Isobaric Vapor−Liquid Equilibria at 6.67 kPa for 1-Octene + 2-Butyl Propenoate

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Isobaric vapor−liquid equilibria for the 1-octene + 2-butyl propenoate system have been determined at 6.67 kPa in a small-capacity recirculating still. Results were found to be thermodynamically consistent, and they were satisfactorily correlated with the van Laar, Wilson, and UNIQUAC equations.

Introduction

2-Butyl propenoate (2-butyl acrylate) is a compound useful in polymerization processes yielding hard polymers with a high thermal resistance and high resistance to hydrolysis. In many cases this acrylate could be a substitute of butyl acrylate in plastic paints to improve their brightness. This compound can be obtained by a heterogeneous direct esterification reaction between 1-butene and acrylic acid, using ion-exchange resins as catalysts.

The product liquid stream coming from the 2-butyl acrylate process (Pérez and Albertos, 1991) is a mixture of butenes, octenes, acrylic acid, and 2-butyl acrylate. Distillation at a reduced pressure avoids polymerization reactions and hence is a good method to purify 2-butyl acrylate. The design and operation of the distillation columns require vapor−liquid equilibrium data, not available in the literature for mixtures containing 2-butyl acrylate.

In this paper isobaric vapor−liquid equilibrium measurements for 1-octene + 2-butyl acrylate are reported at 6.67 kPa as well as the vapor pressures of pure 2-butyl acrylate.

The experimental results were correlated using the van Laar, Wilson, and UNIQUAC equations.

Experimental Section

Materials. 1-Octene (>98%) from Aldrich was purified by distillation in a column (25 mm i.d. and 500 mm long) packed with 2.5 × 2.5 Dixon rings. Gas chromatography analysis after distillation showed less than 0.5% impurities. The physical properties of this component listed in Table 1 result in good agreement with literature values. 2-Butyl acrylate was synthesized in our laboratory, degassed, washed, dried with a molecular sieve (Union Carbide, type 5A), and purified at reduced pressure in a column (25 mm i.d and 500 mm long) packed with 3 mm Fenske rings. The major impurities were acrylic acid (<0.5%) and water (<0.15%).

Apparatus and Procedure. The experimental apparatus, Figure 1, was made of glass with a charge capacity of about 75 cm^3. Both liquid and vapor phases were continuously recirculated in order to provide a good mixing and to ensure that the equilibrium was reached. The vapor condenser was connected to a vacuum controller (Vacuubrand CVC 24) coupled with a vacuum pump (Vacuubrand RZ-2). The equilibrium temperatures were measured with a PT-100. Pressure and temperature were determined with an accuracy of ±1 mbar and ±0.1 K, respectively.

The compositions of liquid and condensed vapor phases were measured by GC using a Varian 3400 GC with a flame ionization detector. A 50 m long and 0.32 mm i.d. 5% phenylmethylsilicone-fused silica capillary column was used. Chromatographic analyses were carried out at the following conditions: oven temperature, 80 °C; injector temperature, 200 °C; detector temperature, 250 °C; carrier gas, nitrogen (1.8 cm^3/min); split ratio (1:100). At least two analyses were carried out for each vapor -and liquid-phase composition, allowing concentration measurements with an accuracy better than 0.001.

Table 1. Refractive Indexes n_D and Boiling Points T_o of the Pure Components

	n_D(298.15 K)		T_o/K	
component	this work	lit.	this work	lit.
1-octene	1.4085	1.4087[a]	395.05[b]	395.03[a]
2-butyl acrylate	1.4130	na	331.25[c]	na

[a] TRC, 1995. [b] At 101.3 kPa. [c] At 6.6 kPa.

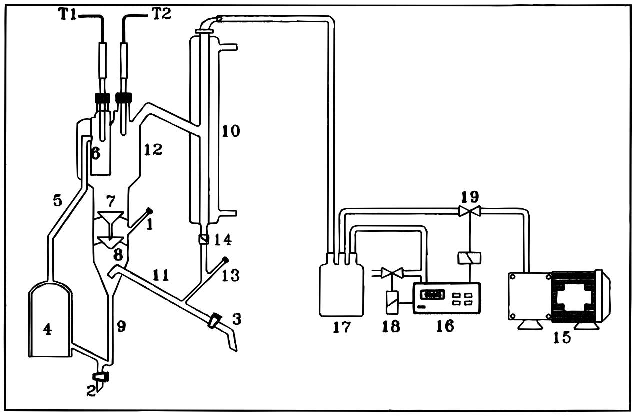

Figure 1. Experimental apparatus: (1) liquid-phase sampling system, (2, 3) cocks, (4) inverted boiling flask, (5) Cottrell pump, (6) vapor tube, (7) liquid-phase receiver, (8) liquid-phase reservoir, (9) recirculating liquid, (10) cooler, (11) vapor-phase condensate recycle, (12) vapor tube, (13) vapor-phase sampling system, (14) drop counter, (15) vacuum pump, (16) vacuum controller, (17) drum, (18, 19) electrically operated valves.

