Supporting Information
for
Accurate effective diffusivities in multicomponent systems

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1 Detailed derivation of the new effective diffusivity model

The first step in the derivation involves equating the molar fraction gradients expressed in terms of effective diffusivities and the generalized Fick's first law:

$$\begin{cases} (\overline{J}) = -C_T[D_{\text{eff}}](\nabla x) \iff (\nabla x) = -[D_{\text{eff}}]^{-1}(\overline{J})\dfrac{1}{C_T} \\ (\overline{J}) = -C_T[D](\nabla x) \iff (\nabla x) = -[D]^{-1}(\overline{J})\dfrac{1}{C_T} \end{cases} \tag{SI-1.1}$$

which results in the following relation:

$$[D_{\text{eff}}]^{-1}(\overline{J}) = [D]^{-1}(\overline{J}) \tag{SI-1.2}$$

An ith row of equation (SI-1.2) is given by:

$$\frac{1}{D_{i,\text{eff}}} = \sum_{j=1}^{n-1} D_{ij}^{inv}\frac{\overline{J}_j}{\overline{J}_i}, \quad i = 1, ..., (n-1) \tag{SI-1.3}$$

where D_{ij}^{inv} represents the ij element of matrix $[D]^{-1}$. This equation will then be used to derive the effective diffusivity of the last component, $D_{n,\text{eff}}$. First, substituting the mole fraction restriction $\sum_{j=1}^{n} x_j = 1 \iff x_n = 1 - \sum_{j=1}^{n-1} x_j$ into the molar diffusion flux of component n, $\overline{J}_n$, one gets:

$$\overline{J}_n = -C_T D_{n,\text{eff}}\nabla x_n = C_T D_{n,\text{eff}} \sum_{j=1}^{n-1} \nabla x_j \tag{SI-1.4}$$

Then, since $\nabla x_j = -\overline{J}_j/(D_{j,\text{eff}}C_T)$, equation (SI-1.4) gives rise to:

$$\overline{J}_n = C_T D_{n,\text{eff}} \sum_{j=1}^{n-1} \frac{-\overline{J}_j}{C_T D_{j,\text{eff}}} = -D_{n,\text{eff}} \sum_{j=1}^{n-1} \frac{\overline{J}_j}{D_{j,\text{eff}}} \tag{SI-1.5}$$

Rearranging the previous equation, one gets the expression for the effective diffusivity of species n:

$$\frac{1}{D_{n,\text{eff}}} = -\sum_{j=1}^{n-1} \frac{1}{D_{j,\text{eff}}}\frac{\overline{J}_j}{\overline{J}_n} \tag{SI-1.6}$$

Taking into account the relationship between Maxwell-Stefan and generalized Fick's first law equations:

$$(\overline{J}) = -C_T[D](\nabla x) = -C_T[B]^{-1}[\Gamma](\nabla x) \tag{SI-1.7}$$

one obtains $[D] = [B]^{-1}[\Gamma]$, which can be substituted in equations (SI-1.3) and (SI-1.6) for calculation purposes.

2 Effective diffusivity model for ideal mixtures

In this section it is derived the new effective diffusivity model for the special case of ideal mixtures, being demonstrated that it corresponds to the model of Bird et al. [1]. In the particular case of ideal solutions, $\gamma_i = 1$. Hence:

$$\ln \gamma_i = 0 \quad (i = 1, 2, ..., n) \Longrightarrow \Gamma_{ij} = \delta_{ij} \iff [\Gamma] = [I]$$

Since $[D] = [B]^{-1}[\Gamma]$, then $[D]^{-1} = [B]$. Now the effective diffusivity can be calculated with the elements of the $[B]$ matrix, and an arbitrary row i of $[D_{\text{eff}}]$ is given by:

$$\frac{\overline{J}_i}{D_{i,\text{eff}}} = \sum_{j=1}^{n-1} B_{ij}\overline{J}_j = B_{ii}\overline{J}_i + \sum_{\substack{j=1\\ j\neq i}}^{n-1} B_{ij}\overline{J}_j \tag{SI-2.1}$$

where:

$$B_{ii} = \frac{x_i}{Đ_{in}} + \sum_{\substack{j=1\\ j\neq i}}^{n} \frac{x_j}{Đ_{ij}} \tag{SI-2.2a}$$

$$B_{ij} = -x_i\left(\frac{1}{Đ_{ij}} - \frac{1}{Đ_{in}}\right) \tag{SI-2.2b}$$

Replacing the definition of B_{ii} and B_{ij} into equation (SI-2.1), one obtains:

$$\begin{aligned}
\frac{1}{D_{i,\text{eff}}}\overline{J}_i &= \overline{J}_i\left(\frac{x_i}{Đ_{in}} + \sum_{\substack{j=1\\ j\neq i}}^{n} \frac{x_j}{Đ_{ij}}\right) - x_i \sum_{\substack{j=1\\ j\neq i}}^{n-1} \overline{J}_j\left(\frac{1}{Đ_{ij}} - \frac{1}{Đ_{in}}\right) \\
&= \frac{x_i\overline{J}_i}{Đ_{in}} + \overline{J}_i \sum_{\substack{j=1\\ j\neq i}}^{n} \frac{x_j}{Đ_{ij}} - x_i \sum_{\substack{j=1\\ j\neq i}}^{n-1} \frac{\overline{J}_j}{Đ_{ij}} + x_i \sum_{\substack{j=1\\ j\neq i}}^{n-1} \frac{\overline{J}_j}{Đ_{in}} \\
&= -x_i \sum_{\substack{j=1\\ j\neq i}}^{n-1} \frac{\overline{J}_j}{Đ_{ij}} + \frac{x_i}{Đ_{in}}\left(\sum_{\substack{j=1\\ j\neq i}}^{n-1} \overline{J}_j + \overline{J}_i\right) + \overline{J}_i \sum_{\substack{j=1\\ j\neq i}}^{n} \frac{x_j}{Đ_{ij}}
\end{aligned} \tag{SI-2.3}$$

Let us now focus the parenthesis term, taking into account the fundamental restriction $\sum_{j=1}^{n} \overline{J}_j = 0$:

$$\sum_{\substack{j=1\\ j\neq i}}^{n-1} \overline{J}_j + \overline{J}_i = \sum_{j=1}^{n-1} \overline{J}_j = -\overline{J}_n \tag{SI-2.4}$$

Substituting this equation into equation (SI-2.3):

$$\begin{aligned}
\frac{1}{D_{i,\text{eff}}}\overline{J}_i &= -x_i \sum_{\substack{j=1\\ j\neq i}}^{n-1} \frac{\overline{J}_j}{Đ_{ij}} - \frac{x_i \overline{J}_n}{Đ_{in}} + \overline{J}_i \sum_{\substack{j=1\\ j\neq i}}^{n} \frac{x_j}{Đ_{ij}} \\
&= -x_i \left(\sum_{\substack{j=1\\ j\neq i}}^{n-1} \frac{\overline{J}_j}{Đ_{ij}} + \frac{\overline{J}_n}{Đ_{in}} \right) + \overline{J}_i \sum_{\substack{j=1\\ j\neq i}}^{n} \frac{x_j}{Đ_{ij}} \\
&= -x_i \sum_{\substack{j=1\\ j\neq i}}^{n} \frac{\overline{J}_j}{Đ_{ij}} + \overline{J}_i \sum_{\substack{j=1\\ j\neq i}}^{n} \frac{x_j}{Đ_{ij}} \\
&= \sum_{\substack{j=1\\ j\neq i}}^{n} \frac{\overline{J}_i x_j - \overline{J}_j x_i}{Đ_{ij}}
\end{aligned} \tag{SI-2.5}$$

