Vapor-Liquid Equilibrium Data for Ternary System Methanol-Ethanol-Water

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The present paper relates to the ternary system methanol-ethanol-water, and its main purpose is to determine whether the classical equations of liquid-vapor equilibrium are capable of representing satisfactorily the experimental data. The components of this mixture show the phenomena of association, and it is known that this may somewhat complicate the relations of liquid-vapor equilibrium.

EXPERIMENTAL PROCEDURE

The ternary system methanol-ethanol-water was studied by Griswold (*9*), who gave a graphical representation of it, but did not test the experimental data by means of the term log y.

Edwards, Hashmael, Gilmont, and Othmer (*7*), examining the possibility of applying thermodynamic relations to this ternary system, observed that, while there is agreement between experience and theory for low water concentrations, there is no agreement for high water concentrations; the error may be as much as 0.1 mole.

Since the publication of Griswold's data, the apparatus and methods for the determination of equilibrium have been improved. For this reason, the experimental study was resumed in order to compare results and correlate experience and theory.

Purity of Components. Methanol was rectified in a high-efficiency column. Ethanol was treated and stirred in anhydrous barium hydroxide for 24 hours, then rectified together with sodium in a similar column. Water was also rectified. During these treatments, precautions were taken to avoid allowing the alcohols to remain in a damp atmosphere.

The physical constants of products are indicated in Table I. A satisfactory standard of purity was obtained.

Experimental Method. The determination of liquid-vapor equilibrium data was carried out using, first, Othmer's apparatus (*20*), then, with slight modifications, the dynamic apparatus, some examples of which have been described (*4,11,13,16,17,23-25,28*).

The most volatile component flows continuously into a saturator or "equilibrium chamber," which is maintained at a definite temperature and contains the ternary mixture to be studied.

The apparatus (Figure 1) consists of three saturators, *A*, *B*, and *C*, the last of which is the "equilibrium chamber;" these three interconnected saturators are completely immersed in a water bath, *G*. *C* is provided with pipes; *D* is used to withdraw a sample of the liquid phase and *I* drains off the condensation vapors. Temperature is measured to within ± 0.05 °C.

The most volatile component, vaporized in container *R*, flows continuously into saturators *A*, *B*, and *C*, and into the equilibrium chamber, *C*, in which the vapors pass through the liquid ternary mixture. The vapors are condensed and collected in a container. Constant temperature is maintained in the bath and, when the equilibrium is established, samples of the liquid phase and of the vapor phase are removed for analysis.

The pressure did not vary much from one experiment to the other. The Clapeyron equation may be conveniently employed, to give a close approximation of the effect of pressure on boiling point for small pressure changes (*5*):

$$\Delta T_b = 0.00012\, T_b\, \Delta_p$$

Results with the system studied show a good correlation with those obtained with Othmer's apparatus. This observation is based rather on the shape of Griswold's curves (*9*) than on the comparison of individual experimental plots given by this author, because there is an insufficient number of plots in the region of high water concentration.

Analysis of Samples. The samples of the liquid and condensed vapor phases were analyzed by taking measurements of refractive index, density, and boiling point. According to Griswold (*8*), the composition of this ternary system may be determined graphically from its boiling point and from the ratio of refractive index to density.

Because of the small volume of samples taken, it was impossible to use a standard ebulliometer, such as Swietoslawsky's, and measurement of the boiling point was somewhat inaccurate. This method was replaced by direct water analysis using Fischer's method (*18*). When the water concentration of the ternary mixture is known, the ratio of refractive index to density is determined and the ethanol concentration is read on the analytical diagram, whereas the methanol concentration is obtained by difference. The precision of Fischer's method was tested in this particular case against samples of known composition, and the results are given in Table II. Because of the instability of the sulfur trioxide-methanol-pyridine solution, daily determination of the equivalence in water is required.

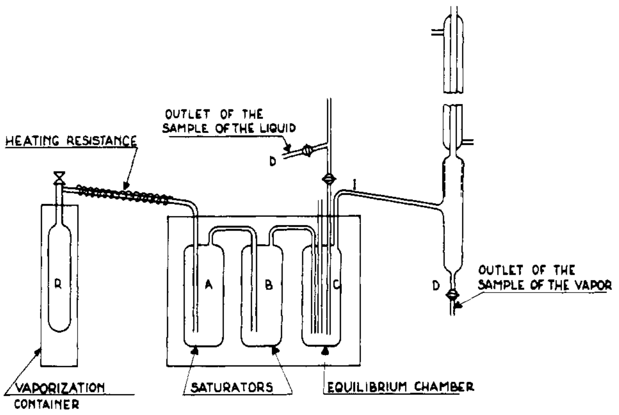

Figure 1. Vapor liquid equilibrium dynamic apparatus

Table I. Purity of Components

	Methanol				Ethanol				Water			
	Exptl.	$T°$	Bibliog. (*10*)	$T°$	Exptl.	$T°$	Bibliog. (*10*)	$T°$	Exptl.	$T°$	Bibliog. (*10*)	$T°$
Refractive Index n_D^t	1.3312	14.5	1.33118	14.5	1.3625	18.5	1.36242	18.5	1.3331	20	1.3330	20
	1.3275	25			1.3596	25						
Density$_4^{25}$	0.7865		0.78643		0.785		0.78505		1		1	

Table II. Water Analysis by Fischer's Method

Weight of Components, Grams			Water Obtained by Fischer's Method, Gram
Methanol	Ethanol	Water	
2.000	2.000	0.800	0.792
2.000	2.000	0.500	0.498
2.000	2.000	0.200	0.196
2.000	2.000	0.100	0.098
0.080	0.100	0.370	0.368
0.075	0.090	0.380	0.378
0.040	0.055	0.400	0.399
0.200	0.300	0.500	0.497
0.400	0.600	0.450	0.447

The figures show that Fischer's method provides exact values of water concentration.

