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Vapor-Liquid Equilibria for Propane-Propylene

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Several authors have reported vapor-liquid equilibrium data for the propane-propylene system (*1* to *5*). We present here the results of data reduction as needed for computer calculations of vapor-liquid equilibria for wide ranges of temperature, pressure, and composition. Our results suggest that the relative volatility of propylene to propane at the propylene-rich end is appreciably lower than that estimated by Zdonik in 1958 (*7*). In view of the large commercial importance of propylene, our results may be of interest for optimum design of propylene plants.

Following the thermodynamic treatment of Prausnitz and Chueh (*6*), the equation of equilibrium is

$$\phi_i\, y_i\, P = \gamma_i^{(P0)}\, x_i\, f_i^{o(P0)} \exp \frac{\bar{v}_i P}{RT} \tag{1}$$

In reducing the experimental data, the standard state fugacity for each component is the fugacity of the pure liquid at system temperature corrected to zero pressure. Equations for standard state fugacities for propane and for propylene are given in reference *6* (Appendix A).

Vapor-phase fugacity coefficients were calculated using a computer program (PHIMIX), and partial molar liquid volumes using a computer program (VOLPAR), as described in reference *6*.

The effect of liquid composition on activity coefficients is given by

$$\ln \gamma_1^{(P0)} = \alpha\, v_{c_1}\, \Phi_2^2 \tag{2}$$

and

$$\ln \gamma_2^{(P0)} = \alpha\, v_{c_2}\, \Phi_1^2 \tag{3}$$

where the volume fractions are defined by

$$\Phi_1 = \frac{x_1\, v_{c_1}}{x_1 v_{c_1} + x_2 v_{c_2}}; \quad \Phi_2 = \frac{x_2\, v_{c_2}}{x_1 v_{c_1} + x_2 v_{c_2}} \tag{4}$$

Using the available experimental data together with a suitable computer program (SYMFIT) from reference *6*, we find that

$$\alpha^{1/2} = 0.305924 - 1.3273 \times 10^{-2} \left[\frac{T}{100}\right] - 1.7922 \times 10^{-3} \left[\frac{T}{100}\right]^2 - 1.431 \times 10^{-4} \left[\frac{T}{100}\right]^3 - 1.71 \times 10^{-5} \left[\frac{T}{100}\right]^4 \tag{5}$$

Equation (5) represents the data over the temperature range 400 to 660°R. The maximum deviation between calculated and observed vapor-phase mole fractions is 0.005.

Figure 1 shows the relative volatility of propylene to propane as a function of pressure for several liquid-phase mole fractions. The relative volatility increases with decreasing pressure; however, this effect becomes very small at high concentrations of propylene. Therefore, in designing separation equipment for very pure propylene, little advantage is gained in operating at low pressures. This conclusion is different from that of Zdonik (*7*) who predicted a significant increase in relative volatility with a

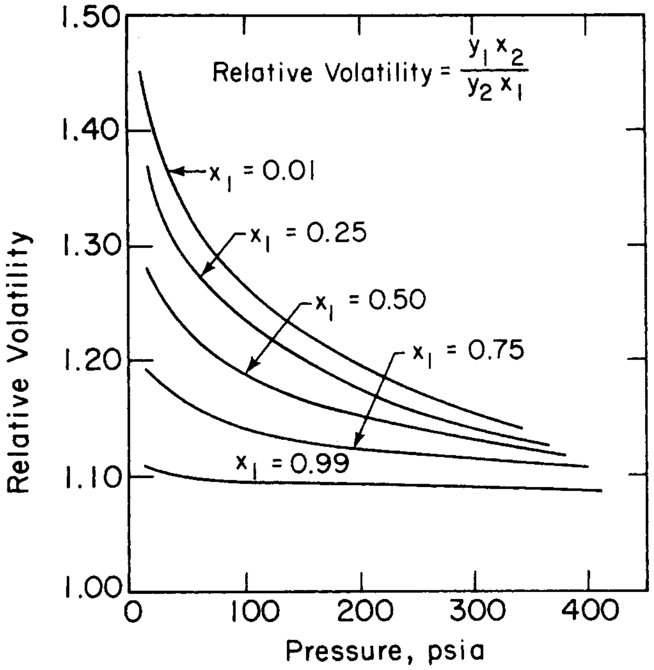

Fig. 1. Relative volatility of propylene (1) to propane (2) as a function of pressure at five liquid-phase mole fractions.

decrease in pressure for high liquid-phase concentrations of propylene. The predictions of Zdonik (7) appear to be based upon an arbitrary extrapolation of the data of Reamer and Sage (4) rather than upon a thermodynamic analysis as used to establish Figure 1.

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NOTATION

f = fugacity, psia.
P = total pressure, psia.
R = gas constant
T = absolute temperature, °R.
$\bar{v}$ = liquid-phase partial molar volume, cu.ft./lb.-mole
v = molar liquid volume, cu.ft./lb.-mole
x = liquid-phase mole fraction
y = vapor-phase mole fraction
α = binary interaction constant (a function of temperature), lb.-mole/cu.ft.
Φ = volume fraction
ϕ = vapor-phase fugacity coefficient
γ = liquid-phase activity coefficient

Subscripts

i = component
c = critical

Superscripts

o = standard state
P0 = corrected to zero pressure

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Comments on Diffusion in Membrane-Limited Blood Oxygenators

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Weissman (*1*) has recently considered oxygen transport to blood through a membrane in the limiting case of no hemodynamic boundary layer. As indicated there, this problem may be solved by use of a linear diffusion equation for the membrane plus a nonlinear diffusion equation for the blood caused by the oxygen capacity of the hemoglobin in the red blood cells. The purpose of this note is to show that the numerical solution by Weissman was unnecessarily complicated and that his results and conclusions may be obtained much more clearly and simply by proper writing of the describing equations and boundary conditions, which lead to an analytical solution.

The usual scheme of making separate balances on the membrane and on the blood with a matching condition at the blood-membrane interface will be followed. Thus, the mathematical problem consists of the steady state diffusion equation for the membrane in the transverse direction with a plug flow (no transverse gradients because no hemodynamic boundary layer resistance) balance for the blood. Such an approach will be followed here.

As much as possible, the original nomenclature of Weissman has been preserved. In addition, the relations between oxygen partial pressure and concentration in the membrane and in the plasma, as defined by Reneau et al. (2), will be used: $C^m{}_{O_2} = c_m\, P_{O_2}$, $C^p{}_{O_2} = c_1\, P^p{}_{O_2}$.

The diffusion of oxygen through the membrane is described by

$$c_m\, D_{O_2,m} \frac{\partial^2 P_{O_2}}{\partial y^{*2}} = 0 \tag{1}$$

where c_m is the oxygen solubility in the membrane, P_{O_2} is the partial pressure in the membrane, and $y^* = y/t$ is the dimensionless distance measured from the membrane-blood interface to the membrane gas interface, $y = t$. The proper boundary conditions on this equation are

$$c_m\, P_{O_2}\big|_{y^*=1} = c_m\, P^\infty{}_{O_2} \tag{2}$$

and

$$c_m\, P_{O_2}\big|_{y^*=0} = \left[\frac{c_m}{c_1}\right] c_1\, P^p{}_{O_2} \tag{3}$$

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