Further, another relationship between *A* and *B* (Figure 3) is given by

$$A = 0.1456\, e^{-21.62 \times 10^{-4} B} \qquad (3)$$

The following equation is obtained by substituting Equations 2 and 3 in Equation 1:

$$\mu_{\text{mix}} = 0.1456\, e^{[(1/T) - 21.62 \times 10^{-4}]\,(1097 + 1286\,\chi^{1.89})} \qquad (4)$$

For associated liquids, the relationship between log μ_l and $1/T$ becomes slightly curved; in the present case this relationship resulted in straight lines. This may be due to negligible effect of association of *n*-butanol in the range of temperatures studied.

By means of Equation 4, viscosity data at any given temperature and composition of the binary mixture can be predicted. Viscosity data predicted through Equation 4 compare well with experimental data (Table II), and the average percent deviation is 2.3.

Nomenclature

A, B = constants in Equation 1
T = absolute temperature, °K
χ = composition, mole fraction *n*-butanol
μ_{mix} = viscosity of mixture, cP

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Total Pressure Method: Binary Systems Cyclohexane–*n*-Pentanol, –*n*-Heptanol, and –*n*-Octanol

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Vapor-liquid equilibria for the binary systems cyclohexane–*n*-pentanol, –*n*-heptanol, and –*n*-octanol were obtained by the total pressure measurement method. Isothermal and isobaric vapor-liquid equilibria were calculated by numerical methods. For the isothermal conditions the calculations were performed at 10°C intervals between 70° and 130°C while for the isobaric conditions, they were performed at 400, 600, 760, and 900 mm Hg. The excess free energy was also calculated under all these conditions.

The total pressure measurement method consists of measuring the total pressures as a function of the composition of only one of the phases (usually the liquid phase) at constant temperature. The composition of the other phase is calculated with the help of the Gibbs-Duhem equation. The main advantage of this method is the great reduction of the experimental work involved.

In previous papers by the same authors *(2, 3)*, the Ramalho and Delmas method *(5)* has been improved and also extended to calculate numerically isobaric data. This modified method has been used in performing the necessary calculations in this work. A brief description of the method used to calculate vapor-liquid equilibrium data has been filed with the ACS Depository Service.

The method of calculation was fully described in previous articles *(2, 3)*. The average deviation of the results obtained by calculation when compared to reliable experimental data was well within 1% and the maximum local error never exceeded 1.5%.

Experimental

Apparatus. The apparatus used in this investigation is, with some modifications, essentially the same as the one used elsewhere *(4, 6)*. The overall experimental setup is illustrated in Figure 1. Four ebulliometers of the Swietoslawski type were operated in parallel at the same pressure to speed the collection of data. With a vacuum pump, the ebulliometers could be operated below atmospheric pressure and operation above was accomplished by using a high-pressure nitrogen cylinder to create the desired pressure. Pressure is finely controlled by a Cartesian manostat. Quartz thermometers were used to measure temperature with a precision of ±0.02°C. Pressure was read with a manometer coupled with a cathetometer. The precision in the measurement of pressure was ±0.5 mm Hg. A quieting reservoir was incorporated before the manometer to eliminate the fluctuations in the manometer owing to the boiling of the solution. The liquid mixtures were prepared by weighing appropriate amounts of the components. The precision in the composition was ±0.001.

Full descriptions of the apparatus with detailed descriptions and precisions of the equipment used can be found elsewhere *(1)*.

Materials. All the materials used were of the chromo quality standard 99+ mol %. The density and index of refraction of these materials were measured and are given in Table I. They were used as received without further purification.

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Table I. Properties of Experimental Materials

Substance[a]	Supplier	Index of refraction at 25°C		Density, 25°C	
		Exptl	Lit. (7)	Exptl	Lit. (7)
Cyclohexane	Fisher Scientific	1.4239	1.4235	0.7750	0.7739
n-Pentanol	Matheson, Coleman and Bell	1.4072	1.4079	0.8120	0.8112
n-Heptanol	Matheson, Coleman and Bell	1.4217	1.4225	0.8200	0.8186
n-Octanol	Fisher Scientific	1.4277	1.4276	0.8237	0.8223

[a] Chromo quality standard, 99+ mol %.

