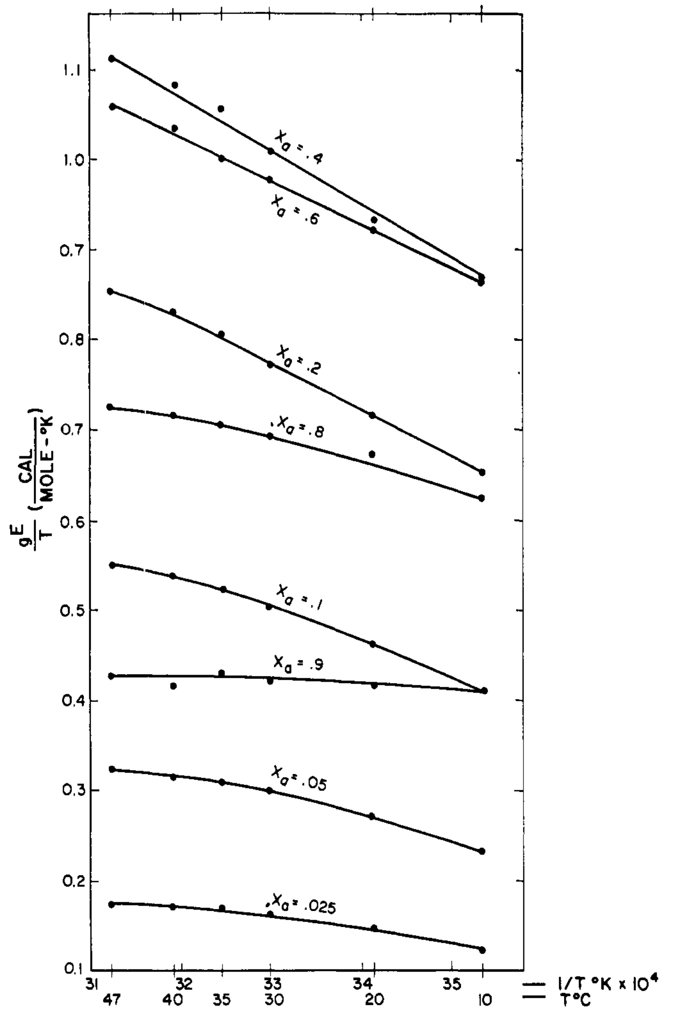

Figure 4. Excess Gibbs free energy for methyldiethylamine-water

Greek Letters

γ = activity coefficient = $f/f^0 X$
Φ = ratio of fugacity coefficient of pure component to component fugacity coefficient in mixture

Subscripts

a = amine
w = water
1 = Component 1
2 = Component 2

Superscript

0 = pure component

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Vapor-Liquid Equilibrium for System Toluene–*n*-Amyl Alcohol

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Total vapor pressures of mixtures of toluene and *n*-amyl alcohol were measured at temperatures from 30° C to the normal boiling point for liquid solutions of known compositions. These data were used to calculate isothermal vapor-liquid equilibrium compositions at five different temperatures from 30–110° C. The calculation procedure to convert the vapor pressure-temperature-liquid composition data to isothermal vapor-liquid equilibrium compositions is discussed.

CALCULATION METHODS

The approach outlined by Van Ness (*13*) was used to calculate the equilibrium compositions from the total vapor pressure data. The general coexistence equation is rigorous and derived from the Gibbs-Duhem equation. For a binary system, this equation is

$$\psi dP + \Omega dT = (y_1 - x_1) d \ln \left(\frac{\gamma_1^V}{\gamma_2^V}\right) + \frac{(y_1 - x_1)}{y_1(1 - y_1)} dy_1 \quad (1)$$

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Total vapor pressures for toluene–*n*-amyl alcohol solutions of 11 different compositions including the pure components were measured over the range 30°C to the normal boiling point with an isoteniscope–mercury barometer system. These data were used to calculate isothermal vapor-liquid equilibrium compositions at 30°, 50°, 70°, 90°, and 110°C by numerical integration of the isothermal coexistence equation.

