I/I_1 = relative intensity, the intensity of a given x-ray diffraction line expressed as a percentage of the intensity of the most intense line of the x-ray powder diffraction pattern

n_1 = refractive index measured on the common orientation parallel to the length of a crystal

n_2 = refractive index measured on the common orientation parallel to the width of a crystal

R = universal gas constant, calories per gram mole -° K.

Greek

β = interaxial angle between the a and c crystallographic axes

ΔH_f = enthalpy change at constant temperature and pressure when 1 gram mole of methylene blue dissolves in an ideal solution; equal to the heat of fusion of methylene blue ($\Delta H_f > 0$ for heat being absorbed), calories per gram mole

Other

$//$ = refers to viewing a crystal when length of crystal is parallel to the plane of polarization

$\perp$ = refers to viewing a crystal when length of crystal is perpendicular to the plane of polarization

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Vapor-Liquid Equilibrium in the System Pyridine-Tetrachloroethylene

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Reliable vapor-liquid equilibrium data obtained with a modified Gillespie equilibrium still are presented for the binary system pyridine(1)-tetrachloroethylene(2) at 60°, 80°, and 100° C. A thermodynamic evaluation proved the data to be consistent. The thermodynamic correlation of the experimental data was made using a fourth-order Margules equation and the series expansion of relative volatility. A minimum boiling azeotrope is formed, whose composition changes very slightly with temperature.

THE literature has recently brought a whole series of theories (*4, 5, 8, 13, 16*) which deal with the thermodynamics of solutions. Most of these theories are, however, applicable only to systems whose components are practically nonpolar or only slightly polar. For proving the validity of those theories, therefore, reliable vapor-liquid equilibrium data are necessary for such systems. The literature dealing with vapor-liquid equilibrium data is very extensive (*5, 9*); nevertheless, there is a lack of good experimental data for systems with the aforementioned properties. Pyridine-tetrachloroethylene belongs to this group of systems, and what is more, the considerable difference in the densities of the components affords the exact analytical determination of both equilibrium phases.

EXPERIMENTAL

Chemicals. Fisher spectroanalyzed pyridine was twice distilled and purified as usual (*6*). The measured density at 30° C. (0.97285 gram per cc.) and the boiling point (115.31° C.) were in good agreement with the values given in the literature (*6, 7, 10, 17*). At atmospheric pressure, the boiling point and the condensation temperature measured with a Beckman thermometer in a modified Swietoslawski differential ebulliometer (*5*) differed by only 0.004° C. This result indicated that the sample did not contain sufficient impurities of different volatilities to have any significant effect on the boiling point measurement. The tetrachloroethylene, an Eastman-Kodak spectrograde product stabilized with thymol, was used without further purification. The experimental values of the density at 30° C. (1.60636 grams per cc.) and the normal boiling point (121.03° C.) agree with the literature values (*17*) very well. The boiling point and condensation temperature difference was 0.005° C. The apparent purity of the product stabilized with thymol, deduced from melting point studies by the time-temperature method, was 99.89 ± 0.04 mole %. Twice distilled deionized water was used as a standard for pressure measurements.

Apparatus and Procedure. The vapor-liquid equilibrium data were determined using a modified Gillespie still (*5*). The still was initially charged with approximately 200 cc. of a binary solution and operated for at least 2 to 3 hours. As has been proved (*2*), the time required to achieve equilibrium depends on the ratio of the condensate receiver volume to the boiling chamber volume. The theoretical calculation of Erdös and Pouchly (*2*) led to the conclusion that the contents of the condensate receiver should be exchanged six or seven times until equilibrium is established. The period can be shortened by decreasing the volume of the receiver and also by filling the receiver with a solution having approximately the equilibrium composition as estimated in some manner—e.g., using Raoult's law.