EXPERIMENTAL RESULTS AND COMPARISON WITH GRISWOLD'S DATA

The results obtained with both methods are presented in Table III, with Griswold's data for comparison. The boiling points of the mixtures are also stated.

In the middle region of the concentrations, the results obtained in both studies agree well. On the other hand, differences in the region of high water concentrations are greater. Methanol concentrations in the vapor phase are lower than those found by Griswold, and concentrations in water are generally higher. Fischer's method is hardly likely to be at fault, in view of the checked data shown in Table II.

If the results of equilibrium determination obtained with both methods are plotted on a large scale ternary diagram, the same equilibrium values may be obtained. As equilibrium was reached, the figures show no systematic error arising from a fractionating effect of Othmer's apparatus.

Table III. Comparison of Experimental Data with Griswold's Data

Temp., °C.	Liquid Compn., Mole Fraction			Vapor Compn., Mole Fraction					
				This Investigation			Data of Griswold (9)		
	x_1	x_2	x_3	y_1	y_2	y_2	y_1	y_2	y_3
				Othmer Type Still					
68.1	0.750	0.141	0.109	0.850	0.096	0.054	0.870	0.105	0.025
68.1	0.756	0.142	0.102	0.852	0.096	0.052	0.870	0.104	0.026
74.2	0.302	0.590	0.108	0.418	0.490	0.092	0.415	0.505	0.080
71.7	0.530	0.230	0.240	0.695	0.180	0.125	0.710	0.195	0.095
75	0.260	0.520	0.220	0.360	0.470	0.170	0.375	0.465	0.160
81.2	0.049	0.248	0.703	0.130	0.512	0.358	0.135	0.510	0.355
74.5	0.360	0.293	0.347	0.525	0.290	0.185	0.535	0.295	0.170
76.3	0.203	0.475	0.322	0.328	0.470	0.202	0.325	0.475	0.200
77.2	0.216	0.310	0.474	0.390	0.365	0.245	0.380	0.380	0.240
71.9	0.490	0.360	0.150	0.635	0.290	0.075	0.650	0.285	0.065
79	0.102	0.368	0.530	0.197	0.510	0.293	0.205	0.515	0.280
75.8	0.284	0.296	0.420	0.440	0.355	0.205	0.470	0.335	0.195
80.5	0.035	0.350	0.615	0.081	0.554	0.365	0.100	0.550	0.350
83	0.043	0.062	0.895	0.185	0.310	0.505	0.210	0.325	0.465
87.5	0.061	0.033	0.906	0.280	0.220	0.500	0.315	0.230	0.465
83	0.138	0.041	0.821	0.425	0.150	0.425	0.495	0.175	0.330
79	0.240	0.060	0.700	0.550	0.160	0.290	0.575	0.140	0.285
81	0.055	0.255	0.690	0.160	0.485	0.355	0.140	0.500	0.360
82.7	0.053	0.145	0.802	0.145	0.430	0.425	0.190	0.450	0.360
82.7	0.093	0.098	0.809	0.310	0.300	0.390	0.355	0.360	0.285
				Dynamic Method					
82.7	0.109	0.081	0.810	0.355	0.250	0.395	0.375	0.335	0.290
83.5	0.09	0.080	0.830	0.308	0.285	0.407	0.375	0.345	0.280
82.5	0.061	0.142	0.797	0.195	0.395	0.410	0.220	0.445	0.335
82.2	0.160	0.037	0.803	0.515	0.105	0.380	0.525	0.125	0.350
81	0.117	0.098	0.785	0.359	0.273	0.368	0.355	0.335	0.310
82.8	0.0515	0.067	0.8815	0.228	0.316	0.456	0.270	0.335	0.395
82.5	0.1	0.096	0.804	0.310	0.295	0.395	0.360	0.360	0.280
76.5	0.110	0.720	0.170	0.180	0.680	0.140	0.160	0.685	0.155

When the equilibrium data of the binary systems are known, it is possible, for some systems which are said to "simple," to deduce equilibrium ternary data from them. It is difficult to know *a priori* whether a system is simple or not, but it is likely to be so in mixtures of components of related structure (homologous) though not in partially miscible systems. Between these extreme cases, it is interesting to examine the possibilities of assuming a simple system in intermediate cases.

The equilibrium ternary data are obtained in one of the following ways:

The values of log γ_1, log γ_2, log γ_3, are first calculated from the concentrations x_1, x_2, x_3, in the liquid phase, by means of the relations:

$$\operatorname{Log} \gamma_1 = F(x_1, x_2, x_3) \tag{1}$$

The concentrations in the vapor phase are deduced by means of the relation:

$$y_1 = \frac{p_1^\circ x_1 \gamma_1}{P} \tag{2}$$

Other relations give the values of the ratios log γ_1/γ_2, log γ_2/γ_3, log γ_3/γ_1 from the concentrations x_1, x_2, x_3.

$$\log \frac{\gamma_1}{\gamma_2} = \Phi(x_1, x_2, x_3) \tag{3}$$

From this, the values of relative volatility of the components 1 and 2, as compared with component 3, may be deduced by means of the relations:

$$\alpha_{23} = \frac{\gamma_2}{\gamma_3}\,\frac{p_2^\circ}{p_3^\circ} \tag{4}$$

and

$$\alpha_{13} = \frac{\gamma_1}{\gamma_3}\,\frac{p_1^\circ}{p_3^\circ} \tag{5}$$

Vapor concentrations y_1, y_2, y_3 are calculated from the equation:

$$y_i = \frac{\alpha_i x_i}{\Sigma(\alpha_i x_i)} \tag{6}$$

The ternary relations (Equations 1 and 3) contain constants, which are either the end values of log γ_1, log γ_2, log γ_3 in the three binary systems, or individual values calculated from equilibrium data of the same binary systems.