Results and Discussion

Table 2 shows the experimental vapor pressure data obtained in this work for the pure 2-butyl acrylate, as well as the parameters *A*, *B*, and *C* of the Antoine equation.

$$\ln(P_i^o/\text{kPa}) = A - \frac{B}{(T/\text{K}) + C} \qquad (1)$$

The values of these constants for 2-butyl acrylate were

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Table 2. Vapor Pressure for 2-Butyl Acrylate as a Function of Temperature T and Antoine Constants A, B, and C

P/kPa	2.27	2.93	3.73	5.47	6.67	10.93
T/K	308.25	312.20	318.75	326.75	331.25	342.35

	A	B	C
1-octene[a]	13.9480	3116.52	−60.39
2-butyl acrylate[b]	12.7448	2721.03	−80.05

$$\ln (P/\text{kPa}) = A - B/(C + T/\text{K})$$

[a] Data from Reid et al., 1987. [b] Data from this work.

Table 3. Experimental Vapor−Liquid Equilibrium Data for 1-Octene (1) + 2-Butyl Acrylate (2) at 6.67 kPa: Liquid-Phase Mole Fraction x_i and Vapor-Phase Mole Fraction y_i

T/K	x_1	y_1	γ_1	γ_2	T/K	x_1	y_1	γ_1	γ_2
331.3	0.000	0.000			323.6	0.362	0.511	1.123	1.041
330.8	0.010	0.021	0.991	1.483	322.9	0.407	0.582	1.177	1.026
328.7	0.071	0.166	1.012	1.417	322.9	0.408	0.564	1.240	0.989
328.1	0.099	0.214	1.004	1.436	321.7	0.504	0.639	1.218	1.001
327.4	0.127	0.266	1.022	1.344	321.2	0.554	0.671	1.319	0.985
327.0	0.164	0.301	1.040	1.237	321.0	0.601	0.699	1.270	0.996
326.8	0.169	0.307	1.058	1.175	320.5	0.656	0.733	1.279	0.989
325.8	0.209	0.377	1.092	1.138	319.8	0.745	0.792	1.431	0.976
324.4	0.306	0.478	1.117	1.097	319.5	0.822	0.847	1.429	0.986
324.1	0.322	0.505	1.153	1.050	319.3	0.850	0.874	1.500	0.985
323.8	0.347	0.510	1.193	1.002	319.2	0.984	0.987	1.244	0.995
					319.0	1.000	1.000		

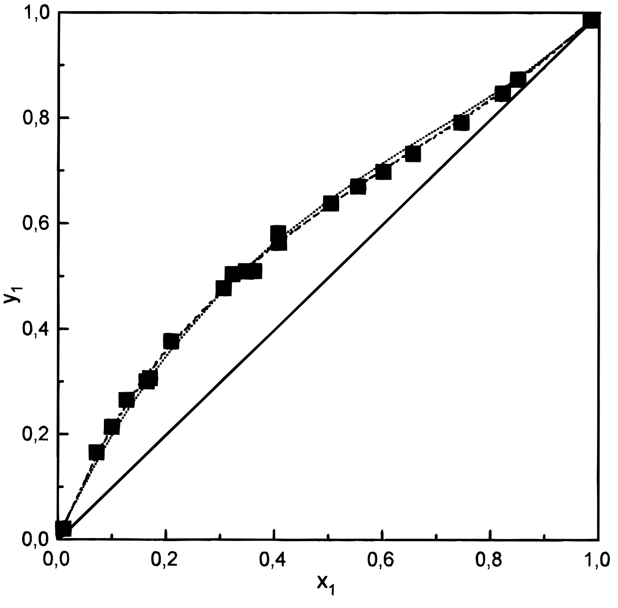

Figure 2. y−x equilibrium diagram for 1-octene (1) + 2-butyl acrylate (2) at 6.67 kPa: (■) experimental; (−··−) Van Laar; (- - -) Wilson; (···) UNIQUAC.

obtained by fitting our experimental data to eq 1 using a nonlinear regression method based on Marquardt's algorithm, in order to minimize the following objective function F:

$$F = \sum (P_{\text{exptl}} - P_{\text{calc}})^2 \tag{2}$$

The Antoine equation constants for 1-octene were obtained from the literature (Reid et al., 1987).