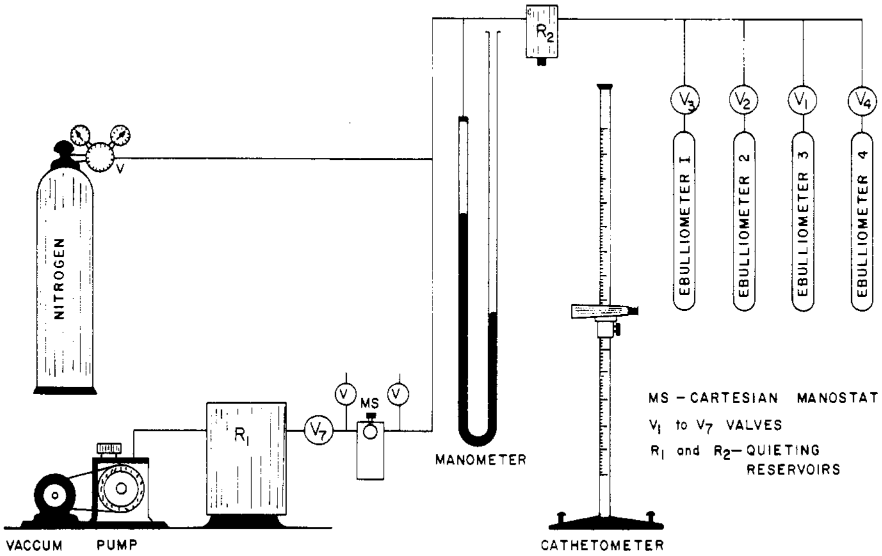

Figure 1. Ebulliometers and peripheral apparatus

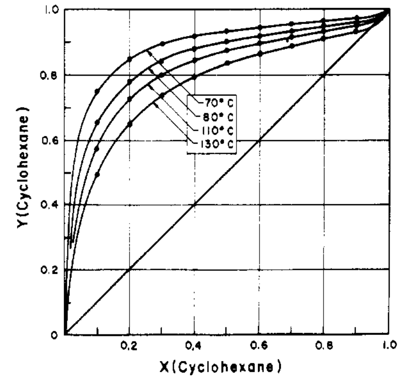

Figure 3. Vapor-liquid equilibrium at constant temperature for the system cyclohexane-*n*-pentanol

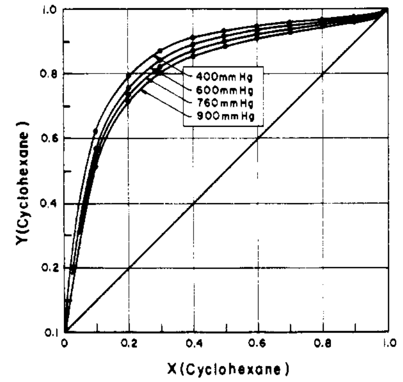

Figure 4. Vapor-liquid equilibrium at constant pressure for the system cyclohexane-*n*-pentanol

