Supplementary material to accompany:

Diffusion of alkane mixtures in zeolites. Validating the Maxwell-Stefan formulation using MD simulations.

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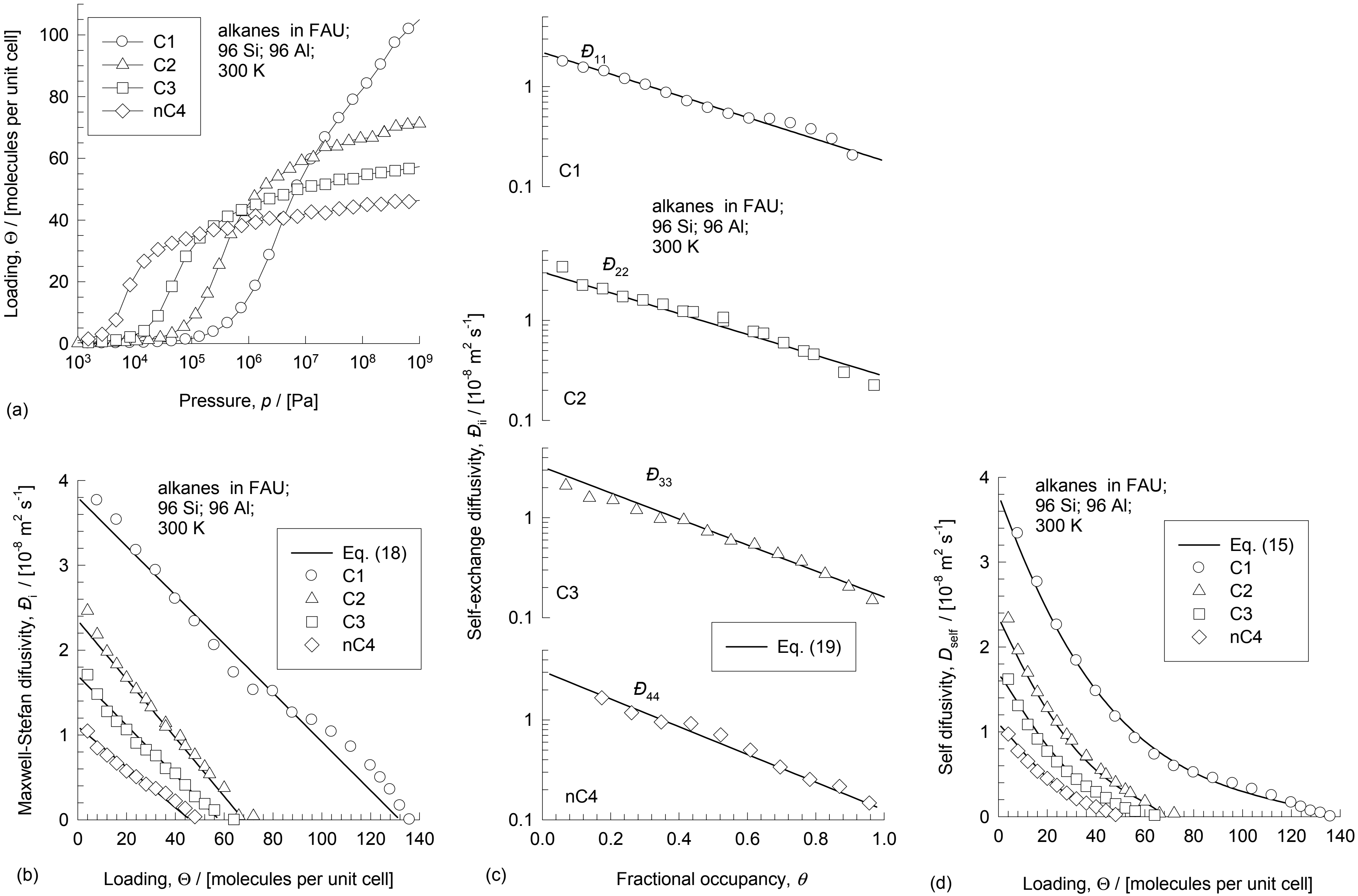
Contents:

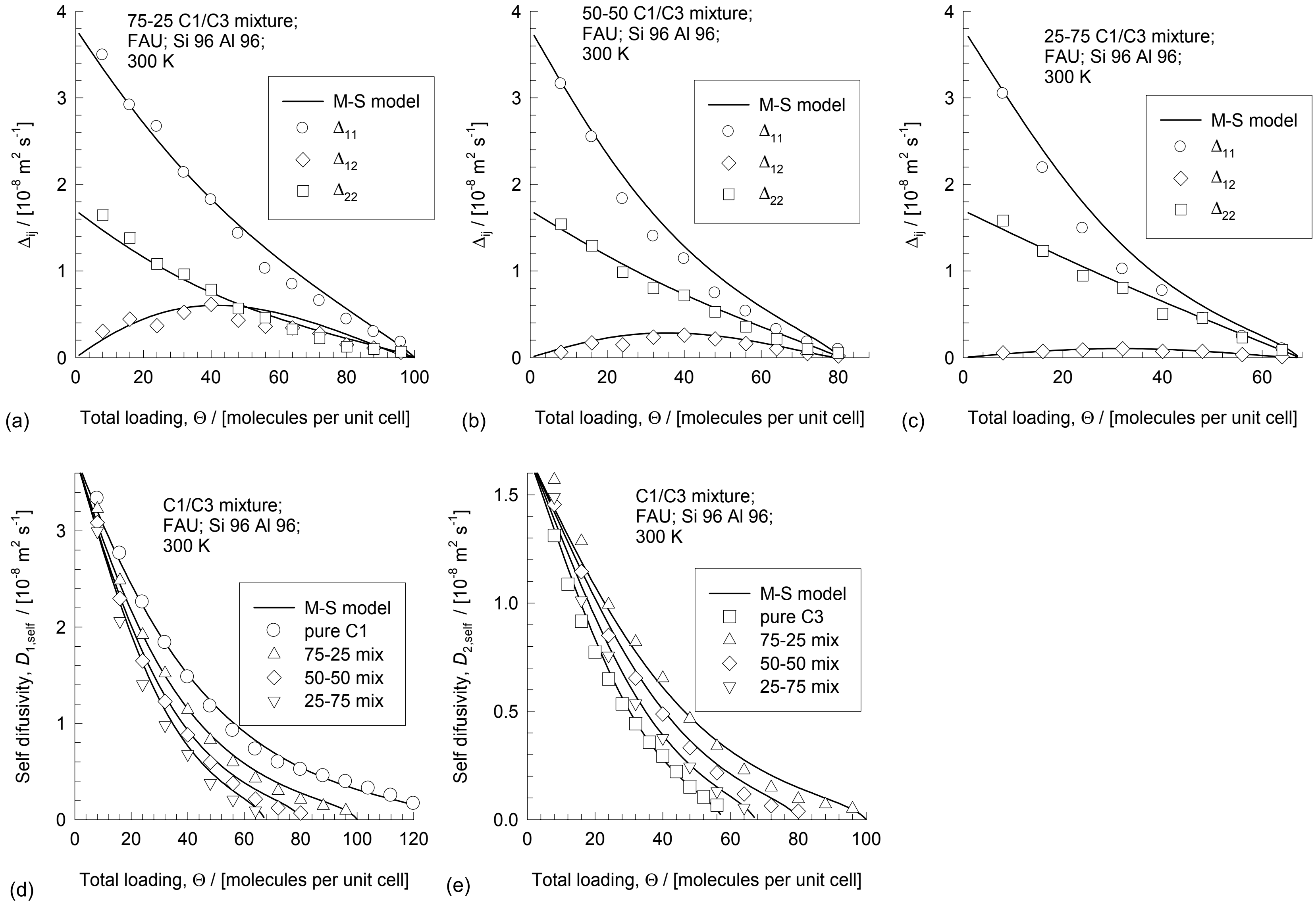
Appendix A

- Contains data on Δ_{ij}, $D_{i,self}$, $Đ_{i}$, $Đ_{ii}$ for all the campaigns listed in Table 1 of the manuscript
- The symbols represent the MD simulated data, or data derived from the MD data using Eqs (12), (13) and (16)
- The continuous solid lines represent calculations based on fits of the pure component parameters listed in Tables 2 and 3.
- The Equation numbers in the graphs refer to the equations in the manuscript of the main paper