The experimental VLE data at 6.67 kPa for the binary system are shown in Table 3 and Figures 2 and 3. Results were checked for thermodynamic consistency by applying three different tests. When the area test (Redlich and Kister, 1948; Herington, 1951) was used, a difference of 0.17% was obtained. The point-to-point test (Van Ness et al., 1973; Fredenslund et al., 1977) gave deviations less than 0.02 in mole fraction. Finally, the L-W method of Wisniak (1993) gave a total deviation of about 1.02%.

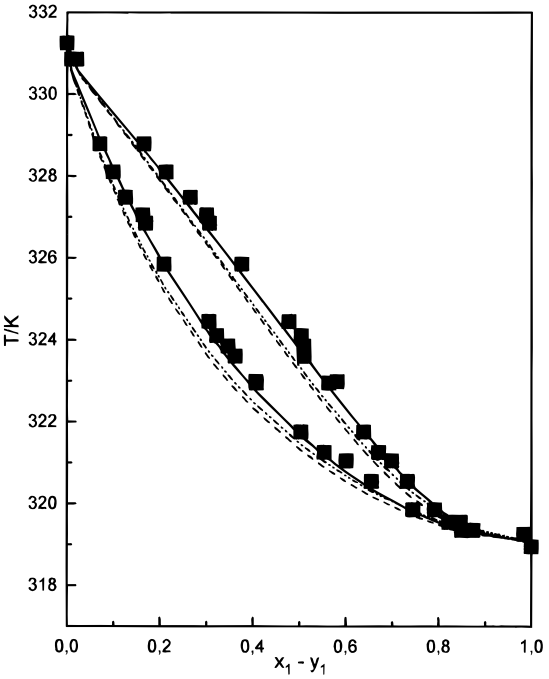

Figure 3. T−y−x diagram for 1-octene (1) + 2-butyl acrylate (2) at 6.67 kPa: (■) experimental; (−··−) Van Laar; (- - -) Wilson; (—) UNIQUAC.

Table 4. Fitting Parameters and Absolute Deviations $|\Delta T|$ and $|\Delta y|$

model	parameters	$\lvert\Delta y\rvert$	$\lvert\Delta T\rvert$/K
Van Laar[a]	$A_{12} = 0.4295$, $A_{21} = 0.4787$	0.008	0.43
Wilson[b]	$A_{12} = 4.1671$, $A_{21} = 1369.30$	0.009	0.46
UNIQUAC[b]	$A_{12} = 1290.67$, $A_{21} = -837.06$	0.011	0.14

[a] Dimensionless. [b] Wilson: A_{12} (J mol^{-1}) = $\lambda_{12} - \lambda_{11}$; A_{21} (J mol^{-1}) = $\lambda_{21} - \lambda_{22}$. UNIQUAC: A_{12} (J mol^{-1}) = $u_{12} - u_{11}$; A_{21} (J mol^{-1}) = $u_{21} - u_{22}$.

The data were correlated using the Van Laar (1910), Wilson (1964), and UNIQUAC (Abrams and Prausnitz, 1975) equations for the liquid phase activity coefficients. The virial equation of state was used to describe the vapor phase by estimating the second virial coefficients by the Hayden−O'Connell method (Prausnitz et al., 1980).

The binary parameters of each model were obtained by using the above mentioned nonlinear regression analysis in order to minimize the objective function F':

$$F' = \left[\left(\frac{T_{\text{expt}} - T_{\text{calc}}}{\sigma_T}\right)^2 + \left(\frac{y_{\text{expt}} - y_{\text{calc}}}{\sigma_y}\right)^2\right] \tag{3}$$

where σ_y and σ_T are the uncertainties for vapor-phase composition and boiling point, respectively. In this work, we have used $\sigma_y = 0.01$ and $\sigma_T = 0.1$ K.

Table 4 summarizes these parameters as well as the average absolute deviations between experimental and calculated temperatures ($|\Delta T|$) and vapor compositions ($|\Delta y|$).

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