From the relation between molar and diffusion fluxes, the following substitutions can be made: $\overline{J}_j = \overline{N}_j - x_j \overline{N}_T$ and $\overline{J}_i = \overline{N}_i - x_i \overline{N}_T$, which yields:

$$\begin{aligned}
\frac{\overline{N}_i - x_i \overline{N}_T}{D_{i,\text{eff}}} &= \sum_{\substack{j=1\\ j\neq i}}^{n} \frac{(\overline{N}_i - x_i \overline{N}_T) x_j - (\overline{N}_j - x_j \overline{N}_T) x_i}{Đ_{ij}} \\
&= \sum_{\substack{j=1\\ j\neq i}}^{n} \frac{\overline{N}_i x_j - x_i \overline{N}_T x_j - \overline{N}_j x_i + x_j \overline{N}_T x_i}{Đ_{ij}} \\
&= \sum_{\substack{j=1\\ j\neq i}}^{n} \frac{\overline{N}_i x_j - \overline{N}_j x_i}{Đ_{ij}} \\
&= -x_i \sum_{\substack{j=1\\ j\neq i}}^{n} \frac{\overline{N}_j}{Đ_{ij}} + \overline{N}_i \sum_{\substack{j=1\\ j\neq i}}^{n} \frac{x_j}{Đ_{ij}}
\end{aligned} \tag{SI-2.6}$$

Isolating $D_{i,\text{eff}}$ in the left hand side of the previous equation, one obtains the expressions by Bird *et al.* [1] for ideal mixtures:

$$D_{i,\text{eff}}^{Ideal} = \frac{\overline{N}_i - x_i \overline{N}_T}{-x_i \sum_{\substack{j=1\\ j\neq i}}^{n} \frac{\overline{N}_j}{Đ_{ij}} + \overline{N}_i \sum_{\substack{j=1\\ j\neq i}}^{n} \frac{x_j}{Đ_{ij}}} \tag{SI-2.7}$$

3 Subsidiary equations for liquid phase effective diffusivities - case of ethyl acetate synthesis

3.1 UNIFAC model

UNIFAC is a group contribution thermodynamic model for the activity coefficient, which is calculated as a sum of a combinatorial term and a residual term [2]:

$$\ln \gamma_j = \ln \gamma_j^{COMB} + \ln \gamma_j^{RES} \tag{SI-3.1}$$

The combinatorial term is:

$$\ln \gamma_j^{COMB} = \ln \frac{\Phi_j}{x_j} + \left[1 - \frac{\Phi_j}{x_j}\right] - 5q_j \left[\ln \frac{\Phi_j}{\theta_j} + \left(1 - \frac{\Phi_j}{\theta_j}\right)\right] \tag{SI-3.2}$$

where Φ_j represents a molecular volume fraction and θ_j a molecular surface fraction, which are based on relative molecule volumes r_j and relative molecule surface areas q_j:

$$\Phi_j = \frac{x_j r_j}{\sum_i x_i r_i} \quad \text{and} \quad \theta_j = \frac{x_j q_j}{\sum_i x_i q_i} \tag{SI-3.3}$$

The r_j and q_j values are calculated from tabulated group parameters R_k (group volume) and Q_k (group surface area):

$$r_j = \sum_k \nu_k^{(j)} R_k \quad \text{and} \quad q_j = \sum_k \nu_k^{(j)} Q_k \tag{SI-3.4}$$

where $\nu_k^{(j)}$ is the number of groups k in molecule j.

The residual contribution is given by:

$$\ln \gamma_j^{RES} = \sum_k \nu_k^{(j)} [\ln \Gamma_k - \ln \Gamma_k^{(j)}] \tag{SI-3.5}$$

where Γ_k is calculated assuming a hypothetical solution of groups found in the mixture, and $\Gamma_k^{(j)}$ is calculated assuming a hypothetical solution of groups in the case of pure component j.

$$\ln \Gamma_k = Q_k \left[1 - \ln\left(\sum_{groups\ m} \Theta_m \Psi_{mk}\right) - \sum_{groups\ n} \frac{\Theta_n \Psi_{kn}}{\sum_{groups\ m} \Theta_m \Psi_{mn}}\right] \tag{SI-3.6}$$

Γ_k requires the following quantities:

- Molecular energy variable, based on tabulated energy of interaction parameters a_{mn}:

$$\Psi_{mn} = \exp\left(\frac{-a_{mn}}{T}\right) \tag{SI-3.7}$$

- Mole fraction of group k:

$$X_k = \frac{\sum_{molecules\ i} \nu_k^{(i)} x_i}{\sum_{molecules\ i} \sum_{groups\ m} \nu_m^{(i)} x_i} \tag{SI-3.8}$$

- Surface area fraction of group k (the denominator represents summation across all groups in the solution of functional groups):

$$\Theta_k = \frac{X_k Q_k}{\sum_{groups\ m} X_m Q_m} \tag{SI-3.9}$$

The energy of interaction between groups that appear in the molecules present in the ethyl acetate synthesis reaction are given in Table SI-3.1. Table SI-3.2 contains the parameters R_k and Q_k, and Table SI-3.3 contains information about the number of times each group appears in each molecule present in the ethyl acetate synthesis reaction.

Table SI-3.1: UNIFAC energy of interaction parameters (K) [2]

Main/Secondary	CH_3	CH_2	OH	H_2O	CH_3COO	COOH
CH_3	0	0	986.5	1318	232.1	663.5
CH_2	0	0	986.5	1318	232.1	663.5
OH	156.4	156.4	0	353.5	101.1	199
H_2O	300	300	-229.1	0	72.87	-14.09
CH_3COO	114.8	114.8	245.4	200.8	0	660.2
COOH	315.3	315.3	-151	-66.17	-256.3	0

Table SI-3.2: UNIFAC group volume and surface area parameters [2]

k	CH_3	CH_2	OH	H_2O	CH_3COO	COOH
R_k	0.9011	0.6744	1	0.92	1.9031	1.3013
Q_k	0.848	0.540	1.2	1.4	1.728	1.224

Table SI-3.3: Groups per molecule

Molecule/Groups	CH_3	CH_2	OH	H_2O	CH_3COO	COOH
CH_3COOH	1	0	0	0	0	1
CH_3CH_2OH	1	1	1	0	0	0
$CH_3COOC_2H_5$	1	1	0	0	1	0
H_2O	0	0	0	1	0	0

3.2 Estimation of infinite dilution binary diffusion coefficients

The Wilke-Chang equation, due to its simplicity and reliable results [3], is employed to estimate diffusion coefficients at infinite dilution in dense phases:

$$D_{ij}^{\circ} = \frac{7.4 \times 10^{-8} (\phi M_j)^{1/2} T}{\mu_j V_{i,bp}^{0.6}} \tag{SI-3.10}$$

D_{ij}° = diffusion coefficient of dilute component i in solvent j (cm^2/s)

M_j = molecular weight of solvent j (g/mol)

ϕ = solvent association factor, equal to 2.6 for water, 1.5 for ethanol, and 1.0 for unassociated solvents.

T = temperature (K)

μ_j = solvent viscosity (cP)

$V_{i,bp}$ = liquid molar volume of solute i at its normal boiling point (cm^3/mol)

Table SI-3.4 contains the necessary data to apply equation (SI-3.10). All data from Table SI-3.4 were taken from *The Properties of Gases and Liquids* [3], except the viscosities at the desired temperature, which were estimated using the following empirical equation taken from *Perry's Chemical Engineers' Handbook* [4]:

$$\mu = \exp\left(C_1 + C_2/T + C_3 \ln T + C_4 T^{C_5}\right) \tag{SI-3.11}$$

Constants C_1, C_2, C_3, C_4, C_5 are listed in Table SI-3.5. The calculated diffusion coefficients of all pairs of components are given in Table SI-3.6.