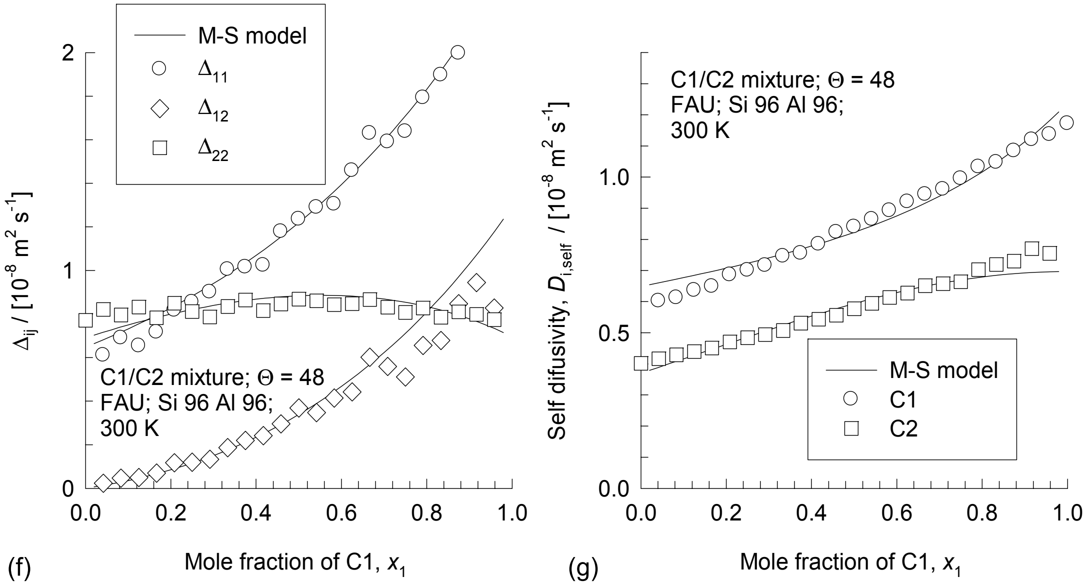
FAU; 300 K; pure component data; C1, C2, C3 and nC4



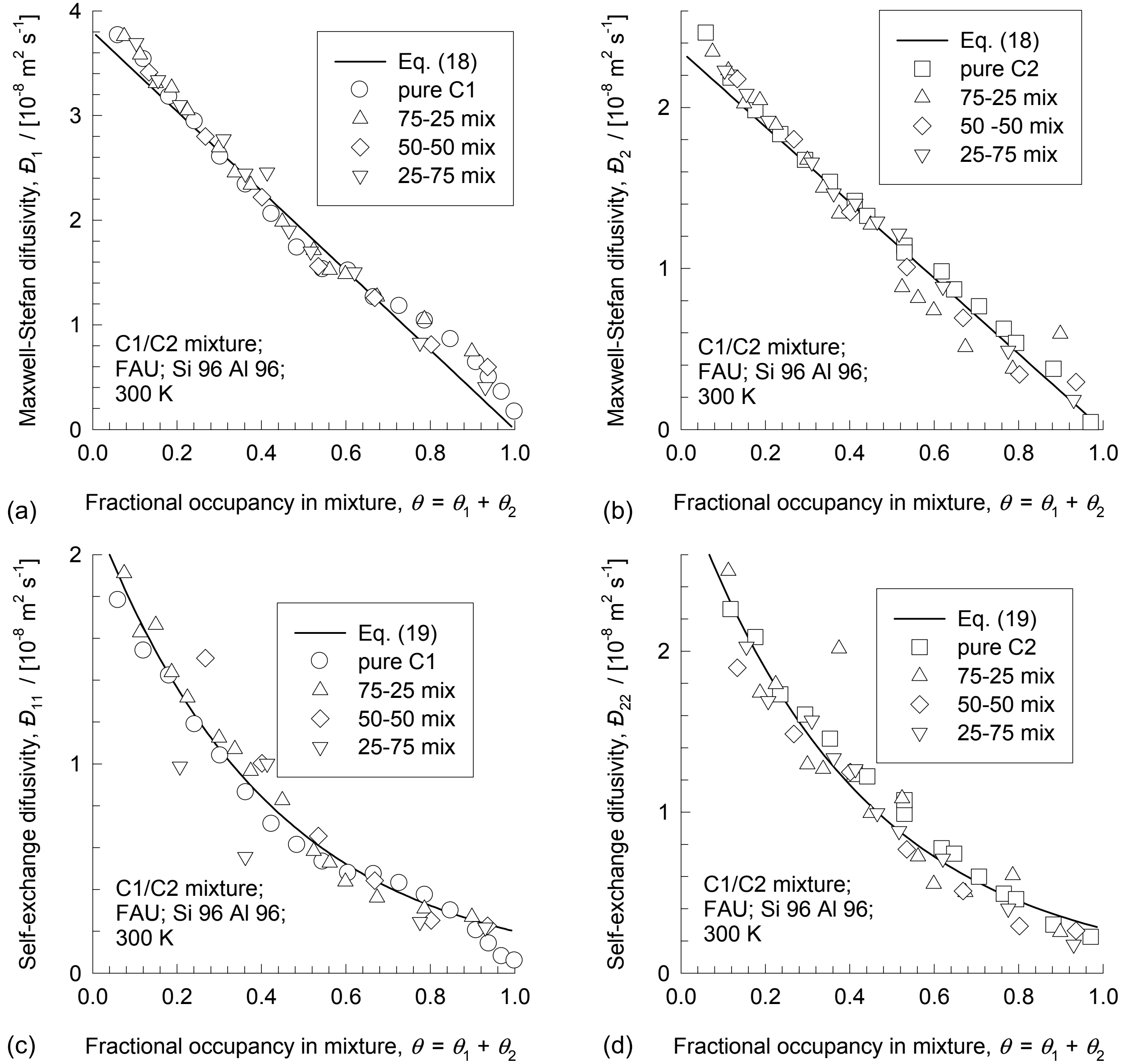
FAU; 300 K; C1/C2 75-25, 50-50, 25-75 mix; varying loadings



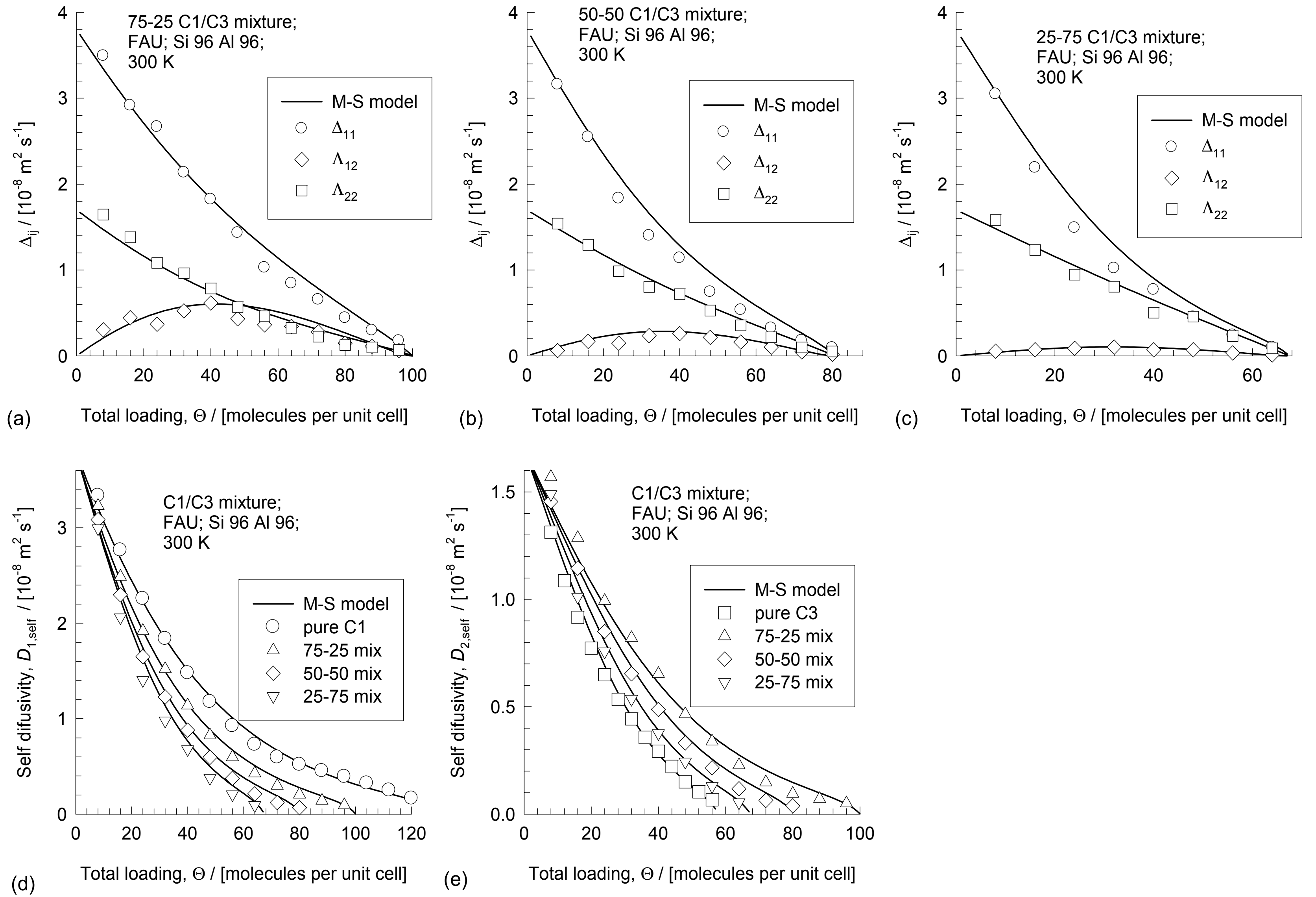
FAU; 300 K; C1/C2 binary; Θ = 48; varying compositions