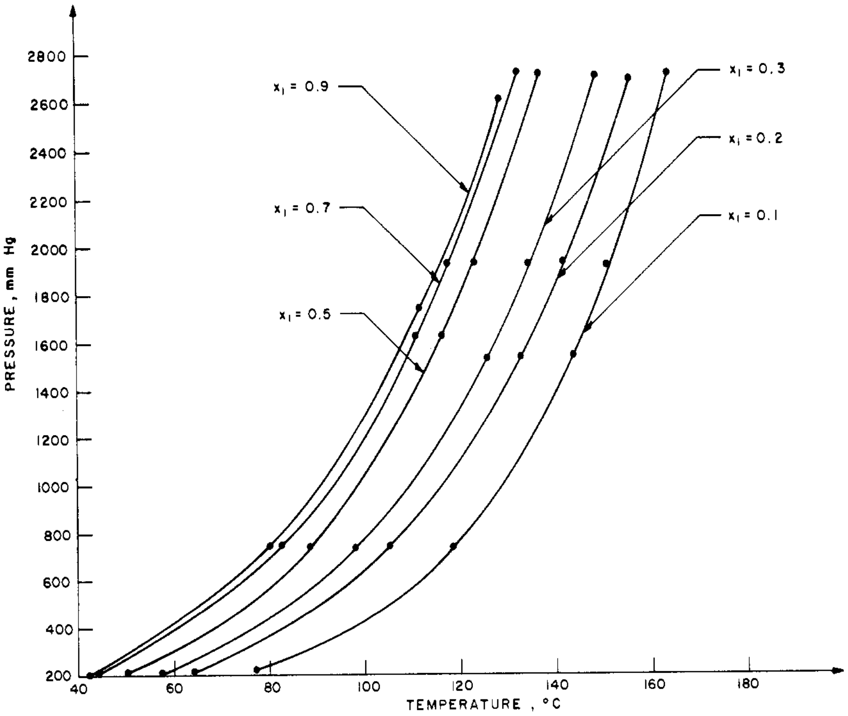

Figure 2. *PTX* values for the system cyclohexane (1)-*n*-pentanol (2)

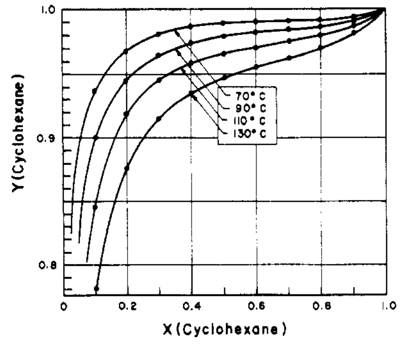

Figure 5. Vapor-liquid equilibrium at constant temperature for the system cyclohexane-*n*-heptanol

Table II. *PTX* Values for Binary Systems Cyclohexane (1)-*n*-Alcohol (2)

$x_1 = 0.1$		$x_1 = 0.2$		$x_1 = 0.3$		$x_1 = 0.4$		$x_1 = 0.5$		$x_1 = 0.6$		$x_1 = 0.7$		$x_1 = 0.8$		$x_1 = 0.9$	
P, mm Hg	*T*, °C	*P*, mm Hg	*T*, °C	*P*, mm Hg	*T*, °C	*P*, mm Hg	*T*, °C	*P*, mm Hg	*T*, °C	*P*, mm Hg	*T*, °C	*P*, mm Hg	*T*, °C	*P*, mm Hg	*T*, °C	*P*, mm Hg	*T*, °C
								Pentanol									
212.8	77.76	212.8	64.64	212.8	58.27	212.2	55.10	212.2	50.16	212.2	45.30	212.2	44.71	192.7	42.23	192.7	42.16
740.3	118.42	740.3	105.31	740.3	97.89	741.1	94.02	741.1	88.78	741.1	85.03	741.1	82.32	739.9	81.50	739.9	80.86
1549.7	143.46	1549.7	132.61	1549.7	125.32	1629.8	123.18	1629.8	116.81	1629.8	113.53	1629.8	110.79	1741.1	112.46	1741.1	111.84
1926.7	151.03	1926.7	141.20	1926.7	134.07	1937.5	130.60	1937.5	123.42	1937.5	120.21	1937.5	117.74	2022.6	118.49	2022.6	117.92
2716.5	163.21	2716.5	155.30	2716.5	148.58	2720.6	144.55	2720.6	136.90	2720.6	133.82	2720.6	132.25	2613.5	129.27	2613.5	128.85
								Heptanol									
192.7	86.11	192.7	68.10	202.7	58.84	202.7	53.42	202.7	46.43	202.7	45.14	214.7	44.79	214.7	44.77	214.7	44.86
739.9	136.50	739.9	113.80	739.9	100.54	739.9	93.16	739.9	87.60	739.9	86.55	740.3	84.27	740.3	82.42	740.3	81.67
1741.1	178.96	1741.1	152.23	1871.2	139.07	1871.2	130.40	1871.2	125.55	1871.2	122.60	1728.5	116.46	1728.5	114.34	1728.5	113.19
2022.6	187.54	2022.6	160.00	2112.4	144.81	2112.4	136.00	2112.4	131.80	2112.4	127.70	2122.3	125.03	2122.3	123.02	2122.3	121.82
2613.5	203.16	2613.5	174.12	2837.6	159.58	2837.6	150.47	2837.6	144.45	2837.6	140.54	2717.6	135.79	2717.6	139.04	2717.6	132.81
								Octanol									
250.2	98.81	222.5	76.08	222.5	65.04	222.5	57.83	222.5	53.77	242.2	54.23	242.2	52.10	242.2	48.97	242.2	47.86
739.4	143.82	741.4	119.06	741.4	107.50	741.4	99.56	741.4	92.73	742.7	88.27	742.7	86.33	742.7	83.90	742.7	82.06
1672.4	184.97	1474.1	147.30	1474.1	134.45	1474.1	126.23	1474.1	119.83	1484.6	113.67	1484.6	111.53	1484.6	109.20	1484.6	106.95
2071.5	197.04	2115.5	163.45	2115.5	149.58	2115.5	141.26	2115.5	135.87	1843.7	122.46	1843.7	120.18	1843.7	117.80	1843.7	115.45
2662.7	211.98	2667.3	174.34	2667.3	159.68	2667.3	151.30	2667.3	146.92	2786.9	140.53	2786.9	137.84	2786.9	135.26	2786.9	132.72