Table SI-3.4: Component data for Wilke-Chang equation

Property/Molecule	CH_3COOH	CH_3CH_2OH	$CH_3COOC_2H_5$	H_2O
M (g/mol) [3]	60.0520	46.0684	88.1051	18.0153
ϕ [3]	1	1.5	1	2.6
μ (cP) at 78 °C [4]	0.5728	0.4409	0.2504	0.3650
V_{bp} (cm^3/mol) [3]	66.0	60.85	106.3	18.8

Table SI-3.5: Constants for viscosity estimation [4] by equation (SI-3.11)

Constants	CH_3COOH	CH_3CH_2OH	$CH_3COOC_2H_5$	H_2O
C_1	-9.03	7.875	14.354	-52.843
C_2	1212.3	781.98	-154.6	3703.6
C_3	-0.322	-3.0418	-3.7887	5.866
C_4	0	0	0	-5.8729×10^{-29}
C_5	0	0	0	10

Table SI-3.6: Estimated binary diffusion coefficients (cm^2/s) at infinite dilution using the Wilke-Chang equation at 351.15 K

	Solvent			
Solute	**CH_3COOH**	**CH_3CH_2OH**	**$CH_3COOC_2H_5$**	**H_2O**
CH_3COOH	-	3.9666×10^{-5}	7.8877×10^{-5}	3.9452×10^{-5}
CH_3CH_2OH	2.9882×10^{-5}	-	8.2817×10^{-5}	4.1422×10^{-5}
$CH_3COOC_2H_5$	2.1382×10^{-5}	2.9800×10^{-5}	-	2.9640×10^{-5}
H_2O	6.0461×10^{-5}	8.4266×10^{-5}	16.7564×10^{-5}	-

4 Subsidiary equations for gas phase effective diffusivities - case of methanol synthesis

4.1 Peng-Robinson equation of state

The Peng-Robinson (PR) equation of state (EoS) in its dimensionless, cubic polynomial format is given by [2]:

$$Z^3 - (1 - B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0 \tag{SI-4.1}$$

where:

$A = a \cdot \frac{P}{R^2T^2}$

$B = b \cdot \frac{P}{RT}$

$a = 0.45723553 \frac{R^2T_c^2}{P_c}\alpha$

$\alpha = [1 + \kappa(1 - \sqrt{T_R})]^2$

$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2$

$b = 0.07779607R\frac{T_c}{P_c}$

T_c = critical temperature (K)

P_c = critical pressure (MPa)

$T_R = T/T_c$ = reduced temperature

ω = acentric factor

$Z = \frac{P}{\rho RT}$ = compressibility factor

R = 8.31446 cm^{3}MPa/(K mol) = ideal gas constant

Roots with imaginary parts, if present, are ignored. If the result consists of three real roots, the highest value corresponds to the gas phase compressibility factor. This value is then used to calculate the pure gas molar density (mol/cm^3):

$$\rho = \frac{1}{Z}\frac{P}{RT} \tag{SI-4.2}$$

The PR expression for the fugacity coefficient of component i, $\hat{\phi}_i$, in a gas mixture is [2]:

$$\ln(\hat{\phi}_i) = -\ln(Z-B) + \frac{B_i}{B}(Z-1) - \frac{A}{B\sqrt{8}}\ln\left[\frac{Z+(1+\sqrt{2})B}{Z+(1-\sqrt{2})B}\cdot\left(\frac{2\sum_j x_j A_{ij}}{A} - \frac{B_i}{B}\right)\right] \tag{SI-4.3}$$

where:

$B_i = b_i \cdot \frac{P}{RT}$

$A_i = a_i \cdot \frac{P}{R^2T^2}$

$A_{ij} = (A_i \cdot A_j)^{1/2} \cdot (1 - k_{ij})$

$B = \sum_j x_j B_j$

$A = \sum_i \sum_j x_i x_j A_{ij}$

k_{ij} = binary interaction parameters

The pure component data necessary for the calculations can be found in Table SI-4.1. The pure component densities at 0.1 MPa and 10 MPa estimated by the PR EoS are listed in Table SI-4.2.

Table SI-4.1: Pure component data/properties [3]

Property	CO	CH_3OH	H_2	H_2O	CH_4	CO_2
T_c (K)	132.85	512.64	33.25	647.14	190.56	304.12
P_c (MPa)	3.494	8.097	1.297	22.064	4.599	7.374
V_c (cm^3/mol)	93.1	118.0	65.00	55.95	98.6	94.07
ω	0.045	0.565	-0.216	0.344	0.011	0.225
M (g/mol)	28.010	32.042	2.016	18.015	16.043	44.010

Table SI-4.2: Pure component densities (mol/cm^3) at high and low pressure, at 573.15 K, estimated by PR EoS

Component	P = 0.1 MPa	P = 10 MPa
CO	2.0978×10^{-5}	2.0264×10^{-3}
CH_3OH	2.1049×10^{-5}	3.1088×10^{-3}
H_2	2.0979×10^{-5}	2.0450×10^{-3}
H_2O	2.1038×10^{-5}	3.1133×10^{-3}
CH_4	2.0984×10^{-5}	2.0794×10^{-3}
CO_2	2.0993×10^{-5}	2.1553×10^{-3}

4.2 PC-SAFT equation of state

SAFT (Statistical Associating Fluid Theory) is an equation of state adequate for associating fluids. Since its conception [5], the original model has been modified by several independent research groups. One of the most widely used variations is the PC-SAFT (Perturbed Chain-SAFT) equation of state, developed by Gross and Sadowski [6], which uses a hard-chain fluid as reference instead of spherical molecules.

For associating components, five pure component parameters must be known in order to apply the model (three for non-associating components). The parameters are estimated from regression of experimental data, usually vapor pressure and liquid densities, in a wide range of temperatures [7]. They are:

- m = number of segments in the chain (chain length)
- ε = dispersion energy of interaction between segments (J)
- σ = temperature-independent Lennard-Jones segment diameter (Å)
- ε^{AB} = association energy (for associating compounds only) (J)
- κ^{AB} = association volume (for associating compounds only) (dimensionless)

In the context of the methanol synthesis reaction considered in this article, the necessary pure component parameters are given in Table SI-4.3. The pure component densities at 0.1 MPa and 10 MPa calculated with PC-SAFT EoS are listed in Table SI-4.4.

Table SI-4.3: Pure component parameters for PC-SAFT EoS calculations

Parameter	CO [6]	CH_3OH [8]	H_2 [9]	H_2O [10]	CH_4 [6]	CO_2 [6]
m	1.3097	1.5143	0.8285	1.0953	1.0000	2.0729
σ (Å)	3.2507	3.2564	2.973	2.8898	3.0739	2.7852
ε/k_B (K)	92.15	193.76	12.53	365.96	150.03	169.21
κ^{AB}	-	0.03522	-	0.03487	-	-
ε^{AB}/k_B (K)	-	2847.81	-	2515.7	-	-

$k_B \equiv$ Boltzmann constant

Table SI-4.4: Pure component densities (mol/cm^3) at high and low pressure, at 573.15 K, estimated by PC-SAFT EoS

Component	P = 0.1 MPa	P = 10 MPa
CO	2.0988×10^{-5}	2.0170×10^{-3}
CH_3OH	2.1048×10^{-5}	2.8603×10^{-3}
H_2	2.0988×10^{-5}	2.0298×10^{-3}
H_2O	2.1033×10^{-5}	2.6455×10^{-3}
CH_4	2.0995×10^{-5}	2.0861×10^{-3}
CO_2	2.1006×10^{-5}	2.1848×10^{-3}

4.3 Estimation of low pressure viscosity, μ^*

The viscosity of polar gases that can establish hydrogen bonds (*e.g.*, methanol and water) at relatively low pressures (0.2 - 5 atm) and reduced temperature $T_R \leq 2.0$ can be estimated by equation (SI-4.4) [11]. For polar gases without hydrogen bonding, equation (SI-4.5) is applicable. For non-polar gases, equations (SI-4.6) and (SI-4.7) may be used, below $T_R = 1.5$ and above $T_R = 1.5$ [11].

$$(\mu^*\xi)Z_c^{5/4} = [7.55T_R - 0.55] \times 10^{-5} \tag{SI-4.4}$$

$$(\mu^*\xi)Z_c^{2/3} = [1.90T_R - 0.29]^{4/6} \times 10^{-4} \tag{SI-4.5}$$

$$\mu^*\xi = 34.0 \times 10^{-5} T_R^{0.94}, \quad T_R \leq 1.50 \tag{SI-4.6}$$

$$\mu^*\xi = 17.78 \times 10^{-5}[4.58T_R - 1.67]^{5/8}, \quad T_R > 1.50 \tag{SI-4.7}$$

In the previous equations, ξ is a viscosity parameter given by:

$$\xi = \frac{T_c^{1/6}}{M^{1/2}P_c^{2/3}} \tag{SI-4.8}$$

with P_c in atm, M (molecular weight) in g/mol and T_c in K.