$$\psi = \frac{V^V - V^L + (y_1 - x_1)(V_2^V - V_1^V)}{RT} \tag{2}$$

$$\Omega = \frac{H^V - H^L + (y_1 - x_1)(H_2^V - H_1^V)}{RT^2} \tag{3}$$

For isothermal conditions and for low pressures, Equation 1 can be reduced to

$$\frac{dy_1}{dP} = \frac{\psi - (1 - 2\,y_1)(y_1 - x_1)(\delta_{12}/RT)}{\dfrac{(y_1 - x_1)}{y_1(1 - y_1)} - (y_1 - x_1)(2\,P\delta_{12}/RT)} \tag{4}$$

Equation 2 becomes

$$\psi = \frac{y_1y_2\delta_{12} - V^L + x_1B_{11} + x_2B_{22}}{RT} + \frac{1}{P} \tag{5}$$

In Equations 4 and 5, the virial equation of state truncated after the second term is used to represent the *PVT* behavior of the gas phase. Only moderate accuracy is required for the second virial coefficients because of the low pressure application. Hence, if experimental data are not available, existing correlations can be used with satisfactory accuracy. B_{11}, B_{22}, and δ_{12} were calculated using procedures suggested by O'Connell and Prausnitz (*8*). The critical properties for toluene required for estimating the second virial coefficient were taken from the data of Rossini (*10*). The critical constants for *n*-amyl alcohol were calculated by Lydersen's method as suggested by Gold and Ogle (*3*).

The liquid molar volume was assumed to be a linear function of mole fraction between the values of molar volume for the pure components. This assumes negligible volume change upon mixing. The volume change of mixing for other alcohol–hydrocarbon systems has been measured by Pardo and Van Ness (*9*) and Van Ness and coworkers (*14*, *15*). For alcohol–aromatic systems, the volume change on mixing was less than 0.2% of the mixture volume. Because of the relative magnitudes of the numbers in Equation 5, the effect of neglecting the volume change of mixing is entirely negligible. In addition, the small variation in molar volume caused by pressure changes was neglected. Liquid molar volumes were derived from the data of Timmermans (*12*).

The experimental data to be used with Equations 4 and 5 are most convenient if in the form of total vapor pressure vs. liquid composition at constant temperature. Thus, *P* is a function of x_1. To get y_1 as a function of x_1, we can integrate the equation

$$\frac{dy_1}{dx_1} = \frac{dy_1}{dP} \cdot \frac{dP}{dx_1} \tag{6}$$

dP/dx_1 can be obtained from the experimental data by differentiation of the *P* vs. x_1 data. dy_1/dP is obtained from Equation 4. Experimental data, combined with Equations 4–6 can then be used to calculate equilibrium y_1 vs x_1 values by numerical integration. In this study, the fourth-order Runge-Kutta integration technique given by Lapidus (*6*) was used with an IBM 360/50 digital computer to perform the integrations. The procedure will now be summarized in a stepwise manner.

For 11 solutions of different and known liquid composition, total vapor pressures were measured at temperatures from 30° C to the normal boiling point. For each mixture, the total vapor pressure data were fitted by a nonlinear least-squares technique to the following integrated form of the Clausius-Clapeyron equation

$$\log_{10} P = A - B/T - C \log_{10} T \tag{7}$$

The set of Equations 7 represented the experimental data and could be used to calculate the vapor pressure for each of the liquid mixtures at any given temperature.

A set of isothermal vapor pressure data as a function of x_1 was calculated from the fitted Equations 7. The calculated data points were used because the experimental measurements could not be made exactly at each temperature desired. This procedure also smoothed the data. A seventh-degree polynomial in x_1 was fitted to the *P* vs. x_1 data using a linear least-squares technique. This latter equation was then differentiated analytically to yield dP/dx_1 values.

Equation 6 was integrated numerically, making use of Equations 4 and 5 and the experimentally derived dP/dx_1 data to yield y_1 vs. x_1 at constant temperature. Because of the nature of the system, all integrations were started at the pure component compositions to obtain proper convergence.

EXPERIMENTAL

The materials used were both of relatively high purity as obtained from the suppliers. Gas chromatographic analysis, however, revealed some impurities, especially in the alcohol. Therefore, the materials were redistilled at high reflux ratio in a 100-cm tall distillation column packed with $^1/_8$-in. glass helices. The samples were taken from heart cuts in which no impurities other than air could be detected by the gas chromatograph.

The toluene used was purchased from the Phillips Petroleum Co., with a specified purity of 99+ mol %. After distillation the refractive index at 20° C was 1.4967 compared to 1.4961 from the literature (*4*).

