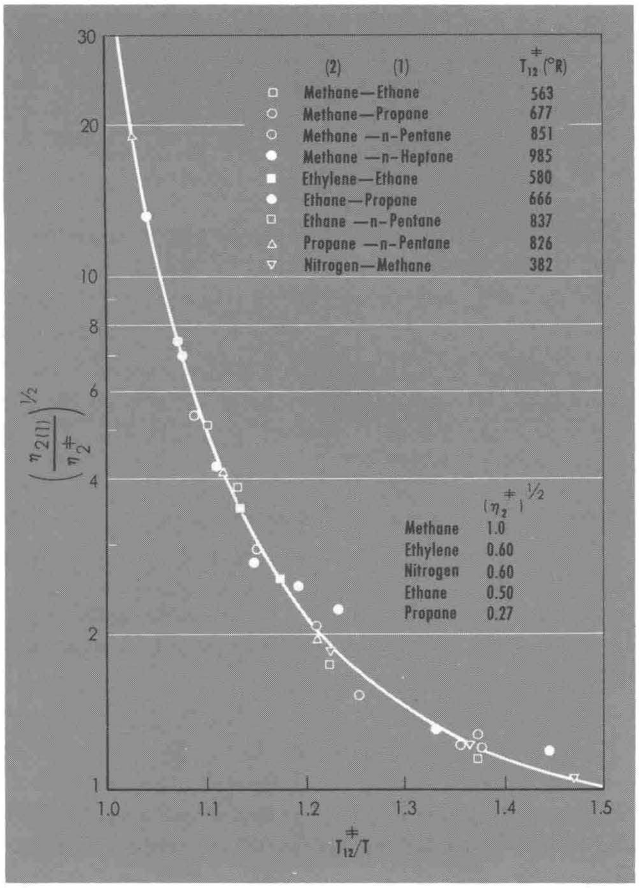

Figure 5. Correlation of dilation constants $\eta_{2(1)}$ for some binary systems

$$\frac{g^E}{RT(x_1 v_{c_1} + x_2 v_{c_2})} = \alpha_{12}\Phi_1\Phi_2 \qquad (37)$$

From Equations 28 and 29 we obtain

$$\ln \gamma_1^{(P^r)} = v_{c_1}\alpha_{12}\Phi_2^2 \qquad (38)$$

$$\ln \gamma_2^{(P^r)} = v_{c_2}\alpha_{12}\Phi_1^2 \qquad (39)$$

where $\gamma_1^{(P^r)}$ is given by Equation 18 and $\gamma_2^{(P^r)}$ by

$$\gamma_2^{(P^r)} = \frac{f_2}{x_2 f_{\text{pure } 2}^{(P^r)}} \exp \int_P^{P^r} \frac{\bar{v}_2^L}{RT}\, dP \qquad (40)$$

It can be shown (*5, 26*) that for the case when both components are subcritical and the excess Gibbs energy can be represented by Equation 37, or by Equation 26 with $q_1 = v_{c_1}$, $q_2 = v_{c_2}$—i.e., $\eta = 0$—there exist rigorous relationships between the constants in the two conventions, viz.:

$$\alpha_{22(1)} = \alpha_{12} \qquad (41)$$

$$\ln H_{2(1)}^{(P^r)} = \ln f_{\text{pure } 2}^{(P^r)} + v_{c_2}\alpha_{12} \qquad (42)$$

Dilated van Laar model for a multicomponent liquid mixture. Extension of the dilated van Laar model to the multicomponent case is best illustrated for a four-component system containing two solvents and two solutes. The results may then be generalized for a solution containing any number of solutes and solvents as shown elsewhere (*26*).

We use the following notation:

Components 1 and 2	Solvents ($T_{R_i} \leq 0.93$)
Components 3 and 4	Solutes ($T_{R_i} > 0.93$)

In the subsequent discussion of excess Gibbs energy we consider only the excess energy due to the interaction of solute molecules in the mixed solvent—i.e., the excess Gibbs energy is taken relative to a solution infinitely dilute with respect to components 3 and 4 in the mixed solvent and does not include the excess Gibbs energy due to the nonideality of the solute-free solvent mixture.

