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

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Measurements of liquid-liquid equilibria in the system water + *n*-propanol + *n*-butanol between 20° and 60°C are reported. A new method is described for the determination of the liquid-liquid tie lines.

This paper reports results of a systematic and comprehensive series of measurements of the thermodynamic properties of liquid mixtures of water, *n*-propanol, and *n*-butanol. Enthalpies of mixing for this system and also for the appropriate binary mixtures have been reported previously (*3*, *4*). We present results of measurements of liquid-liquid equilibria for the ternary system in the range 20–60°C. This system has previously been investigated at 20°C (*2*) and 37.8°C (*5*). Vapor-liquid equilibrium data will be reported elsewhere.

MATERIALS

The *n*-propanol (SLR grade, Fisons Ltd., U.K.) was purified by refluxing with anhydrous potassium carbonate and fractional distillation from a 30-cm long Vigreux column. The first and last fractions were discarded. The *n*-butanol (AR Grade, Fisons Ltd.,) was used as received, and water was taken from a conventional laboratory still.

EXPERIMENTAL

Liquid-liquid equilibria were investigated using two separate techniques. First, the binodal curves were determined by titrating binary mixtures of known composition with the third component. Whatever the starting composition, the end point was detected by the onset or disappearance of turbidity in the sample. During titration, the samples were maintained at the desired temperature by means of a water thermostat whose temperature remained steady to within ±0.01°C. The amount of the third component required could be reproduced to within about 0.2% of the total volume (~30 cm^3).

Second, the liquid-liquid tie lines were determined by equilibrating two-phase ternary mixtures of known overall composition and then removing portions of each liquid layer with a pipet for analysis. The following method was developed for the analysis of the samples. The experimental technique, similar to that described by Smith (*6*), is illustrated in Figure 1. The original mixture, *A*, is separated into two layers, *B* and *C*. A weighed amount of liquid of composition *B* is taken and, to this, a known amount of pure 3 is added when the composition changes to that at *D*. The mixture is then titrated with pure 2 until the end point *E* is reached when, of course, the turbidity in the sample disappears.

Care must be taken that *E* does not lie near the Plait point *P*, as this results in the end point of the titration being obscured by critical opalescence. This means that point *D* must be suitably placed by addition of the appropriate amount of pure 3. The required composition, *B*, cannot be obtained directly from the known weights of the materials used in the titrations since, initially, only the composition at *A* is known. In this work a graphical method was used to determine the required compositions, and in this respect our method differs from that of Smith (*6*). He employed a procedure which depended on fitting an equation to the binodal curve.

The graphical procedure is illustrated in Figure 2. The curve YGY' is the locus of points G which satisfy the material balance $FG/G3' = M_3/M_B$ where M_3 is the weight of pure 3 added to the sample of composition B and M_B is the weight of sample B. The curve XDX' is the locus of points H which satisfy the material balance $HJ/J2 = M_2/M_D = M_2/M_3+M_B$. The intersection of YGY' and XDX' gives the composition at D from which the required composition B can readily be obtained by calculation or by extrapolating the line $D3$ back to the binodal curve. A similar experimental and analytical procedure is used for determining the composition of layer C. The success of the method, of course, depends largely on an accurate knowledge of the binodal curve. The results can be checked, however, because the points A, B, and C must lie on a straight line.

In the present experiments, about 50 cm^3 of the ternary heterogeneous mixture was used and about 10 cm^3 each of layers *B* and *C* were taken for analysis. Prior to separation, the mixtures were left in a water thermostat for at least 3 hr with intermittent shaking.