It is necessary, therefore, to have accurate equilibrium data of the binary systems: methanol-water, ethanol-water, and methanol-ethanol.

VAPOR LIQUID EQUILIBRIUM DATA FOR ETHANOL-WATER, METHANOL-WATER, METHANOL-ETHANOL

System Ethanol-Water. There is a fair measure of agreement in the experimental data quoted by the different authors (*3,12,15,19*) and further experimental verifications were considered unnecessary.

System Methanol-Water. As the data of the different authors vary widely, further study was given to this binary system; the experimental values were found to confirm those of Cornell and Montonna (*6*).

System Methanol-Ethanol. As no recent data were available for this system, new calculations were worked out for it. The results are given in Table IV and shown in Figures 2 and 3.

Table IV. Vapor Liquid Equilibrium Data for Methanol-Ethanol

Temp., °C.	Mole Fraction			
	Methanol in liquid, x_1	Methanol in vapor, y_1	Log γ_1	Log γ_2
65.8	0.888	0.932	0.00014	0.019
67.6	0.725	0.820	0.0015	0.012
69.2	0.600	0.725	0.0025	0.0075
70.9	0.470	0.600	0.005	0.0045
72.3	0.375	0.505	0.007	0.0035
74	0.248	0.362	0.010	0.0015
75.8	0.142	0.222	0.014	0.001
77	0.073	0.120	0.0175	0.00021

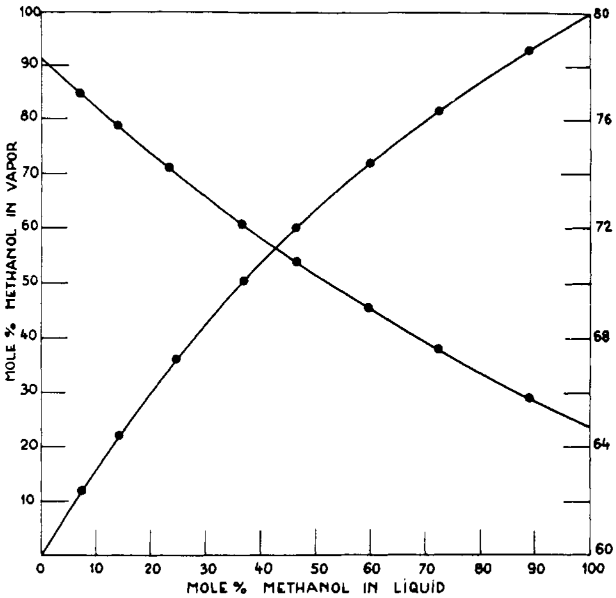

Figure 2. Vapor liquid and composition relationships for methanol-ethanol system

For each of the three binary systems, the thermodynamical consistence of the equilibrium data was tested by means of the integrated forms of Duhem-Margules' equation:

Margules' equations:

$$\text{Log}\ \gamma_1 = (2A_{21} - A_{12})x_2^2 + 2(A_{12} - A_{21})x_2^3 \qquad (7a)$$

$$\text{Log}\gamma_2 = (2A_{12} - A_{21})x_1^2 + 2(A_{21} - A_{12})x_1^3 \qquad (7b)$$

From these two relations, the following equation for log γ_1/γ_2 is deduced:

$$\text{Log}\frac{\gamma_1}{\gamma_2} = A_{12}(1 - x_1)(1 - 3x_1) + A_{21}x_1(2 - 3x_1) \qquad (8)$$

Constants A_{12} and A_{21} are the end values of log γ_1 and log γ_2 for $x_1 = 0$ and $x_2 = 0$, respectively.

Redlich and Kister's equation (22):

$$\text{Log}\frac{\gamma_1}{\gamma_2} = B(1 - 2x_1) + C[6x_1(1 - x_1) - 1] + D(1 - 2x_1)[1 - 8x_1(1 - x_1)] \qquad (9)$$

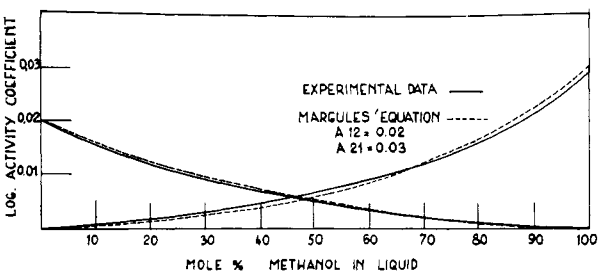

Figure 3. Methanol-ethanol system

$$\text{Log}\frac{\gamma_1}{\gamma_2}\ vs.\ \text{composition}$$

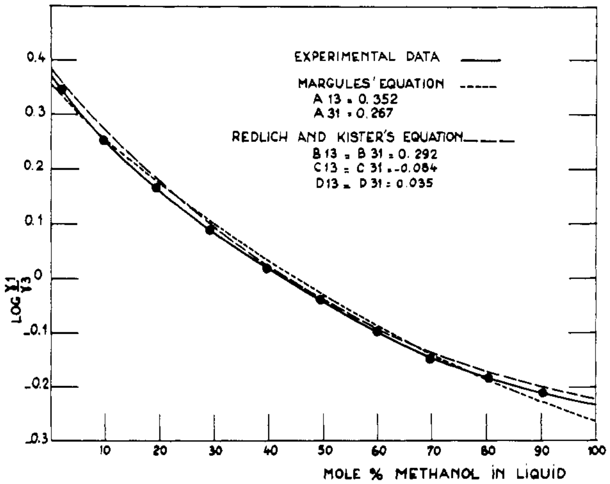

Figure 4. Methanol-water system

$$\text{Log}\frac{\gamma_1}{\gamma_3}\ vs.\ \text{composition}$$

The difference between this equation and Margules' relation (Equation 8) lies in the fact that the binary system is represented by a three-constant equation. The values of *B*, *C*, and *D* are calculated by applying Equation 9 to certain individual points (Table V) (22).

