Isopiestic Binary Vapor-Liquid Equilibria

System: Carbon Tetrachloride–*n*-Butanol

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Reliable vapor-liquid equilibrium data are presented on the carbon tetrachloride–*n*-butanol system. These data have been correlated with several estimating equations, and satisfactory agreement was obtained in all cases.

CARBON TETRACHLORIDE forms azeotropes with acetone and methanol. A separation of the azeotropic mixtures of the systems, acetone–carbon tetrachloride and methanol–carbon tetrachloride, might be effected either by azeotropic or by extractive distillation techniques; *n*-butanol might be used as a third component to effect this separation. Prior to the study of the ternary systems, acetone–carbon tetrachloride–*n*-butanol and methanol–carbon tetrachloride–*n*-butanol, a knowledge of the vapor-liquid equilibrium data of the constituent binaries is essential. The vapor-liquid equilibrium data of all the constituent binaries of the above ternary systems were available in literature except the binary system, carbon tetrachloride–*n*-butanol. The present investigation on this system was, therefore, undertaken to study its behavior, to obtain reliable vapor-liquid equilibrium data, and to correlate the data so obtained.

CHEMICALS USED

Carbon tetrachloride from the British Drug Houses, Ltd., London, containing 0.0015% nonvolatile matter, 0.0025% absorbed oxygen 0.0005% carbon disulfide and 0.02% water as impurities, and *n*-butanol from E. Merck Agri. Darmstadt, Germany, were used after further purification in a laboratory fractionating column, collecting the fractions boiled at their respective boiling points. The physical properties of the chemicals were compared with literature values and presented in Table I.

EXPERIMENTAL AND ANALYTICAL DATA

The vapor-liquid equilibrium data were obtained at 760 ± 1 mm. of Hg using a modified Colburn still (*15, 16*), Table II.

Specific gravity was used as a basis for analysis. Specific gravity was a linear function of mole composition, the standard error of estimate of the 11 data points from the equation of regression line (*18*) of specific gravity on mole per cent carbon tetrachloride being 0.0044. The composition of the unknown vapor and liquid samples was determined by reference to the standard plot after specific gravities of the samples were determined. The accuracy of the composition measurement was within 0.5 mole %.

CALCULATIONS

The activity coefficient data of the experimental runs were calculated by the following relation:

$$\rho_i = \frac{Z_1 P y_i}{P_i^\circ X_i}$$

The vapor phase nonideality correction factor was estimated for all the runs by the following relation (*11*).

$$Z_i = \exp^{10} \frac{(P_i^\circ - P)(V_i - \beta_i)}{2.303\, RT}$$

The vapor pressure data of the components were determined using Antoine type of vapor pressure equations taken from literature (*1, 7*). Liquid molal volumes were calculated at the desired temperatures by the method of Lydersen, Greenkorn, and Hongen (*10*), using the values of pure liquid density at 30° C. The second virial coefficients, β, were calculated at the desired temperatures using the relation given by Wohl (*20*). The critical constants required in the estimation of the second virial coefficients were taken from literature (*6*).

Serious error might result in this case, if the nonideality correction factor were omitted as it varied from 1.000 to 1.047 for carbon tetrachloride and from 0.9679 to 0.9910 for *n*-butanol.

DISCUSSION AND CORRELATION OF RESULTS

This system formed a minimum boiling azeotrope at 94.75 mole % carbon tetrachloride and at 76.5° C. This was further confirmed by distilling a liquid mixture of pseudo-azeotropic composition at total reflux in a laboratory distillation column and analyzing the samples after the attainment of equilibrium. This was repeated with a different mixture around that composition until the azeotropic point was located. Lecat (*8*) reported the azeotropic data for this system at 97.5 weight % carbon tetrachloride—i.e., 94.95 mole % carbon tetrachloride—and at 76.55° C.