μ^* = low pressure (0.2 - 5 atm) viscosity (cP)

$T_R = T/T_c$ = reduced temperature

$Z_c = P_c V_c/(RT_c)$ = compressibility factor at the critical point

The low pressure (0.1 MPa) viscosity estimated for all components can be found in Table SI-4.5.

Table SI-4.5: Pure component viscosity at low pressure (0.1 MPa) and 573.15 K

Component	μ^* (cP)
CO	0.022257
CH_3OH	0.018992
H_2	0.011661
H_2O	0.020188
CH_4	0.017950
CO_2	0.026661

4.4 Estimation of high pressure viscosity, μ

Correlations for viscosity at high pressure have been developed as function of reduced density by Jossi, Stiel and Thodos [12]. The general equation over a wide range of reduced densities (0.002 - 4) is given by:

$$[(\mu - \mu^*)\xi + 10^{-4}]^{1/4} = 0.10230 + 0.023364\rho_R + 0.058533\rho_R^2 - 0.040758\rho_R^3 + 0.0093324\rho_R^4 \quad \text{(SI-4.9)}$$

Less complex expressions have been developed by the same authors for a restricted range of reduced densities:

$$(\mu - \mu^*)\xi = [23.12e^{1.079\rho_R} - 25] \times 10^{-5}, \quad 0.3 \leq \rho_R \leq 2.0 \quad \text{(SI-4.10)}$$

$$(\mu - \mu^*)\xi = 11.0 \times 10^{-5}[e^{1.584\rho_R} - 1], \quad \rho_R < 0.3 \quad \text{(SI-4.11)}$$

The relationship described by equation (SI-4.9) deviates significantly for hydrogen and water. For these substances, the following expressions are valid:

- Hydrogen

$$[(\mu - \mu^*)\xi + 10^{-4}]^{1/4} = 0.10616 - 0.042426\rho_R + 0.17553\rho_R^2 - 0.12295\rho_R^3 + 0.028149\rho_R^4 \quad \text{(SI-4.12)}$$

- Water

$$[(\mu - \mu^*)\xi + 10^{-4}]^{1/4} = 0.10721 + 0.040646\rho_R + 0.0026282\rho_R^2 - 0.0054430\rho_R^3 + 0.0017979\rho_R^4 \quad \text{(SI-4.13)}$$

where:

ξ = viscosity parameter (equation (SI-4.8))

μ^* = low pressure viscosity (cP) (calculated in Section 4.3)

$\rho_R = \rho/\rho_c = \rho \cdot V_c$ = reduced density, with ρ calculated with an equation of state (in this work, PR and PC-SAFT EoS)

μ = high pressure viscosity (cP)

The estimated viscosity at high pressure for all components, using the densities calculated by both PR and PC-SAFT EoS, is given in Table SI-4.6.

Table SI-4.6: Pure component viscosities at high pressure (10 MPa) and 573.15 K with densities computed with PR and PC-SAFT EoS

Component	μ_{PR} (cP)	$\mu_{\text{PC-SAFT}}$ (cP)
CO	0.023208	0.023203
CH_3OH	0.022462	0.022065
H_2	0.011722	0.011722
H_2O	0.023893	0.023562
CH_4	0.018847	0.018850
CO_2	0.028519	0.028549

4.5 Estimation of low pressure gas diffusion coefficients, D^*_{ij}

The Fuller-Giddings-Schettler equation can be utilized to estimate binary diffusion coefficients of gases at low pressure [3]. In this case, composition does not heavily affect binary diffusivities, therefore infinite dilution coefficients are obtained from equation (SI-4.14) directly, $D^*_{ij} = D^*_{ji} = D^{*\circ}_{ji} = D^{*\circ}_{ij}$.

$$D^*_{ij} = D^*_{ji} = \frac{0.00143T^{1.75}}{PM_{ij}^{1/2}[\upsilon_i^{1/3} + \upsilon_j^{1/3}]^2} \tag{SI-4.14}$$

where:

D^*_{ij} = binary diffusion coefficient at low pressure (cm^2/s)

T = temperature (K)

$M_{ij} = 2[(1/M_i) + 1/M_j]^{-1}$, M_i and M_j are component molecular weights (g/mol)

P = pressure (bar)

υ = diffusion volume of the molecule (can be estimated by the summation of tabulated atomic diffusion volumes)

Necessary data to apply this correlation are presented in Table SI-4.1. The required diffusion volumes are: 18.0 (CO), 31.25 (CH_3OH), 6.12 (H_2), 13.1 (H_2O), 25.14 (CH_4) and 26.9 (CO_2). The diffusion coefficients at low pressure for all pairs of components are given in Table SI-4.7.

Table SI-4.7: Estimated binary diffusion coefficients at infinite dilution (cm^2/s) using the Fuller-Giddings-Schettler equation at 0.1 MPa and 573.15 K. Note: $D^{*\circ}_{ij} = D^{*\circ}_{ji}$

Components	**CO**	**CH_3OH**	**H_2**	**H_2O**	**CH_4**	**CO_2**
CO	-	0.5274	2.5000	0.8273	0.6900	0.5201
CH_3OH	0.5274	-	1.9885	0.6592	0.5618	0.4174
H_2	2.5000	1.9885	-	2.8766	2.2402	2.0999
H_2O	0.8273	0.6592	2.8766	-	0.8338	0.6625
CH_4	0.6900	0.5618	2.2402	0.8338	-	0.5638
CO_2	0.5201	0.4174	2.0999	0.6625	0.5638	-

4.6 Estimation of high pressure diffusion coefficients, D_{ij}

Binary diffusion coefficients at high pressure can be estimated by the correlation developed by Riazi and Whitson [3]:

$$\frac{\rho D_{ij}}{(\rho D_{ij})^*} = 1.07\left(\frac{\mu}{\mu^*}\right)^{b+cP_R} \tag{SI-4.15}$$

where:

$b = -0.27 - 0.38\omega$

$c = -0.05 + 0.1\omega$

$\omega = x_i\omega_i + x_j\omega_j$ = acentric factor of the binary mixture

μ^* = viscosity at low pressure

$P_R = P/P_c$ = reduced pressure of the mixture

$P_c = x_iP_{ci} + x_jP_{cj}$ = critical pressure of the binary mixture

$(\rho D_{ij})^*$ = product of density and binary diffusion coefficient evaluated at low pressure

In the present work, only infinite dilution binary coefficients are needed. Thus, the physical properties of the mixture are approximated by the solvent properties: as $x_i \to 0$, $P_c \to P_{cj}$, $\omega \to \omega_j$, $\mu \to \mu_j$, $\rho \to \rho_j$, $D_{ij} \to D^{\circ}_{ij}$.

Tables SI-4.8 and SI-4.9 contain the high pressure binary diffusion coefficients at infinite dilution calculated with pure component densities obtained with PR and PC-SAFT EoS, respectively.