Table V. Calculation of Constants *B*, *C*, and *D* in Redlich and Kister's Equation

$x_1 = 0.5$	$\log\frac{\gamma_1}{\gamma_2} = C/2$
$x_1 = 0.1464$	$\log\frac{\gamma_1}{\gamma_2} = 0.7071B - C/4$
$x_1 = 0.8536$	$\log\frac{\gamma_1}{\gamma_2} = -0.7071B - C/4$
$x_1 = 0.2113$	$\log\frac{\gamma_1}{\gamma_2} = 0.5773(B - D/3)$
$x_1 = 0.7887$	$\log\frac{\gamma_1}{\gamma_2} = -0.5773(B - D/3)$
$x_1 = 0.2959$	$\log\frac{\gamma_1}{\gamma_2} = 0.4082\left(B - \frac{2D}{3}\right) + C/4$
$x_1 = 0.7041$	$\log\frac{\gamma_1}{\gamma_2} = -0.4082\left(B - \frac{2D}{3}\right) + C/4$

By using the Equations 8 and 9, it was possible to calculate the values of the constants, which are given in Table VI.

In addition, in Figures 4 and 5, for the systems methanol-water and ethanol-water, the experimental curves log γ_1/γ_3, and γ_1/γ_2 calculated by means of Margules' and Redlich's equations, have been presented, taking the values indicated in Table VI. These curves are reasonably in agreement in every case; equality of areas situated above and below the line log $\gamma = 0$ is obtained within 1 %.

For the system methanol-ethanol, the thermodynamical consistence was tested only by Margules' equations log $\gamma = f(x)$. The results agree well with the experimental findings.

The binary constants having been computed in this way, it is possible to apply the ternary relations to Equations 1 and 3 to calculate the concentrations in the vapor phase from the mole fractions in the liquid phase.

Table VI. Values of Binary Constants

Constants of Margules' Equation	Constants of Redlich and Kister's Equation
$A_{12} = 0.020$	$B_{12} = B_{21} = 0.02$
$A_{21} = 0.030$	$B_{23} = B_{32} = 0.513$
$A_{23} = 0.700$	$B_{13} = B_{31} = 0.272$
$A_{32} = 0.400$	$C_{12} = C_{21} = 0$
$A_{31} = 0.267$	$C_{23} = C_{32} = -0.138$
$A_{13} = 0.352$	$C_{13} = C_{31} = -0.084$
	$D_{12} = D_{21} = 0.015$
	$D_{23} = D_{32} = 0.074$
	$D_{13} = D_{31} = 0.035$

FORECASTING OF TERNARY SYSTEM EQUILIBRIUM DATA FROM THOSE OF BINARY SYSTEMS

Ternary Relationships, Activity-Molar Concentration. The free energy of a system is expressed by the following equation:

$$G = \Sigma n G_i^\circ + \Sigma n\, RT \ln x + (\Sigma n)\, \Delta G \qquad (10)$$

From this equation, Van Laar (*27,29*), Wohl (*29*), and Redlich and Kister (*14,22*) have deduced ternary relations by which either $\log \gamma_1$, $\log \gamma_2$, $\log \gamma_3$, or $\log \gamma_1/\gamma_2$, $\log \gamma_2/\gamma_3$, $\log \gamma_3/\gamma_1$, may be calculated.

In Van Laar's and Wohl's equations, constants A_{12}, A_{23}, A_{31}, etc... are the end values of $\log \gamma_1$, $\log \gamma_2$, $\log \gamma_3$, in the three binary systems presented in Table VI.

Constants B_{12}, C_{12}, D_{12}, etc... of Redlich and Kister's equation are individual values calculated by Equation 9.

C, which figures in Wohl's and Redlich's equations, is that of the ternary system, calculated from the experimental data for several liquids of known composition.

Calculation of Ternary Constant C^+. It is generally advisable to calculate the ternary constant, C^+, from the experimental values of x and y, by means of the equation $\log \gamma_1$ or $\log \gamma_1/\gamma_2$.

If this is done, values of C^+ are obtained which vary widely, in absolute value (Table VII).

Table VII. Calculation of Values of C^+

Mole Fraction in Liquid			According to Margules' Equations		According to Redlich and Kister's Equations	
x_1	x_2	x_3	By $\log \frac{\gamma_2}{\gamma_3}$	By $\log \frac{\gamma_3}{\gamma_1}$	By $\log \frac{\gamma_3}{\gamma_2}$	By $\log \frac{\gamma_1}{\gamma_3}$
0.750	0.141	0.109	− 0.774	− 0.035	+ 0.416	+ 0.076
0.260	0.520	0.220	− 0.455	− 2.425	+ 0.680	+ 3.820
0.102	0.368	0.530	− 2.370	− 0.367	+ 2.680	+ 0.950
0.216	0.310	0.474	− 0.528	− 1.080	+ 0.153	+ 0.950
0.049	0.248	0.703	− 1.8	− 0.704	+ 2.51	+ 1.045
0.302	0.590	0.108	− 0.333	− 0.450	+ 0.423	+ 0.603
0.043	0.062	0.895	− 1.880	− 1.430	+ 1.445	+ 2.290

The scatter of numerical values of C^+ is not peculiar to the system studied. It recurs in the ternary system methyl ethyl ketone-*n*-heptane-toluene. Kortum (*2*) gives a single value of C^+ calculated from Steinhauser and White's experimental data (*26*). But if other values are calculated, the results given in Table VIII are obtained, which confirm this scatter.

As the values of C^+ deduced from experimental readings are subject to experimental errors from y, the most divergent values of Table VII (say − 2.370, column 4 and − 2.425, column 5) may be disregarded. On this basis, for the system studied, the mean value of C_m^+ has been chosen equal to − 1 for Margules' equation, and the mean value of C_r^+, equal to + 1, for Redlich and Kister's equation.