RESULTS

The coordinates of the binodal curves for temperatures in the range 20–60°C are presented in Table I and also in Figure 3

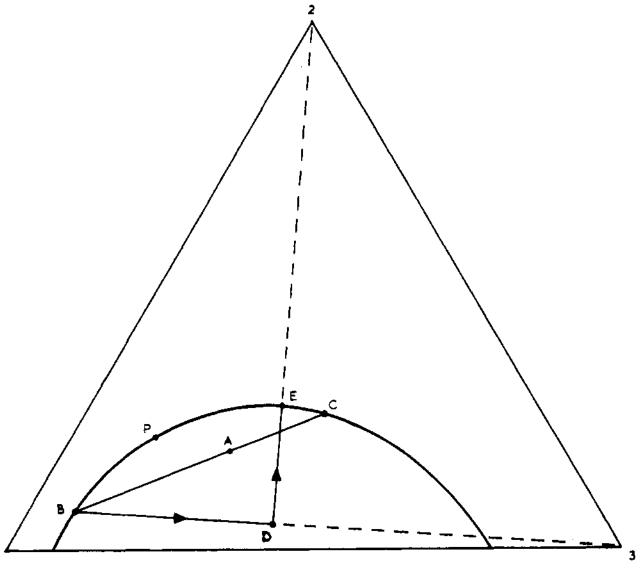

Figure 1. Illustration of experimental procedure for determining composition of liquid layer B

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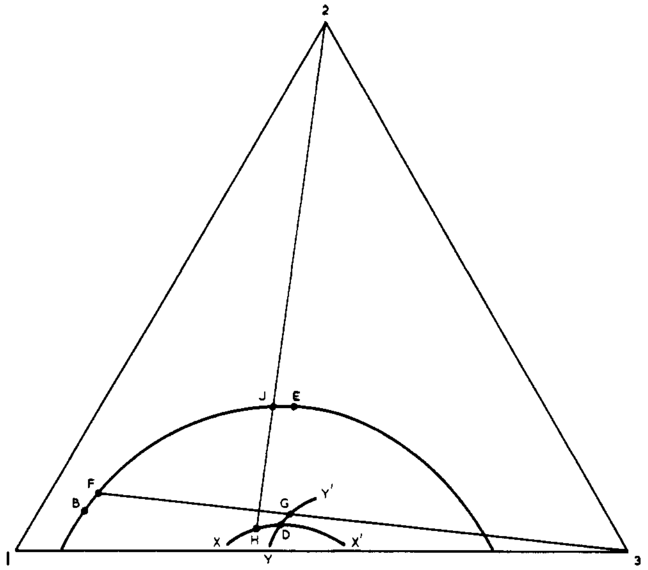

Figure 2. Graphical procedure for estimating composition at point *B*

Table I. Limits of Solubility for System Water + *n*-Propanol + *n*-Butanol

20.1°C		25.9°C		31.2°C		48.5°C		60.0°C	
W_1	W_2	W_1	W_2	W_1	W_2	W_1	W_2	W_1	W_2
39.9	28.1	21.3	3.8	21.7	4.2	22.1	4.9	23.9	1.7
47.3	27.5	21.5	6.6	33.8	24.7	22.8	2.6	27.5	1.6
58.5	24.1	28.0	18.9	40.3	26.7	27.1	16.4	28.1	13.0
68.4	19.2	33.5	25.0	48.3	26.5	34.2	24.4	35.7	21.1
78.4	13.6	40.0	27.4	57.3	23.5	40.9	26.1	43.0	22.6
76.3	14.8	48.0	26.8	68.0	18.3	47.8	25.4	50.6	22.5
33.1	25.9	56.9	24.0	70.8	17.1	59.4	21.8	66.0	17.0
26.2	19.1	67.9	18.8			70.6	16.3	71.0	14.8
21.6	8.0								