Table SI-4.8: Binary diffusion coefficients at infinite dilution (cm^2/s) of each pair of components at 573.15 K and high pressure (10 MPa). Densities were estimated by PR EoS

	Solvent					
Solute	**CO**	**CH_3OH**	**H_2**	**H_2O**	**CH_4**	**CO_2**
CO	-	0.003527	0.027337	0.005585	0.007314	0.005279
CH_3OH	0.005740	-	0.021743	0.004449	0.005955	0.004236
H_2	0.027213	0.013298	-	0.019417	0.023745	0.021313
H_2O	0.009006	0.004408	0.031455	-	0.008838	0.006724
CH_4	0.007511	0.003757	0.024496	0.005628	-	0.005723
CO_2	0.005661	0.002791	0.022962	0.004472	0.005976	-

Table SI-4.9: Binary diffusion coefficients at infinite dilution (cm^2/s) of each pair of components at 573.15 K and high pressure (10 MPa). Densities were estimated by PC-SAFT EoS

	Solvent					
Solute	**CO**	**CH_3OH**	**H_2**	**H_2O**	**CH_4**	**CO_2**
CO	-	0.003866	0.027553	0.006608	0.007293	0.005209
CH_3OH	0.005770	-	0.021915	0.005265	0.005938	0.004180
H_2	0.027355	0.014577	-	0.022976	0.023679	0.021030
H_2O	0.009053	0.004832	0.031703	-	0.008813	0.006635
CH_4	0.007550	0.004118	0.024690	0.006660	-	0.005647
CO_2	0.005691	0.003060	0.023143	0.005291	0.005960	-

5 Detailed results for the liquid and gas phase effective diffusivities

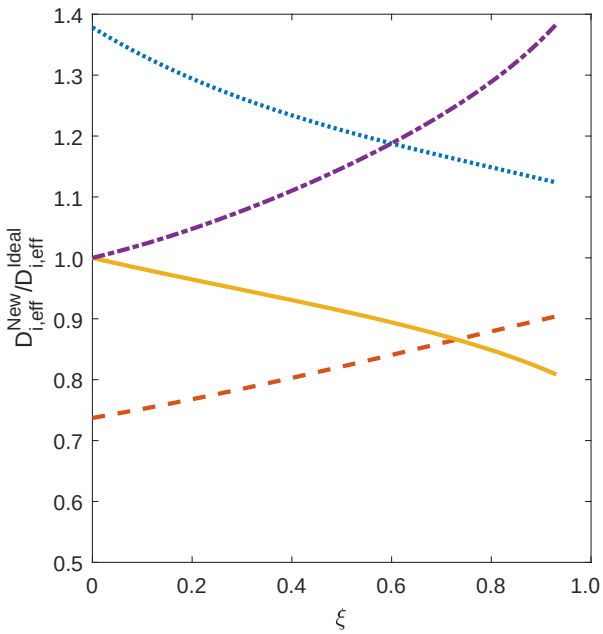
This section contains detailed figures and results for the models that were not emphasized in the main text of the article, namely those by Burghardt and Krupiczka [13], Kubota *et al.* [14], and Kato *et al.* [15].

5.1 Liquid phase reaction: ethyl acetate synthesis

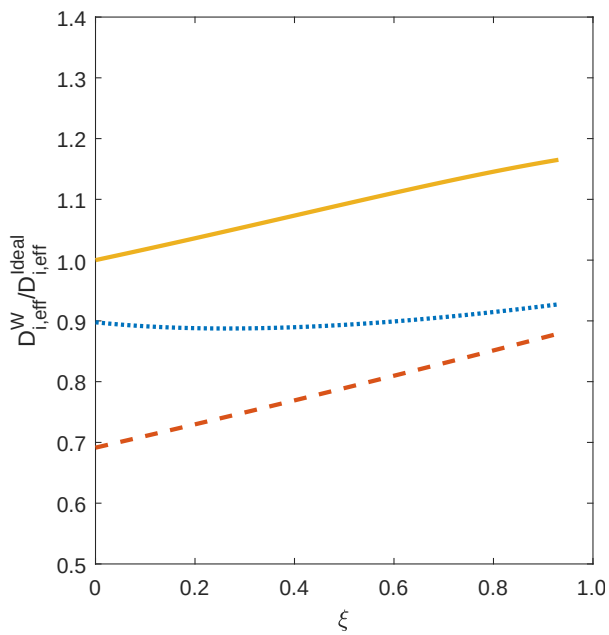
Results for the $D_{i,\text{eff}}^{Model}/D_{i,\text{eff}}^{Ideal}$ ratios at the initial and final (equilibrium) compositions of the reaction mixture are shown in Table SI-5.1. Figure SI-5.1 illustrates these ratios as function of the extent of reaction for the new model and other models, except that by Kubota *et al.*

Table SI-5.1: Effective diffusivities ratios $D^{Model}_{i,\text{eff}}/D^{Ideal}_{i,\text{eff}}$ for an initial equimolar reactants mixture at the beginning ($\xi = 0$; values enclosed in parentheses) and equilibrium ($\xi_{eq} = 0.931$) at 78 °C, using UNIFAC model for the activity coefficients

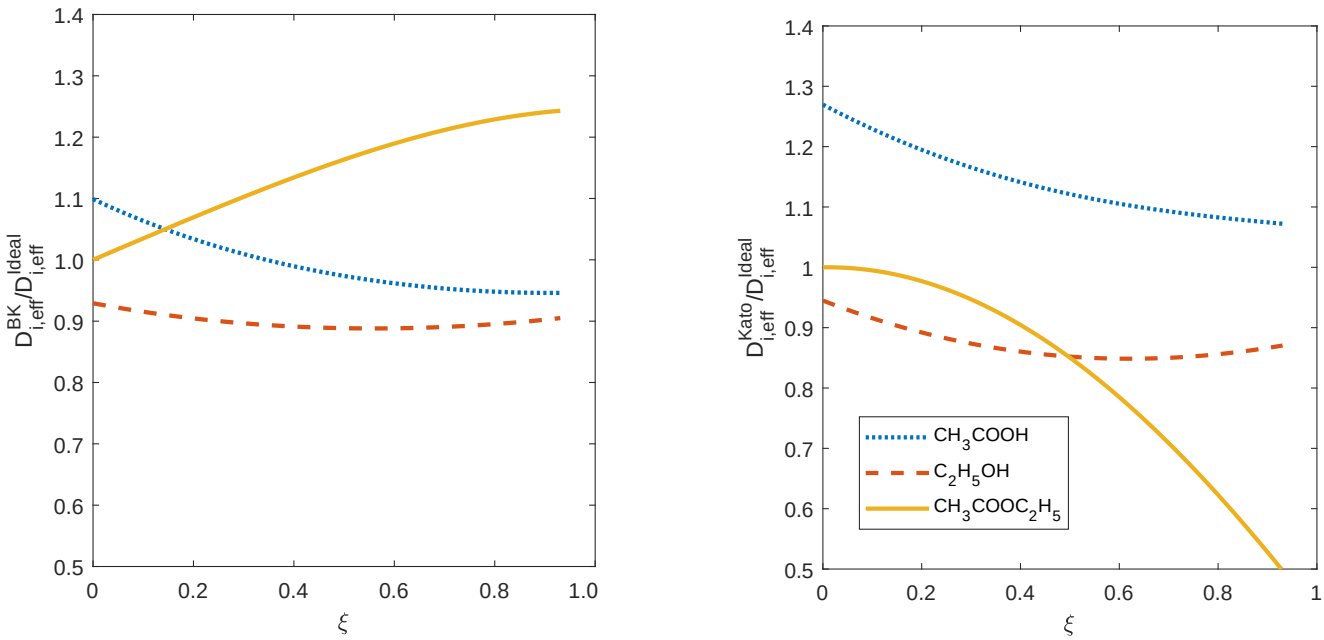
Component		**CH_3COOH**	**CH_3CH_2OH**	**$CH_3COOCH_2CH_3$**	**H_2O**
Initial mole fractions		(0.500)	(0.500)	(0.000)	(0.000)
Equilibrium mole fractions		0.190	0.190	0.310	0.310
Ratio	**Reference Model**				
$D^{New}_{i,\text{eff}}/D^{Ideal}_{i,\text{eff}}$	New	(1.379)	(0.737)	(1.0000	(1.000)
	Eqs. (11), (14)	1.124	0.904	0.809	1.384
$D^{W}_{i,\text{eff}}/D^{Ideal}_{i,\text{eff}}$	Wilke	(0.898)	(0.691)	(1.000)	-
	Eq. (5)	0.927	0.879	1.651	
$D^{BK}_{i,\text{eff}}/D^{Ideal}_{i,\text{eff}}$	Burghardt and	(1.099)	(0.929)	(1.000)	-
	Krupiczka Eq. (8)	0.946	0.905	1.243	
$D^{Kato}_{i,\text{eff}}/D^{Ideal}_{i,\text{eff}}$	Kato *et al.*	(1.270)	(0.945)	(1.000)	-
	Eq. (9)	1.072	0.870	0.498	



