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

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Isobaric vapor−liquid equilibria for both 1-octene + propenoic acid and 2-butyl propenoate + propenoic acid systems have been determined at 6.67 kPa in a small-capacity recirculating still. Results were found to be thermodynamically consistent by using the *L*−*W* method of Wisniak and they were satisfactorily correlated with the van Laar, Wilson, and UNIQUAC equations, considering propenoic acid as an associating compound in both liquid and vapor phases.

Introduction

2-Butyl propenoate (2-butyl acrylate) is a monomer that has received recent industrial interest in polymerization processes and it is considered a possible substitute of butyl acrylate.

This compound can be obtained by a direct esterification reaction between propenoic acid (acrylic acid) and 1-butene (Pérez and Albertos, 1991). The reaction product is a mixture containing butenes, different branched chain octenes, acrylic acid, and 2-butyl acrylate. Distillation at a reduced pressure avoids polymerization reactions, and therefore is a good method to purify 2-butyl acrylate. The design of distillation separation processes requires vapor−liquid equilibrium data, not available in the literature.

In a previous paper (Aguado et al., 1996) we have reported the vapor−liquid equilibrium data for the 1-octene + 2-butyl acrylate system at 6.67 kPa as well as the vapor pressures of pure 2-butyl acrylate. In this paper vapor−liquid equilibria for 1-octene + acrylic acid and 2-butyl acrylate + acrylic acid are reported at 6.67 kPa.

The experimental results were correlated using van Laar, Wilson, and UNIQUAC equations for activity coefficients, considering acrylic acid association in both liquid and vapor phases.

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. Acrylic acid (>99%) from Aldrich was used with 0.02% hidroquinone monomethyl ether as the polymerization inhibitor. 2-Butyl acrylate was synthesized in our laboratory, degassed, washed, dried with a 5A molecular sieve (Union Carbide), 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%). The physical properties of these compounds listed in Table 1 are in agreement with literature values.

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

component	n_D (298.15 K) this work	n_D (298.15 K) lit.	T_o/K this work	T_o/K lit.
1-octene	1.4085	1.4087[a]	395.05[d]	395.03[a]
acrylic acid	1.4215	1.4185[a]	342.95[c]	343.15[b]
2-butyl acrylate	1.4130	n.a.	331.25[c]	n.a.

[a] TRC, 1991−6. [b] Nemec and William, 1984. [c] At 6.67 kPa. [d] At 101.33 kPa.

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

T/K	x_1	y_1	T/K	x_1	y_1
342.9	0.000	0.000	320.9	0.611	0.758
332.3	0.099	0.397	319.4	0.791	0.831
332.2	0.103	0.423	319.3	0.865	0.870
327.3	0.160	0.511	319.1	0.886	0.889
326.3	0.175	0.532	319.0	0.922	0.937
326.3	0.182	0.525	318.9	0.935	0.944
324.0	0.305	0.557	318.9	0.948	0.954
323.0	0.348	0.608	318.8	1.000	1.000
322.1	0.443	0.661			

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

T/K	x_1	y_1	T/K	x_1	y_1
342.9	0.000	0.000	333.5	0.762	0.820
337.9	0.241	0.308	333.4	0.789	0.852
337.6	0.282	0.367	332.7	0.831	0.876
337.4	0.330	0.401	332.3	0.904	0.946
336.3	0.489	0.571	331.8	0.963	0.986
334.5	0.658	0.739	331.3	1.000	1.000
334.3	0.719	0.779			

Apparatus and Procedure. The experimental apparatus used in this work was a glass recirculating still with a vacuum controller (Vacuubrand CVC24) connected to a vacuum pump (Vacuubrand RZ-2). It has been described in a previous work (Aguado et al., 1996). 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

