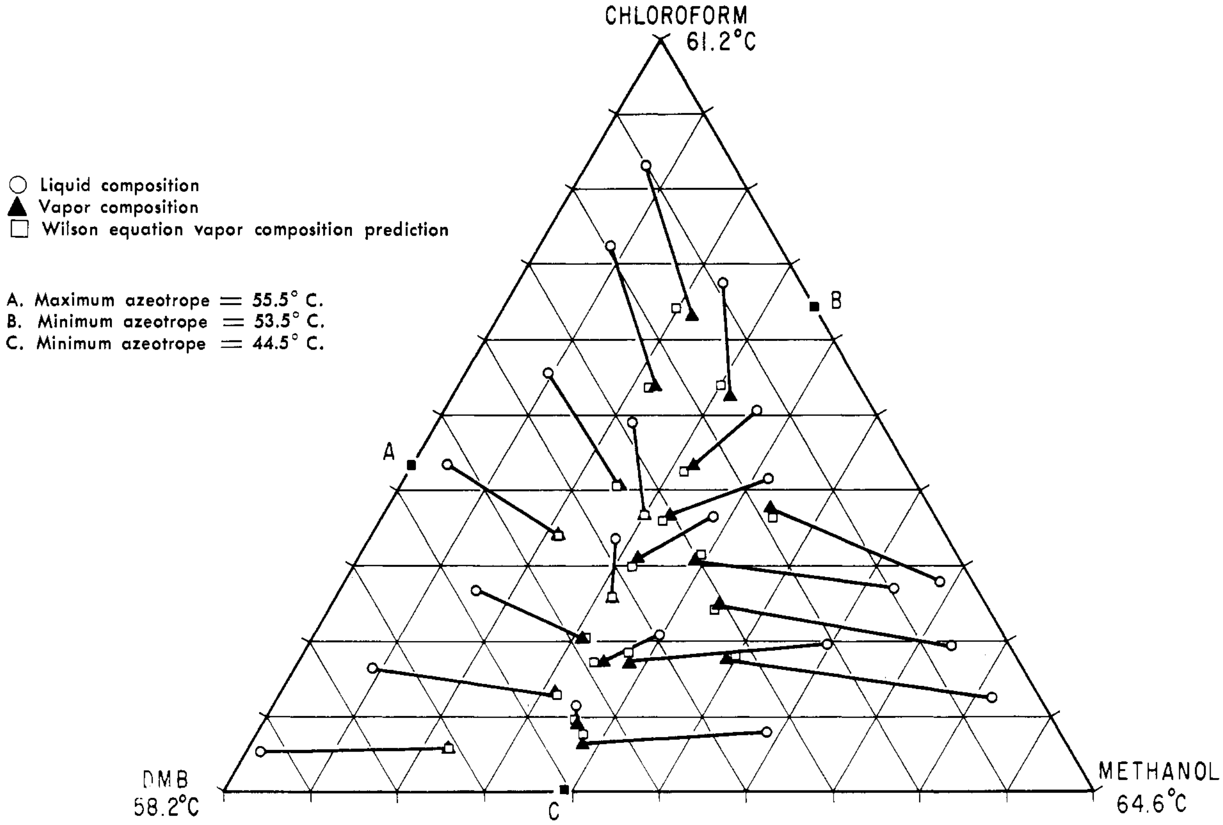

Figure 3. Experimental and calculated values of vapor compositions for selected liquid compositions; 2,3-dimethylbutane–methanol–chloroform system

data. These parameters were needed to characterize the 2,3-dimethylbutane–methanol–chloroform ternary. All three binaries have minimum-boiling azeotropes, with the methanol-2,3-dimethylbutane azeotrope at the lowest temperature: 2,3-dimethylbutane–chloroform, azeotrope 53.5° C. at 0.65 mole fraction of chloroform; methanol-chloroform, azeotrope 55.5° C. at 0.43 mole fraction of chloroform; 2,3-dimethylbutane–methanol, azeotrope 44.5° C. at 0.390 mole fraction of methanol.