(a)



(b)



(c) (d)

Figure SI-5.1: Effective diffusivities ratios from $\xi = 0$ up to equilibrium ($\xi_{eq} = 0.931$) for an initial equimolar reactants mixture at 78 °C: (a) $D^{New}_{i,\text{eff}}/D^{Ideal}_{i,\text{eff}}$, (b) $D^{W}_{i,\text{eff}}/D^{Ideal}_{i,\text{eff}}$, (c) $D^{BK}_{i,\text{eff}}/D^{Ideal}_{i,\text{eff}}$, and (d) $D^{Kato}_{i,\text{eff}}/D^{Ideal}_{i,\text{eff}}$

The model by Kato *et al.* [15] (Figure SI-5.1d) for ethyl acetate ($CH_3COOC_2H_5$) diverges quite significantly from the results achieved with Burghardt and Krupiczka, and Wilke equations, as its curve is monotonically decreasing, while these two are strictly increasing. In this sense, its trend is similar to the new model, though with a higher slope in absolute value, which results in a large difference of effective diffusivities ratios at equilibrium, as can be seen in Table SI-5.1. Furthermore, the curve for ethanol in Figure SI-5.1d is very different from that of the new model, almost plateauing after an initial descent, which is distinct from Figure SI-5.1a, where the curve for this component increases almost linearly with the extent of reaction. Hence, despite the fact the Kato *et al.* equation [15] is the unique reference model that accounts for the non-ideal behavior of the mixture, the method by which the effective diffusivities are calculated (by simply equating them to the main diagonal elements of matrix $[D]$), clearly gives rise to substantial discrepancies in comparison with the new model.

In Table SI-5.1, little agreement is observed amongst the values of all models. For instance, at $\xi = 0$, the acetic acid effective diffusivities ratio is greatly underestimated by the Wilke [16] and Burghardt and Krupiczka models [13], whereas ethanol tends to be overestimated by Burghardt and Krupiczka [13], and Kato *et al.* [15]. At equilibrium, $\xi_{eq} = 0.931$, the models of Wilke [16] and Burghardt and Krupiczka [13] exhibit a large degree of similarity between the effective diffusivities ratios of CH_3COOH and CH_3CH_2OH (*ca.* 5% difference), whereas the new model achieves values *ca.* 24% different.

5.2 Gas phase reaction: high pressure methanol synthesis

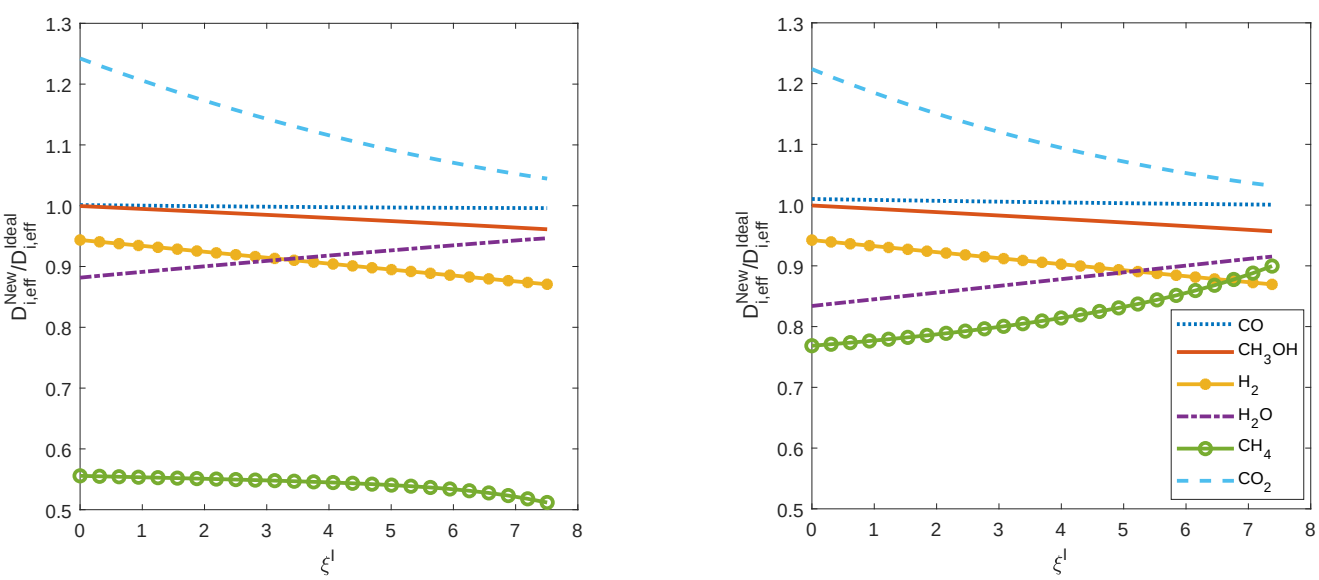
Tables SI-5.2 and SI-5.3 contain the $D_{i,\text{eff}}^{Model}/D_{i,\text{eff}}^{Ideal}$ ratios using PR and PC-SAFT EoS, respectively. Figures SI-5.2 through SI-5.4 show the evolution of these ratios as function of ξ^I for both EoS, respectively. The discussion pertaining the results in Figure SI-5.2 can be read in the main text of the article.

Table SI-5.2: Effective diffusivities ratios $D_{i,\text{eff}}^{Model}/D_{i,\text{eff}}^{Ideal}$ at the beginning ($\xi^I = 0$; $\xi_{eq}^{II} = 0.1014$; values enclosed in parentheses) and equilibrium ($\xi_{eq}^{I} = 7.5068$; $\xi_{eq}^{II} = 0.2994$), calculated using Peng-Robinson EoS for the fugacity coefficients at 573.15 K and 10 MPa

Component		**CO**	**CH_3OH**	**H_2**	**H_2O**	**CH_4**	**CO_2**
Initial mole fractions		(0.1224)	(0.0012)	(0.7084)	(0.0026)	(0.1490)	(0.0164)
Equilibrium mole fractions		0.0580	0.0897	0.6545	0.0054	0.1753	0.0170
Ratio	**Reference Model**						
$D_{i,\text{eff}}^{New}/D_{i,\text{eff}}^{Ideal}$	New	(1.0011)	(0.9994)	(0.9436)	(0.8818)	(0.5557)	(1.2420)
	Eqs. (11), (14)	0.9961	0.9612	0.8708	0.9467	0.5114	1.0444
$D_{i,\text{eff}}^{W}/D_{i,\text{eff}}^{Ideal}$	Wilke	(1.5792)	(1.0003)	(1.3823)	(0.6567)	(0.1049)	-
	Eq. (5)	1.2087	1.0210	1.2789	0.8182	0.0495	
$D_{i,\text{eff}}^{K}/D_{i,\text{eff}}^{Ideal}$	Kubota *et al.*	(1.3296)	(0.9976)	(3.3785)	(0.7039)	(0.0000)	-
	Eqs. (7)	1.1428	0.8450	2.7918	0.9059	0.0000	
$D_{i,\text{eff}}^{BK}/D_{i,\text{eff}}^{Ideal}$	Burghardt and	(1.2416)	(0.9979)	(1.2745)	(0.6543)	(0.0812)	-
	Krupiczka Eq. (8)	1.1177	0.8645	1.2579	0.8124	0.0393	
$D_{i,\text{eff}}^{Kato}/D_{i,\text{eff}}^{Ideal}$	Kato	(1.2875)	(0.9972)	(1.3175)	(0.6546)	(0.0827)	-
	Eq. (9)	1.1343	0.8131	1.2418	0.8125	0.0400	

