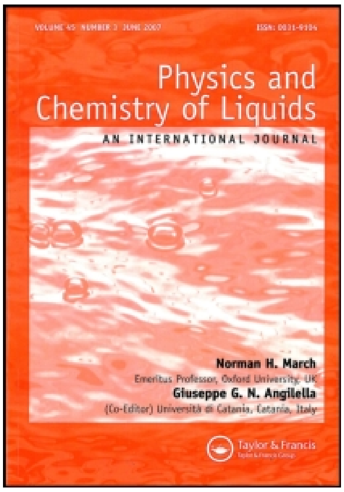

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ISOBARIC VAPOUR—LIQUID EQUILIBRIUM IN THE *n*-BUTANOL (1) + *n*-BUTYLCHLOROACETATE (2) SYSTEM AT 94.83 kPa⁺

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Isobaric Vapour-liquid equilibrium of the *n*-butanol (1) + *n*-butylchloroacetate (2) system has been measured at 94.83 kPa. The activity coefficients are evaluated and correlated by Wilson equation.

Keywords: Vapour–liquid equilibrium; *n*-butanol; *n*-butylchloroacetate; Wilson parameters

INTRODUCTION

Mixtures of *n*-butanol and *n*-butylchloroacetate appear as process streams in the manufacture of butachlor (a well known pesticide). Phase equilibrium (T-x-y) measurements on the binry mixtures of these compounds at the locally prevailing pressure of 94.83 kPa, have been carried out for use in the design of the equipment and process for the separation.

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APPARATUS AND EXPERIMENTAL

A circulation type still, very similar to the one described by Boublik and Benson[1], has been used for these experiments. The still is carefully lagged by insulating materials such as asbestos rope and powder to minimise the loss of heat to the surroundings by conduction. By means of a large buffer vessel, a Cartesian monostat and a vacuum pump, connected in series the pressure is maintained within ± 0.133 kPa. The temperatures are measured by means of a carefully calibrated mercury-in-glass ther mometer to an accuracy of ± 0.1 K.

The attainment of equilibrium conditions is judged by maintenance of the equilibrium temperature constant for at least half an hour. Constancy of the composition of the liquid and vapour phase samples, drawn at three succesive half an hour intervals, is used as an additional check for the attainment of the equilibrium conditions. The observed values of the equilibrium temperature (T), the composition of the liquid phase (x_1) and the vapour phase (y_1) under equilibrium conditions are noted.

The pure substances used in the present experiments are expected to be at least 99.8% pure based on a comparison of the physical properties with the literature data [2] presented in Table I.

The compositions of the liquid and vapour samples are measured by using gas–liquid chromatography. Based on the analysis of the samples prepared from known masses of the components carried out apriori, the compositions of the liquid and vapour samples reported in this paper are expected to be within ± 0.1% of their true values.

TABLE I Comparison of physical properties of pure liquids with literature data[2]

Substance	*Refractive-index at 298.15* K		*Normal Boiling Point* (K)	
	This work	*Literature*	*This work*	*Literature*
n-Butanol	1.3392	1.3391	390.05	391.15
n-Butylchloroacetate	1.4260	1.4259	454.35	454.45

RESULTS

The phase equilibrium data presented in Table II, are the equilibrium temperature (T), the liquid phase mole fraction (x_1) and the vapour phase mole fraction (y_1), resulting from at least three successive measurements on the test samples.

The liquid phase activity coefficients (γ_1 and γ_2) are calculated by using

$$\gamma_1 = z_1 y_1 p / x_1 p_1^\circ \tag{1}$$

$$\gamma_2 = z_2 y_2 p / x_2 p_2^\circ \tag{2}$$

The prue component vapour pressures (p_1° and p_2°) at the required temperatures are calculated from Antoine equation

$$\ln p^\circ = A - B/(T + C) \tag{3}$$

Where p° is the vapour pressure in kPa and T is the absolute temperature in k, using the values of A, B and C given in Table III. The vapour

TABLE II Vapour–liquid equilibrium data of *n*-Butanol (1) + *n*-Butylchloroacetate at 94.83 kpa

Wilson Parameters: $(\lambda_{12} - \lambda_{11})/R = 322.22$ K;

$(\lambda_{12} - \lambda_{22})/R = -365.69$ K

Temperature	x_1	y_1	γ_1	γ_2
448.75	0.0000	0.0000	0.5814	1.0000
444.35	0.0908	0.4202	0.6638	0.9927
441.85	0.1388	0.5830	0.7103	0.9879
416.45	0.2635	0.7304	0.7335	0.9644
412.35	0.3238	0.8272	0.8032	0.9490
408.05	0.4109	0.8400	0.8406	0.9095
405.65	0.4755	0.8743	0.8863	0.9076
402.45	0.5233	0.8813	0.9141	0.8730
401.65	0.5616	0.9086	0.9316	0.8546
398.75	0.6937	0.9365	0.9438	0.8398
395.35	0.8178	0.9598	0.9753	0.7900
390.05	0.9686	0.9910	0.9971	0.7450
389.05	0.9959	0.9950	0.9958	0.6958
389.05	1.0000	0.0000	1.0000	0.6861