The *n*-amyl alcohol was purchased from Baker Chemical Co., with a specified boiling range of 137.4–8.0° C. After distillation, the refractive index at 20° C was 1.4099 compared to 1.4101 from the literature (*4*).

Despite the extensive initial purification, the materials contained appreciable amounts of dissolved gases, such as air, even though all sample transfers to the vapor pressure measuring cell were conducted in a glass apparatus from which air had been previously evacuated to 10 μ absolute pressure. The alcohol was easily degassed by repeatedly freezing the liquid with liquid nitrogen, thawing, refreezing, and evacuating the vapor space above the frozen sample. When no gas bubbles were seen rising to the liquid surface on thawing, the degassing was complete as the vapor pressure showed. The toluene required much more extensive degassing. After drawing the toluene vapor first through a bed of Dehydrite and then through Ascarite, the toluene was condensed and subjected to the same degassing-by-freezing technique as the alcohol. The toluene was vacuum distilled into a specially designed glass still with a 21-cm long packed section containing $^1/_4$-in. Intalox saddles.

Vaporization in the still pot was supplied by a thermosyphon reboiler made from 2-mm id capillary tubing wound outside with resistance heating wire. The thermosyphon reboiler eliminated the violent bumping that otherwise occurred when the toluene boiled. Toluene vapors were condensed by a water-cooled condenser built into the upper section of the still. Every few hours the vapor space above the condenser was isolated by closing a stopcock and was completely evacuated, thus removing any noncondensables that had collected there. The stopcock was reopened and the refluxing continued. Periodically, a portion of the toluene was removed from the still, and its vapor pressure was measured at several temperatures to check on the progress of the degassing. Table I shows the progress of the toluene degassing operation, essentially complete after 144 hr.

Vapor pressures were measured in a Booth-type isoteniscope (*2*) in a constant temperature bath. Pressure measurements were made by balancing the pressure exerted by the sample with dry air and measuring the air pressure with an absolute mercury manometer which was read by a cathetometer. After the isoteniscope was loaded, the sample was sealed in with mercury, connected to the absolute manometer system, and placed in a well-stirred constant-temperature bath. The sample inside the isoteniscope was stirred continuously by a magnetic stirring bar driven from beneath the bath. The sample temperature was measured using a copper-constantan thermocouple immersed in the bath near the isoteniscope. The thermocouple was calibrated against an NBS-certified platinum-resistance thermometer. The bath temperature could be controlled to within ±0.05° C, and no temperature gradients could be detected with the thermocouple near the isoteniscope.

For each sample, the first vapor pressure measurement was made at room temperature after which successive vapor pressures were determined at approximatly 10° C intervals up to the sample's normal boiling point. The sample was vacuum distilled from the isoteniscope into a trap and taken for composition analysis with a refractometer. The isoteniscope was so constructed that the uncertainty in liquid-phase composition introduced by assigning the composition of the entire sample to the liquid phase was less than ±0.001 mole fraction. The following is a summary of the maximum expected experimental errors for this study: temperature, ±0.05° C; pressure, ±0.2 mm Hg; composition, ±0.005 mole fraction.

EXPERIMENTAL RESULTS

Table II gives the constants in the integrated Clausius-Clapeyron equation (Equation 7) for the vapor pressures as functions of temperature for each mixture investigated. All barometric measurements were corrected for capillarity of the manometer and mercury vapor pressure and are given corrected to a mercury column at 0° C and gravity as at sea level and 45° latitude.

The pure-component data (Tables III and IV) are in good agreement with that of Rossini (*10*) in the case of toluene and with the data of Kemme and Krepps (*5*) for *n*-amyl alcohol.

Figure 1 shows the variation in total vapor pressure with liquid composition at the five temperatures for which the isothermal coexistence equation was solved. An azeotrope is evident at 110° C but not seen at the four lower temperatures.