Table SI-5.3: Effective diffusivities ratios $D^{Model}_{i,\text{eff}}/D^{Ideal}_{i,\text{eff}}$ at the beginning ($\xi^I = 0$; $\xi^{II}_{eq} = 0.0935$; values enclosed in parentheses) and equilibrium ($\xi^I_{eq} = 7.3797$ and $\xi^{II}_{eq} = 0.2894$) calculated using PC-SAFT EoS for the fugacity coefficients at 573.15 K and 10 MPa

Component		**CO**	**CH_3OH**	**H_2**	**H_2O**	**CH_4**	**CO_2**
Initial mole fractions		(0.1223)	(0.0012)	(0.7085)	(0.0025)	(0.1490)	(0.0165)
Equilibrium mole fractions		0.0592	0.0880	0.6557	0.0053	0.1748	0.0170
Ratio	**Reference Model**						
$D^{New}_{i,\text{eff}}/D^{Ideal}_{i,\text{eff}}$	New	(1.0100)	(0.9994)	(0.9424)	(0.8336)	(0.7685)	(1.2244)
	Eqs. (11), (14)	1.0007	0.9569	0.8695	0.9152	0.8996	1.0319
$D^{W}_{i,\text{eff}}/D^{Ideal}_{i,\text{eff}}$	Wilke	(1.5479)	(0.9675)	(1.3535)	(0.6644)	(0.1659)	-
	Eq. (5)	1.1855	0.9827	1.2464	0.7727	0.1102	
$D^{K}_{i,\text{eff}}/D^{Ideal}_{i,\text{eff}}$	Kubota *et al.*	(1.3034)	(0.9649)	(3.3085)	(0.7086)	(0.0000)	-
	Eqs. (7)	1.1165	0.8188	2.6910	0.7899	0.0000	
$D^{BK}_{i,\text{eff}}/D^{Ideal}_{i,\text{eff}}$	Burghardt and	(1.2171)	(0.9652)	(1.2481)	(0.6614)	(0.1284)	-
	Krupiczka Eq. (8)	1.0938	0.8346	1.2246	0.7673	0.0876	
$D^{Kato}_{i,\text{eff}}/D^{Ideal}_{i,\text{eff}}$	Kato	(1.2715)	(0.9644)	(1.2649)	(0.6618)	(0.1320)	-
	Eq. (9)	1.1136	0.7820	1.1901	0.7676	0.0899	



(a) (b)

Figure SI-5.2: Effective diffusivities ratios $D^{New}_{i,\text{eff}}/D^{Ideal}_{i,\text{eff}}$ as function of extent of reaction I, up to equilibrium, at 573.15 K and 10 MPa, using (a) PR EoS ($\xi^I_{eq} = 7.5068$; $\xi^{II}_{eq} = 0.2994$), and (b) PC-SAFT EoS ($\xi^I_{eq} = 7.3797$; $\xi^{II}_{eq} = 0.2894$)

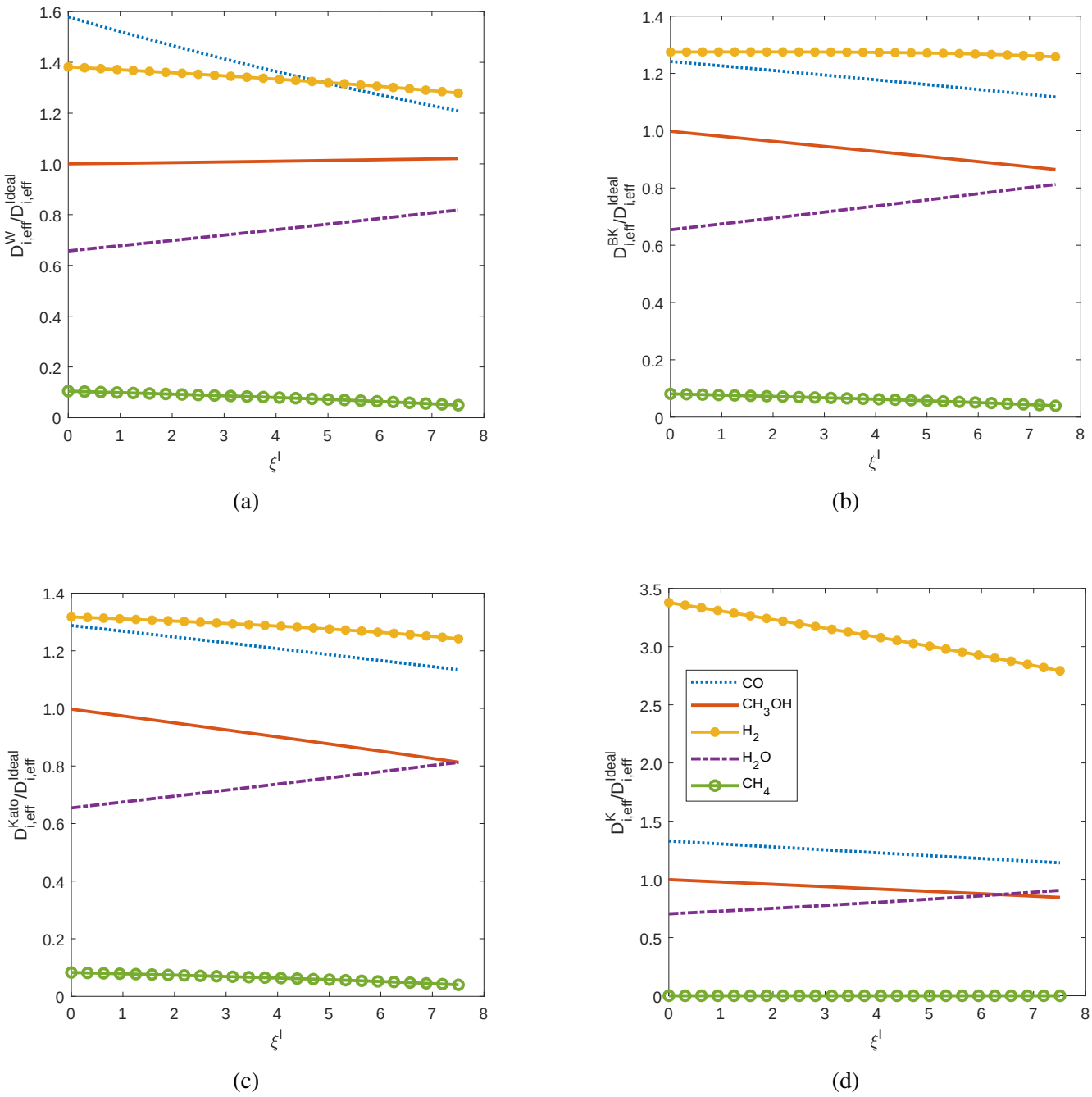


Figure SI-5.3: Effective diffusivities ratios $D_{i,\text{eff}}^{Model}/D_{i,\text{eff}}^{Ideal}$ with fugacity coefficients computed with PR EoS at 573.15 K and 10 MPa: (a) Wilke, (b) Burghardt and Krupiczka, (c) Kato *et al*., and (d) Kubota *et al*.