2,3-Dimethylbutane–Methanol–Chloroform System. The data points for the 2,3-dimethylbutane–methanol–chloroform system are shown in Table IV and on Figure 3. The experimental vapor compositions and those predicted utilizing the Wilson equation compare favorably, as shown on Figure 3. For a majority of the points, the predicted composition differed by less than 0.01 mole fraction from the experimental vapor mole fraction. Estimated average deviation in y, because of the assumption of ideal gas behavior, is ±0.005 mole fraction. The largest difference between the predicted equilibrium temperature and experimental temperature for the 21 points was 0.3° C. The maximum and average deviations in the predicted activity coefficients, expressed as a per cent of the experimental activity coefficients, were 6.8 and 2.3% for 2,3-dimethylbutane, 11.0 and 2.3% for methanol, and 8.3 and 2.2% for chloroform.

Figure 4 depicts the vapor and liquid surfaces in an "exploded" view. The liquid surface has a flat "valley," extending from the methanol-2,3-dimethylbutane azeotrope to the chloroform-methanol azeotrope. On either side of the valley are steeply rising "embankments." The vapor surface slopes gradually into a deep trough between the methanol-2,3-dimethylbutane azeotrope and the methanol-chloroform azeotrope. This is also indicated by the isothermal lines of the liquid and vapor surfaces (Figures 5 and 6). The isothermal lines are