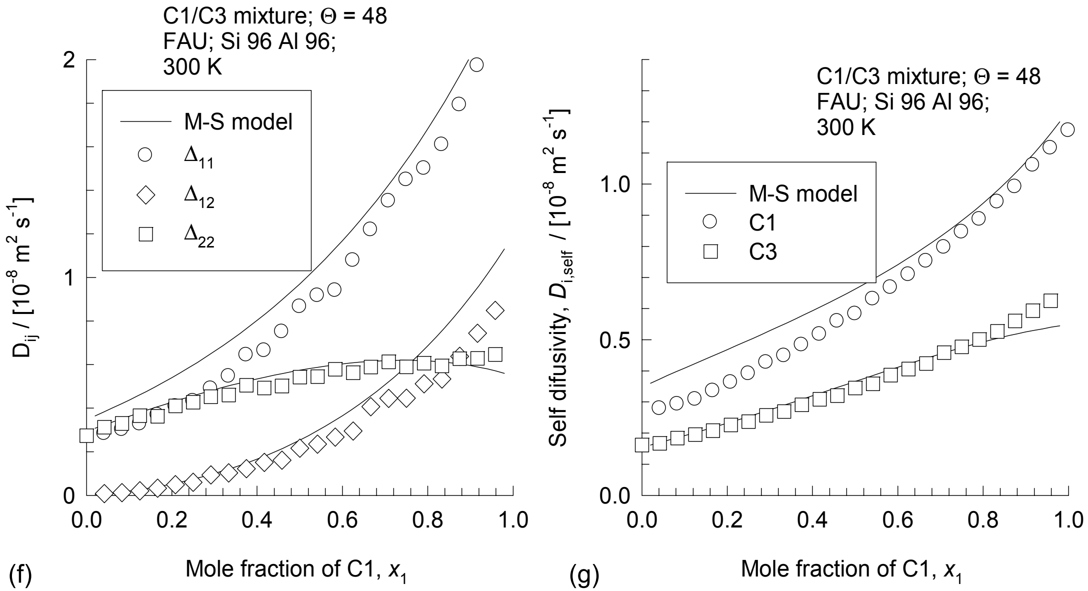
FAU; 300 K; C1/C2 75-25, 50-50, 25-75 binary mixtures; Data on $Đ_i$ and $Đ_{ii}$ backed out from MD simulations



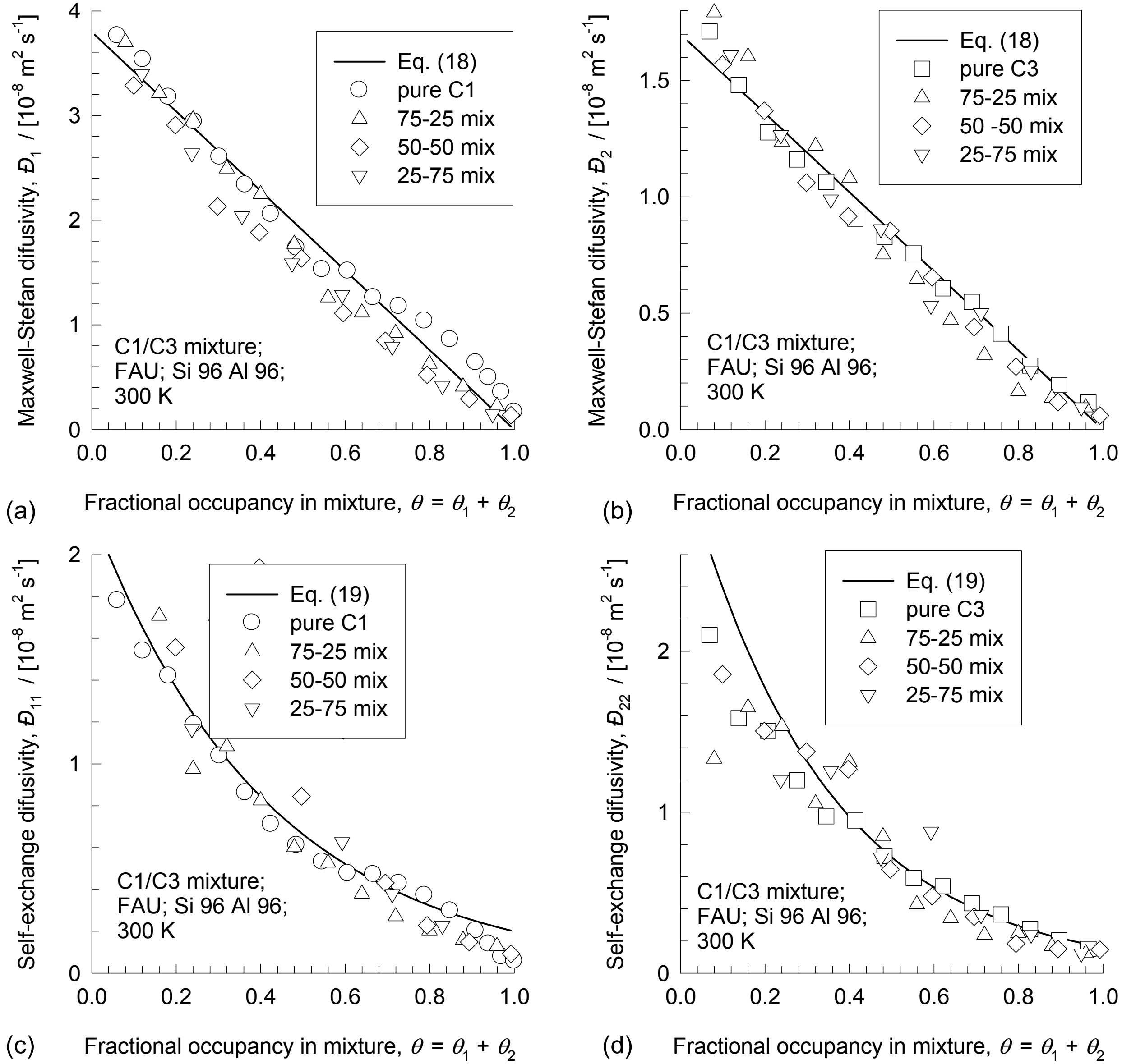
FAU; 300 K; C1/C3 75-25, 50-50, 25-75 mix; varying loadings