For the accurate measurement of vapor-liquid equilibrium data, it is necessary to have perfect control of both the temperature and pressure. To get the most accurate readings of the pressure, a Swietoslawski-type ebulliometer (*5*) filled with deionized and distilled water was connected in parallel into the system. From the boiling point of water, the corresponding pressure of the system was determined.

The vapor pressure of water as a function of temperature is known very accurately (*11*), so that the pressure of the system was measured with high accuracy as well. This arrangement eliminates even the errors in the boiling point measurements owing to changes in the barometric pressure during the experiment. Because of the hygroscopic nature of pyridine, all measurements were made in an inert, dry atmosphere. The temperature was measured with a mercury thermometer calibrated by the National Bureau of Standards. The uncertainty in the temperature readings was ±0.015° C.

Vapor and liquid equilibrium samples were analyzed by density measurements at 30° ± 0.02° C. using a standard pycnometric technique. For this purpose, a density composition curve was plotted from measurements with samples of known composition. An accuracy in the density measurements of ±0.0002 gram per cc. allowed an accuracy in the determination of the composition of better than 0.1 mole %. The experimental density composition data are shown in Table I.

RESULTS AND DISCUSSION

The experimental vapor-liquid equilibrium data are presented in Table II, and Figures 1, 2, and 3.

For the thermodynamic correlation two types of equations have been used. The Margules fourth-order equation (*5*) in the form

$$\log\left[\frac{\gamma_1}{\gamma_2}\right] = x_2^2 A_{12} - x_1^2 A_{21} - 2x_1 x_2 \left[A_{12} - A_{21} + (x_2 - x_1)\, D\right] \tag{1}$$

and the series expansion of the relative volatility (*5*)

$$\alpha_{12} = \frac{\gamma_1 P_1^0}{\gamma_2 P_2^0} \tag{2}$$

which can be written

$$\log \frac{\gamma_1}{\gamma_2} = \log\left[\frac{1 + a_{12}x_2 + a_{122}x_2^2}{1 + a_{21}x_1 + a_{211}x_1^2}\right] - \log \frac{P_1^0}{P_2^0} \tag{3}$$

The activity coefficients of both components in the mixture were calculated from the following equation

$$\gamma_i = \left[\frac{y_i P}{x_i P_i^0}\right] \exp\left[\frac{(P - P_i{}^0)(B_i - \bar{V}_i)}{RT}\right] \tag{4}$$

and they are plotted in Figures 4, 5, and 6.

Table I. Densities of the System Pyridine(1)-Tetrachloroethylene(2) at 30° C.

x_1	d_4^{30}	x_1	d_4^{30}
0.0000	1.6063	0.5030	1.3223
0.0648	1.5727	0.6414	1.2333
0.1297	1.5380	0.6887	1.2017
0.1306	1.5378	0.7119	1.1861
0.2318	1.4823	0.7427	1.1647
0.2434	1.4759	0.7742	1.1424
0.3377	1.4218	0.8027	1.1222
0.3553	1.4115	0.8309	1.1018
0.3660	1.4053	0.8622	1.0790
0.3949	1.3886	0.8956	1.0538
0.4389	1.3617	0.9275	1.0296
0.4464	1.3573	1.0000	0.9728

Table II. Vapor-Liquid Equilibrium in the System Pyridine(1)-Tetrachloroethylene(2)