The experimental data were tested for thermodynamic consistency by applying Herington criteria (*3*). The "*D*"

Table I. Physical Properties of the System Components

	Density at 30° C.		Ref. Index at 30° C.		Boiling point ° C.	
Chemical	Exptl.	Lit. (*17*)	Exptl.	Lit. (*17*)	Exptl.	Lit. (*17*)
Carbon tetrachloride	1.5746	1.5748	1.4547	1.45475	76.7	76.7
n-Butanol	0.8020	0.80206	1.3950	1.39505	117.7	117.7 to 118

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Table II. Experimental and Estimated Vapor-Liquid Equilibrium Data at 760 ± 1 mm. of Hg

System: Carbon Tetrachloride–*n*-Butanol Composition on Mole % Basis

				Experimental		Two-Suffix van Laar Equations	
Run No.	Temp. ° C.	x_1	y	γ_1	γ_2	γ_1	γ_2
1	108.3	4.62	30.60	2.858	1.017	2.509	1.001
2	105.8	6.20	37.50	2.774	1.024	2.469	1.002
3	105.3	6.56	39.60	2.804	1.013	2.460	1.002
4	101.6	9.64	49.00	2.589	1.020	2.383	1.005
5	101.8	10.60	49.50	2.366	1.013	2.359	1.007
6	100.5	11.72	52.90	2.364	1.007	2.331	1.008
7	99.5	12.00	54.00	2.417	1.027	2.325	1.008
8	97.3	14.44	58.90	2.317	1.030	2.266	1.012
9	97.0	16.24	61.20	2.157	1.006	2.222	1.016
10	94.5	19.86	66.00	2.030	1.020	2.136	1.024
11	90.0	27.26	74.00	1.869	1.035	1.970	1.051
12	90.2	27.94	74.20	1.820	1.028	1.954	1.054
13	89.1	29.18	75.50	1.826	1.039	1.912	1.059
14	86.5	35.08	80.00	1.730	1.034	1.804	1.093
15	85.5	39.12	81.60	1.625	1.059	1.723	1.123
16	85.5	39.86	81.60	1.595	1.072	1.708	1.129
17	85.1	40.38	82.00	1.599	1.076	1.698	1.134
18	84.3	42.30	82.40	1.569	1.126	1.662	1.152
19	83.2	47.16	84.00	1.480	1.172	1.571	1.205
20	82.0	52.40	85.50	1.402	1.243	1.480	1.279
21	80.8	57.42	87.00	1.348	1.314	1.397	1.371
22	79.9	64.20	88.00	1.251	1.501	1.296	1.542
23	79.3	66.72	88.50	1.231	1.588	1.262	1.624
24	79.0	70.60	89.00	1.181	1.742	1.212	1.774
25	78.5	75.72	90.00	1.129	1.965	1.152	2.038
26	78.3	79.96	91.00	1.088	2.158	1.109	2.334
27	77.5	86.96	92.80	1.044	2.755	1.050	3.071
28	77.5	90.76	93.96	1.013	3.248	1.026	3.681
29	77.1	93.02	94.70	1.007	3.857	1.016	4.151
30	77.4	93.38	95.20	1.000	3.630	1.014	4.235
31	77.1	96.16	96.00	0.9873	5.287	1.002	4.991

and "J" values of Herington test were 3.1880 and 17.63, respectively. Thus, since the value of D is less than the value of J, the experimental data are thermodynamically consistent.

Figure 2 shows that this system is not ideal and does not show maxima and minima in the log γ *vs.* x curves. The experimental activity coefficient data of this system were, therefore, correlated by Wohl's (*19*) two-suffix van Laar equations. The end values were determined by extrapolation and by trial and error until good agreement with the experimental data was obtained, and the values were A_{12} = 0.42., A_{21} = 0.81. The average error between the estimated and experimental activity coefficient data expressed as

$$\frac{(\gamma \text{ cal.} - \gamma \text{ Expt.})100}{\gamma \text{ cal.}}$$

was +0.86% in "γ_1" and +2.74% in "γ_2," and these are within the limits of experimental accuracy. The recommended forms of Wohl's two-suffix van Laar equations for this system are:

$$\log \gamma_1 = \frac{0.42 x_2^2}{(0.52\, x_1 + x_2)^2}$$

$$\log \gamma_2 = \frac{0.81\, x_1^2}{(x_1 + 1.93)^2}$$

Besides Wohl's equation (*19*), various other correlations such as Li and Coull (*9*),

$$\left(\frac{b_1}{b_2}\right)\left(\frac{b_2}{K_{12}}\right)^{0.5} = 0.045,\ \left(\frac{b_2}{b_1}\right)\left(\frac{b_1}{K_{12}}\right)^{0.5} = 0.11,$$

$$\left(\frac{b_2}{K_{12}}\right)^{0.5} = 0.08,\ \left(\frac{b_1}{k_{12}}\right)^{0.5} = 0.06$$

and Prahl (*14*) correlations (A = 1.0, B = −2.5, C = −21.9), and the stepwise integration method of Othmer (*13*) were applied with a view to test their applicability to this system. The base point used in the stepwise integration method of Othmer (*13*) and in Prahl Correlation (*14*) is: x_1 = 10.6 and y_1 = 49.5 mole percent CCl_4.