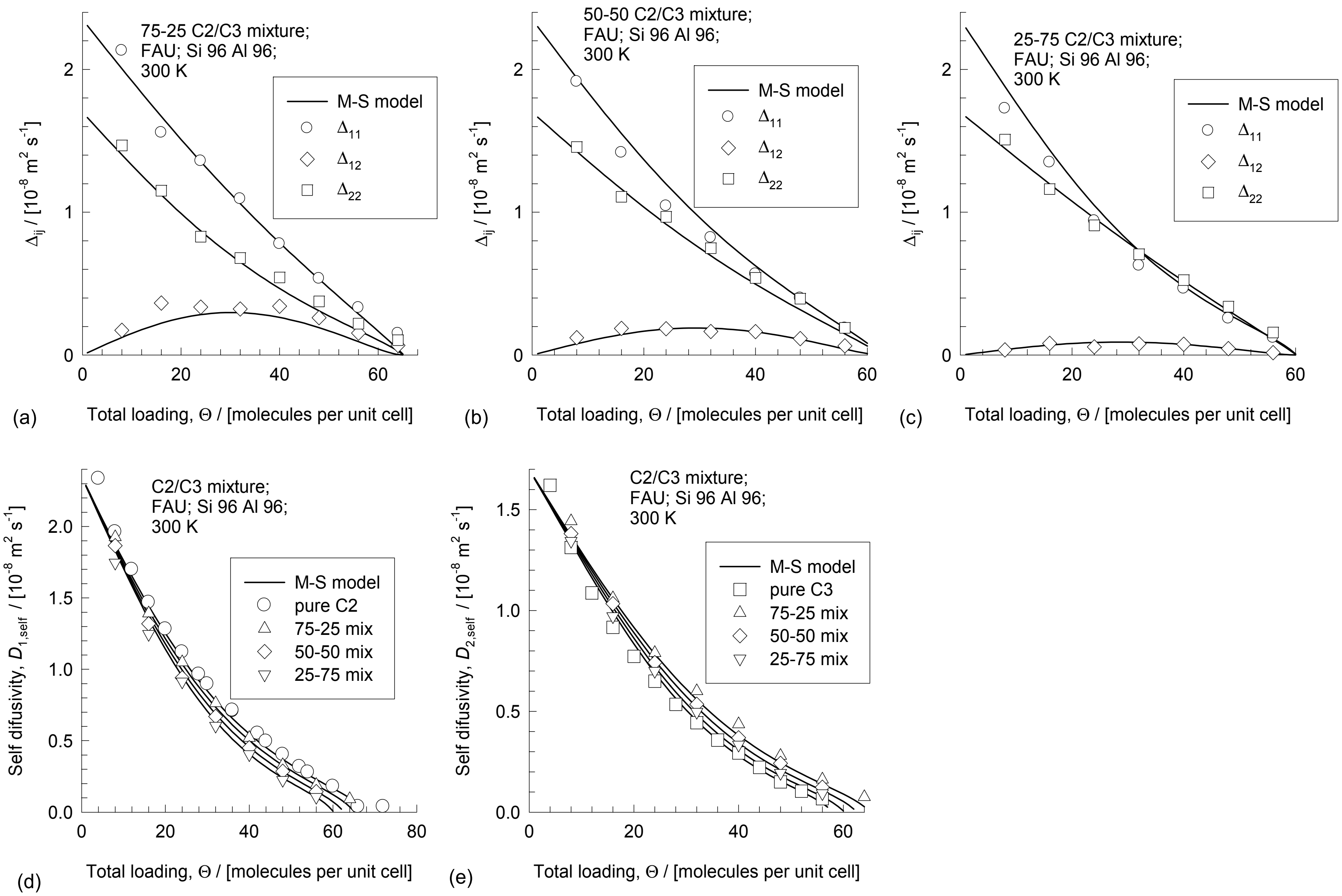
FAU; 300 K; C1/C3 binary; Θ = 48; varying compositions



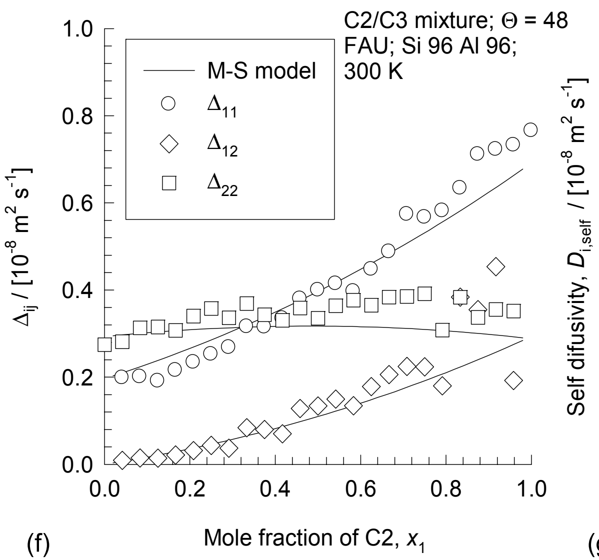
FAU; 300 K; C1/C3 75-25, 50-50, 25-75 binary mixtures; Data on $Đ_i$ and $Đ_{ii}$ backed out from MD simulations



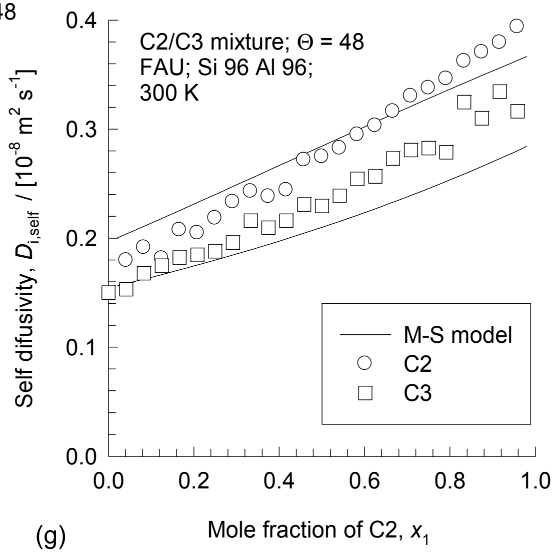
FAU; 300 K; C2/C3 75-25, 50-50, 25-75 mix; varying loadings



FAU; 300 K; C2/C3 binary; Θ = 48; varying compositions

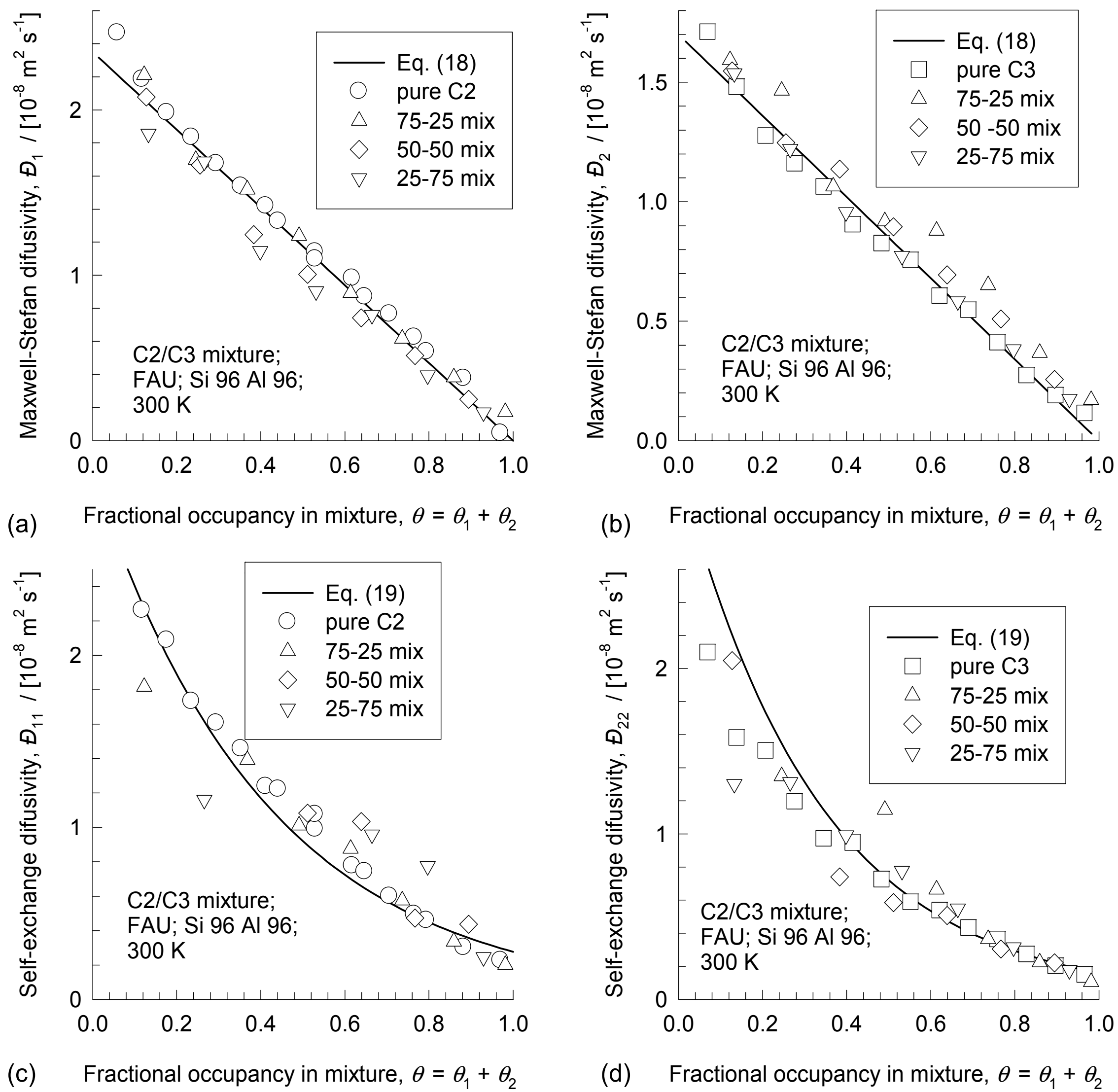


(f)