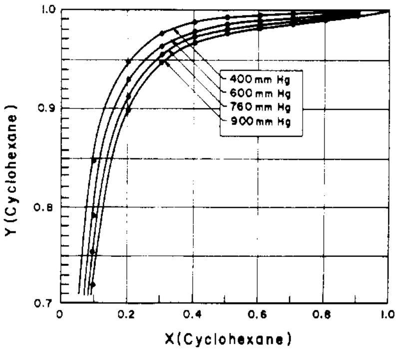

Figure 6. Vapor-liquid equilibrium at constant pressure for the system cyclohexane-*n*-heptanol

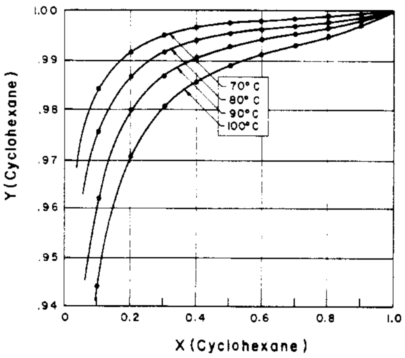

Figure 7. Vapor-liquid equilibrium at constant temperature for the system cyclohexane-*n*-octanol

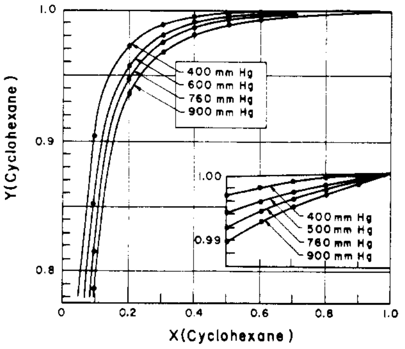

Figure 8. Vapor-liquid equilibrium at constant pressure for the system cyclohexane-*n*-octanol

Results. PTX data were determined and are tabulated in Table II, and Figure 2 illustrates a portion of the experimental data obtained for one system. Experimental determinations were carried out for the complete concentration range at intervals of 0.1 mole concentration.

Isothermal vapor-liquid equilibrium were calculated from 70° to 130°C at 10°C intervals. Isobaric data were also calculated at 400, 600, 760, and 900 mm Hg. Redlick and Kister consistency tests were performed and were well within 1% for all systems studied. The test, with this procedure verifies only the accuracy of the calculation and not the consistency of the data since the Gibbs-Duhem equation is used in this method. Figures 3-8 illustrate some of the calculated results. A complete set of calculated data have been filed with the ACS Microfilm Depository Service.