Moreover, calculation shows that relatively large variations of C^+—for instance, ± 0.3—have no great effect on the value of $\log \gamma$ or of y. The effect is much smaller than that of binary constants.

Comparison of Vapor Concentration, Experimental and Calculated, for Identical Liquid Composition. A comparison of experimental results and the values calculated by means of Van Laar's, Margules', and Redlich and Kister's equations is shown in Table IX, and on the ternary diagrams (Figures 6 to 8). Figure 6 includes the experimental results and the values calculated by means of Van Laar's equation from the same liquid points. Figure 7 includes the experimental results and the values calculated by means of Margules' equation, and Figure 8 includes the experimental results and the values calculated by means of Redlich and Kister's equation.

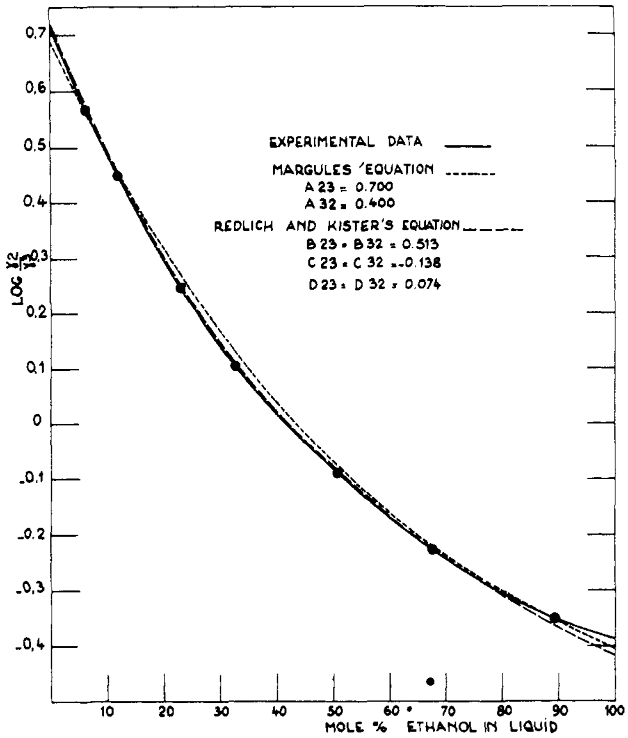

Figure 5. Ethanol-water system

$\text{Log}\,\frac{\gamma_2}{\gamma_3}$ vs. composition

The region of vapors with a high concentration of water ($y_3 > 0.60$) was not studied because such vapors are in equilibrium with liquid mixtures of very high water concentration. In these mixtures, titration of methanol and ethanol would be too inaccurate.

Figures 6 and 8 show that the experimental results agree fairly well with the values calculated by means of Van Laar's, and Redlich and Kister's equations in the region of vapors of low water concentration. On the other hand, for water concentrations of more than 40% in the vapor phase, the differences are considerable.

Figure 7 shows that Margules' two-constant equation gives in both regions a somewhat better agreement than the former, although the two-constant equation (Margules' equation) does not give such a good picture of the binary data.

Table VIII. Calculation of Values of C^+ for Methyl Ethyl Ketone-*n*-Heptane-Toulene

Mole Fraction in Liquid$^{(a)}$			Value of C^+	
Methyl ethyl ketone x_1	*n*-Heptane x_2	Toluene x_3	$\text{Log}\,\frac{\gamma_3}{\gamma_2}$	$\text{Log}\,\frac{\gamma_1}{\gamma_3}$
0.738	0.217	0.045	+ 0.355	+ 1.720
0.658	0.196	0.146	− 1.025	+ 1.625
0.191	0.705	0.104	+ 0.526	+ 0.943
0.282$^{(b)}$	0.477	0.241	+ 0.111	+ 2.091
0.350	0.113	0.537	+ 0.117	+ 2.590
0.198	0.112	0.690	− 0.069	− 1.135

(a) Steinhauser and White's data (*26*).

(b) From this mixture, Kortum has calculated C^+ by Margules' equation, $\log \gamma_1 = F(x_1, x_2, x_3)\, C^+ = +\,0.13$.

Despite the scatter of the values of C^+, a study of the figures of Table VII suggests that parameter C^+ varies with composition. Moreover methanol and ethanol, as homologous terms, are very similar in their power of association, while pure water possesses a high degree of association (*21*).