x_1	y_1	P, Mm. Hg	Deviation in Vapor Phase Composition: Margules	Deviation in Vapor Phase Composition: α-series
		60° C.		
0.0652	0.1354	104.65	0.0021	0.0011
0.0837	0.1654	106.21	0.0026	0.0014
0.1628	0.2727	113.06	−0.0006	−0.0020
0.2115	0.3225	116.60	−0.0006	−0.0019
0.2465	0.3507	118.11	0.0026	0.0015
0.3500	0.4307	122.14	0.0020	0.0015
0.4462	0.4985	124.52	−0.0017	−0.0018
0.5035	0.5348	125.66	−0.0013	−0.0013
0.5546	0.5655	126.08	0.0010	0.0010
0.6209	0.6113	126.16	−0.0003	−0.0006
0.6578	0.6357	125.98	0.0013	0.0009
0.6912	0.6600	125.48	0.0017	0.0011
0.7357	0.6957	124.76	0.0010	0.0001
0.7820	0.7362	123.64	0.0001	−0.0010
0.8567	0.8092	120.92	0.0002	−0.0012
0.9200	0.8815	118.04	0.0018	0.0006
0.9525	0.9248	115.61	0.0022	0.0020
		Mean	0.0014	0.0012
		80° C.		
0.0301	0.0661	217.00	0.0010	−0.0003
0.0763	0.1473	229.18	0.0035	0.0015
0.1315	0.2277	240.21	0.0019	0.0000
0.1703	0.2788	245.72	−0.0032	−0.0050
0.2188	0.3237	251.58	0.0015	0.0000
0.2372	0.3415	253.39	0.0008	−0.0006
0.2567	0.3583	255.31	0.0012	−0.0001
0.3537	0.4292	263.08	0.0065	0.0051
0.3825	0.4545	264.62	0.0017	0.0002
0.4160	0.4773	266.57	0.0021	0.0002
0.5003	0.5330	268.73	0.0026	0.0001
0.5683	0.5793	270.08	0.0016	−0.0014
0.6401	0.6270	270.50	0.0037	0.0003
0.6890	0.6641	270.09	0.0027	−0.0007
0.7190	0.6878	269.53	0.0023	−0.0009
0.7425	0.7065	269.19	0.0027	−0.0003
0.7657	0.7253	268.43	0.0035	−0.0004
0.7970	0.7553	266.69	0.0014	−0.0009
0.8207	0.7760	265.44	0.0031	0.0011
0.8600	0.8173	261.90	0.0015	0.0004
0.9374	0.9087	253.51	0.0011	0.0014
0.9797	0.9677	246.60	0.0010	0.0014
		Mean	0.0023	0.0010
		100° C.		
0.0593	0.1196	436.53	−0.0021	0.0014
0.0992	0.1780	451.56	0.0016	0.0023
0.1537	0.2537	469.58	−0.0039	0.0033
0.2470	0.3448	489.80	0.0002	0.0005
0.3028	0.3898	498.76	0.0028	0.0030
0.3613	0.4365	507.42	0.0014	0.0016
0.4545	0.5087	518.50	−0.0040	−0.0039
0.5035	0.5390	523.00	−0.0004	−0.0003
0.5102	0.5445	523.52	−0.0013	−0.0012
0.6036	0.6079	526.49	0.0006	0.0007
0.6362	0.6323	526.62	−0.0002	−0.0001
0.7007	0.6803	526.30	0.0007	0.0008
0.7077	0.6837	526.21	0.0028	0.0029
0.7366	0.7109	525.40	−0.0010	−0.0008
0.8280	0.7928	517.00	−0.0011	−0.0008
0.8655	0.8312	513.10	−0.0015	−0.0011
0.8862	0.8522	510.01	0.0000	0.0004
0.9058	0.8753	506.49	−0.0009	−0.0004
0.9585	0.9403	492.02	0.0001	0.0004
		Mean	0.0014	0.0014

All the data necessary for calculating the activity coefficients are summarized in Tables III and IV. It was further proved that the ratio of the two exponents is very close to unity at all concentrations and temperatures, so that the ratio of both activity coefficients can be written in the form

$$\frac{\gamma_1}{\gamma_2} = \frac{x_2 y_1 P_2^0}{x_1 y_2 P_1^0} \tag{5}$$

The values calculated from this relation were inserted into Equations 1 and 3, and the constants of both equations were found by the method of least squares. Table V presents the values of these constants.