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Table 4. Deviations in Tests of Thermodynamic Consistency

	area test		point-to-point test		*L*−*W* test	
system	experimental deviation	consistency requirements	experimental deviation	consistency requirements	experimental deviation	consistency requirements
1-octene + acrylic acid	42.8%	<10%	0.01-0.25	<0.01	0.42%	<5%
2-butyl acrylate + acrylic acid	78.3%	<10%	0.001-0.05	<0.01	0.85%	<5%

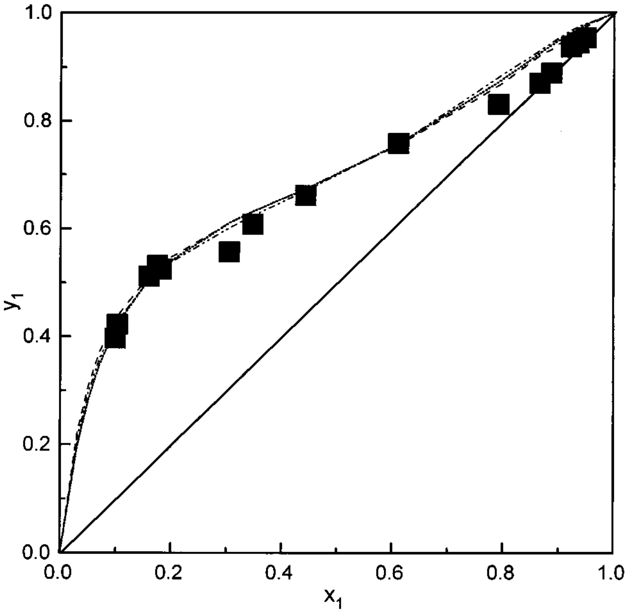

Figure 1. *y*−*x* equilibrium diagram for 1-octene (1) + acrylic acid (2) at 6.67 kPa: (■) experimental; (— · · —) Van Laar; (- - -) Wilson; (···) UNIQUAC.

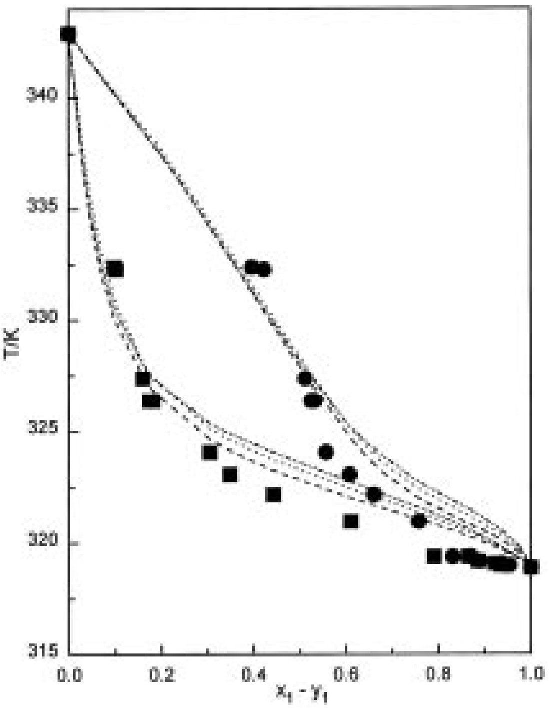

Figure 2. *T*−*y*−*x* equilibrium diagram for 1-octene (1) + acrylic acid (2) at 6.67 kPa: (■) experimental liquid phase; (●) experimental vapor phase; (— · · —) Van Laar; (- - -) Wilson; (···) UNIQUAC.

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 0.002.

