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Vapor–Liquid Equilibria of the System 2-Butanol–Chlorobenzene

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Isobaric vapor–liquid equilibrium data for the system 2-butanol + chlorobenzene are measured at 760 ± 1 mmHg pressure and reported. The system is nonideal and shows positive deviations from Raoult's law. Equilibrium temperature and liquid composition are correlated by the Danciu equation and the vapor and liquid compositions are correlated by the Norrish–Twigg equation.

Some alcohol–chlorobenzene systems exhibit azeotropic behavior (*3*) and form symmetrical solutions. Vapor–liquid equilibrium data of chlorobenzene with methanol (*4*, *7*), 1-propanol, 1-butanol (*10*), 2-propanol, 2-butanol (*5*), 2-methyl-2-propanol (*8*), and 3-methyl-1-butanol (*9*) have been reported. So far vapor–liquid equilibrium data on 2-butanol–chlorobenzene is not studied. Hence vapor–liquid equilibrium data for the system 2-butanol–chlorobenzene are obtained at 760 mmHg pressure with a view to study its behavior in comparison with the aforementioned systems.

Experimental Section

Analytical reagent grade 2-butanol and chlorobenzene are used after double distillation in a laboratory packed distillation column. The physical properties (refractive index and boiling point) of the chemicals are presented in Table I along with the literature values for comparison (*12*).

The equilibrium still used in the present work is of the type designed by Jones, Schoenborn, and Colburn as modified by Ward (*11*). Equilibrium condition is attained in 45 min. However, the vapor and liquid samples are withdrawn for analysis after maintaining the equilibrium condition for 2 h. The equilibrium temperature is measured with a mercury-in-glass thermometer having an accuracy of 0.1 °C.

Vapor and liquid samples are analyzed by refractive index measurements at 30 °C. The composition in mole percent of each component of the binary mixture is determined by a standard calibration chart of refractive index vs. composition prepared earlier. Refractive index measurements are taken for sodium light using Abbe's refractometer having a precision of 0.001 and the last significant digit in the refractive index value is determined through eye approximation.

Results and Discussion

The liquid-phase activity coefficients for the components are determined from the equation

$$\gamma_i = Z_i \pi y_i / P^\circ_i x_i$$

where

$$Z_i = \exp[(\pi - P^\circ_i)(B_i - V_i)/RT]$$

Table I. Physical Properties of Chemicals

	bp, °C		refractive index at 25 °C	
chemical	exptl	lit.[12]	exptl	lit.[12]
2-butanol	99.5	99.53	1.3952	1.3953[a]
chlorobenzene	132.0	131.687	1.4750	1.4750 (24.6 °C)

[a] Calculated using dn/dt.

Table II. Experimental Data of the System 2-Butanol + Chlorobenzene

				exptl	
no.	temp, °C	x_1	y_1	γ_1	γ_2
1	122.7	0.041	0.231	2.56	1.03
2	119.4	0.054	0.280	2.61	1.08
3	117.8	0.112	0.403	1.90	0.99
4	112.8	0.137	0.443	2.02	1.11
5	111.6	0.162	0.466	1.87	1.14
6	102.9	0.501	0.663	1.17	1.59
7	101.7	0.581	0.699	1.11	1.76
8	100.9	0.660	0.748	1.08	1.86
9	100.0	0.766	0.814	1.04	2.06
10	99.7	0.814	0.846	1.03	2.16
11	99.8	0.910	0.920	1.00	2.32

Table III. Correlating Equations

1. Danciu Equation

$$\log X_2 = 0.92 + (1.05 \log \theta_1)$$

where $X_2 = x_2/x_1$ and $\theta_1 = (t - t_1)/(t_2 - t)$, t_1 and t_2 are boiling points of pure components and t is the boiling point of a binary mixture

2. Norrish–Twigg Equation

$$\log \frac{y_1}{x_1}\left[\frac{x_2}{y_2}\right]^K = 2.6875 - 2.5x_1$$

where K, the ratio of molar heats of vaporization of the lower boiling component to that of the higher boiling component, = 3.0652.

The second virial coefficients for both the components are calculated by using Wohl's (*13*) generalized correlation and molar volumes by the expansion factor method of Hala et al. (*2*). The following equations are used to calculate the pure-component vapor pressures: 2-butanol

$$\log P = 46.42483 - 4261.0/T - 12.4877 \log T$$

chlorobenzene

$$\log P = 7.18473 - 1556.6/(230 + t)$$

The experimental vapor–liquid equilibrium data along with activity coefficients are presented in Table II and the t–$(x - y)$

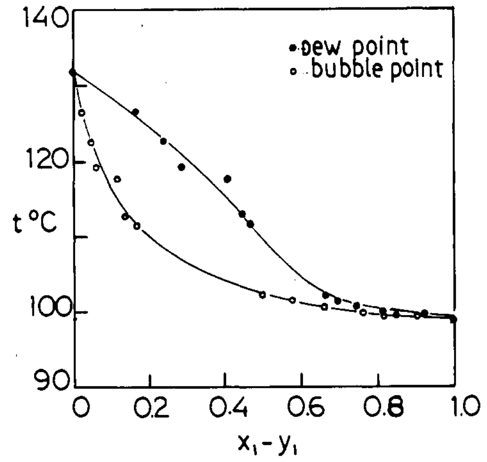

Figure 1. *t–x,y* diagram.

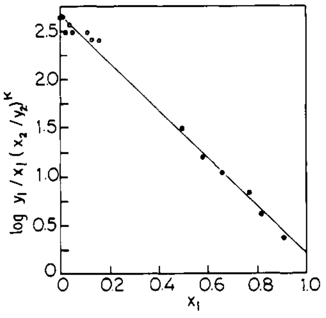

Figure 2. Danciu correlation.

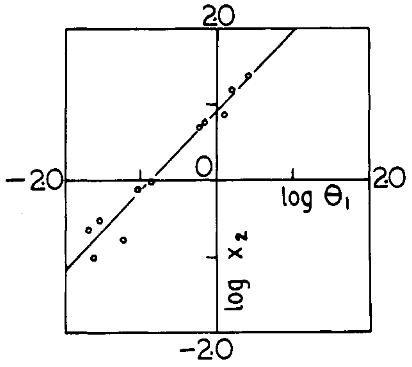

Figure 3. Norrish–Twigg correlation.

diagram is shown in Figure 1. As is observed from the data, the system is nonideal and shows positive deviations from Raoult's law. The activity coefficient data, unlike that of other systems mentioned earlier, could not be correlated satisfactorily with the Margules or the Reddlich–Kister equations. However, the equilibrium temperature and composition are well correlated by the Danciu equation (*1*). The Norrish–Twigg (*6*) equation is used for the correlation of vapor and liquid compositions. The two correlations are given in Table III and shown in Figures 2 and 3.

Since the Norrish–Twigg correlation gives a straight line, the data are thermodynamically consistent.

Glossary

P°_i	vapor pressure of pure component, mmHg
R	gas constant, 82.06 atm cm^3 $g\text{-}mol^{-1}$ K^{-1}
t	equilibrium temperature, °C
T	absolute temperature, K
V	liquid molar volume, cm^3 $g\text{-}mol^{-1}$
x	mole fraction of the component in liquid phase
y	mole fraction of the component in vapor phase
Z	vapor-phase nonideality factor
B	second virial coefficient, cm $g\text{-}mol^{-1}$
γ	activity coefficient
π	total pressure, mmHg

Subscripts

1	more volatile component
i	any component

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