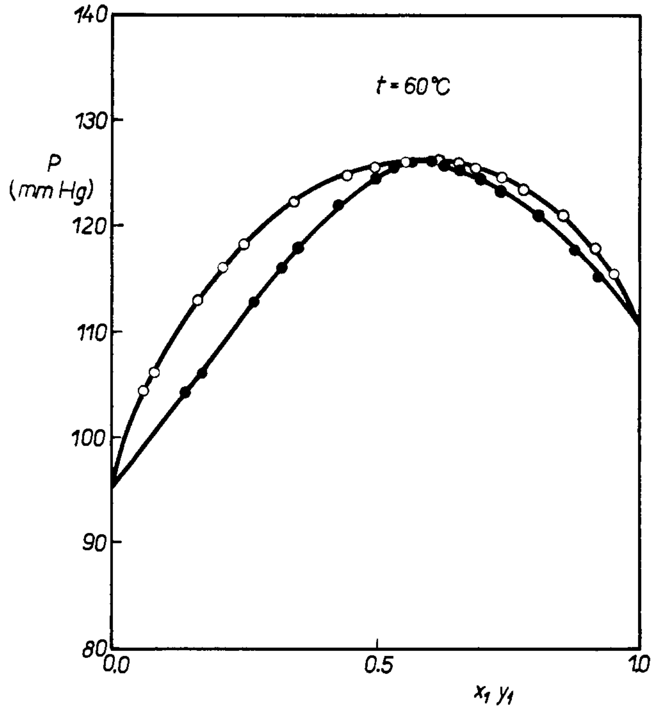

Figure 1. Vapor-liquid equilibrium
System pyridine(1)-tetrachloroethylene(2) at 60° C.

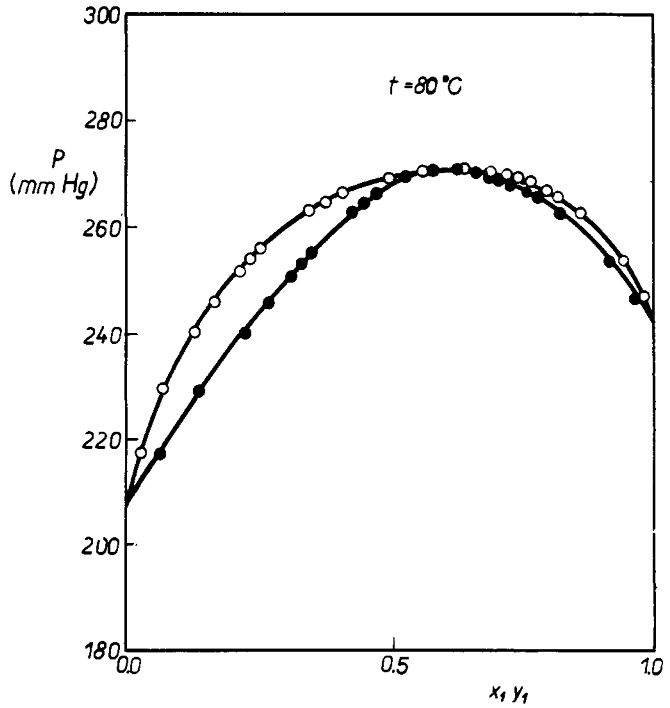

Figure 2. Vapor-liquid equilibrium
System pyridine(1)-tetrachloroethylene(2) at 80° C.

The vapor phase composition was then calculated using the relation

$$y_1 = \frac{\left(\frac{\gamma_1 P_1^0}{\gamma_2 P_2^0}\right) x_1}{1 + x_1 \left(\frac{\gamma_1 P_1^0}{\gamma_2 P_2^0} - 1\right)} \qquad (6)$$

Deviations in the calculated vapor phase composition presented in Table II indicate that the Margules equation and the series expansion of relative volatility correlate the experimental data very well. The deviations calculated from the second order Van Laar equation (5) were much greater.