Table V presents the isothermal vapor-liquid equilibrium compositions at five temperatures from 30–110° C. In addition, the liquid-phase activity coefficient, vapor pressure, and excess free energy, ΔG^E, are tabulated. Values for ΔG^E were calculated using the equation

$$\Delta G^E = RT(x_1 \ln \gamma_1^L + x_2 \ln \gamma_2^L) \qquad (8)$$

Activity coefficients were calculated from the equation

$$\gamma_i^L = \frac{y_iP}{x_iP_i^o} + \frac{(B_{ii} - V_i^L)(P - P_i^o)}{RT} + \frac{P\delta_{ij}}{RT} y_i^2 \qquad (9)$$

Table I. Toluene Degassing Times

	Vapor Pressure,[a] mm Hg after			
t, ° C	0 hr	72 hr	144 hr	170 hr
70.0	215.08	203.92	203.17	203.21
110.0	779.56	746.48	746.36	745.49

[a] Vapor pressures are smoothed values calculated from Equation 7 which was fitted to the particular set of experimental data.

Table II. Integrated Clausius-Clapeyron Equation[a] Constants

Mole fraction toluene	Standard error estimate, mm Hg	A	B, ° K⁻¹	C
0.000	0.415	51.02254	4878.576	13.877430
0.125	0.698	6.23402	2018.146	−0.641210
0.295	0.389	8.77065	2015.623	0.300993
0.418	1.397	13.80306	2241.971	2.000000
0.528	0.320	13.35838	2197.996	1.861322
0.595	0.154	14.28155	2239.237	2.170832
0.717	0.321	17.37152	2390.385	3.206628
0.819	0.484	16.75390	2352.509	3.000000
0.880	0.088	18.88354	2458.569	3.715066
0.940	1.774	25.76370	2813.330	6.018566
1.000	0.471	21.36637	2573.199	4.559219

[a] The integrated Clausius-Clapeyron equation is given by Equation 7, where *P* is in mm Hg and *T* is degrees Kelvin. The multiple correlation coefficient was 0.999+ for each data set, indicating excellent correlations. The standard error of estimate is defined as follows: $SE = Phi/(n - k)$ where

$$Phi = \sum_{i=1}^{n} (\text{observed pressure} - \text{predicted pressure})^2$$

Table III. Toluene Vapor Pressures

	Vapor pressure, mm Hg, from the data of		
Temp., ° C	Rossini (*10*)[a]	Van Ness (*15*)[a] et al.	Sadler (*11*)[b]
30.0	36.67	37.95	36.64
50.0	92.10	93.32	91.78
70.0	203.72	204.67	203.21
90.0	406.65	408.66	406.20
110.0	746.41	754.76	745.49

[a] Vapor pressures were calculated from the Antoine equation fitted by the investigator to his experimental data. [b] Vapor pressures were calculated from a fit of the experimental data to the integrated form of the Clausius-Clapeyron equation by the indicated investigator.

Table IV. *n*-Amyl Alcohol Vapor Pressures

	Vapor pressure, mm Hg, from the data of		
Temp., ° C	Butler (*1*)[a]	Kemme (*5*)[b] and Krepps	Sadler (*11*)[a]
30.0	3.65	3.17	3.10
50.0	14.22	12.92	12.64
70.0	45.18	42.06	41.66
90.0	121.46	115.06	115.15
110.0	284.14	274.16	275.03
130.0	591.65	584.36	581.25

[a] Vapor pressures were calculated from a fit of the experimental data to the integrated form of the Clausius-Clapeyron equation by the indicated investigator. [b] Vapor pressures were calculated from the Antoine equation fitted by the investigator to his experimental data.

Table V. Isothermal Vapor-Liquid Equilibrium Compositions

Vapor-Liquid Equilibrium at 30° C

Toluene mole fraction		Liquid-phase activity coefficient		Total pressure, mm Hg	Excess free energy, cal/g mol
Liquid	Vapor	Toluene	*n*-Amyl alcohol		
0.010	0.323	4.010	0.999	4.53	7.67
0.050	0.674	3.358	1.004	9.09	38.96
0.100	0.783	2.813	1.019	13.12	72.22
0.150	0.832	2.466	1.038	16.25	100.39
0.200	0.861	2.238	1.059	18.99	124.80
0.250	0.883	2.077	1.083	21.51	145.88
0.300	0.899	1.949	1.108	23.80	163.89
0.350	0.911	1.836	1.141	25.82	179.77
0.400	0.920	1.730	1.182	27.54	192.58
0.450	0.927	1.630	1.236	28.95	202.42
0.500	0.934	1.535	1.306	30.13	209.39
0.550	0.938	1.450	1.390	31.14	212.41
0.600	0.942	1.376	1.492	32.08	211.69
0.650	0.947	1.312	1.617	32.98	207.51
0.700	0.951	1.256	1.769	33.85	199.14
0.750	0.956	1.204	1.975	34.62	186.42
0.800	0.959	1.152	2.306	35.19	168.69
0.850	0.961	1.095	2.933	35.47	143.78