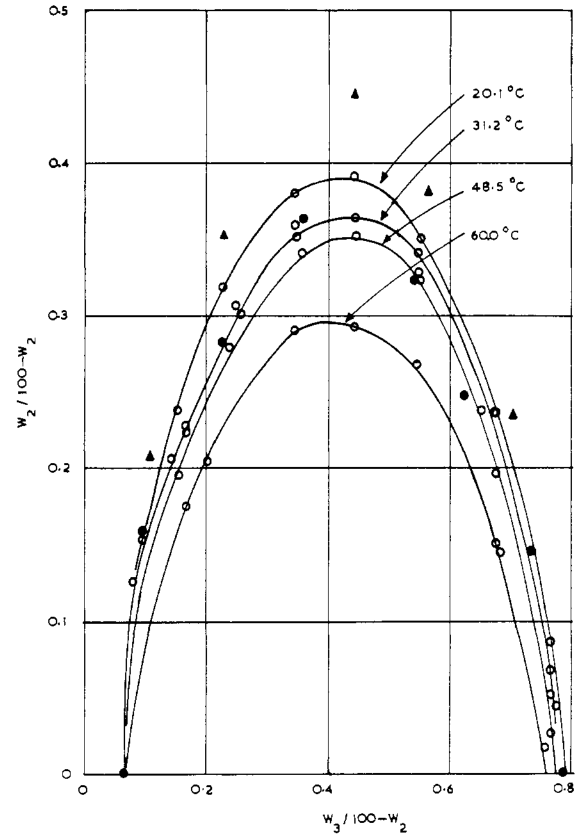

Figure 3. Binodal curves for water + *n*-propanol + *n*-butanol

○, this work; ▲, Bogin, 20°C (2); ●, McCants el al., 37.8°C (5)

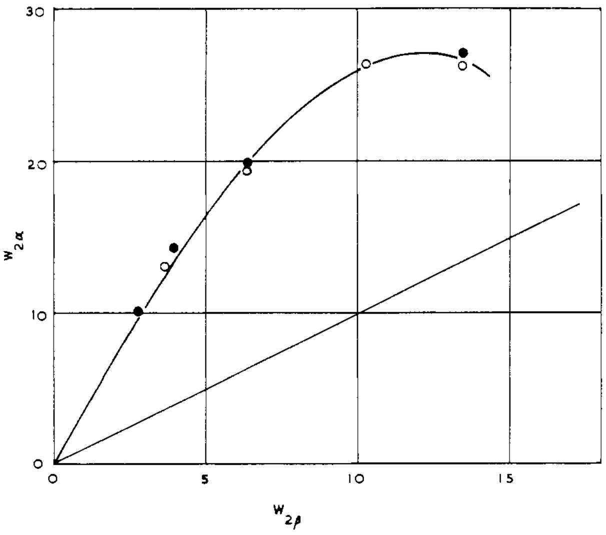

Figure 4. Distribution curve for *n*-propanol between *n*-butanol and water

○, this work, 30°C; ●, McCants et al., 37.8°C (5)

where they are compared with the results of McCants et al. (*5*) and of Bogin (*2*) on a solvent-free composition diagram. The agreement with the data of McCants et al. is satisfactory. The earlier data of Bogin do not agree with either set of results. The estimated error in the compositions quoted in Table I is ±0.2 wt %. The mutual solubilities for *n*-butanol and water were taken from the International Critical Tables. For clarity, the data for 25.9°C have been omitted from Figure 3.

The results of the tie-line determinations are given in Table II and also in Figure 4 where the composition of *n*-propanol in the butanol-rich layer has been plotted against that in the water-rich layer. The agreement with the measurements of McCants et al. (*5*) is good, although our results were obtained at 30°C and the former at 37.8°C. With the enthalpy data of ref. *2*, it can be estimated that over this temperature range the limiting slope of the curve of Figure 4 (the distribution ratio at infinite dilution) should not change by more than 10%.