Table IX. Calculated Vapor Liquid Equilibria for Methanol-Ethanol-Water System

Liquid Compn., Mole Fraction (Column 1)			Vapor Compn., Mole Fraction														
						Calculated Data											
			Data of This Investigation (Column 2)			Van Laar's Equation (Column 3)			Redlich and Kister's Equation (Column 4)			Margules' Equation $C^+ = -1$ (Column 5)			Margules' Equation $C^+ = -x_3$ (Column 6)		
x_1	x_2	x_3	y_1	y_2	y_3	y_1	y_2	y_3	y_1	y_2	y_3	y_1	y_2	y_3	y_1	y_2	y_3
0.750	0.141	0.109	0.850	0.096	0.054	0.850	0.100	0.050	0.842	0.0965	0.0615	0.824	0.112	0.064	0.846	0.100	0.054
0.302	0.590	0.108	0.418	0.490	0.092	0.425	0.496	0.079	0.430	0.464	0.106	0.430	0.462	0.108	0.424	0.490	0.086
0.530	0.230	0.240	0.695	0.180	0.125	0.693	0.188	0.119	0.652	0.212	0.136	0.646	0.211	0.143	0.675	0.193	0.132
0.260	0.520	0.220	0.360	0.470	0.170	0.375	0.475	0.150	0.402	0.430	0.168	0.394	0.434	0.172	0.380	0.463	0.157
0.049	0.248	0.703	0.130	0.512	0.358	0.109	0.496	0.394	0.133	0.493	0.374	0.147	0.494	0.359	0.134	0.497	0.369
0.360	0.293	0.347	0.525	0.290	0.185	0.529	0.285	0.186	0.515	0.301	0.184	0.505	0.302	0.193	0.510	0.296	0.194
0.203	0.475	0.322	0.328	0.470	0.202	0.314	0.480	0.206	0.347	0.444	0.209	0.338	0.444	0.218	0.308	0.472	0.220
0.216	0.310	0.474	0.390	0.365	0.245	0.352	0.382	0.266	0.381	0.379	0.240	0.380	0.376	0.244	0.366	0.378	0.256
0.490	0.360	0.150	0.635	0.290	0.075	0.638	0.2875	0.0745	0.632	0.280	0.088	0.596	0.286	0.118	0.620	0.285	0.095
0.102	0.368	0.530	0.197	0.510	0.293	0.183	0.505	0.312	0.232	0.476	0.292	0.240	0.472	0.288	0.214	0.486	0.300
0.284	0.296	0.420	0.440	0.355	0.205	0.455	0.345	0.200	0.465	0.343	0.192	0.446	0.332	0.222	0.440	0.331	0.229
0.035	0.350	0.615	0.081	0.554	0.365	0.070	0.564	0.366	0.099	0.540	0.361	0.103	0.550	0.347	0.090	0.556	0.354
0.043	0.062	0.895	0.185	0.310	0.505	0.162	0.275	0.563	0.148	0.318	0.534	0.182	0.297	0.521	0.180	0.297	0.523
0.061	0.033	0.906	0.280	0.220	0.500	0.256	0.163	0.581	0.220	0.204	0.576	0.262	0.185	0.553	0.262	0.183	0.555
0.032	0.051	0.917	0.160	0.284	0.556	0.132	0.259	0.609	0.118	0.294	0.588	0.150	0.277	0.573	0.149	0.275	0.576
0.138	0.041	0.821	0.425	0.150	0.425	0.413	0.137	0.450	0.382	0.191	0.427	0.421	0.1685	0.4105	0.422	0.162	0.416
0.109	0.081	0.810	0.355	0.250	0.395	0.315	0.250	0.435	0.305	0.259	0.436	0.326	0.281	0.393	0.325	0.275	0.400
0.09	0.08	0.830	0.308	0.285	0.407	0.274	0.276	0.450	0.260	0.288	0.452	0.297	0.295	0.408	0.294	0.292	0.414
0.061	0.142	0.797	0.195	0.395	0.410	0.166	0.396	0.438	0.170	0.417	0.413	0.195	0.407	0.398	0.189	0.403	0.408
0.160	0.037	0.803	0.515	0.105	0.380	0.464	0.118	0.415	0.477	0.118	0.405	0.461	0.146	0.393	0.461	0.140	0.399
0.0515	0.067	0.8815	0.228	0.316	0.456	0.186	0.272	0.542	0.168	0.323	0.509	0.204	0.302	0.494	0.202	0.300	0.498
0.1	0.096	0.804	0.310	0.295	0.395	0.284	0.286	0.432	0.265	0.334	0.401	0.301	0.309	0.390	0.300	0.312	0.388
0.110	0.720	0.170	0.180	0.680	0.140	0.186	0.686	0.128	0.200	0.650	0.150	0.180	0.680	0.140	0.175	0.679	0.146
0.117	0.098	0.785	0.359	0.273	0.368	0.315	0.270	0.415	0.299	0.322	0.379	0.330	0.300	0.370	0.327	0.295	0.378
0.240	0.060	0.700	0.550	0.160	0.290	0.512	0.180	0.308	0.508	0.190	0.302	0.522	0.173	0.305	0.528	0.159	0.313

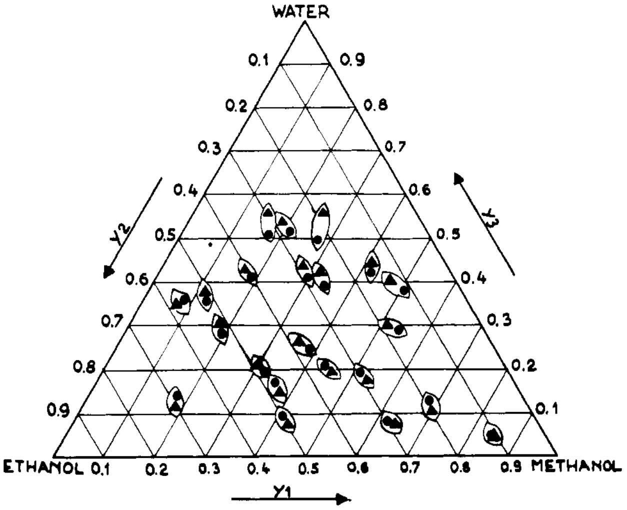

Figure 6. Liquid vapor equilibrium diagram for ternary system methanol-ethanol-water

●Experimental data
▲Van Laar's equation

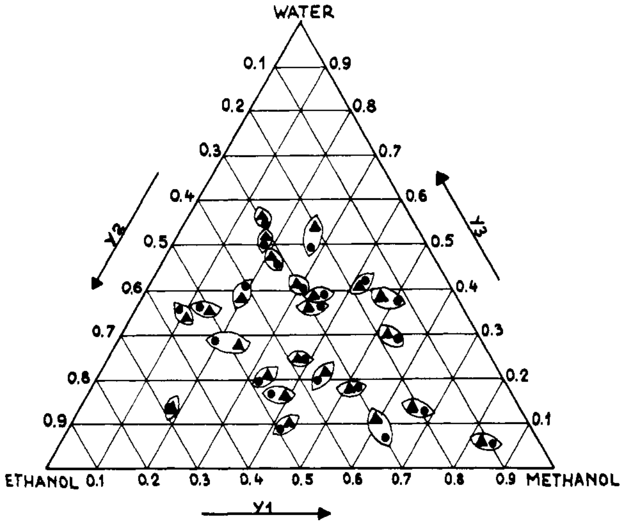

Figure 7. Liquid vapor equilibrium diagram for ternary system methanol-ethanol-water