Vapor-Liquid Equilibrium at 50° C

Toluene mole fraction		Liquid-phase activity coefficient		Total pressure, mm Hg	Excess free energy, cal/g mol
Liquid	Vapor	Toluene	*n*-Amyl alcohol		
0.010	0.208	3.617	1.000	15.81	8.26
0.050	0.539	3.100	1.005	26.21	39.17
0.100	0.675	2.646	1.018	35.75	72.54
0.150	0.741	2.337	1.036	43.18	100.95
0.200	0.783	2.123	1.057	49.53	124.99
0.250	0.814	1.966	1.080	55.23	145.78
0.300	0.837	1.842	1.108	60.41	168.68
0.350	0.855	1.736	1.140	65.03	178.58
0.400	0.870	1.640	1.179	69.07	190.49
0.450	0.882	1.551	1.229	72.53	199.58
0.500	0.891	1.468	1.292	75.47	205.54
0.550	0.899	1.392	1.371	78.01	207.87
0.600	0.907	1.324	1.466	80.27	206.38
0.650	0.914	1.264	1.584	82.36	201.05
0.700	0.922	1.211	1.733	84.33	191.84
0.750	0.929	1.163	1.924	86.15	177.93
0.800	0.936	1.119	2.201	87.73	159.10
0.850	0.943	1.076	2.659	88.96	133.97
0.900	0.950	1.033	3.548	89.81	99.97
0.950	0.962	0.999	5.345	90.50	53.24

Vapor-Liquid Equilibrium at 70° C

Toluene mole fraction		Liquid-phase activity coefficient		Total pressure, mm Hg	Excess free energy, cal/g mol
Liquid	Vapor	Toluene	*n*-Amyl alcohol		
0.010	0.135	3.227	1.000	47.75	8.15
0.050	0.414	2.813	1.005	68.10	38.19
0.100	0.561	2.436	1.016	87.28	70.57
0.150	0.641	2.171	1.033	102.39	98.03
0.200	0.693	1.982	1.053	115.25	121.45
0.250	0.733	1.840	1.076	126.73	141.40
0.300	0.764	1.729	1.101	137.17	158.06
0.350	0.789	1.635	1.132	146.61	172.11
0.400	0.810	1.551	1.168	155.00	183.15
0.450	0.827	1.473	1.213	162.33	191.33
0.500	0.842	1.401	1.269	168.64	196.33
0.550	0.854	1.334	1.341	174.08	197.98
0.600	0.865	1.272	1.430	178.85	195.93
0.650	0.876	1.217	1.539	193.16	189.91
0.700	0.887	1.169	1.674	187.18	179.88
0.750	0.898	1.127	1.842	191.00	165.31
0.800	0.911	1.091	2.064	194.58	146.20
0.850	0.924	1.058	2.381	197.78	121.64
0.900	0.939	1.029	2.910	200.38	90.29
0.950	0.959	1.005	3.917	202.19	49.59

Vapor-Liquid Equilibrium at 90° C

Toluene mole fraction		Liquid-phase activity coefficient		Total pressure, mm Hg	Excess free energy, cal/g mol
Liquid	Vapor	Toluene	*n*-Amyl alconol		
0.010	0.091	2.881	1.000	125.59	7.86
0.050	0.313	2.529	1.004	160.68	36.37
0.100	0.454	2.207	1.015	194.12	67.03
0.150	0.539	1.983	1.031	220.86	92.78
0.200	0.599	1.824	1.049	243.94	114.51
0.250	0.647	1.706	1.070	264.79	132.83
0.300	0.686	1.614	1.093	283.94	148.30
0.350	0.718	1.536	1.119	301.40	161.02
0.400	0.745	1.465	1.151	317.04	171.08
0.450	0.768	1.399	1.191	330.77	178.39
0.500	0.788	1.337	1.241	342.64	182.59
0.550	0.805	1.278	1.305	352.87	183.67
0.600	0.821	1.223	1.384	361.82	181.04
0.650	0.836	1.175	1.481	369.89	174.67
0.700	0.852	1.133	1.596	378.45	164.35
0.750	0.868	1.099	1.732	384.71	149.92
0.800	0.887	1.070	1.896	391.65	131.45
0.850	0.907	1.046	2.110	397.65	108.53
0.900	0.929	1.025	2.449	403.04	80.37
0.950	0.956	1.006	3.097	406.10	44.61