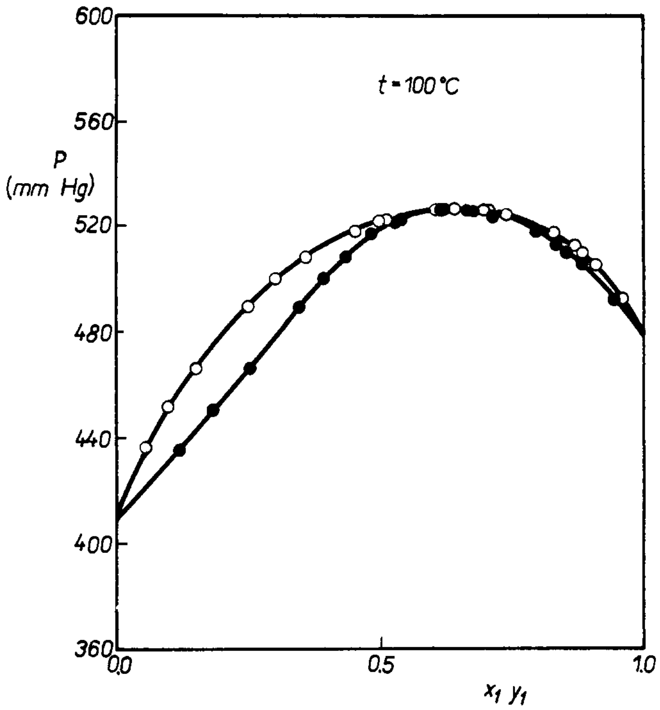

Figure 3. Vapor-liquid equilibrium
System pyridine(1)-tetrachloroethylene(2) at 100° C.

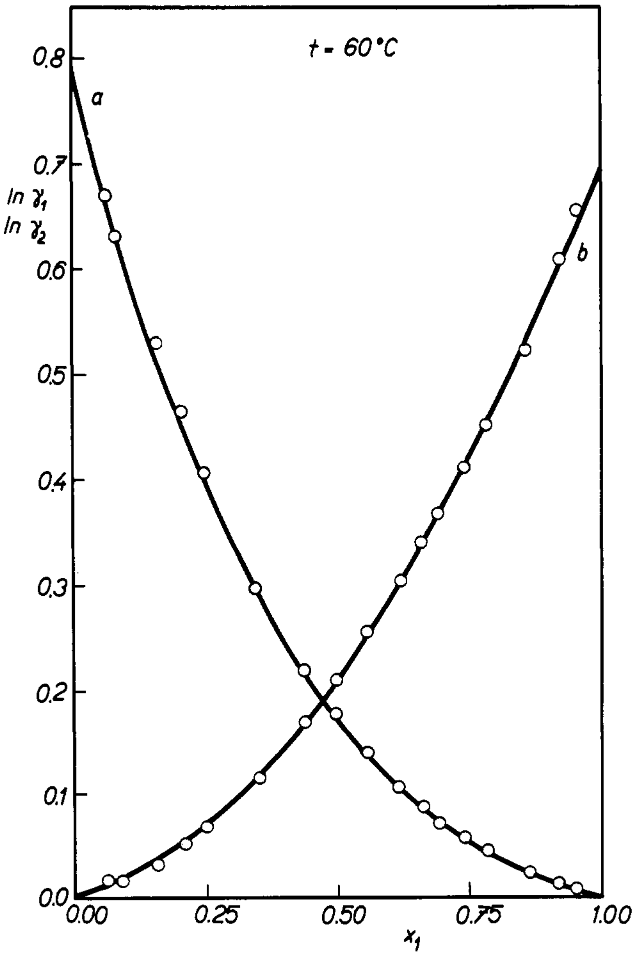

Figure 4. The logarithm of the activity coefficients as a function of the composition
System pyridine(1)-tetrachloroethylene(2)
a. ln γ_1
b. ln γ_2