●Experimental data
▲Margules' equation, $C^+ = -1$

As parameter C^+ expresses the forces involved in the ternary interaction—such forces depend on the degree of association—it is reasonable to assume that C^+ varies according to the ratio:

$$\frac{\text{Concn. of more associated components}}{\text{Concn. of less associated components}}$$

Similar notions were arrived at in a somewhat different form by Redlich and Kister (*22*) for the ternary heptane-toluene-methanol, and by Atkins and Boyer (*1*) for the system C_4 hydrocarbons-acetone-water. These authors also drew a distinction between the more associated component and the less associated one in calculating the liquid-vapor equilibrium.

The effect of the molecular association is to increase the relative volatility of the less associated components (methanol and ethanol for the system in question) with respect to the more associated component (water). These relative volatilities α_{23} and α_{13} are correlated with the activity coefficients by Relations 4 and 5. Because of the association, the ratios log γ_2/γ_3 and log γ_1/γ_3 increase.

According to Margules' equation, these ratios take the form:

$$\text{Log}\ \frac{\gamma_2}{\gamma_3} = M - Cx_1(x_3 - x_2)$$

and

$$\text{Log}\ \frac{\gamma_3}{\gamma_1} = N - Cx_2(x_1 - x_3)$$

where M and N indicate the amount of all terms of this equation which are not affected by C^+.

If parameter C^+ is made to vary from 0 (for $x_3 = 0$) to -1 (for $x_3 = 1$), as suggested by Table VII, the ratios log γ_2/γ_3 and log γ_1/γ_3 increase simultaneously when x_3 is larger than x_2 and x_1. In the region where $x_3 \ll x_1$ and $x_3 \ll x_2$ these ratios are not greatly affected by the factor $Cx_1 (x_3 - x_2)$ or $Cx_2 (x_1 - x_3)$, because the parameter C^+ is then small. On the other hand, the influence of C^+ is high where x_3 is high. Now, the differences between the experimental and calculated values are important for the high water concentration mixtures—i.e., in the region where x_3 is very high with respect to x_1 and x_2. It may be assumed that these differences are due to the association of water, and that they may be reduced by varying the value of C^+ to state the effect of the association.

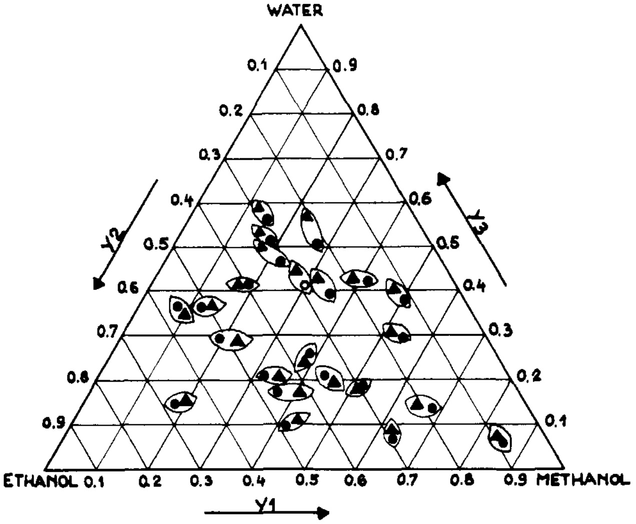

Figure 8. Liquid vapor equilibrium diagram for ternary system methanol-ethanol-water

●Experimental data
▲Redlich and Kister's equation

In view of the standard of accuracy of the various experimental measurements, it suffices to take a linear variation of C^+ with the water-concentration, x_3, such that:

$$C^+ = C_0^+ x_3$$

For low water concentrations, satisfactory agreement is observed between experimental results and calculated values for C_m^+ equal to 0; for high water concentrations the value of C_m^+ may be taken as equal to -1 for Margules' equation; this gives the following linear relation:

$$C_m^+ = -x_3$$

A comparison between the experimental results and the values calculated by means of Margules' two-constant equation, with C_m^+ varying according to the relation $C_m^+ = -x_3$, is shown in Table IX and Figure 9.

The behavior of methanol obtained with Margules' equation taking $C_m^+ = -x_3$ is illustrated by Figure 10, which shows lines of constant methanol activity coefficient. Similar plots for ethanol and water are shown in Figures 11 and 12.

This method of calculation gives the best representation of equilibrium data. In the region of vapors with low water concentrations, the differences between the calculated and experimental readings are small. In the high water concentrations, they are slightly greater; but representation is satisfactory for the whole diagram.

The purely empirical equation $C_m^+ = -x_3$ indicates only a trend within certain ranges of composition; but use of

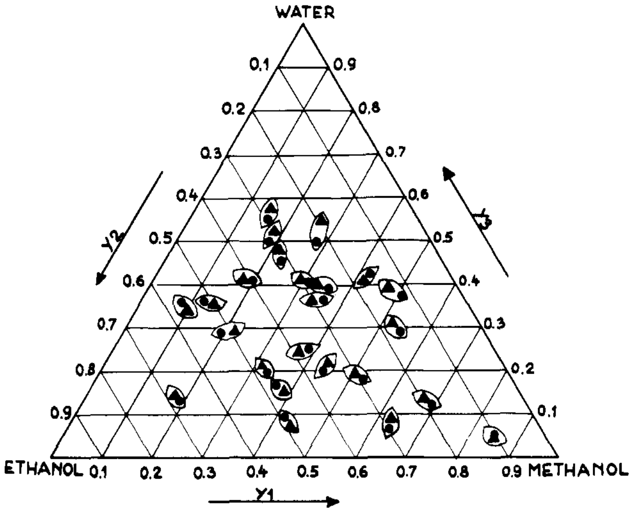

Figure 9. Liquid vapor equilibrium diagram for ternary system methanol-ethanol-water