Vapor-Liquid Equilibrium at 110° C

Toluene mole fraction		Liquid-phase activity coefficient		Total pressure, mm Hg	Excess free energy, cal/g mol
Liquid	Vapor	Toluene	*n*-Amyl alconol		
0.010	0.065	2.644	1.000	291.76	7.56
0.050	0.238	2.293	1.005	346.90	34.88
0.100	0.361	1.992	1.016	398.46	63.30
0.150	0.444	1.795	1.031	440.06	86.54
0.200	0.509	1.666	1.047	477.00	105.85
0.250	0.563	1.575	1.064	511.42	122.12
0.300	0.609	1.506	1.083	543.66	135.81
0.350	0.649	1.446	1.104	573.31	147.30
0.400	0.682	1.389	1.131	599.82	156.38
0.450	0.711	1.334	1.166	622.92	162.84
0.500	0.735	1.279	1.210	642.77	166.45
0.550	0.757	1.228	1.267	659.88	166.96
0.600	0.778	1.181	1.335	675.03	164.00
0.650	0.798	1.141	1.415	688.97	157.57
0.700	0.820	1.107	1.504	702.25	147.62
0.750	0.843	1.081	1.604	714.97	134.29
0.800	0.867	1.059	1.722	726.72	117.55
0.850	0.893	1.039	1.888	736.59	97.06
0.900	0.918	1.018	2.179	743.43	71.42
0.950	0.951	1.003	2.612	746.36	38.44
0.970	0.969	1.001	2.741	746.42	23.49
0.980	0.979	1.000	2.797	746.24	15.79
0.990	0.982	0.992	4.948	745.96	6.22

To calculate the vapor composition, dP/dx_1 must be evaluated by differentiating a seventh-degree polynomial that was fitted to isothermal P-x data by a least-squares technique. Differentiation of a high-degree polynomial can give erratic derivatives if the fitted data are not smooth. Two checks were made to be certain that the calculated derivatives were reasonable. First, the computer terminated integration whenever a zero derivative occurred, indicating an azeotrope. The only isotherm for which an azeotrope was indicated was at 110° C. Second, values of dP/dx_1 were printed by the computer and were checked to be certain the derivatives were reasonable. Figure 2 gives dP/dx_1 as a function of x_1 for the 110° C isotherm as obtained by differentiation of the polynomial. Individual points are not shown on the figure because they were calculated from the equation at intervals of 0.01 in x_1. This figure shows the derivatives dP/dx_1 to be reasonably smooth.

In addition to the equilibrium data calculated from the total vapor pressure measurements, some direct equilibrium measurements at atmospheric pressure were made using an equilib-