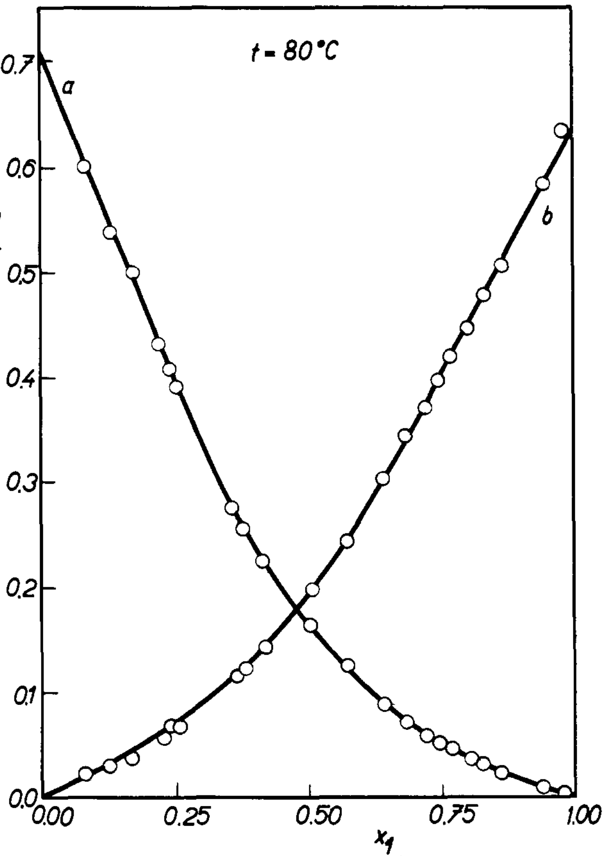

Figure 5. The logarithm of the activity coefficients as a function of the composition

System pyridine(1)-tetrachloroethylene(2)

a. ln γ_1 b. ln γ_2

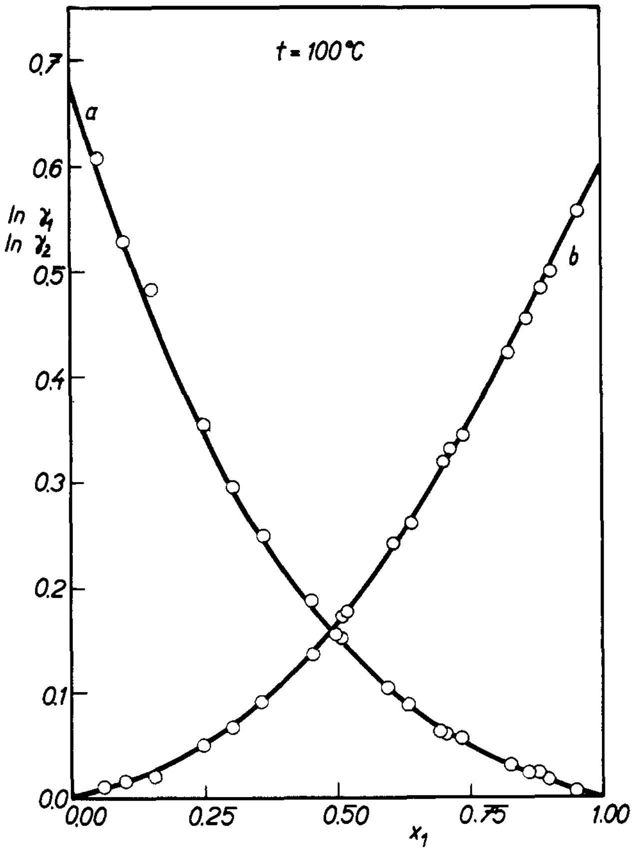

Figure 6. The logarithm of the activity coefficients as a function of the composition

System pyridine(1)-tetrachloroethylene(2)

a. ln γ_1 b. ln γ_2

The thermodynamic consistency of the experimental data was proved by the equation (*16*)

$$\int_0^1 \ln\left[\alpha_{12}\frac{P_2^0}{P_1^0}\right]dx_1 = \frac{(P_2^0 - P_1^0)(\bar{V}_1 + \bar{V}_2 - B_1 - B_2)}{2RT} \tag{7}$$