The reference fugacity of component 3 is Henry's constant for 3 in the mixed solvent; and similarly for component 4. The reference fugacity of component 1 (or 2) is not the fugacity of the pure liquid, but is modified by the activity coefficient of component 1 (or 2) in the solute-free mixed solvent (see Equations 65 and 66).

According to our solution model, we write for the excess Gibbs energy due to interactions of solute molecules in the mixed solvent:

$$\frac{g^{E*}_{(\text{MS})}}{RT(x_1q_1 + x_2q_2 + x_3q_3 + x_4q_4)} = - \alpha_{33(\text{MS})}\Phi_3^2 - \alpha_{44(\text{MS})}\Phi_4^2 - 2\,\alpha_{34(\text{MS})}\Phi_3\Phi_4 \qquad (43)$$

where

$$q_i = v_{c_i}[1 + (\eta_{3(\text{MS})}\Phi_3^2 + \eta_{4(\text{MS})}\Phi_4^2 + 2\,\eta_{34(\text{MS})}\Phi_3\Phi_4)] \quad (i = 1, 2, 3, 4) \qquad (44)$$

and subscript (MS) refers to mixed solvent. Here, $\alpha_{33(\text{MS})}$ is the self-interaction constant of solute molecules 3 in the environment of mixed solvent, and $\eta_{3(\text{MS})}$ is the dilation constant of solute molecules 3 in the mixed solvent. By introducing as before (*6*) the assumptions

$$\alpha_{34(\text{MS})} = \sqrt{\alpha_{33(\text{MS})}\alpha_{44(\text{MS})}} \qquad (45)$$

$$\eta_{34(\text{MS})} = \sqrt{\eta_{3(\text{MS})}\eta_{4(\text{MS})}} \qquad (46)$$

Equation 43 can then be rearranged to read

$$\frac{g^{E*}_{(\text{MS})}}{RT} = -(\alpha_{33(\text{MS})}{}^{1/2}\Phi_3 + \alpha_{44(\text{MS})}{}^{1/2}\Phi_4)^2 \times [1 + (\eta_{3(\text{MS})}{}^{1/2}\Phi_3 + \eta_{4(\text{MS})}{}^{1/2}\Phi_4)^2](x_1v_{c_1} + x_2v_{c_2} + x_3v_{c_3} + x_4v_{c_4}) \qquad (47)$$

The self-interaction constant of solute molecules in an environment of mixed solvent is assumed to be given by a linear average in the solute-free solvent mole fraction; results are not sensitive to this combination rule since, in most cases, the components in the mixed solvent are similar in their behavior toward the particular solute. Thus,

$$\alpha_{33(\mathrm{MS})}{}^{1/2} = \frac{\Phi_1\alpha_{33(1)}{}^{1/2} + \Phi_2\alpha_{33(2)}{}^{1/2}}{\Phi_1 + \Phi_2} \tag{48}$$

and similarly,

$$\ln\left(\frac{\eta_{3(\mathrm{MS})}}{\eta_3{}^{\ddagger}}\right)^{1/2} = f_\eta\left(\frac{T_{3(\mathrm{MS})}{}^{\ddagger}}{T}\right) \tag{49}$$

where

$$T_{3(\mathrm{MS})}{}^{\ddagger} = \frac{\Phi_1 T_{3(1)}{}^{\ddagger} + \Phi_2 T_{3(2)}{}^{\ddagger}}{\Phi_1 + \Phi_2} \tag{50}$$

and f_η is given by Equation 36. The activity coefficients can be obtained by differentiating Equation 47. They are:

$$\ln \gamma_{1(\mathrm{MS})}{}^{(P^r)} = v_{c_1}\{\Phi_\alpha{}^2(1 + 3\,\Phi_\eta{}^2 + 2\,DM_1\Phi_\eta) - 2\,AM_1\Phi_\alpha(1 + \Phi_\eta{}^2)\} \tag{51}$$

