

## APPENDICES

### A. Wilson Model:

The Wilson model, consistent with the Flory Huggins relation, uses the concept of “local composition” and accounts for the differences in both molecular and intermolecular forces. The overall solution ( $\Phi_i = V_{iL} / V_L$ ) is replaced by local-volume fractions  $\bar{\Phi}_i$  given by Equation (1):

$$\bar{\Phi}_i = \frac{V_{iL} x_i \exp(-\lambda_{ii} / RT)}{\sum_{j=1}^C V_{jL} x_j \exp(-\lambda_{ij} / RT)} \quad (1)$$

where interaction energies  $\lambda_{ij} = \lambda_{ji}$ , but  $\lambda_{ij} \neq \lambda_{ji}$ .

For a binary system, the Wilson model for the excess Gibbs energy can be expressed as follows:

$$\frac{G^E}{RT} = -x_1 \ln(x_1 + \Lambda_{12} x_2) - x_2 \ln(\Lambda_{21} x_1 + x_2) \quad (2)$$

where  $G^E$  is the Gibbs energy. Values of  $\Lambda_{ij} < 1$  correspond to positive deviation from Raoult’s law while values greater than 1 result in slightly negative deviations. An ideal solution is observed when  $\Lambda_{ij} = 1$ . The interaction parameters  $\Lambda_{ij}$  can be expressed as follows:

$$\Lambda_{12} = \frac{V_2^L}{V_1^L} \exp\left(\frac{-\Delta\lambda_{12}}{RT}\right) \quad (3)$$

$$\Lambda_{21} = \frac{V_1^L}{V_2^L} \exp\left(\frac{-\Delta\lambda_{21}}{RT}\right) \quad (4)$$

where  $\Delta\lambda_{ij} = \lambda_{ij} - \lambda_{ji}$  are the binary parameters. It is known that  $\lambda_{ii}$  and  $\lambda_{ij}$  are temperature dependent and that  $V_{iL} / V_{jL}$  are dependent on temperature, but the variation is small compared to the effect of temperature on the exponential terms in Equations (3) and (4).

For a binary mixture, the activity coefficients  $\gamma_1$  and  $\gamma_2$  can be obtained from the following equations:

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12} x_2) + x_2 \left( \frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2} \right) \quad (5)$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21} x_1) - x_1 \left( \frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2} \right) \quad (6)$$

When insufficient data are available to determine binary parameters from the best fit of activity coefficients, infinite dilution or single-point values can be used. At infinite dilution, the Wilson equation becomes:

$$\ln \gamma_1^\infty = 1 - \ln \Lambda_{12} - \Lambda_{21} \quad (7)$$

$$\ln \gamma_2^\infty = 1 - \ln \Lambda_{21} - \Lambda_{12} \quad (8)$$

### B. UNIFAC Model

The UNIFAC model represents the activity coefficient as the sum of a combinatorial part (the contribution due to differences in the molecular size and shape of the molecules in the mixture) and a residual one (the contribution due to the molecular interactions or energy interactions).

$$\ln \gamma_i = \ln \gamma_i^{com} + \ln \gamma_i^{res} \quad (9)$$

The two contributions are determined by three parameters, namely, the group surface area parameter  $\Phi$ , the group volume contribution (Q), and the binary interaction parameter  $a_{mm}$ . The combinatorial part is obtained as follows:

$$\ln \gamma_i^{com} = \ln \frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\Phi_i} + \ell_i - \frac{\Phi_i}{x_i} \sum_{j=1}^{N_c} x_j \ell_j \quad (10)$$

$$\Phi_i = \frac{r_i x_i}{\sum_{j=1}^{N_c} r_j x_j} \quad (11)$$

$$\theta_i = \frac{q_i x_i}{\sum_{j=1}^{N_c} q_j x_j} \quad (12)$$

$$\ell_i = \frac{z}{2} (r_i - q_i) - r_i + 1 \quad (13)$$

where  $z$  is the coordination number, generally set to be equal to 10.  $\Phi_i$  and  $\theta_i$  are the volume fraction and surface fraction of molecule  $i$  in the system, respectively. Two sets of structural parameters are introduced, one for the compound,  $r$  and  $q$ , and one for the molecular groups,  $R$  and  $Q$ . Both sets of structural parameters are related to the van der Waals volume and surface area of either a compound or a molecular group. The parameters  $r_i$  and  $q_i$  are calculated as the sum of the area parameters and volume of groups, as shown below:

$$r_i = \sum_{k=1}^{N_{g,j}} v_k^{(i)} R_k \quad (14)$$

$$q_i = \sum_{k=1}^{N_{g,j}} v_k^{(i)} Q_k \quad (15)$$

The residual part is obtained by the solution concept in groups:

$$\ln \gamma_i^{res} = \sum_{k=1}^{N_{g,j}} v_k^{(i)} [\ln \Gamma_k - \ln \Gamma_k^{(i)}] \quad (16)$$

where  $\Gamma_k$  is the activity coefficient of a molecular group,  $\Gamma_k^i$  is the residual activity coefficient of group  $k$  in a reference solution containing only molecules of type  $i$ , and  $v$  refers to the number of a group per compound. The residual activity coefficients are obtained by Equation (17):

$$\ln \Gamma_k = Q_k \left[ 1 - \ln \left( \sum_{m=1}^{N_g} \Theta_m \Psi_{mk} \right) - \sum_{m=1}^{N_g} \frac{\Theta_m \Psi_{km}}{\sum_{n=1}^{N_g} \Theta_n \Psi_{nm}} \right] \quad (17)$$

where  $\Theta_m$  is the area-fraction of molecular group  $m$  and is calculated by Equation (18):

$$\Theta_m = \frac{Q_m X_m}{\sum_{n=1}^{N_g} Q_n X_n} \quad (18)$$

where  $X_m$ , the mole fraction of a molecular group, is calculated by Equation (19):

$$X_m = \frac{\sum_{i=1}^{N_c} v_m^{(i)} x_i}{\sum_{i=1}^{N_c} \sum_{j=1}^{N_g} v_j^{(i)} x_i} \quad (19)$$

where  $\Psi_{mn}$  are the energy interaction parameters between groups  $m$  and  $n$ , and are calculated by Equation (20):

$$\Psi_{mn} = \exp\left[-\frac{U_{mn} - U_{nn}}{RT}\right] = \exp\left[-\frac{a_{mn}}{RT}\right] \quad (20)$$

where  $U_{mn}$  is a measure of the interaction energy between groups  $m$  and  $n$ .

### C. Deviations between the Experimental and Predicted Data in the *n*-Butane + Methanol System

Table A. MRD (Mean Relative Deviation) and BIAS (on  $x$  and  $y$ ) Obtained in Fitting the Experimental VLE Data (*n*-butane + methanol) with PR, PC-SAFT, and SAFT-VR EoS [1]

The <i>n</i> -butane+ methanol system	PR				SAFT-VR				PC-SAFT			
T(K)	BIAS $x$	BIAS $y$	MRD $x$	MRD $y$	BIAS $x$	BIAS $y$	MRD $x$	MRD $y$	BIAS $x$	BIAS $y$	MRD $x$	MRD $y$
	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
323.22 [1]	-7.4	0.5	7.6	0.6	-6.9	-0.1	10.5	0.3	-1.1	-0.2	5.6	1.0
373.19 [1]	-0.1	0.9	4.1	1.6	-0.5	-0.5	5.7	1.8	0.1	-1.8	2.2	2.2
403.13 [1]	-0.1	-0.5	3.6	2.5	-3.2	-1.3	5.8	2.7	0.0	-1.5	4.0	2.2
423.09 [1]	-0.7	-2.6	9.3	4.8	-8.0	-1.8	11.7	3.3	8.4	-0.9	10.6	3.3
Literature data												
273.15 [28]	5.3	-1.1	17.1	30.	-3.2	1.3	5.8	2.7	-4.8	1.7	28.4	2.6
323.15 [28]	-4.1	-1.7	8.8	1.7	-12.0	-2.6	16.5	2.6	2.0	2.1	7.5	2.1
373.15 [28]	-0.8	-3.4	2.6	3.4	-4.9	-3.1	8.7	3.8	-1.1	1.9	2.9	2.0

Table B. AAE, AAD (%), and BIAS (%) between the Experimental and predicted (PR-MHV2-UNIFAC and GC-PR-CPA) Data in the *n*-Butane + Methanol Mixture

System	T(K)	PR-MHV2-UNIFAC			GC-PR-CPA		
		AAE (mole fraction)	AAD (%)	BIAS (%)	AAE (mole fraction)	AAD (%)	BIAS (%)
<i>n</i> -butane + methanol	323.2[29]	0.01	5.4	-4.2	0.01	13	5.1
	373.2[29]	0.02	9.1	-8.4	0.02	11	-4.2
	403.1[29]	0.02	8.3	-5.8	0.02	7.4	1.6