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Vapor–Liquid Equilibrium for the *n*-Pentane–Dichloromethane System at 298.15 K

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Isothermal vapor–liquid equilibrium data were determined by using a modified Boublik–Benson still for the *n*-pentane–dichloromethane system at 298.15 K. This system shows an azeotropic point at $x_1 = 0.55$ and at 82.0 kPa. A test of thermodynamic consistency was applied to the activity coefficients. The results obtained were correlated in terms of the liquid activity coefficients of Margules, van Laar, Wilson, and UNIFAC equations. The best agreement with experimental data was given by Wilson's equations.

Introduction

Vapor–liquid data are necessary for interpretation of distillation processes. This paper reports the results of measurements on vapor–liquid equilibrium for the *n*-pentane–dichloromethane system at 298.15 K. Experimental data for this system have not been reported in the literature, and this system was chosen because *n*-pentane (component 1) is nonpolar and dichloromethane (component 2) is polar. This work is a continuation of our studies on the thermodynamic properties of mixtures (*1*, *2*).

Experimental Section

n-Pentane (Carlo Erba p.a.) was distilled over dried P_2O_5 and only the middle half of each distillation was recovered. Dichloromethane (Merck p.a.) was distilled over calcium chloride and again only the middle half of each distillation was recovered.

Densities were determined with a Robertson specific gravity bottle with an accuracy of ±0.1 kg m^{-3}. The refractive indexes for the sodium D line were measured with a Jena dipping refractometer with an accuracy of ±0.000 02.

Equilibrium data were determined by using a modified version of the equilibrium still described by Boublik and Benson (*3*). The still and a water ebulloscope were attached to a large pressure vessel which could be maintained at any required pressure. The equilibrium value of the pressure was calculated from the boiling point of water in the ebulloscope. The latter could be determined with an accuracy of 0.01 °C with a Digitec digital thermometer. The temperature in the still was also measured at 0.01 °C with a calibrated thermometer.

Barometric pressure and room temperature were recorded for each experimental run, and necessary corrections were made in the observed pressure values. Compositions of the equilibrium liquid and the condensed vapor phases were determined from measurements of their refractive indexes at 298.15 K by using eq 1, where x_1 is the mole fraction *n*-pentane, and n_1 and n_2 are the refractive indexes of the pure components. This equation was determined empirically with coefficients calculated by a computation program and correlates the results of a series of mixtures of the two components of known composition. Table I gives values of densities, refractive indexes and vapor pressures of the pure components and literature values for comparison.

$$n_D(x_1) = n_1x_1 + n_2x_2 + x_1x_2[-0.0484944 + 0.0121661(2x_1 - 1) - 0.0096753(2x_1 - 1)^2 - 0.0142016(2x_1 - 1)^3 - 0.0148441(2x_1 - 1)^4] \quad (1)$$

Table I. Physical Properties of Pure Components at 298.15 K

	ρ, kg m^{-3}		n_D		$P_i°$, kPa	
	expt	lit.	expt	lit.	expt	lit.
n-pentane	621.9	621.39[a]	1.35466	1.35472[a]	68.25	68.37[b]
dichloromethane	1315.2	1316.8[a]	1.42119	1.4211[c]	57.80	57.36[d]

[a] Reference *4*. [b] Reference *5*. [c] Reference *6*. [d] Reference *7*.

Table II. Experimental and Calculated Isothermal Vapor–Liquid Equilibrium Results for *n*-Pentane (1) + Dichloromethane System at 298.15 K

x_1	y_1	P, kPa	γ_1	γ_2
0.0369	0.1023	63.30	2.585	1.016
0.0644	0.1592	67.06	2.436	1.040
0.1090	0.2380	70.73	2.264	1.044
0.1606	0.3163	74.45	2.144	1.047
0.2515	0.3870	77.01	1.729	1.088
0.3226	0.4333	79.01	1.553	1.141
0.4208	0.4898	80.78	1.367	1.220
0.5561	0.5593	81.98	1.180	1.380
0.6364	0.6063	81.31	1.127	1.510
0.6507	0.6169	81.18	1.118	1.532
0.7774	0.7046	78.25	1.033	1.782
0.8448	0.7651	76.11	1.005	1.982

Results

The liquid-phase activity coefficients were estimated from the experimental data, taking into account the nonideality of the vapor phase, by employing the following equation

$$\ln \gamma_i = \ln \frac{y_iP}{x_iP_i^0} + \frac{(B_{ii} - V_i^0)(P - P_i^0)}{RT} + (1 - y_i)^2\frac{P\delta}{RT} \quad (2)$$

where

$$\delta = 2B_{12} - B_{11} - B_{22} \quad (3)$$

For *n*-pentane at 298.15 K, $B_{11} = -1.184 \times 10^{-3}$ m^3 mol^{-1}; for dichloromethane at the same temperature, $B_{22} = -0.862 \times 10^{-3}$ m^3 mol^{-1} and $B_{12} = -0.921 \times 10^{-3}$ m^3 mol^{-1}. These values were estimated from the Hayden and O'Connell method (*8*).

Values of the mole fraction of *n*-pentane in the liquid and vapor phases and values of pressures and activity coefficients of both components are summarized in Table II.

Figure 1 shows the vapor pressure of this system against the mole fraction of *n*-pentane with an azeotrope at $x_1 = 0.55$ and a pressure of 82.0 kPa approximately.