$$\ln \gamma_{2(\mathrm{MS})}{}^{(P^r)} = v_{c_2}\{\Phi_\alpha{}^2(1 + 3\,\Phi_\eta{}^2 + 2\,DM_2\Phi_\eta) - 2\,AM_2\Phi_\alpha(1 + \Phi_\eta{}^2)\} \tag{52}$$

$$\ln \gamma_3{}^*{}_{(\mathrm{MS})}{}^{(P^r)} = v_{c_3}\{\Phi_\alpha{}^2(1 + 3\,\Phi_\eta{}^2 - 2\,\eta_{3(\mathrm{MS})}{}^{1/2}\Phi_\eta) - 2\,\alpha_{33(\mathrm{MS})}{}^{1/2}\Phi_\alpha(1 + \Phi_\eta{}^2)\} \tag{53}$$

$$\ln \gamma_4{}^*{}_{(\mathrm{MS})}{}^{(P^r)} = v_{c_4}\{\Phi_\alpha{}^2(1 + 3\,\Phi_\eta{}^2 - 2\,\eta_{4(\mathrm{MS})}{}^{1/2}\Phi_\eta) - 2\,\alpha_{44(\mathrm{MS})}{}^{1/2}\Phi_\alpha(1 + \Phi_\eta{}^2)\} \tag{54}$$

where

$$\Phi_\alpha = \alpha_{33(\mathrm{MS})}{}^{1/2}\Phi_3 + \alpha_{44(\mathrm{MS})}{}^{1/2}\Phi_4 \tag{55}$$

$$\Phi_\eta = \eta_{3(\mathrm{MS})}{}^{1/2}\Phi_3 + \eta_{4(\mathrm{MS})}{}^{1/2}\Phi_4 \tag{56}$$

$$AM_l = \frac{(\alpha_{33(l)}{}^{1/2} - \alpha_{33(\mathrm{MS})}{}^{1/2})\Phi_3 + (\alpha_{44(l)}{}^{1/2} - \alpha_{44(\mathrm{MS})}{}^{1/2})\Phi_4}{\Phi_1 + \Phi_2} \quad (l = 1, 2) \tag{57}$$

$$DM_l = \Phi_3 DN_{3(l)} + \Phi_4 DN_{4(l)} \quad (l = 1, 2) \tag{58}$$

$$DN_{j(l)} = \frac{DS_j}{T}\,\frac{T_{j(\mathrm{MS})}{}^{\ddagger} - T_{j(l)}{}^{\ddagger}}{v_{c_l}(\Phi_1/v_{c_1} + \Phi_2/v_{c_2})}, \ (j = 3, 4) \tag{59}$$

$$DS_j = \eta_j{}^{\ddagger 1/2}\left[\frac{\partial(\eta/\eta^{\ddagger})^{1/2}}{\partial(T^{\ddagger}/T)}\right]_{T^{\ddagger} = T_{i(\mathrm{MS})}{}^{\ddagger}} \tag{60}$$

The fugacity of each component is given by:

$$f_1{}^{(P)} = \gamma_{1(\mathrm{MS})}{}^{(P^r)}x_1 f_{1(\mathrm{MS})}{}^{o(P^r)} \exp \int_{P^r}^{P} \frac{\bar{v}_1{}^L}{RT}\,dP \tag{61}$$

$$f_2{}^{(P)} = \gamma_{2(\mathrm{MS})}{}^{(P^r)}x_2 f_{2(\mathrm{MS})}{}^{o(P^r)} \exp \int_{P^r}^{P} \frac{\bar{v}_2{}^L}{RT}\,fP \tag{62}$$

$$f_3{}^{(P)} = \gamma_{3(\mathrm{MS})}{}^{*(P^r)}x_3 H_{3(\mathrm{MS})}{}^{(P^r)} \exp \int_{P^r}^{P} \frac{\bar{v}_3{}^L}{RT}\,dP \tag{63}$$

$$f_4{}^{(P)} = \gamma_{4(\mathrm{MS})}{}^{*(P^r)}x_4 H_{4(\mathrm{MS})}{}^{(P^r)} \exp \int_{P^r}^{P} \frac{\bar{v}_4{}^L}{RT}\,dP \tag{64}$$