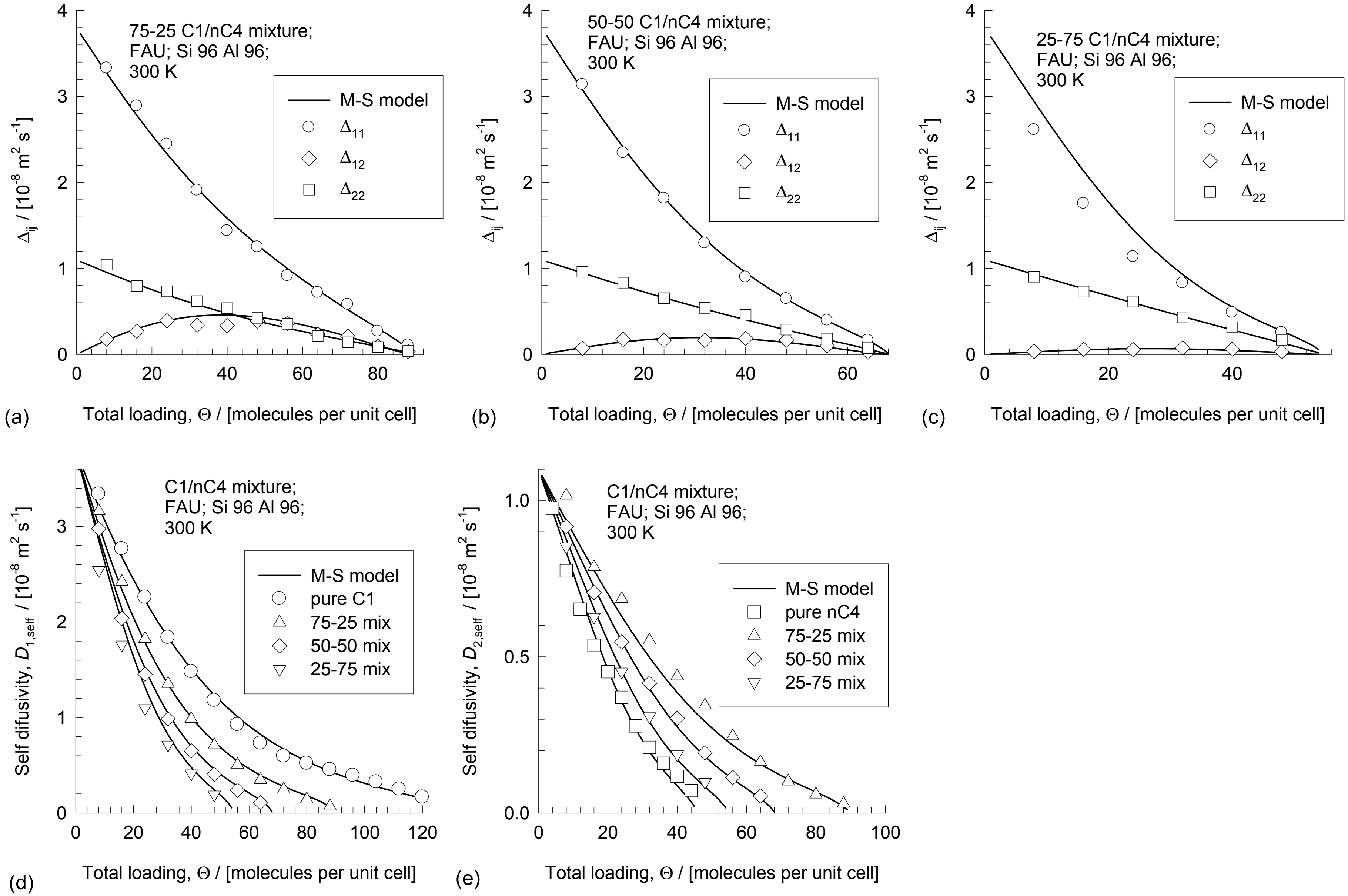


(g)

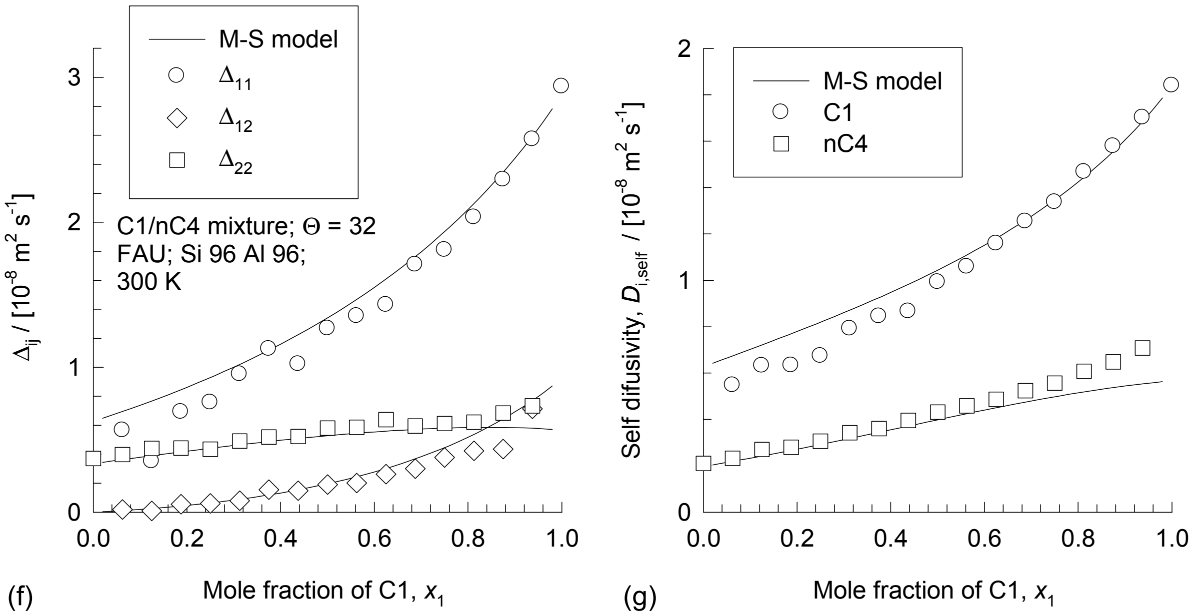
FAU; 300 K; C2/C3 75-25, 50-50, 25-75 binary mixtures; Data on $Đ_i$ and $Đ_{ii}$ backed out from MD simulations



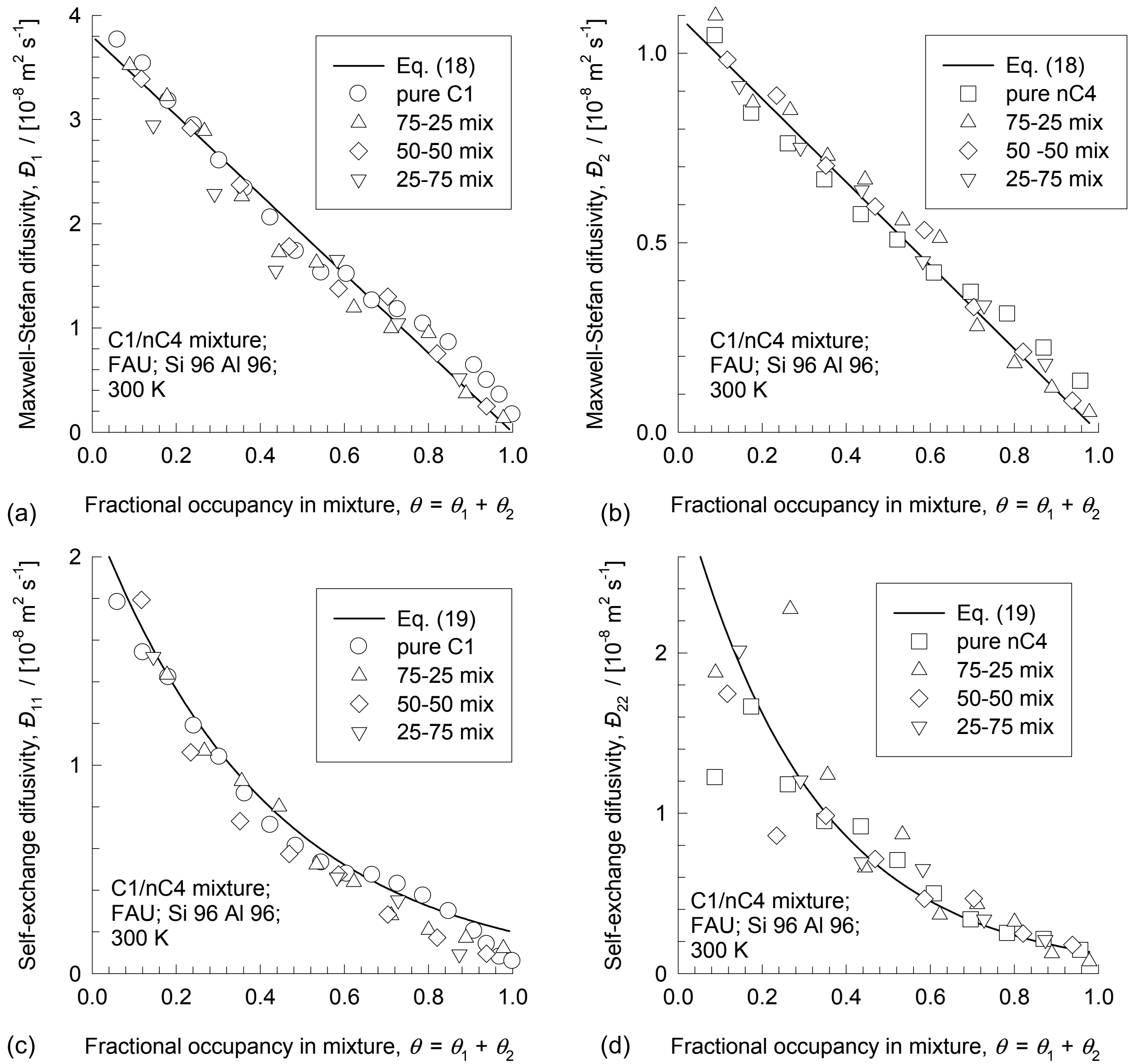
FAU; 300 K; C1/nC4 75-25, 50-50, 25,75 mix; varying loadings