TABLE III Antoine constants of the pure liquids used in connection with equation (1)

Substance	*A*	*B*	*C*
n-Butanol	14.9411	3005.87	−99.72
n-Butylchloroacetate	16.2532	4959.74	−24.86

pressure data of the pure substances, including the boiling point observations of this work, recorded as the first and last entries in Table II, are represented by Antoine equation with the constants given in Table III within ± 0.1 kpa.

The vapour phase imperfection coefficients z_1 and z_2 are calculated from

$$z_1 = \exp\left[\{(p - p_1^\circ)(B_{11} - V_1^L) + p y_2^2 \delta_{12}\}/RT\right] \tag{4}$$

$$z_2 = \exp\left[\{(p - p_2^\circ)(B_{22} - V_2^L) + p y_1^2 \delta_{12}\}/RT\right] \tag{5}$$

with

$$\delta_{12} = 2B_{12} - B_{11} - B_{22} \tag{6}$$

The pure component second virial coefficients B_{11} and B_{22} are calculated from the generalized correlation proposed by Tsonopoulos[3]. Cross second virial coefficients are calculated from the Pitzer and Curl type generalization method described by Van Ness and Abbott[4]. Yen and Woods correlation[5] is used to calculate the molar volumes V_1^L and V_2^L. The critical properties and the other data needed in the calculations are collected from Reid *et al.*[6]

THERMODYNAMIC CONSISTENCY

To test the thermodynamic consistency, the practical procedure described by Fredenslund *et al.*[7], based on the ideas originally proposed by Van Ness *et al.*[8] and Abbott and Van Ness[9] is used. The excess Gibbs free energy is related to the liquid phase mole fraction in the form

$$G^E/RT = x_1 \ln \gamma_1 + x_2 \gamma_2 = g = x_1(1 - x_1)\sum^{k} a_k L_k(x_1) \tag{7}$$

where L_k (x_1) represents the Legendre function given by

$$L_k(x_1) = [(2k-1)(2x_1-1)\,L_{k-1}(x) - (k-1)\;L_{k-2}(x)]/k \tag{8}$$

with $k = 1,2,\ldots\ldots n$. The systems studied in the present work could be represented to good accuracy by the first order Legendre polynomial with the coefficients A and B given in Table IV. The coefficients are used to calculate the activity coefficient γ_1 through the equation

$$\ln\gamma_1 = g + (1-x_1)(dg/dx_1) \tag{9}$$

Values of y_1 calculated from equation (1) after substituting the values of the other variables, compared with the measured values of y_1, with an average absolute deviation of less than 0.01 units are shown in Table IV, indicating that the data are thermodynamically consistent.

CORRELATION OF ACTIVITY COEFFICIENTS

The activity coefficient data have been fitted to the Wilson [10] equation

$$g = -x_1\ln(x_1 + \Lambda_{12}x_2) - x_2\ln(x_2 + \Lambda_{21}x_1) \tag{10}$$

where

$$\Lambda_{12} = (V_2^L/V_1^L)\ \exp - [(\lambda_{12} - \lambda_{11})/RT] \tag{11}$$

and

$$\Lambda_{21} = (V_1^L/V_2^L \exp - [(\lambda_{12} - \lambda_{22})/RT] \tag{12}$$

TABLE IV Coefficients of the Legendre polynomial and average absolute departure in the values of y_1 calculated from experimental data

System	*Coefficients of Legendre Polynomial*	*No. of Observations*	*Av. Abs. Deviation in* y_1
n-Butanol (1) + *n*-Butylchloro-acetate (2) at 94.83 kpa	$A_0 = -0.4521$ $A_1 = 0.0638$	15	0.008

V_1^L and V_2^L are the molar volumes of pure liquids and $(\lambda_{12}-\lambda_{11})/R$ and $(\lambda_{12}-\lambda_{22})/R$ are the Wilson parameters. λ'^{s} are the energies of interaction between the molecules denoted by the subscripts. The optimum Wilson parameters are obtained by minimising the objective function ϕ defined as

$$\phi = [(p_{\text{cal}}/P_{\text{expt}}) - 1]^2 \tag{13}$$

Nelder-Mead optimization technique described in detail by kuester and Mize[11] is used. The optimum values of the Wilson parameters are given in Table II along with the percent average absolute deviation in the liquid phase activity coefficient γ_1. The representation of the data by the Wilson model is good.

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