The reference fugacities $f_{1(\mathrm{MS})}{}^{o(P^r)}$ and $f_{2(\mathrm{MS})}{}^{o(P^r)}$ in Equations 61 and 62 are given by (reference *26*):

$$f_{1(\mathrm{MS})}{}^{o(P^r)} = \gamma_{1(\mathrm{SF})}{}^{(P^r)} f_{\mathrm{pure}\ 1}{}^{(P^r)} \tag{65}$$

$$f_{2(\mathrm{MS})}{}^{o(P^r)} = \gamma_{2(\mathrm{SF})}{}^{(P^r)} f_{\mathrm{pure}\ 2}{}^{(P^r)} \tag{66}$$

where $\gamma_{1(\mathrm{SF})}{}^{(P^r)}$ and $\gamma_{2(\overset{SF}{\cancel{\mathrm{MS}}})}{}^{(P^r)}$ are the activity coefficients of components 1 and 2 in the solute-free (SF) mixed solvent, as given by:

$$\ln \gamma_{1(\mathrm{SF})}{}^{(P^r)} = v_{c_1}\alpha_{12}\Psi_2{}^2 \tag{67}$$

$$\ln \gamma_{2(\mathrm{SF})}{}^{(P^r)} = v_{c_2}\alpha_{12}\Psi_1{}^2 \tag{68}$$

where α_{12} is the interaction constant of solvent molecules 1 and 2, and Ψ is the solute-free solvent volume fraction,

$$\Psi_1 = \frac{\Phi_1}{\Phi_1 + \Phi_2},\ \Psi_2 = \frac{\Phi_2}{\Phi_1 + \Phi_2} \tag{69}$$

As shown elsewhere (*26*), Henry's constants $H_{3(\mathrm{MS})}{}^{(P^r)}$ and $H_{4(\mathrm{MS})}{}^{(P^r)}$ are related to Henry's constants in the pure solvents by

$$\ln H_{3(\mathrm{MS})}{}^{(P^r)} = \Psi_1 \ln H_{3(1)}{}^{(P^r)} + \Psi_2 \ln H_{3(2)}{}^{(P^r)} - v_{c_3}\alpha_{12}\Psi_1\Psi_2 \tag{70}$$

$$\ln H_{4(\mathrm{MS})}{}^{(P^r)} = \Psi_1 \ln H_{4(1)}{}^{(P^r)} + \Psi_2 \ln H_{4(2)}{}^{(P^r)} - v_{c_4}\alpha_{12}\Psi_1\Psi_2 \tag{71}$$

Figure 6 presents calculated activity coefficients for the ternary system *n*-pentane(1)–propane(2)–methane-(3) at 220° F; only binary constants were used in these calculations. At 220° F, there are one solvent, *n*-pentane, and two solutes, propane and methane. This case is the same as the one discussed previously (*6*). In this case the mixed-solvent reference state discussed above automatically reduces to the simple case of a single-reference solvent discussed before (*6*).

C. Liquid-Phase Activity Coefficients: Effect of Pressure

As indicated in the previous section, a useful thermodynamic analysis of high-pressure vapor-liquid equilibria requires information on the effect of pressure on liquid-phase fugacities; this information is given by partial molar volumes in the liquid mixture.

At low or moderate pressures, liquid-phase activity coefficients are weakly dependent on pressure and, as a result, it has been customary to assume that, for practical purposes, activity coefficients depend only on temperature and composition. In many cases this is a good assumption but for phase equilibria at high pressures, especially for those near critical conditions, it can lead to serious error.

When the standard-state fugacity is defined at a constant pressure, for any component i, the pressure de-