The precision of the measurements is about 0.5 wt % of *n*-propanol. The overall compositions of the original mixtures

Table II. Compositions of Liquid Phases at Equilibrium for System Water + *n*-Propanol + *n*-Butanol at 30°C

Butanol-rich		Water-rich	
$W_{1\alpha}$	$W_{2\alpha}$	$W_{1\beta}$	$W_{2\beta}$
24.5	13.0	89.5	3.7
38.8	26.4	82.1	10.3
28.1	19.3	86.6	6.5
47.5	26.2	77.5	13.5

and those of the two conjugate layers (points *A*, *B*, and *C* of Figure 1) lay on straight lines to within 0.5 wt % of *n*-propanol, thus confirming the suitability of the analytical procedure, particularly for systems having binodal curves similar to that of Figure 1. Where more substantial immiscibility occurs, then the method of Bancroft and Hubard (*1*) may be used which corresponds to continuing the titration illustrated in Figure 1 along the extension of *BD* to the binodal curve. This method was, in fact, attempted for the present system but the end points of the titrations were not well defined.

By extrapolation of our results, the composition of the Plait point is estimated to be 19 wt % *n*-propanol, 68 wt % water, 13 wt % *n*-butanol.

NOMENCLATURE

W_i = percentage by weight
M_i = mass of liquid i

SUBSCRIPTS

1 = water
2 = *n*-propanol
3 = *n*-butanol
α = butanol-rich
β = water-rich

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Diffusion and Density Data for One Composition of System H_2O–*n*-Pr_4NBr–β-Alanine at 25°C

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The four diffusion coefficients necessary to describe diffusion in ternary systems are reported at 25°C for the composition of the system H_2O–*n*-Pr_4NBr–β-alanine with the concentrations of *n*-Pr_4NBr and β-alanine equal to 0.75 mol dm^{-3} and 0.50 mol dm^{-3}, respectively. Auxiliary data for solution densities, partial molar volumes, and refractive index derivatives are also included.

To conclude a program for studying diffusion in aqueous ternary systems by means of the Gouy diffusiometer, it was decided to obtain some data for the system water–*n*-propyl ammonium bromide–β-alanine. This paper reports values for the four diffusion coefficients of this system for solutions with the concentrations of tetra-*n*-propyl ammonium bromide and β-alanine equal to 0.75 mol dm^{-3} and 0.50 mol dm^{-3}, respectively.

EXPERIMENTAL

We use the numbers 0, 1, and 2 to denote the components water, *n*-Pr_4NBr, and β-alanine, respectively.

The tetra-*n*-propyl ammonium bromide was Eastman Kodak material twice recrystallized from ANALAR acetone (a British Drug House product). The molecular weight of the sample was taken to be 266.28, and its density determined to be 1.17 g cm^{-3}. The salt was dried in a vacuum oven at 105°C for two days and then stored in a desiccator over $CaCl_2$.

β-Alanine was obtained from two sources; one a grade A Calbiochem, and the other a British Drug House product. Both samples were recrystallized from conductance water, dried in an oven at 50°C, and then stored in a desiccator over phosphorus pentoxide. The molecular weight was taken to be 89.09, and the density 1.437 g cm^{-3}.

Procedures for preparing solutions and calculating their concentrations have been described elsewhere (*9*). All solutions were prepared using conductance quality, singly distilled, but previously demineralized rain water with specific conductance less than 10^{-6} ohm^{-1} cm^{-1}. Each solution density, ρ, in g cm^{-3} was obtained by averaging data from triplicate measurements in matched, single-neck, 30-cm^3 pyrex pycnometers; the density of water at 25°C was taken to be 0.997048 g cm^{-3}.

To obtain the desired diffusion data for the composition investigated, four diffusion experiments were performed with a Gouy diffusiometer which has been previously described (*3*). The reader is referred to earlier articles (*3, 9*) for information about the apparatus, for equations defining the various quantities, for a description of the method of performing the experiments, and for calculation procedures for obtaining the final results. The same fused quartz diffusion cell was used for all experiments; its thickness, *a*, along the light path was 2.5053 cm, and the optical lever arm, *b*, of the Gouy diffusiometer

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