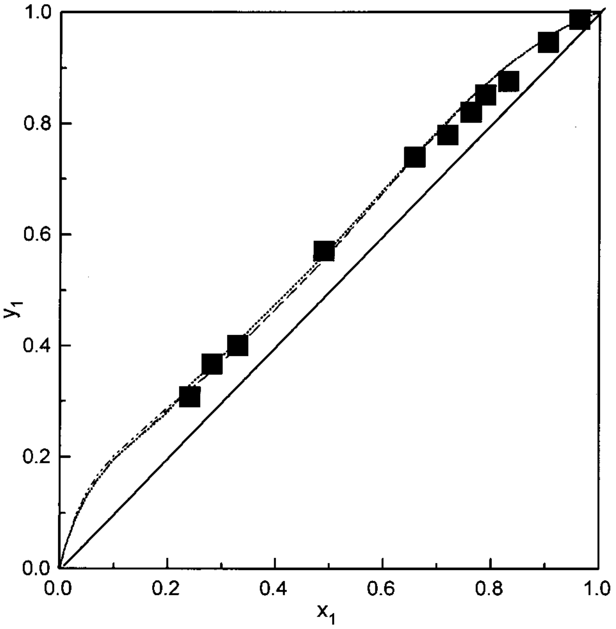

Figure 3. *y*−*x* equilibrium diagram for 2-butyl acrylate (1) + acrylic acid (2) at 6.67 kPa: (■) experimental liquid phase; (●) experimental vapor phase; (— · · —) Van Laar; (- - -) Wilson; (···) UNIQUAC.

Table 5. Antoine Constants A, B, and C

	A	*B*	*C*
1-octene[a]	13.9533	3121.06	−60.10
acrylic acid[a]	16.4649	4485.21	−35.75
2-butyl acrylate[b]	12.7448	2721.03	−80.05

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

[a] Data from TRC, 1991−6. [b] Data from a previous work (Aguado, 1996).

A qualitative test (Rohm & Haas Co., 1961) was used in order to ensure that the components do not polymerize before the equilibrium is reached. This test was carried out by dilution of the mixture in methanol, the formation of a white−yellow turbidity indicates the presence of polymer.

Results and Discussion

The experimental VLE data at 6.67 kPa are shown in Table 2 and Figures 1 and 2 for the 1-octene + acrylic acid system and in Table 3 and Figures 3 and 4 for 2-butyl acrylate + acrylic acid mixtures.

Results were checked for thermodynamical consistency by applying three different tests: the area test (Redlich and Kister, 1948; Herington, 1951), the point-to-point test (Van Ness et al., 1973; Fredenslund et al., 1977), and the *L*−*W* method of Wisniak (Wisniak and Tamir, 1975; Wisniak, 1993). Table 4 shows the deviation of our experimental data for each test as well as the maximum deviation values for thermodynamical consistency. The experimental results are only in agreement with the consistency requirements of the *L*−*W* method. This fact can be explained by taking into account that the *L*−*W*

Table 6. Fitting Parameters and Absolute Deviations $|\Delta T|$ and $|\Delta y|$

system	model	A_{12}	A_{21}	$\|\Delta y\|$	$\|\Delta T\|$/K
1-octene (1) + acrylic acid (2)	Van Laar[a]	1.6575	0.9722	0.026	2.73
	Wilson[b]	1750.5	3262.0	0.025	0.96
	UNIQUAC[b]	1296.1	47.18	0.025	1.18
2-butyl acrylate (1) + acrylic acid (2)	Van Laar[a]	1.4643	0.3765	0.015	0.38
	Wilson[b]	4040.6	592.2	0.016	0.31
	UNIQUAC[b]	−335.2	1207.9	0.013	0.25

[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} = $u_{21} - u_{22}$.