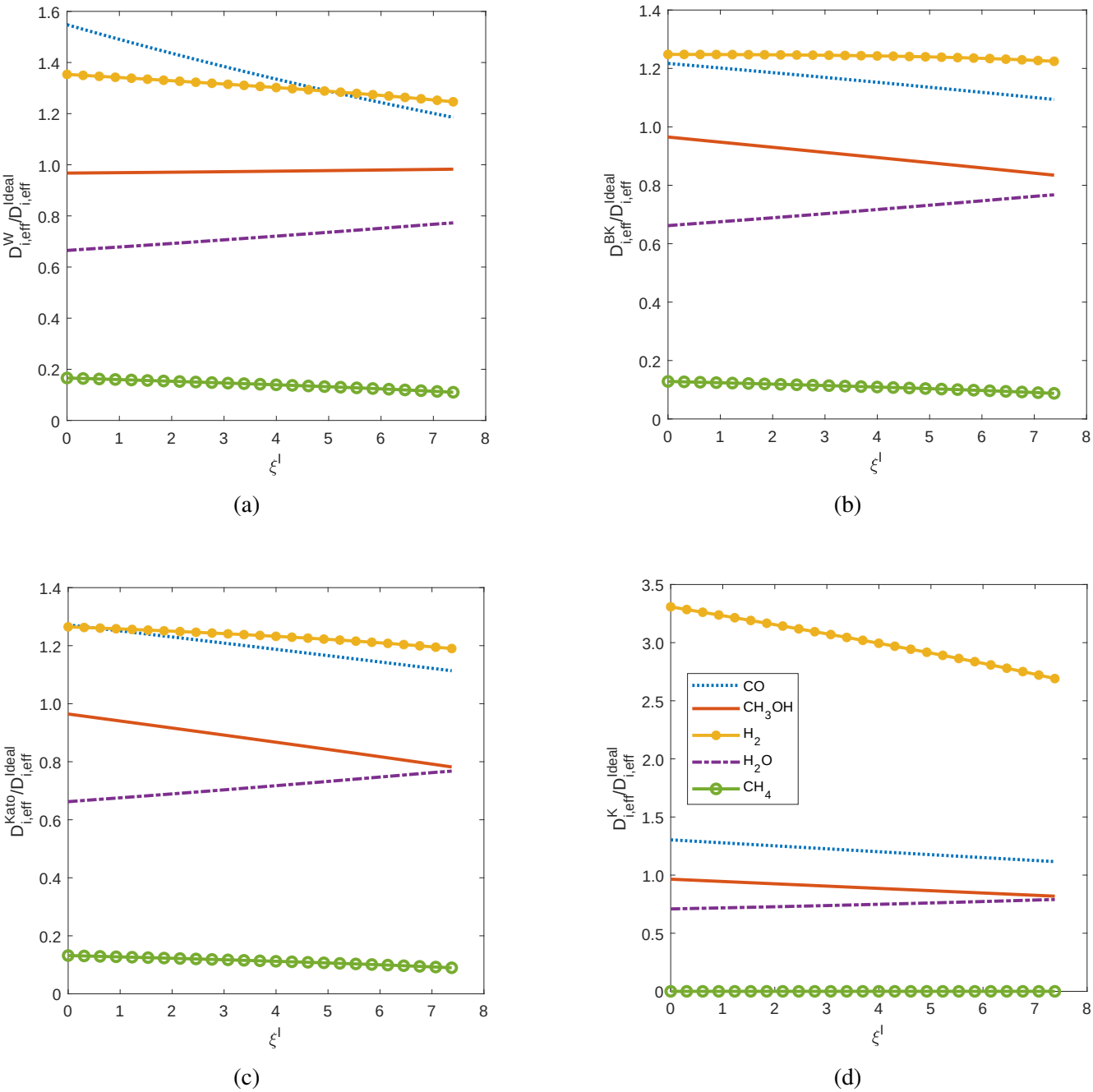


Figure SI-5.4: Effective diffusivities ratios $D_{i,\text{eff}}^{Model}/D_{i,\text{eff}}^{Ideal}$ with fugacity coefficients computed with PC-SAFT EoS at 573.15 K and 10 MPa: (a) Wilke, (b) Burghardt and Krupiczka, (c) Kato *et al.*, and (d) Kubota *et al.*

For models that do not directly involve fugacity coefficients in the determination of effective diffusivities (such as the models of Wilke [16], Burghardt and Krupiczka [13], Kubota *et al.* [14]), one would expect, at first glance, equal results between PR EoS and PC-SAFT EoS. However, all models embody diffusion fluxes ratios, which depend on the derivatives $d\xi_{eq}^{II}/d\xi^{I}$, where ξ_{eq}^{II} is obtained by solving an equation that is a function of the fugacity coefficients. Moreover, the Maxwell-Stefan (MS) diffusivities depend on the estimated high pressure binary diffusivities at infinite dilution, which requires pure component densities

at high pressure, whose values change according to the employed equation of state. This explains slight differences between the curves of the aforementioned models in Figures SI-5.3 and SI-5.4, and between the values in Tables SI-5.2 and SI-5.3.

In Table SI-5.2 at $\xi^I = 0$, the component whose effective diffusivity exhibits the smallest deviation to the ideal expression is methanol, as the ratios calculated by all models are very close to unity. This has been the unique agreement found amongst all models. On the other hand, large deviations are observed for CH_4 in Tables SI-5.2 and SI-5.3, for which the majority of the effective diffusivities ratios is almost null, which, when compared with the values yielded by the new model, show that they are greatly underestimated. Additionally, the model of Kubota *et al.* [14] shows large deviations for H_2, with ratios above 3 that are not found by any of the other models. In contrast, the equations of Burghardt and Krupiczka [13] and Kato *et al*. [15] tend to yield close results for most components, given that their equations are somewhat similar by neglecting the off-diagonal elements of matrices $[B]$ and $[D]$, respectively.

Nomenclature

a	UNIFAC energy of interaction parameter, K
B	Coefficients defined by equations (SI-2.2a) and (SI-2.2b), s/cm^2
C_T	Total concentration, mol/cm^3
D	Diffusion coefficient, cm^2/s
$Đ$	Maxwell-Stefan diffusion coefficient, cm^2/s
EoS	Equation of state
$\overline{J}$	Molar diffusion flux, mol/(cm^2 s)
k_{ij}	Binary interaction parameter
k_B	Boltzmann constant, J/K
M	Molecular weight, g/mol
$\overline{N}$	Molar flux, mol/(cm^2 s)
n	Number of components in a mixture
P	Pressure, MPa
PC-SAFT	Perturbed-Chain Statistical Associating Fluid Theory
PR	Peng-Robinson
Q	UNIFAC group surface area
q	UNIFAC relative molecule surface area
R	Ideal gas constant, cm^3 MPa/(K mol), or UNIFAC group volume
r	UNIFAC relative molecule volume
T	Temperature, K
X	UNIFAC group mole fraction
x	Mole fraction in the liquid phase
y	Mole fraction in the gas phase
Z	Compressibility factor

Greek Letters

Γ_{ij}	UNIFAC group activity coefficient or element of [Γ] matrix
γ	Activity coefficient
δ	Kronecker function
Θ	UNIFAC group surface fraction
θ	UNIFAC molecular surface fraction
μ	Viscosity, cP
ξ	Viscosity parameter as defined by equation (SI-4.8)
ρ	Molar density, mol/cm^3
υ	Fuller-Giddings-Schettler equation molecular diffusion volume
Φ	UNIFAC molecular volume fraction
ϕ	Solvent association factor of Wilke-Chang equation
$\hat{\phi}$	Fugacity coefficient
Ψ	UNIFAC molecular energy parameter
ω	Acentric factor

Subscripts

bp	Boiling point
c	Critical point
eff	Effective
ij	Refers to the pair of components ij
i, j, n	Arbitrary component identification
p	Pure component
R	Reduced

Superscripts

$*$	Low pressure
$\circ$	Infinite dilution
BK	Burghardt and Krupiczka effective diffusivity model
$COMB$	UNIFAC combinatorial part of the activity coefficient
$Ideal$	Ideal (Bird *et al.*) effective diffusivity model
ig	Ideal gas
inv	Element of inverse matrix
K	Kubota *et al.* effective diffusivity model
$Kato$	Kato *et al.* effective diffusivity model
New	New effective diffusivity model
RES	UNIFAC residual part of the activity coefficient
W	Wilke effective diffusivity model

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