This equation yields a convenient and generally accurate test of the consistency of measurements of isothermal vapor-liquid equilibrium data for binary mixtures of nonpolar or weakly polar substances. Because of the small difference in the vapor pressures of both components, the value of the right-hand side of Equation 7 is negligible (1.3×10^{-3}, 2.5×10^{-3}, and 4.0×10^{-3} at 60°, 80°, and 100° C.). Thus, Equation 7 reduces to the Redlich-Kister consistency test method (*14*, *15*). This method requires the net area of the graph $\ln[\alpha_{12}(P_2^0)/(P_1^0)]$ against x_1 to be equal to zero. This requirement is met in Figure 7 at all three temperatures. The ratio of the areas above and below the zero line at 60°, 80°, and 100° C. are 0.985, 1.008, and 1.003.

Evidently (Figures 1, 2, and 3), the system pyridine-tetrachloroethylene forms a minimum boiling azeotrope, whose composition and pressure at the three temperatures are shown in Table VI. The experimental data (Table VI) indicate that the composition of the azeotropic mixture changes only slightly with the temperature.

For an azeotrope, the following equation can be written:

$$\left(\frac{P_1^0}{P_2^0}\right)_{az} = \left(\frac{\gamma_2}{\gamma_1}\right)_{az} \tag{8}$$

By taking the logarithm of both sides, Equation 8 can be rearranged into the form

Table III. Constants of the Antoine Equations

Substance	$-A$	B	C	Ref.
Pyridine	1374.103	7.04162	215.014	(*10*)
Tetrachloroethylene	1531.460	7.21511	232.379	(*3*)

Table IV. Virial Coefficients and Molar Volumes of Pyridine(1) and Tetrachloroethylene(2)

Temp., ° C.	$\bar{V}_1$, Ml. Mole^{-1}	$-B_1$, Ml. Mole^{-1}	$\bar{V}_2$, Ml. Mole^{-1}	$-B_2$, Ml. Mole^{-1}
60	84.039 (*3*)	1453 (*1*, *10*)	106.570 (*3*)	1762[a]
80	85.849 (*3*)	1226 (*1*, *10*)	108.788 (*3*)	1504[a]
100	87.659 (*3*)	1044 (*1*, *10*)	111.006 (*3*)	1294[a]

[a] Data calculated from Pitzer's equation (*12*).

Table V. Constants of the Margules Equation and Series Expansion of the Relative Volatility

Temp., ° C.	Margules			α-Series			
	A_{12}	A_{21}	D	a_{12}	a_{122}	a_{21}	a_{211}
60	0.3438	0.2900	0.0141	1.0215	0.5399	1.1158	−0.4243
80	0.3148	0.2739	0.0065	0.4963	0.8811	0.5826	−0.0170
100	0.2932	0.2571	0.0179	0.9931	0.3495	0.9586	−0.4387

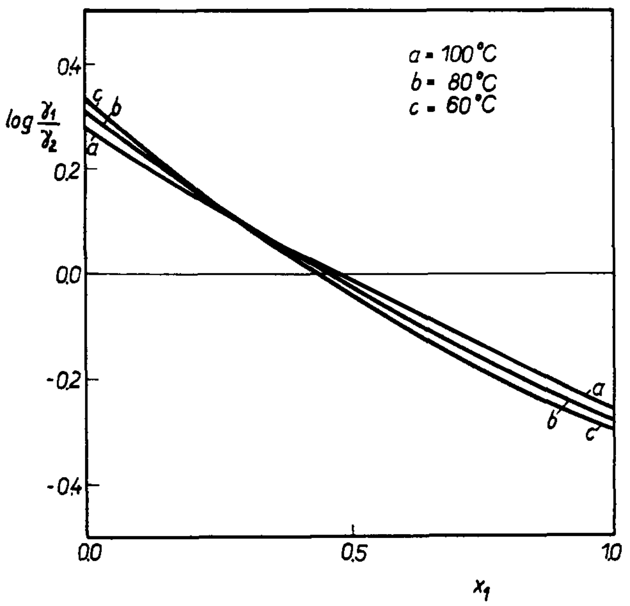

Figure 7. Thermodynamic consistency test
System pyridine(1)-tetrachloroethylene(2)