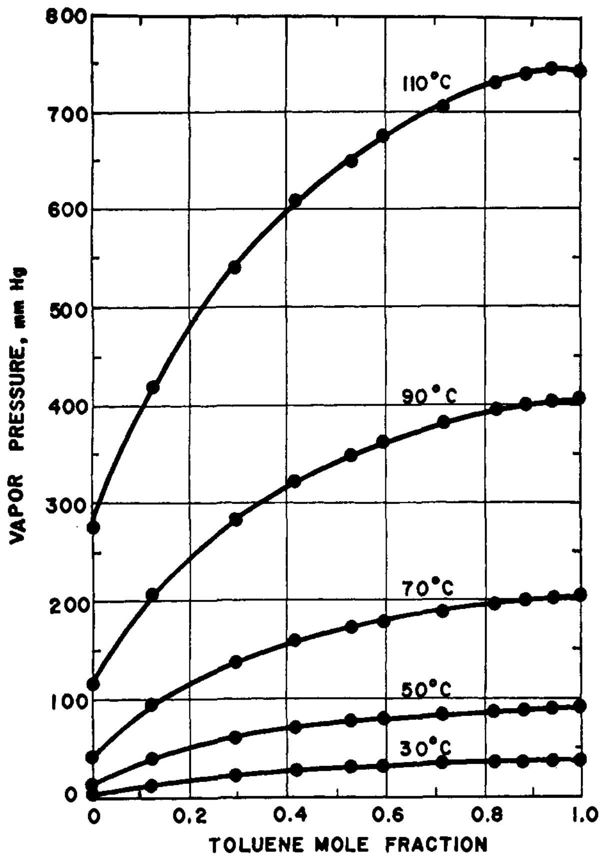

Figure 1. Isothermal total vapor pressure–composition curves

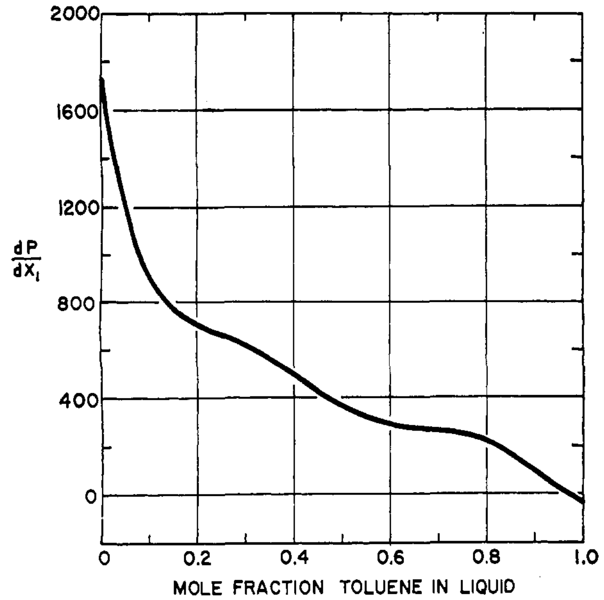

Figure 2. Slope of total vapor pressure curve from seventh degree polynomial

rium still. The materials were the same as previously described, and the still was essentially the same as that used by Nagata (*7*). The results of the measurements with the equilibrium still are given in Table VI. No data are presented for compositions below $x_1 = 0.465$ because as the liquid became more concentrated in *n*-amyl alcohol, severe bumping occurred and it was not possible to obtain reliable data.

The data from the equilibrium still are compared with the data from the total vapor pressure measurements in Figure 3.

Table VI. Isobaric Vapor-Liquid Equilibrium Data

x_1	y_1	Temp, ° C	P, mm Hg	γ_1^L	γ_2^L
0.465	0.685	116.8	760	1.257	1.214
0.530	0.725	115.8	761	1.198	1.257
0.593	0.757	113.4	752	1.177	1.390
0.600	0.765	114.3	763	1.164	1.342
0.635	0.776	113.2	762	1.147	1.460
0.685	0.800	112.4	754	1.108	1.545
0.710	0.825	112.0	757	1.118	1.499
0.767	0.847	111.4	760	1.083	1.678
0.826	0.875	111.0	760	1.050	1.870
0.863	0.900	110.5	758	1.045	1.936
0.920	0.935	110.1	756	1.026	2.191
0.960	0.975	110.2	752	1.018	1.677
0.995	0.995	110.7	762	1.001	2.191

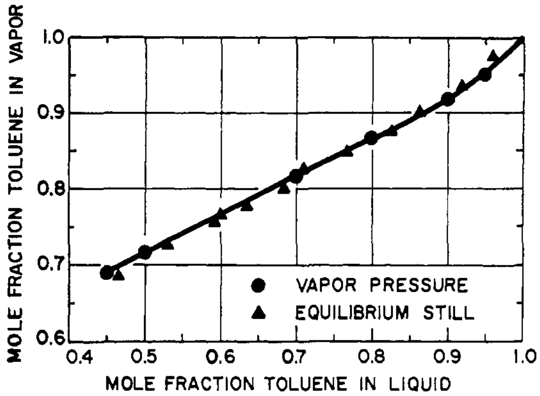

Figure 3. Isobaric equilibrium at 1 atm

The highest isotherm calculated from the total vapor pressure measurements was 110° C, but the isobaric data from the equilibrium still covered a temperature range of 110.1–16.8° C. For a liquid solution of a given composition, the effect of temperature on the vapor composition was not large, and it was easy graphically to extrapolate the data from the total vapor pressure measurements to the temperature observed in the isobaric measurements with the equilibrium still. These extrapolated values are plotted in Figure 3 along with data from the equilibrium still. The agreement is good, and the validity of the calculations from the total vapor pressure measurements is confirmed.