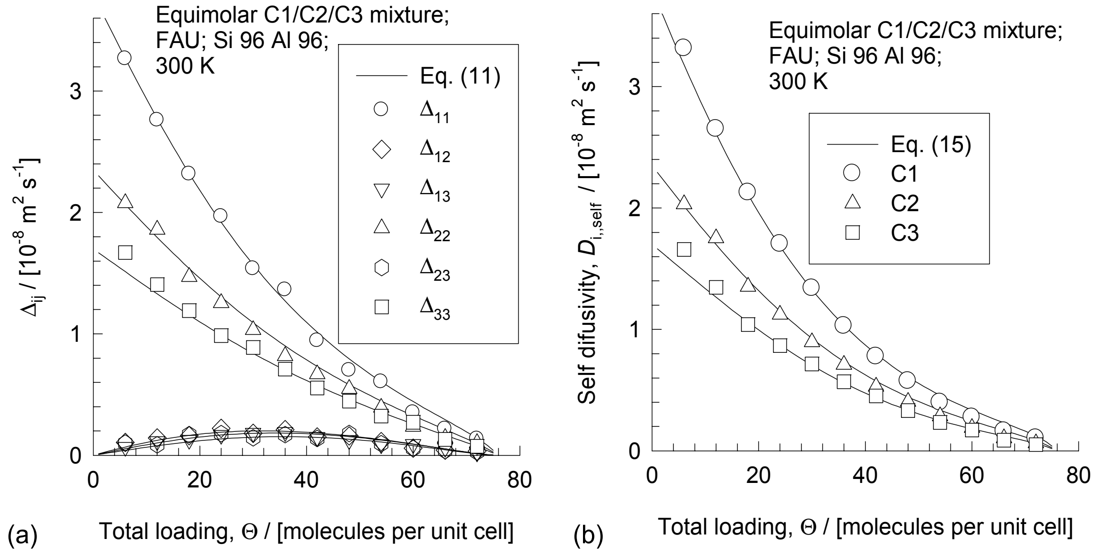
FAU; 300 K; C1/nC4 binary; Θ = 32; varying compositions



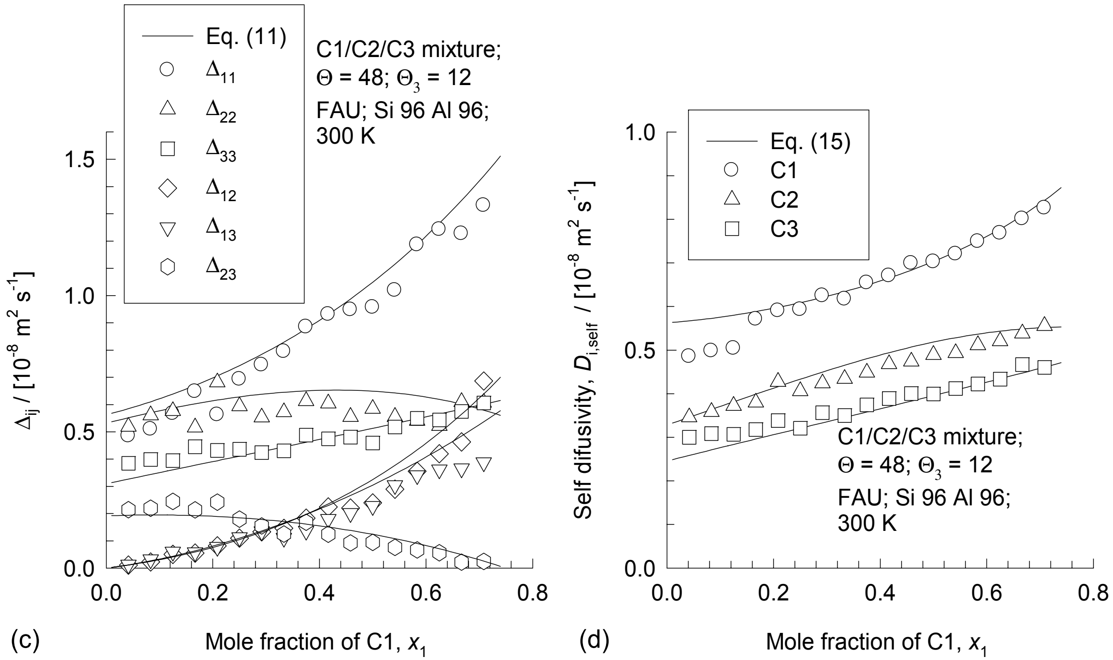
FAU; 300 K; C1/nC4 75-25, 50-50, 25-75 binary mixtures; Data on $Đ_i$ and $Đ_{ii}$ backed out from MD simulations



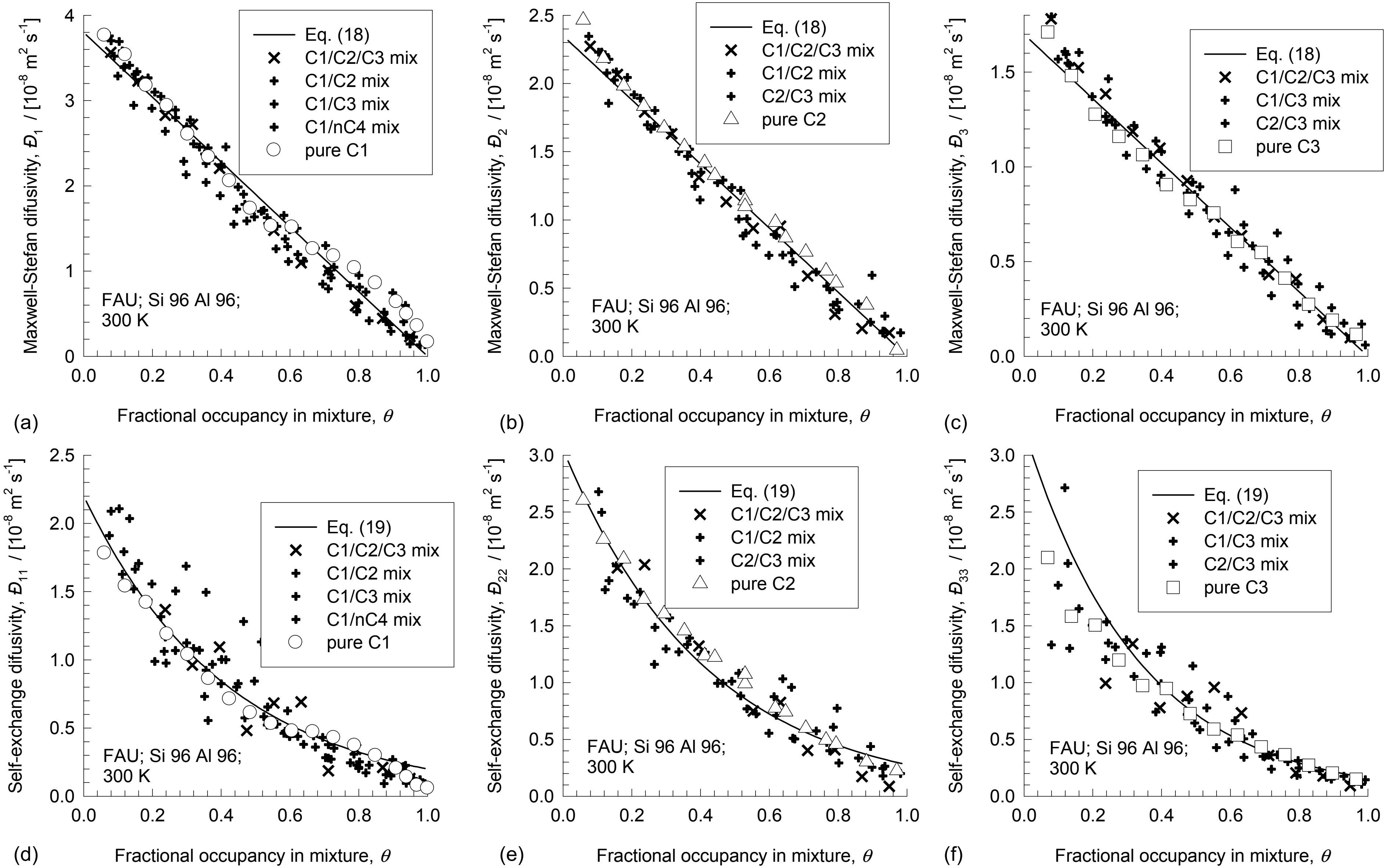
FAU; 300 K; C1/C2/C3 equimolar ternary; varying loadings