Table VI. Composition of the Azeotrope at Different Temperatures

Temp., ° C.	Pressure, Mm. Hg	Composition, Mole %
100	526.57	62.13
80	270.29	59.78
60	126.11	58.95

$$\log\left(\frac{P_1^0}{P_2^0}\right) = \log\gamma_2 - \log\gamma_1 \qquad (9)$$

In the limit when $x_1 \rightarrow 1$, $\gamma_1 \rightarrow 1$, $\log\gamma_1 \rightarrow 0$, and $\log\gamma_2 = A_{21}$. This means that the azeotrope will disappear at the temperature at which $\log(P_1^0/P_2^0)$ will be equal to the constant A_{21}. This temperature can be found out graphically by plotting both $\log(P_1^0/P_2^0)$ and A_{21} on a graph against the temperature. The point of intersection of the two curves gives the desired temperature.

This procedure could not be used for the system pyridine-tetrachloroethylene. The small temperature range in which the vapor-liquid equilibrium was measured and the slight changes in the composition of the azeotrope do not justify the extrapolation of the curves to the condition where $x_1 \rightarrow 1$.

This method can be extended to multicomponent systems. From the azeotropic condition in a ternary system ($x_1 = y_1$, $x_2 = y_2$, $x_3 = y_3$), the following equation can be derived:

$$\frac{\gamma_2\gamma_3}{\gamma_1} = \frac{P P_1^0}{P_2^0 P_3^0} \qquad (10)$$

After taking the logarithm and limiting the expression to $x_1 \rightarrow 1$, we get ($\log\gamma_1 = 0$, $\log\gamma_2 = A_{21}$, $\log\gamma_3 = A_{31}$)

$$\lim_{\substack{x_1 \rightarrow 1 \\ x_2 = x_3 \rightarrow 0}} \log\left(\frac{P P_1^0}{P_2^0 P_3^0}\right) = A_{21} + A_{31} \qquad (11)$$

Similarly,

$$\lim_{\substack{x_2 \rightarrow 1 \\ x_1 = x_3 \rightarrow 0}} \log\left(\frac{P P_2^0}{P_1^0 P_3^0}\right) = A_{12} + A_{32} \qquad (12)$$

and

$$\lim_{\substack{x_3 \rightarrow 1 \\ x_1 = x_2 \rightarrow 0}} \log\left(\frac{P P_3^0}{P_1^0 P_2^0}\right) = A_{13} + A_{23} \qquad (13)$$

All of these equations can be solved graphically by plotting the sum of the constants and the respective logarithmic term against the temperature. The intersection of the two lines again gives the condition (pressure, temperature) at which the azeotrope disappears. This procedure, however, needs very accurate values of the constants.

NOMENCLATURE

a_{12}, a_{21}, a_{122}, a_{2111} = constant of the series expansion of relative volatility
A_{12}, A_{21}, A_{13}, A_{31}, A_{23}, A_{32} = constants of the Margules equation
B_i = virial coefficient of component i
P = total pressure of the system
P_i^0 = vapor pressure of pure component i
R = gas-law proportionality constant
t = temperature, ° C.
T = temperature, absolute
$\bar{V}_i$ = molar volume of pure component i
x_i = liquid phase composition of component i (mole fraction)
y_i = vapor phase composition of component i (mole fraction)

Greek Letters

α_{12} = relative volatility of the binary system 1–2
γ_i = activity coefficient of component i in the liquid phase (standard state is the pure component at the temperature and pressure of the system)

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