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APPENDICES

Appendix A Calculation of molar volume and van der Waals volume.

Molar volume of component i

The group contribution method given by Elbro *et al.* (1991) was used to calculate molar volume of n-alkane and aromatic compound. This method can not be used to calculate the molar volume for cycloalkane which has carbon number less than 9. The liquid density is used to obtain the molar volume of cyclohexane and cyclopentane and the density is obtained from Yaws (1999). The molar volume (V_i) and density (ρ_i) of component i is calculated from the following equations,

$$V_i = A_i + B_i T \tag{A1}$$

$$V_i = \frac{MW_i}{\rho_i} \tag{A2}$$

$$\rho_i = C_i \times D_i^{-\left(1 - \frac{T}{T_c}\right)^n} \tag{A3}$$

where T is the temperature, T_c is the critical temperature and MW is the molecular weight. The parameters A_i, B_i, C_i, D_i and n are shown in the Table A1 and Table A2.

Table A1 Group contributions for saturated molar volume (Fredenslund *et al.*, 1977)

Group	A(cm^3/mol)	B(cm^3/mol K)
CH_3	18.960	45.58
CH_2	12.520	12.94
ACH	10.090	17.37
$ACCH_3$	23.58	24.43

Table A2 The parameters calculating the liquid density (Elbro *et al.*, 1990)

Solvent	C	D	T_c (K)	n
Cyclohexane	0.27376	0.27408	553.54	0.28511
Cyclopentane	0.27236	0.27247	511.76	0.28571

Van der Waals volume of component *i*

Van der Waals volume of component *i* was calculated from the group contribution method given by Bondi (1968).

$$V_{wi} = \sum_k v_k^i \times V_w^k$$

The term of v_k^i is the number of group k in the component *i*. The values for cycloalkane were adjusted to account for the intramolecular crowding losses which also described by Bondi (1968). Table A3 shows the Van der Waals volume (V_w^k) of different groups.

Table A3 Group Van der Waals volume (Bondi, 1968)

Group (k)	V_w^k (cm^3/mol)
CH_3	13.67
CH_2	10.23
ACH	8.06
AC	5.54
CH_2 (cyclohexane)	9.78
CH_2 (cyclopentane)	9.83

Appendix B Calculation of residual activity coefficient.

System: Octacosane-Cyclohexane mixture at octacosane mole fraction = 0.015

and $T = 291.25$ K

The residual activity coefficient is calculated from Equation (3.5). For this system, Equation (3.5) can be written as,

$$\ln \gamma_{C28}^{res} = 2 \times [\ln \Gamma_{CH_3}^{mix} - \ln \Gamma_{CH_3}^{pur}] + 26 \times [\ln \Gamma_{CH_2}^{mix} - \ln \Gamma_{CH_2}^{pur}] \qquad (B1)$$

where $\Gamma_{k_3}^{mix}$ is the activity coefficient of group k in the mixture composition and $\Gamma_{k_3}^{pur}$ is the activity coefficient of group k in the pure octacosane. Both $\Gamma_{k_3}^{mix}$ and $\Gamma_{k_3}^{pur}$ are calculated from Equation (3.6). Table C1 shows the groups and its surface area parameter used in this calculation. The calculation consisted of 2 part, mixture composition and pure octacosane composition.

Table B1 Group surface area parameter and group number (Fredenslund *et al.*, 1977)

Group number	Name	Q_k
1	CH3	0.848
2	CH2	0.540
3	c-CH2	0.540

Mixture composition

There are 3 groups in this system which are CH_3, CH_2 in n-alkane and CH_2 group in cyclohexane (c-CH_2) so Equation (3.6) can be written as

$$\ln \Gamma_{CH_3}^{mix} = Q_{CH_3} \left[\begin{array}{c} 1 - \ln(\theta_1 \psi_{11} + \theta_2 \psi_{21} + \theta_3 \psi_{31}) - \dfrac{\theta_1 \psi_{11}}{\theta_1 \psi_{11} + \theta_2 \psi_{21} + \theta_3 \psi_{31}} \\[2ex] - \dfrac{\theta_2 \psi_{12}}{\theta_1 \psi_{12} + \theta_2 \psi_{22} + \theta_3 \psi_{32}} - \dfrac{\theta_3 \psi_{13}}{\theta_1 \psi_{13} + \theta_2 \psi_{23} + \theta_3 \psi_{33}} \end{array} \right] \qquad (B2)$$