Nomemclature

G^E = excess Gibbs free energy, cal/g-mol
x_1 = mole fraction of the more volatile component of a binary mixture in the liquid phase
y_1 = mole fraction of the more volatile component of a binary mixture in the vapor phase
γ_1,γ_2 = activity coefficients for components 1 and 2 in the liquid phase
ϕ_1,ϕ_2 = coefficient of correction for nonideality of the vapor phase for components 1 and 2
π = total pressure, mm Hg

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Vapor-Liquid Equilibria in Mixtures of Water, *n*-Propanol, and *n*-Butanol

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Measurements of vapor-liquid equilibria in the systems water-*n*-propanol and water-*n*-propanol-*n*-butanol at atmospheric pressure are reported. The results for the ternary system have been compared with those predicted from the binary mixtures using the equation of Renon and Prausnitz. Agreement is very satisfactory. Densities and refractive indices of the binary and ternary mixtures at 25°C are also reported and the excess volumes of binary mixing have been calculated.

This paper reports the results of measurements of vapor-liquid equilibria for the systems water-*n*-propanol and water-*n*-propanol-*n*-butanol at atmospheric pressure. Enthalpies of mixing for these systems have previously been reported (*5, 6*) and liquid-liquid equilibrium studies have also been published (*10*).

Vapor-liquid equilibria in the system water-*n*-propanol have been extensively investigated (*7*) and this system is therefore suitable for testing the performance of the equilibrium still used in the present work. No measurements of vapor-liquid equilibria in the system water-*n*-propanol-*n*-butanol have previously been reported.

Experimental

Materials used in this investigation were purified as described in ref. *5* and *6*.

For the measurements of vapor-liquid equilibria, an equilibrium flow still similar to that described by Vilim et al. (*14*) was constructed. This instrument has the advantage that it avoids recirculation of the condensed vapor, which enables reasonably precise results to be obtained in a short time (15 min). The still used in this work differed from that of Vilim et al. in that the thermometer well was designed to accommodate a 50-ohm capsule-type platinum resistance thermometer (Rosemount Engineering Co. Ltd.) and the vacuum jacket that insulated the equilibrium chamber was extended to include the droplet separator (Figure 1) in order to minimize thermal

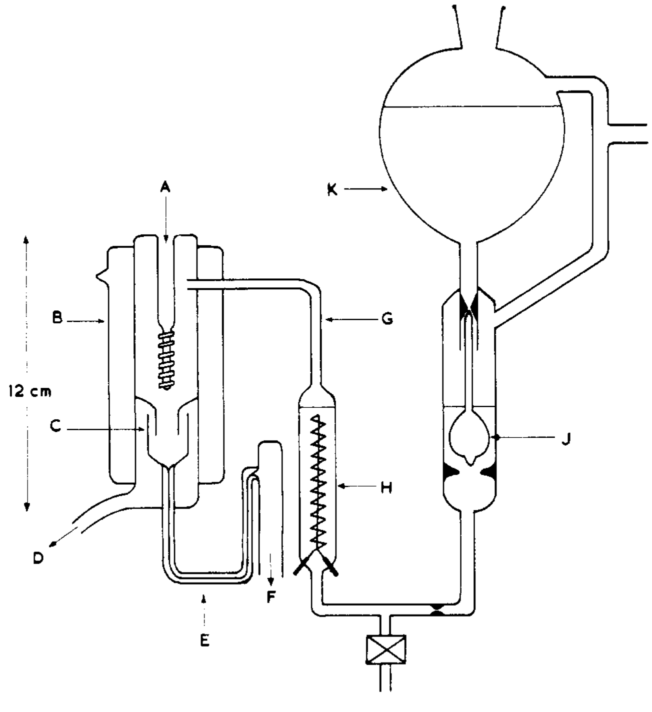

Figure 1. Equilibrium chamber of the flow still
A, thermometer well; B, vacuum jacket; C, droplet separator; D, to vapor condenser; E, 3-mm capillary; F, to liquid cooler; G, Cottrell pump; H, boiler; J, float-valve; K, reservoir

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