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

LITERATURE CITED

(1) Bancroft, W. D., Hubard, S. S., *J. Am. Chem. Soc.*, **64**, 347 (1942).
(2) Bogin, C. D., *Ind. Eng. Chem.*, **16**, 380 (1924).
(3) Goodwin, S. R., Newsham, D. M. T., *J. Chem. Thermodynamics*, **3**, 325 (1971).
(4) Goodwin, S. R., Newsham, D. M. T., *ibid.*, in press, 1971.
(5) McCants, J. F., Jones, J. H., Hopson, W. H., *Ind. Eng. Chem.*, **45**, 454 (1953).
(6) Smith, A. S., *ibid.*, **37**, 185 (1945).

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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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was 304.85 cm. Each experiment was performed within ±0.003° and 25°C, and the Stokes-Einstein relationship was used to convert each reduced height-area ratio to 25.000°C.

Table I. Diffusion Data for Ternary System H_2O–*n*-Pr_4NBr–β-alanine at 25°C[a,b,c]

1	Expt no.	1	2	3	4
2	$(C_1)_A$	0.75104	0.74626	0.73172	0.72706
3	$(C_2)_A$	0.43891	0.45075	0.48768	0.48924
4	ρ_A	1.03436	1.03464	1.03521	1.03541
5	$(C_1)_B$	0.74946	0.75351	0.76809	0.77299
6	$(C_2)_B$	0.56230	0.55067	0.51221	0.49756
7	ρ_B	1.03800	1.03786	1.03722	1.03697
8	$\bar{C}_1$	0.74980	0.74989	0.74991	0.75003
9	$\bar{C}_2$	0.50060	0.50071	0.49995	0.49790
10	J_{exptl}	88.23	86.80	89.09	90.35
11	J_{calcd}	88.02	86.67	89.51	90.17
12	α_1	−0.0152	0.1650	0.8016	1.0055
13	$(\mathfrak{D}_A)_{\text{exptl}} \times 10^5$	0.9362	0.8157	0.5604	0.5031
14	$(\mathfrak{D}_A)_{\text{calcd}} \times 10^5$	0.9297	0.8220	0.5603	0.5026
15	$Q_{\text{exptl}} \times 10^4$	−256.6	−141.4	31.2	48.3
16	$Q_{\text{calcd}} \times 10^4$	−250.3	−148.7	32.4	48.6
17	$R_1 \times 10^3 = 43.004$ $R_2 \times 10^3 = 15.785$				
18	$\bar{V}_0 = 18.097$ $\bar{V}_1 = 232.85$ $\bar{V}_2 = 59.65$				
19	$(D_{11})_V \times 10^5 = 0.4625 \mp 0.0035$				
20	$(D_{12})_V \times 10^5 = 0.092 \mp 0.0014$				
21	$(D_{21})_V \times 10^5 = 0.1862 \pm 0.0160$				
22	$(D_{22})_V \times 10^5 = 0.5197 \pm 0.0060$				

[a] 0 = water, 1 = *n*-Pr_4NBr, 2 = β-alanine. [b] Units: concentrations, C_i, mol dm^{-3}; densities ρ, g cm^{-3}; reduced height-area ratios $\mathfrak{D}_A$, cm^2 sec^{-1}; partial molar volumes $\bar{V}_i$, cm^3 mol^{-1}; refractive index increments R_i, dm^3 mol^{-1}, referred to the velocity of light in air at standard temperature and pressure and for wave length 5460.7 × 10^{-8} cm in air; diffusion coefficients $(D_{ij})_V$, cm^2 sec^{-1}. [c] Quantities which were calculated as intermediate data are $I_A = 329.70$, $S_A = 115.72$, $E_0 = -7.910$, $E_1 = 17.620$, and $E_2 = 7.558$.

RESULTS

Table I summarizes the results from this study. Lines 2–9 give the solute concentrations, C_i, in mol dm^{-3} for the upper (A) and the lower (B) solutions which were prepared for use in each experiment, together with the corresponding measured densities and the mean solute concentrations, $\bar{C}_i = [(C_i)_A + (C_i)_B]/2$. The total number of fringes, J_{exptl}, obtained in each experiment is given in line 10. These values and the corresponding concentration differences, $\Delta C_i = (C_i)_B - (C_i)_A$, were used to compute the values of the refractive index derivatives, R_1 and R_2, listed in line 17 of the table. Then from the R_i and the ΔC_i for each experiment, values of J_{calcd}, line 11, were calculated for comparison with J_{exptl} and, in addition, values were computed for α_1, the fraction of the total refractive increment between solutions B and A contributed by component 1, and are listed in line 12. The reduced height-area ratio, $(\mathfrak{D}_A)_{\text{exptl}}$, and the area, Q_{exptl}, of the fringe deviation graph for each experiment are listed in lines 13 and 15.