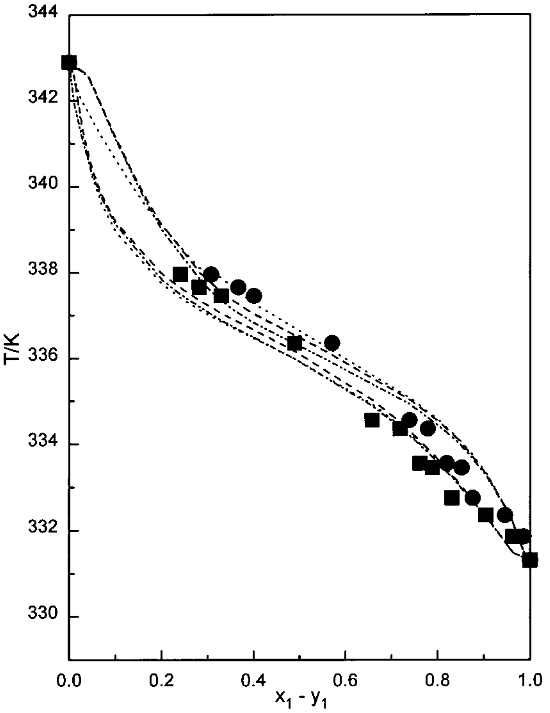

Figure 4. $T-y-x$ equilibrium diagram for 2-butyl acrylate (1) + acrylic acid (2) at 6.67 kPa: (■) experimental; (— • • —) Van Laar; (- - -) Wilson; (•••) UNIQUAC.

method of Wisniak is the unique consistency test that considers the effect of the heat of mixing. However, it does not require direct information on heats of mixing as a function of temperature and composition. Instead, it requires the knowledge of heats of vaporization of pure components, they can be obtained from the literature or estimated using the Pitzer correlation (Reid et al., 1987).

Our results were correlated using the Van Laar, Wilson, and UNIQUAC equations for the liquid phase activity coefficients. The vapor pressures of the pure components have been calculated with the Antoine equation using the coefficients reported in Table 5. The effect of the acrylic acid association in both phases (Marek and Standard, 1954, 1955; Prausnitz et al., 1980) has been included in the analysis.

The binary parameters of each model were obtained by using a nonlinear regression method based on Marquardt's algorithm (Marquardt, 1963) in order to minimize the objective function F:

$$F = \left[\left(\frac{T_{\mathrm{expt}} - T_{\mathrm{calc}}}{\sigma_T}\right)^2 + \left(\frac{y_{\mathrm{expt}} - y_{\mathrm{calc}}}{\sigma_y}\right)^2\right] \tag{1}$$

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 6 includes these parameters as well as the average absolute deviations between experimental and calculated temperatures $|\Delta T|$ and composition $|\Delta y|$.

Appendix

The basic equilibrium relations for systems having a component associating to dimers can be written as follows:

For the associating compound (A)

$$Py_{\mathrm{A}}Z_{\mathrm{As}} = P^{\circ}_{\mathrm{Ac}}x_{\mathrm{A}}\gamma_{\mathrm{As}} \tag{2}$$

where Z_{As} is the vapor phase association factor, P°_{Ac} is the corrected vapor pressure, and γ_{As} is the corrected activity coefficient including the liquid phase dimerization.

$$Z_{\mathrm{As}} = \frac{\sqrt{1 + 4KPy_{\mathrm{A}}(2 - y_{\mathrm{A}})} - 1}{2KPy_{\mathrm{A}}(2 - y_{\mathrm{A}})} \tag{3}$$

$$P_{\mathrm{Ac}} = \frac{\sqrt{1 + 4KP^{\circ}_{\mathrm{A}}} - 1}{2K} \tag{4}$$

K being the vapor phase association constant. For acrylic acid K can be expressed by the following equation (Gmehling and Onken, 1977; Fu et al., 1995)

$$\ln K/\mathrm{kPa}^{-1} = -22.952 + \frac{7635}{T/\mathrm{K}} \tag{5}$$

For the nonassociating component (B)

$$Py_{\mathrm{B}}Z_{\mathrm{B}} = P^{\circ}_{\mathrm{B}}x_{\mathrm{B}}\gamma_{\mathrm{Bs}} \tag{6}$$

$$Z_{\mathrm{B}} = \frac{2[1 - y_{\mathrm{A}} + \sqrt{1 + 4KPy_{\mathrm{A}}(2 - y_{\mathrm{A}})}]}{(2 - y_{\mathrm{A}})(1 + \sqrt{1 + 4KPy_{\mathrm{A}}(2 - y_{\mathrm{A}})})} \tag{7}$$

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