Figure 1 shows that for this system, the vapor composition values estimated by the stepwise integration

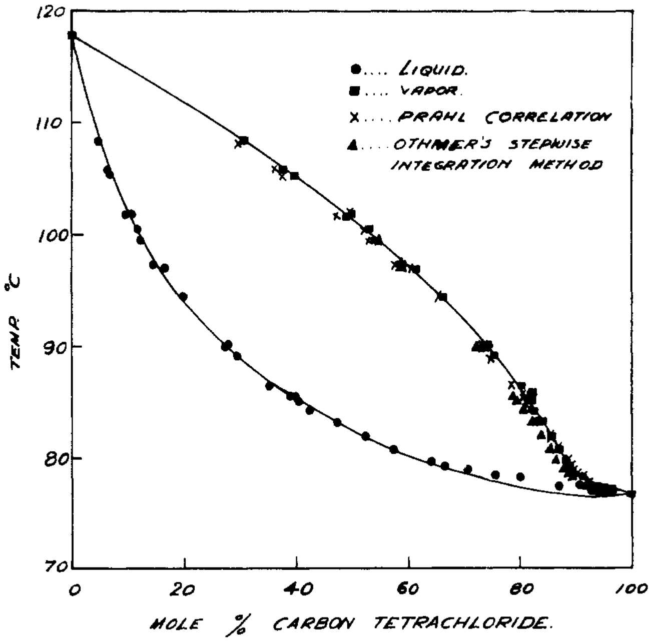

Figure 1. *t* -x- y diagram at 760 mm. of Hg.
System: Carbon tetrachloride–*n*-butanol

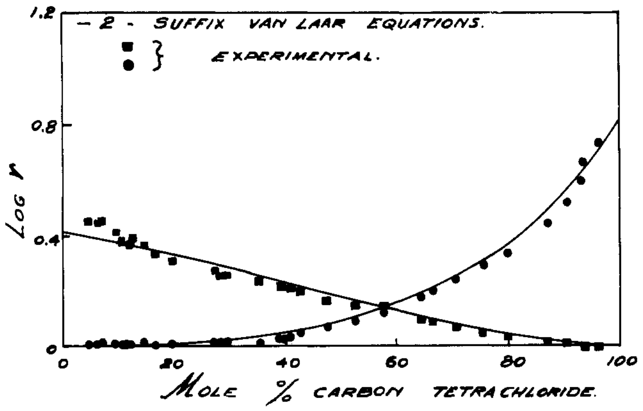

Figure 2. Logarithm of the activity coefficient *vs.* composition
System: Carbon tetrachloride–*n*-butanol

method of Othmer (*13*) are slightly lower than the experimental values. However, the deviations were within the limits of experimental accuracy, and also the accuracy of the correlations used in estimating the heat of vaporization data (*2*, *4*, *5*, *12*). A single set of constants in Prahl correlation (*14*) gave an excellent fit of the experimental data with the estimated values. The recommended form of Prahl correlation for estimating the $x - y$ data of this system is

$$y = \frac{21.9355x(x - 1.0061)}{21.9355x(x - 1.0061) + (1 - x)(x - 2.4945)}$$

CONCLUSION

Of the various correlations tried, Wohl's two-suffix van Laar equations for estimating the activity coefficient data and Prahl correlation for estimating the $x - y$ data are recommended for this system.

NOMENCLATURE

A_{12}, A_{21} = end values of the logarithms of the activity coefficients
$b_1, b_2, K_{12}, A, B, C$ = Constants in equations
D = precentage deviation of areas in Herington test
J = a value of Herington test
P° = pure component vapor pressure
P = total pressure
R = gas constant
t = temperature, ° C.
T = absolute temperature, ° K.
v = liquid molal volume
x = mole fraction of component in liquid
y = mole fraction of component in vapor
Z = correction factor for the nonideality in vapor phase
γ = activity coefficient
δ = density
β = second virial coefficient

Subscripts

$1, 2 \ldots i$ = components $1, 2 \ldots i$
c = critical properties

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