The desired volume fixed diffusion coefficients, $(D_{ij})_V$, for this composition of the system were computed (*2*, *9*) from the values of J_{exptl}, ΔC_i, $(\mathfrak{D}_A)_{\text{exptl}}$, and Q_{exptl}, and are reported in lines 19–22. The estimates of accuracy shown were obtained by recalculating the $(D_{ij})_V$ after changing each Q_{exptl} by its estimated error; the upper sign corresponds to an increase of every Q by 0.0004 and the lower sign to a decrease in every Q by the same amount. An increase of each value of $(\mathfrak{D}_A)_{\text{exptl}}$ by 0.3% (without change in any Q) would increase each $(D_{ij})_V$ by less than 0.5% of its value. Values of I_A and S_A (equation 42 of ref. *9*) together with values of E_0, E_1, and E_2 (equation 43 of ref. *9*), which were intermediate quantities obtained in the calculation of the $(D_{ij})_V$ are reported in footnote *c* of Table I. The values of $(\mathfrak{D}_A)_{\text{calcd}}$ and Q_{calcd} in lines 14 and 16 were computed from the values of ΔC_i, R_i, and the $(D_{ij})_V$ for comparison with the $(\mathfrak{D}_A)_{\text{exptl}}$ and Q_{exptl}. These comparisons, and those of the J_{exptl} with the J_{calcd}, indicate somewhat greater deviations from the experimental data than have usually been obtained in this laboratory for other three-component systems. For this reason the diffusion data in this paper and the ternary activity data (*5*) determined in this laboratory were not used to test the Onsager Reciprocal Relation (*4*) for isothermal diffusion.

It is believed that all the concentration differences, ΔC_i, were sufficiently small so that the effects of concentration dependencies of the $(D_{ij})_V$, of the R_i, and of the $\bar{V}_i$ (see below) do not affect the values reported in lines 17–22 by amounts significantly greater than the experimental error of measurement (*6*). When the ΔC_i are sufficiently small, the volume-fixed frame of reference becomes identical with the cell-fixed frame of reference, and the $(D_{ij})_V$ may be identified with flows relative to the diffusion cell (*4*). Application of criteria given elsewhere (*7*, *8*) indicates that in all four experiments reported in Table I, the liquid columns in the diffusion cell were gravitationally stable.

To calculate the partial molar volumes, $\bar{V}_i$, of the components, the constants in the following equation were determined by the method of least squares to fit the density data in Table I:

$$\rho = 1.03624 + 0.03447(C_1 - 0.75) + 0.02971(C_2 - 0.50)$$

These constants, which reproduced the experimental density data with an average error of ±0.001%, were used to calculate the $\bar{V}_i$ in line 18 by using equations derived previously (*1*).

LITERATURE CITED

(1) Dunlop, P. J., Gosting, L. J., *J. Phys. Chem.*, **63**, 86 (1959).
(2) Ellerton, H. D., Dunlop, P. J., *ibid.*, **71**, 1291 (1967).
(3) Ellerton, H. D., Reinfelds, G., Mulcahy, D., Dunlop, P. J., *ibid.*, **68**, 403 (1964).
(4) Kirkwood, J. G., Baldwin, R. L., Dunlop, P. J., Gosting, L. J., Kegeles, G., *J. Chem. Phys.*, **33**, 1505 (1960).
(5) Pepela, C. N., Dunlop, P. J., Chemical Thermodynamics, in press (1972).
(6) Pepela, C. N., Steel, B. J., Dunlop, P. J., *J. Amer. Chem. Soc.*, **92**, 6743 (1970).
(7) Reinfelds, G., Gosting, L. J., *J. Phys. Chem.*, **68**, 2464 (1964).
(8) Wendt, R. P., *J. Phys. Chem.*, **66**, 1740 (1962).
(9) Woolf, L. A., Miller, D. G., Gosting, L. J., *J. Amer. Chem. Soc.*, **84**, 317 (1962).

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