The activity coefficients at 110° C calculated from the total vapor pressure measurements were fitted by nonlinear least squares to the following three equations:

Van Laar

$$\ln \gamma_1 = \frac{A_{12}}{\left(1 + \dfrac{x_1 A_{12}}{x_2 A_{21}}\right)^2} \qquad \ln \gamma_2 = \frac{A_{21}}{\left(1 + \dfrac{x_2 A_{21}}{x_1 A_{12}}\right)^2} \tag{9}$$

3-Suffix Margules

$$\ln \gamma_1 = x_2^2[A_{12} + 2\,x_1(A_{21} - A_{12})] \qquad \ln \gamma_1 = x_1^2[A_{21} + 2\,x_2(A_{12} - A_{21})] \tag{10}$$

Wilson

$$\ln \gamma_1 = -\ln (x_1 + \Lambda_{12}x_2) + x_2\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right]$$
$$\ln \gamma_2 = -\ln (x_2 + \Lambda_{21}x_1) - x_1\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right] \tag{11}$$

Table VII. Correlating Parameters for Activity Coefficient at 110° C

Eq	Parameters	Standard error estimate	Correlation coefficient
Van Laar	$A_{12} = 0.92639$ $A_{21} = 0.83855$	0.0796	0.992
3-Suffix Margules	$A_{12} = 0.92144$ $A_{21} = 0.84992$	0.0802	0.992
Wilson	$\Lambda_{12} = 0.55283$ $\Lambda_{21} = 0.65866$	0.0737	0.993

Table VII shows how well each equation represents the activity coefficients at 110° C. Although all three equations correlate the data well, the Wilson equation fits slightly better and is recommended for the toluene–*n*-amyl alcohol binary system.

The equipment, procedures, and raw data can be found in more detail in the work of Sadler (*11*). The original data (Table VIII) have been placed on deposit with the ACS Microfilm Depository Service.

ACKNOWLEDGMENT

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NOMENCLATURE

A = constant in the integrated Clausius-Clapeyron equation
A_{12}, A_{21} = parameters in the Van Laar and 3-suffix Margules equations
B = constant in the integrated Clausius-Clapeyron equation
B_{ii}, B_{ij}, B_{jj} = second virial coefficient for pure component i, a mixture of components i and j, and for pure component j, respectively, cc/g mol
C = constant in the integrated Clausius-Clapeyron equation
ΔG^E = excess Gibbs Free energy, cal/g mol
H^L = enthalpy of liquid solution, cal/g mol
H^V = enthalpy of vapor mixture, cal/g mol
H_i^L = enthalpy of pure component in liquid state, cal/g mol
H_i^V = enthalpy of pure component in vapor state, cal/g mol
i = index of summation
k = number of adjustable parameters in correlating equation
P = total vapor pressure, mm Hg
P_i^o = vapor pressure of pure component i
n = number of data points
R = gas constant, 62,361 mm Hg, cc/g mol, °K
t = temperature, °C
T = absolute temperature, °K
V^L = molar volume of liquid solution, cc/g mol
V^V = molar volume of vapor mixture, cc/g mol
V_i^L = liquid molar volume of pure component, i, cc/g mol
V_i^V = vapor molar volume of pure component i, cc/g mol
x_i = mole fraction of component i in the liquid phase
y_i = mole fraction of component i in the vapor phase

Greek Letters

γ_i^L = liquid-phase activity coefficient for component i
γ_i^V = vapor-phase activity coefficient for component i
δ_{ij} = $2\,B_{ij} - B_{ii} - B_{jj}$, cc/g mol
ψ = parameter in the coexistence equation
Ω = parameter in the coexistence equation
Λ_{12}, Λ_{21} = parameters in the Wilson equation

Subscripts

1 = toluene
2 = *n*-amyl alcohol
i, j = general index denoting either component 1 or component 2

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RECEIVED for review August 20, 1970. Accepted March 22, 1971. Table VIII (data on total vapor pressure from 1.000 mole fraction toluene to 0.000, three manuscript pages) will appear following these pages in the microfilm edition of this volume of the Journal. Single copies may be obtained from the Reprint Department, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit by check or money order $3.00 for photocopy or $2.00 for microfiche.