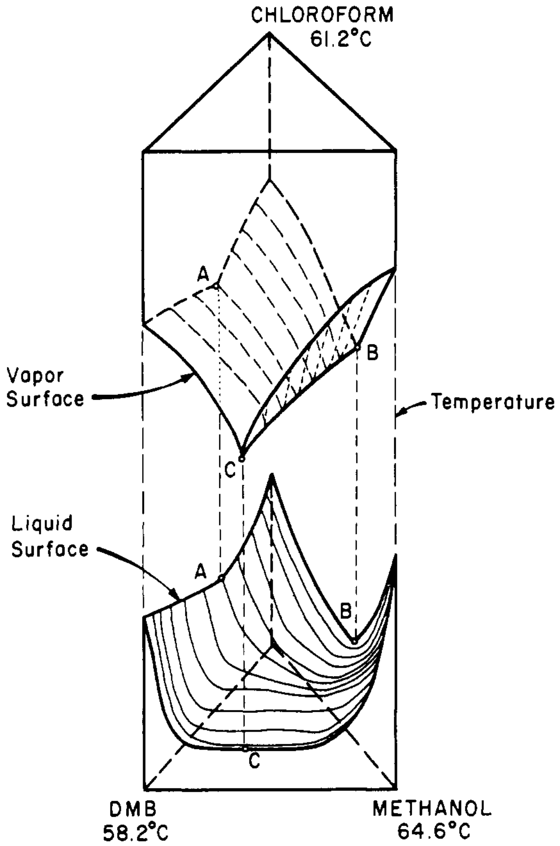

Figure 4. Exploded view of vapor and liquid surfaces

A. Maximum azeotrope = 55.5° C.
B. Minimum azeotrope = 53.5° C.
C. Minimum azeotrope = 44.5° C.

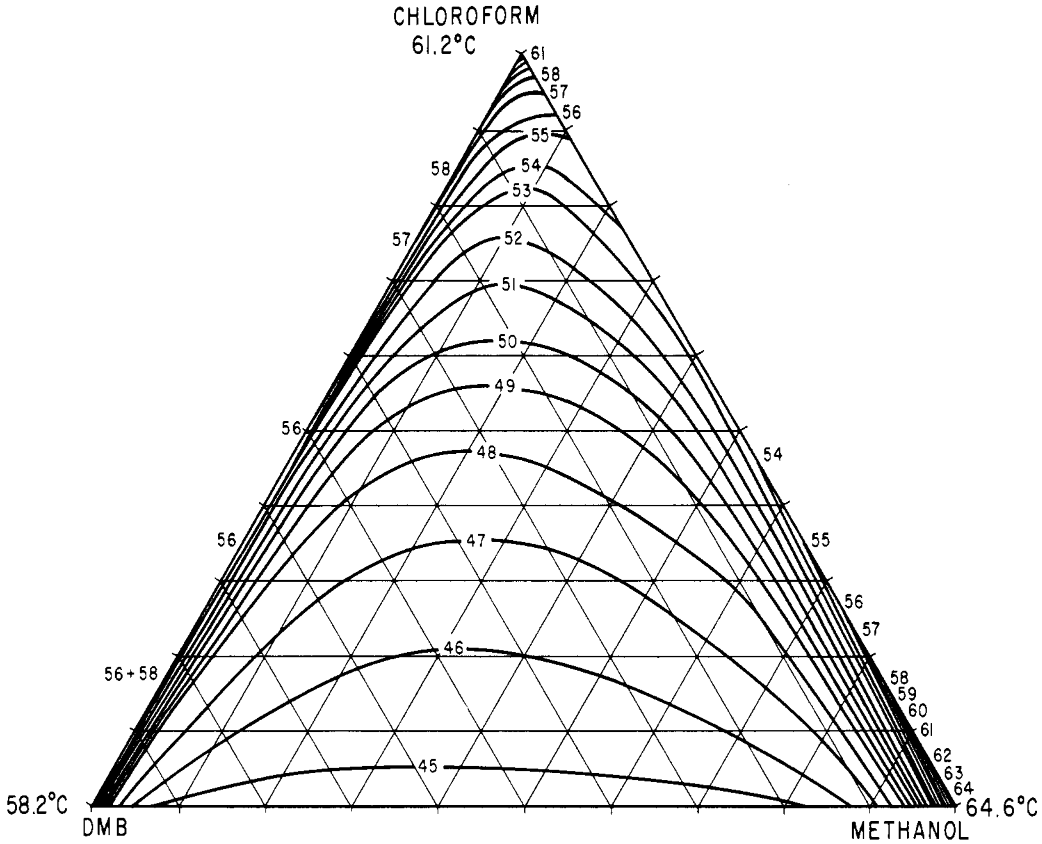

Figure 5. Isothermal lines of the ternary liquid surface

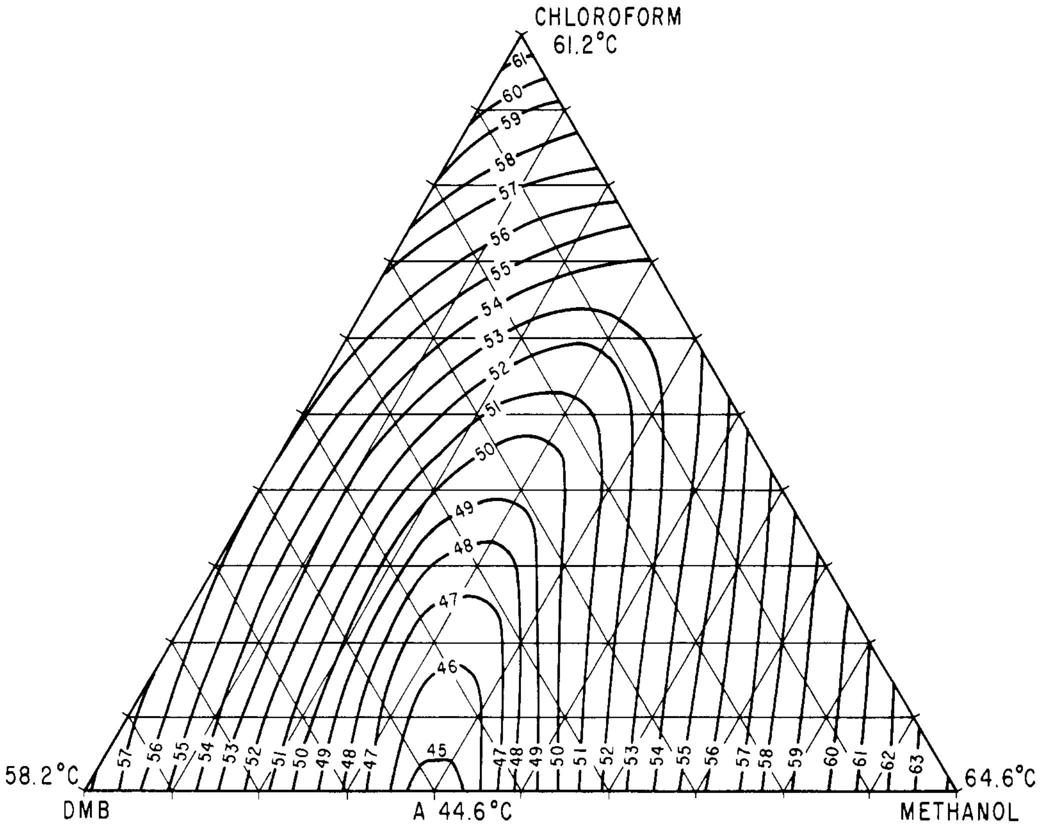

Figure 6. Isothermal lines of the ternary vapor surface

only semiquantitative, because both the experimental and calculated temperature-composition points were used to draw the constant-temperature lines. The greater distance between the liquid isothermal lines shows the flatness of surface in the middle of the ternary composition diagram. The close proximity of the lines near the 2,3-dimethylbutane–chloroform and chloroform-methanol surfaces depict the steeply rising liquid surface.

NOMENCLATURE

A, B, C = Antoine constants
P_i = vapor pressure of component i, mm. of Hg
P_T = total pressure, mm. of Hg
T_c = calculated temperature, ° C.
T_e = experimental temperature, ° C.
x_{ic} = calculated mole fraction of component i in the liquid phase
x_{ic} = experimental mole fraction of component i in the liquid phase
y_{ic} = calculated mole fraction of component i in the vapor phase
y_{ie} = experimental mole fraction of component i in the vapor phase
α_{ij} = relative volatility of component i to component j
γ = activity coefficient
γ_{ie} = calculated activity coefficient of component i
γ_{ie} = experimental activity coefficient of compound i
λ = Wilson parameter, cal. per gram mole

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Critical Properties and Vapor Pressures of Some Organic Nitrogen and Oxygen Compounds