●Experimental data
▲Margules' equation, $C^+ = -x_3$

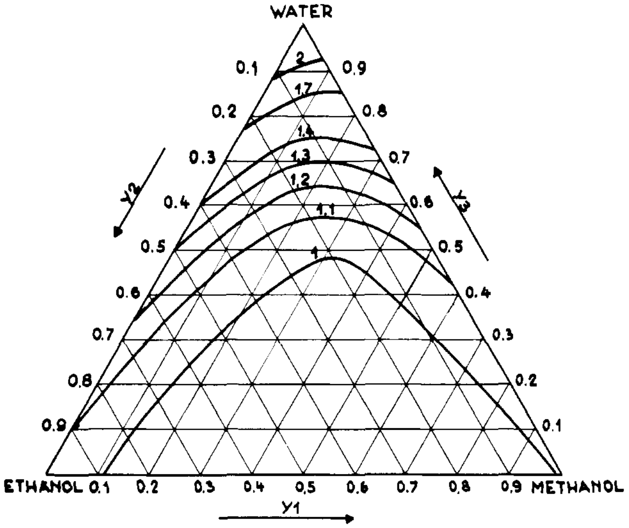

Figure 10. Methanol-ethanol-water system

Activity coefficient of methanol, Margules' equation, $C^+ = -x_3$

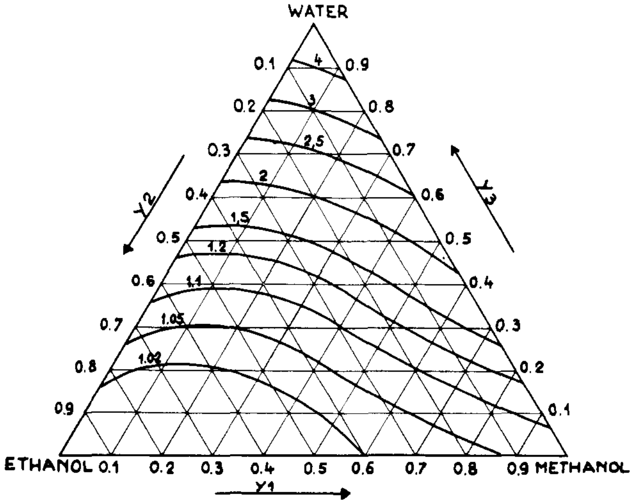

Figure 11. Methanol-ethanol-water system

Activity coefficient of ethanol, Margules' equation, $C^+ = -x_3$

parameter C^+, in the absence of other data, enables a better representation to be obtained, although it has no thermodynamical significance. If a good representation is required for industrial purposes, a corrective coefficient such as $C^+ = -x_3$ may be used.

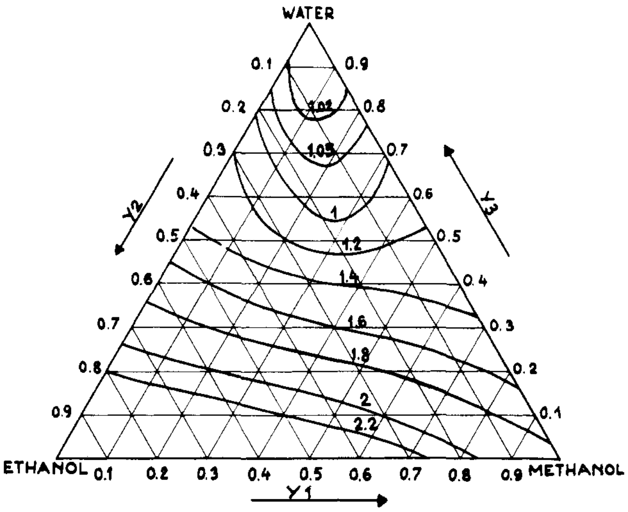

Figure 12. Methanol-ethanol-water system

Activity coefficient of water, Margules' equation, $C^+ = -x_3$

Application of variations in parameter C^+ to Redlich and Kister's equation should also lead to a better representation. This was not considered necessary since, even with C^+_m fixed, Margules' equation gives a better representation than Redlich and Kister's equation.

CONCLUSIONS

The liquid-vapor equilibrium of the ternary system methanol-ethanol-water was studied experimentally by means of Othmer's recirculation apparatus and by dynamic apparatus. The equilibrium data obtained by both methods are closely similar.

In the region of low water concentrations, the figures obtained usually agree fairly well with those previously obtained (*9*). Moreoever differences are greater for liquids very rich in water and poor in methanol.

The results obtained in the present study approximate rather more to the values calculated by means of Van Laar's equation or Margules' two- or three-constant equations; but systematic differences remain which must be attributed to ternary interactions; these are expressed by the ternary parameter, C^+.

The determination of this parameter from experimental data is rather a complicated matter, because the data are liable to unavoidable errors. It is shown that this is not peculiar to the system studied. Values of C^+, other than zero, are obtained by means of Margules' two- and three-constant equations.

A substantial improvement is obtained by letting C^+ vary with the water concentration. Although the relation adopted is wholly empirical, it provides satisfactory agreement between experimental results and calculated values.

NOMENCLATURE

A = binary constants of Van Laar and Margules' equations
B, C, D = binary constants of Redlich and Kister's equation
C^+ = ternary constant of Margules and Redlich and Kister's equations
P = total pressure
p° = vapor pressure of pure component
x = mole concentration in liquid
y = mole concentration in vapor
α = relative volatility = $\dfrac{p^\circ}{p_3^\circ}\;\dfrac{\gamma}{\gamma_3}$
γ = activity coefficient
Subscript 1, 2, or 3 = methanol-ethanol-water under study.

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