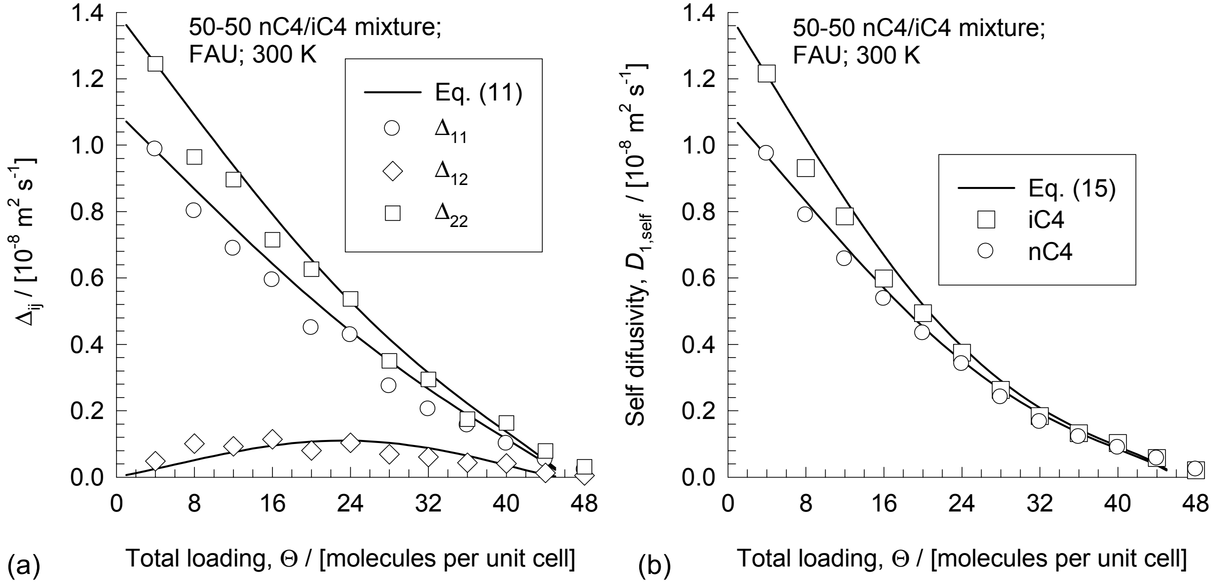
FAU; 300 K; C1/C2/C3 ternary; Θ = 48; varying compositions



FAU; 300 K; pure, binary and ternary; C1, C2, C3
Data on $Đ_i$ and $Đ_{ii}$ backed out from all MD simulations

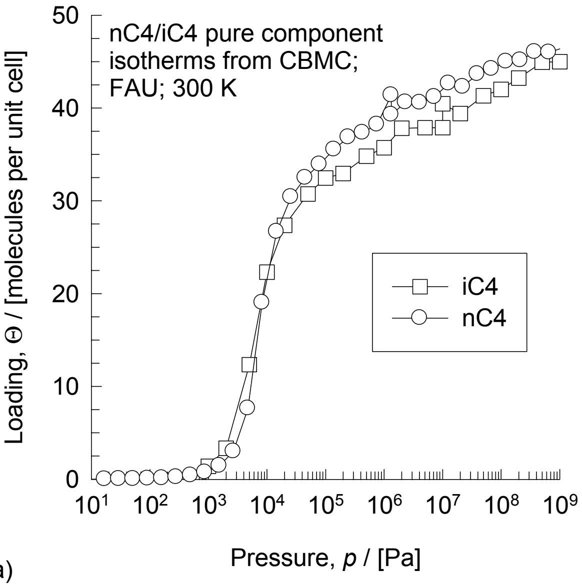


FAU; 300 K; nC4/iC4, 50-50 mix; varying loadings

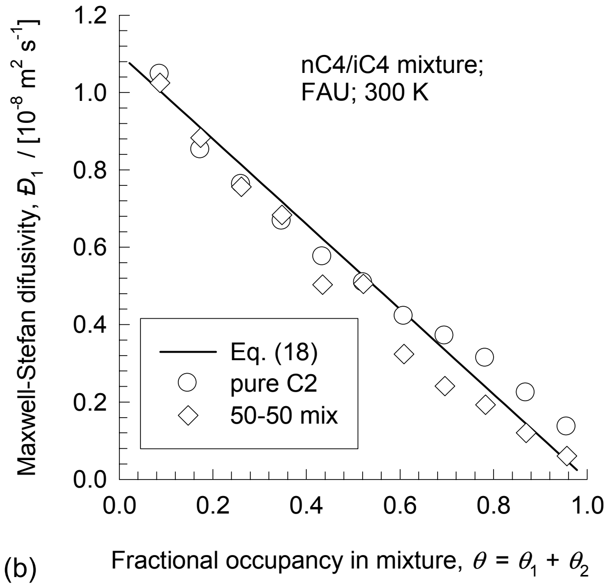


It is noteworthy that iC4 diffuses faster than nC4
In FAU

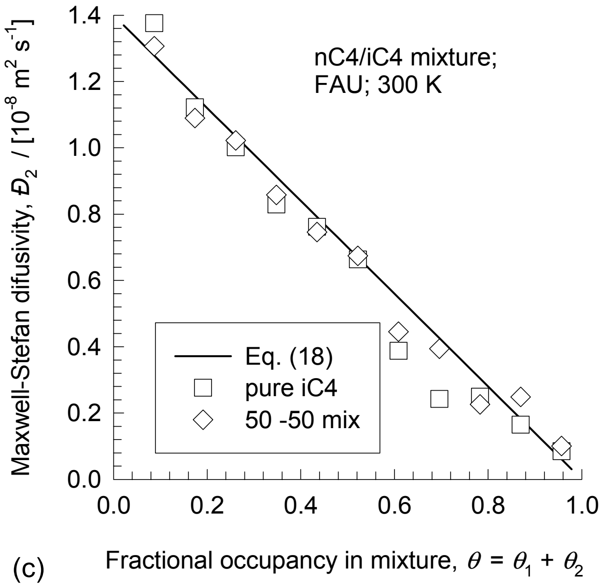
FAU; 300 K; nC4/iC4 50-50 binary mixture; Data on $Đ_i$ and $Đ_{ii}$ backed out from MD simulations



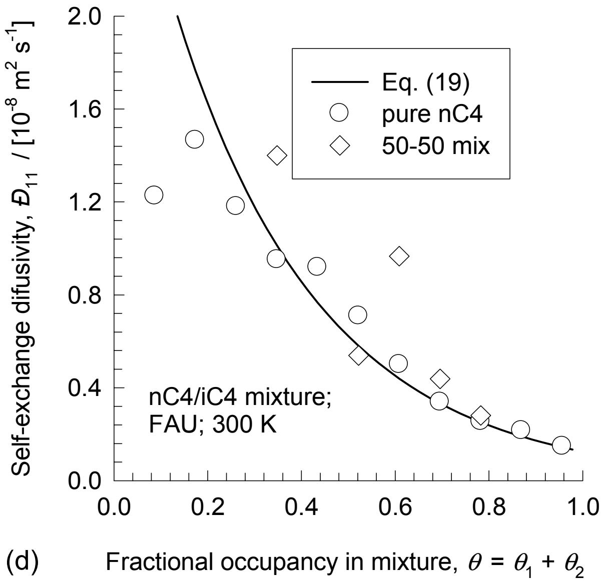
(a)