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EXPERIMENTAL values of *P-V-T* and other thermodynamic properties are available for only the most common substances. Usually these properties have to be estimated. One of the most frequently used tools is the Law of Corresponding States, or one of its modifications, which requires a knowledge of critical properties. Gas and liquid compressibility factors, vapor pressures, heats of vaporization, and other thermodynamic properties are given in the literature as functions of reduced temperature, reduced pressure, and usually a third parameter.

The purpose of this work was to determine the critical properties of selected organic nitrogen and oxygen compounds. Other experimental data include: vapor pressures; rectilinear diameters in the critical region for isopropylamine, *n*-heptane, and benzene; boiling points; indices of refraction; and some information on the stability of the compounds at elevated temperature and pressure. Calculated values of critical compressibility, "acentric factor," and "critical parameter" are presented to expedite the estimation of thermodynamic properties of these compounds.

PURIFICATION OF COMPOUNDS

The compounds listed in Table I were distilled by the authors. The pyrans, picolines, isopropylamine, 1,1-dimethyl hydrazine, and dimethoxymethane were treated with Drierite before distillation. In general, 80% heart cuts were taken the number of times specified in Table I in a 48- × 3/4-inch glass column packed with 1/4-inch glass helices. Reflux ratios of 60 to 80:1 were used. The boiling ranges and boiling temperatures of the final products were measured with a double-junction Chromel-Alumel thermopile capable of measuring temperature differences of the order of 0.0125° C. Attempts to purify 2-methyl pyrazine and *cis*-2,5-dimethyl piperazine

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