The subscribed number represents the group number shown in the Table B1. Surface area fraction is calculated from Equation (3.7) which can be written as following equation,

$$\theta_1 = \frac{Q_1 X_1}{Q_1 X_1 + Q_2 X_2 + Q_3 X_3}$$

$$\theta_2 = \frac{Q_2 X_2}{Q_1 X_1 + Q_2 X_2 + Q_3 X_3}$$

$$\theta_3 = \frac{Q_3 X_3}{Q_1 X_1 + Q_2 X_2 + Q_3 X_3}$$

with

$$X_1 = \frac{v_1^{C28} x_{C28} + v_1^{cC6} x_{cC6}}{v_1^{C28} x_{C28} + v_1^{cC6} x_{cC6} + v_2^{C28} x_{C28} + v_2^{cC6} x_{cC6} + v_3^{C28} x_{C28} + v_3^{cC6} x_{cC6}}$$

$$X_2 = \frac{v_2^{C28} x_{C28} + v_2^{cC6} x_{cC6}}{v_1^{C28} x_{C28} + v_1^{cC6} x_{cC6} + v_2^{C28} x_{C28} + v_2^{cC6} x_{cC6} + v_3^{C28} x_{C28} + v_3^{cC6} x_{cC6}}$$

$$X_3 = \frac{v_3^{C28} x_{C28} + v_3^{cC6} x_{cC6}}{v_1^{C28} x_{C28} + v_1^{cC6} x_{cC6} + v_2^{C28} x_{C28} + v_2^{cC6} x_{cC6} + v_3^{C28} x_{C28} + v_3^{cC6} x_{cC6}}$$

where v_k^i is the number of group k in component i and x_i is the mole fraction of component i. The values of v_k^i and calculated θ_k are shown in the Table B2.

Table B2 The number of group in each component and group surface area fraction of each group

k	v_k^{C28}	v_k^{cC6}	θ_k
1	2	0	0.0074
2	26	0	0.0615
3	0	6	0.9311

The interaction terms, ψ_{mn}, are calculated from Equations (3.8) and (3.9). The interaction parameters used in this calculation are shown in the Table 5.1.

$$\psi_{13} = \psi_{23} = \exp\left(-\frac{73.3124 - 0.1627 \times (291.25 - 298.15))}{291.25}\right)$$

$$= 0.77447$$

$$\psi_{31} = \psi_{32} = \exp\left(-\frac{-69.0285 - 0.1627 \times (291.25 - 298.15)}{291.25}\right)$$

$$= 1.26257$$

$$\psi_{11} = \psi_{12} = \psi_{22} = \psi_{21} = \exp\left(-\frac{0}{291.25}\right) = 1$$

From Equation (B2),

$$\ln \Gamma_{CH_3}^{mix} = 0.848 \times -0.00658$$

$$= -0.00558$$

Similarly for $\Gamma_{CH_2}^{mix}$,

$$\ln \Gamma_{CH_3}^{mix} = 0.540 \times -0.00658$$

$$= -0.00355$$

Pure octacosane composition

      There are 2 groups in octacosane which are CH_3 and CH_2. The surface area fractions for each group are needed to be evaluated for this system. The interaction parameters between CH_2 and CH_3 groups are zero ($\psi_{ij} = 1$) and $\theta_1 + \theta_2 = 1$. The equation (3.6) can be written as

$$\ln \Gamma_{CH_3}^{pur} = 0.848\left[1 - \ln(\theta_1\psi_{11} + \theta_2\psi_{21}) - \frac{\theta_1\psi_{11}}{\theta_1\psi_{11} + \theta_2\psi_{21}} - \frac{\theta_2\psi_{12}}{\theta_1\psi_{12} + \theta_2\psi_{12}}\right]$$

$$= 0.848\left[1 - \ln(\theta_1 + \theta_2) - \frac{\theta_1}{\theta_1 + \theta_2} - \frac{\theta_2}{\theta_1 + \theta_2}\right]$$

$$= 0$$

Similarly, $\Gamma_{CH_2}^{pur} = 0$

The residual activity coefficient of octacosane in cyclohexane can be calculated by Equation (3.5).

$$\ln \gamma_{C28}^{res} = 2 \times (-0.00558 - 0) + 26 \times (-0.00355 - 0)$$
$$= -0.10346$$

Appendix C Structural parameters of component i (r_i and q_i) for solid phase activity coefficient.

Values of r_i and q_i used in the solid phase activity coefficient calculations were obtained from the following equations,

$$r_i = 0.1483 \times r_{i,org} \qquad (C1)$$

$$q_i = 0.1852 \times q_{i,org} \qquad (C2)$$

where $r_{i,org}$ and $q_{i,org}$ are calculated from the group volume parameters (R_k) and group surface area parameters (Q_k),

$$r_{i,org} = \sum_k v_k^i R_k \qquad (C3)$$

$$q_{i,org} = \sum_k v_k^i Q_k \qquad (C4)$$

where v_k^i is the total number of group k in component i. Group volume and surface area has been determined by Abrams and Prausnitz (1975) and used in both UNIQUAC and UNIFAC model. The values of both R_k and Q_k are shown in Table C1.

Table C1 The values of group structural parameters

Group	R_k	Q_k	Group	R_k	Q_k
CH_3	0.9011	0.848	ACH	0.5313	0.400
CH_2	0.6744	0.540	AC	0.3652	0.120

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