parameters and obtain

Example 12.7: Fitting Experimental Activity Coefficients

Use the data in Example 12.6 to fit the excess Gibbs free energy of the system ethanol/acetonitrile to a Redlich-Kister polynomial with two parameters, obtain equations for the activity coefficients. Use these equations to obtain the activity coefficients at infinite dilution and to construct the *Pxy* graph of this system at 40 °C.

Solution We fit the ratio G^{E}/RT to a two-parameter Redlich-Kister polynomial

$$\frac{G^{\mathrm{E}}}{RT} = x_1 x_2 (a_0 + a_1(x_1 - x_2)).$$

By least-squares fitting we find

$$a_0 = 1.27729, \quad a_1 = 0.06540.$$

The activity coefficients are obtained by applying eqs. (12.25) and (12.26) to the fitted expression:

$$\begin{aligned}
\ln\gamma_1 &= (x_1 - 1)^2 (a_0 - a_1 + 4a_1 x_1) \\
&= 1.21188 - 2.16215x_1 + 0.688648x_1^2 + 0.261617x_1^3, \\
\ln\gamma_2 &= x_1^2 (a_0 - 3a_1 + 4a_1 x_1) \\
&= 1.08107x_1^2 + 0.261617x_1^3.
\end{aligned}$$

The solid lines in Figure 12-8 were calculated using these coefficients. As we see, the fitted expressions provide a very accurate description of the experimental data, both for the activity coefficients and the excess Gibbs free energy.

The activity coefficients at infinite dilution are obtained by setting $x_1 = 0$ and $x_2 = 0$:

$$\begin{aligned}
x_1 = 0: \quad \ln\gamma_1^{\infty} &= a_0 - a_1 = 1.2119 \\
x_2 = 0: \quad \ln\gamma_2^{\infty} &= a_0 + a_1 = 1.3427
\end{aligned}$$

Calculation of Pxy graph. The starting point is eq. (12.24), which we apply to each component:

$$\begin{aligned}
y_1 P &= \gamma_1 x_1 P_1^{\mathrm{sat}} \\
y_2 P &= \gamma_2 x_2 P_2^{\mathrm{sat}}.
\end{aligned}$$

(It is left as an exercise to show that the assumptions that allow us to use the simplified form of the equilibrium criterion are valid in this case). Adding these equations we obtain

$$P = \gamma_1 x_1 P_1^{\mathrm{sat}} + \gamma_2 x_2 P_2^{\mathrm{sat}}.$$