A conventional thermodynamic consistency test was applied to the present system (*9*). Thermodynamically consistent isothermal binary data should satisfy eq 4.

$$\int_0^1 \ln \frac{\gamma_1}{\gamma_2}\, dx_1 = 0 \quad (4)$$

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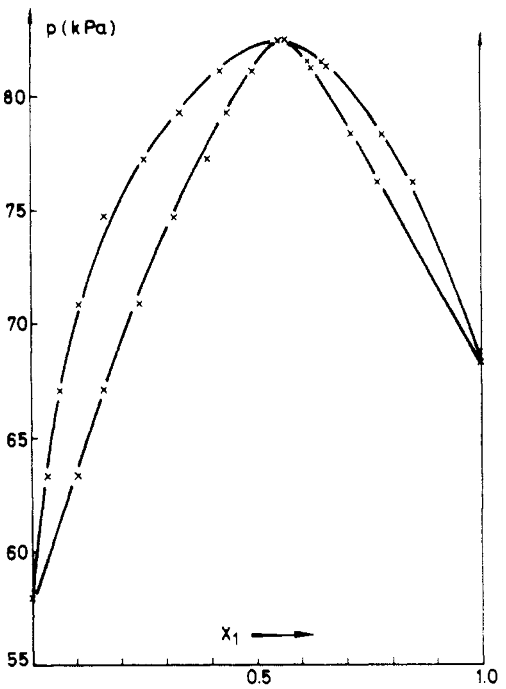

Figure 1. Pressures vs. mole fractions of *n*-pentane for the *n*-pentane (1) + dichloromethane (2) system at 298.15 K.

However, some experimental error is inevitably involved in the observed data. Practically, it may be acceptable to assume that a given set of data is consistent, Herington's test, if

$$0.02 > D = \frac{|\text{area above } x \text{ axis} - \text{area below } x \text{ axis}|}{|\text{area above } x \text{ axis} + \text{area below } x \text{ axis}|} \qquad (5)$$

For the present system $D = 0.01$.

Experimental data were correlated with the following two-suffix Margules equation

$$\log \gamma_1 = x_2^2[A + 2x_1(B - A)]$$
$$\log \gamma_2 = x_1^2[B + 2x_2(A - B)] \qquad (6)$$

With a computation program (using a Radio Shack TRS 80 microcomputer) the following constants were obtained: $A = 0.3596$ and $B = 0.5778$.

In a similar way, the data were compared with the following two-suffix van Laar equation modified by Carlson and Colburn (*10*)

$$\log \gamma_1 = \frac{A}{\left(1 + \frac{x_1 A}{x_2 B}\right)^2}; \quad \log \gamma_2 = \frac{B}{\left(1 + \frac{x_2 B}{x_1 A}\right)^2} \qquad (7)$$

with $A = 0.5562$ and $B = 0.3140$.

The data were also compared with Wilson (*11*) equations

$$\ln \gamma_1 = -\ln (x_1 + Ax_2) + x_2\left[\frac{A}{x_1 + Ax_2} - \frac{B}{x_2 + Bx_1}\right]$$
$$\ln \gamma_2 = -\ln (x_2 + Bx_1) - x_1\left[\frac{A}{x_1 + Ax_2} - \frac{B}{x_2 + Bx_1}\right] \qquad (8)$$

where the constant values obtained were $A = 0.2653$ and $B = 0.8220$.

Finally, UNIFAC (*12*) method was applied. It is known that

$$\ln \gamma_i = \ln \gamma_i^{C} + \ln \gamma_i^{R} \qquad (9)$$

where γ_i^{C} is the combinatorial activity coefficient and γ_i^{R} is the residual activity coefficient. Using the R_k, Q_k, and a_{mn} parameters it was possible to obtain γ_i from eq 9.

The values of P and y_i were computed by the following equations:

$$P_{\text{calcd}} = x_1\gamma_1 P_1^{s} + x_2\gamma_2 P_2^{s} \qquad (10)$$

$$y_{\text{calcd}} = x_1\gamma_1 P_1^{s}/P_{\text{calcd}} \qquad (11)$$

The correct vapor pressures of the components were calculated by the following equation:

$$P_i^{s} = P_i^{0} \exp\left\{\frac{[(V_i^{0} - B_{ii})(P - P_i^{0})] - P\delta(1 - y_i)^2}{RT}\right\} \qquad (12)$$

The calculated results were compared with the experimental values as shown in Table III, with the standard deviations included.

Table III. Standard Deviations in Pressures and in Gas-Phase Mole Fractions

	σ_P	σ_y
eq 6	1.05	0.019
eq 7	0.80	0.017
eq 8	0.51	0.015
eq 9	6.89	0.032

Equation 8 (of Wilson) gives the best agreement with the experimental values for this system.

Glossary

A, B	coefficients of eq 6, 7, and 8, nondimensional
B_{11}, B_{22}	gas-phase second virial coefficients, m^3 mol^{-1}
B_{12}	gas-phase second cross virial coefficient, m^3 mol^{-1}
D	area test constant, nondimensional
n_D	refractive index, nondimensional
P	total pressure, kPa
P_i^0	vapor pressure of component i, kPa
P_i^s	corrected vapor pressure of component i, kPa
R	gas constant, 8.319 J mol^{-1} K^{-1}
T	absolute temperature, K
V_i^0	molar volume of component i, m^3 mol^{-1}
x_i	liquid-phase mole fraction of component 1
y_i	vapor-phase mole fraction of component i

Greek Letters

γ_i	activity coefficient of component i, nondimensional
ρ	liquid density of component i, kg m^{-3}
σ	standard deviation

Registry No. *n*-Pentane, 109-66-0; dichloromethane, 75-09-2.

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