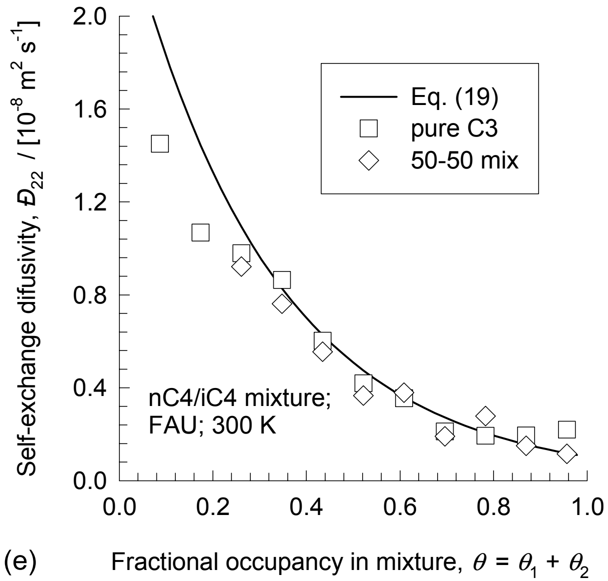
(b)



(c)



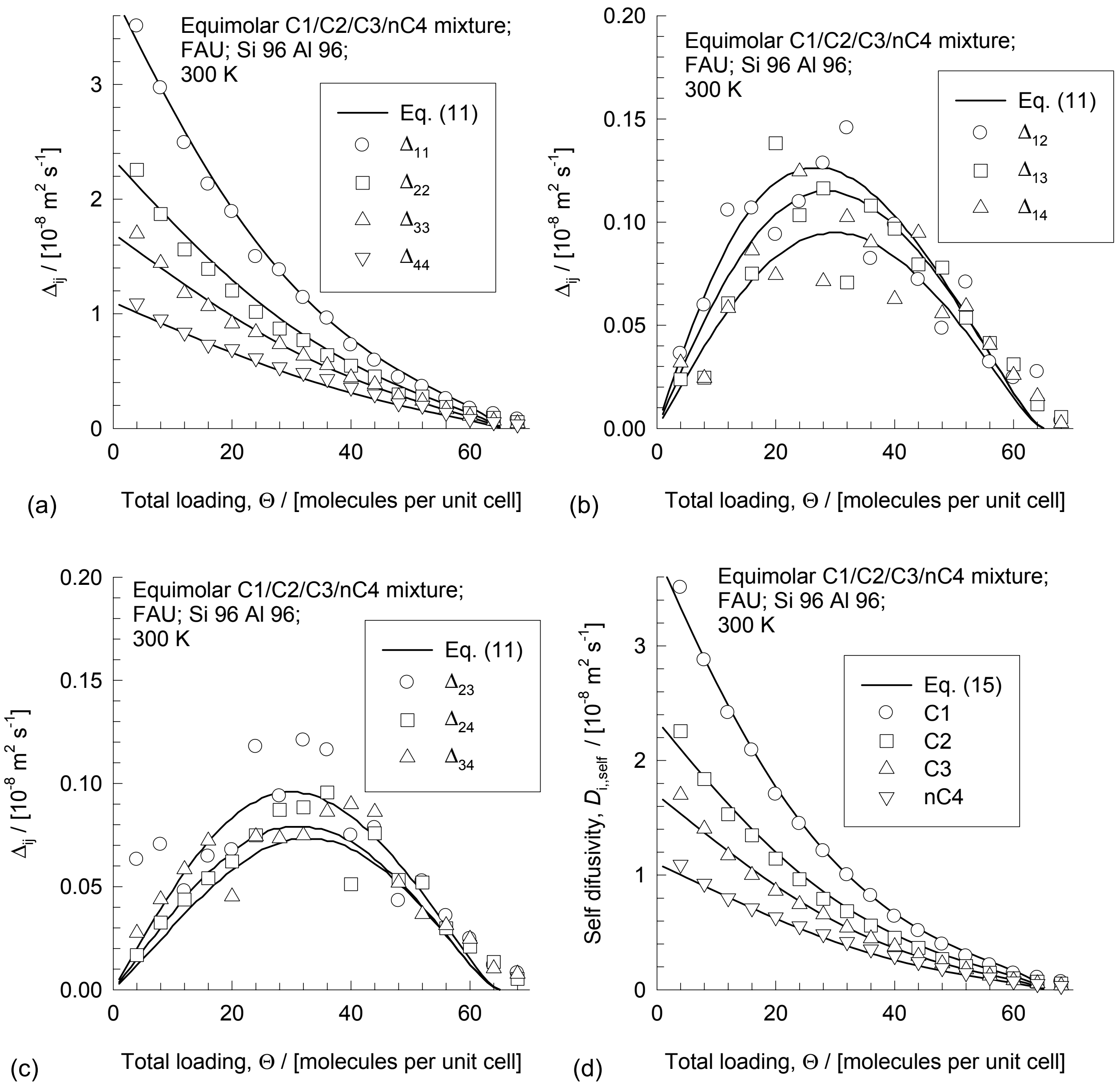
(d)



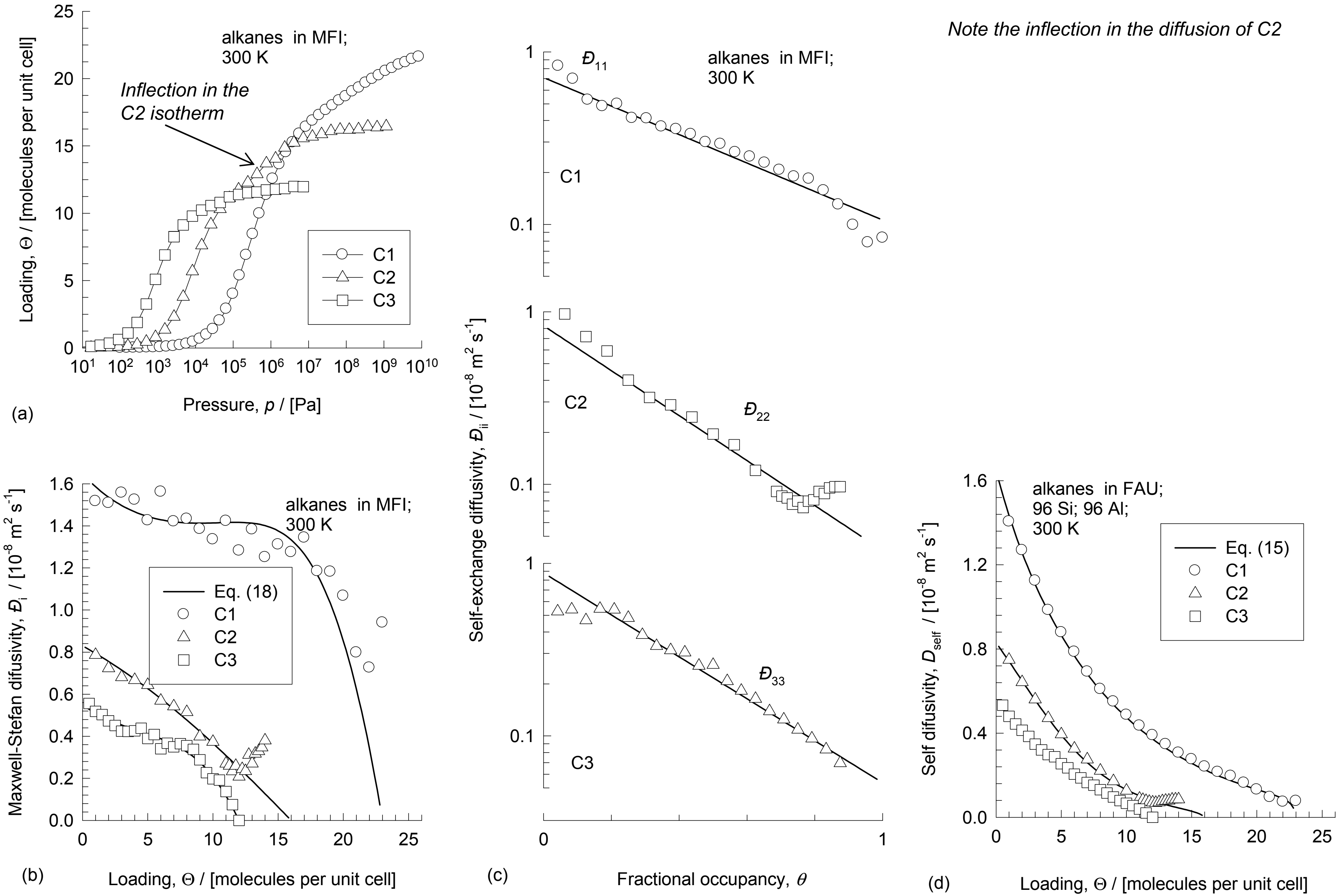
(e)

It is noteworthy that iC4 diffuses faster than nC4 In FAU

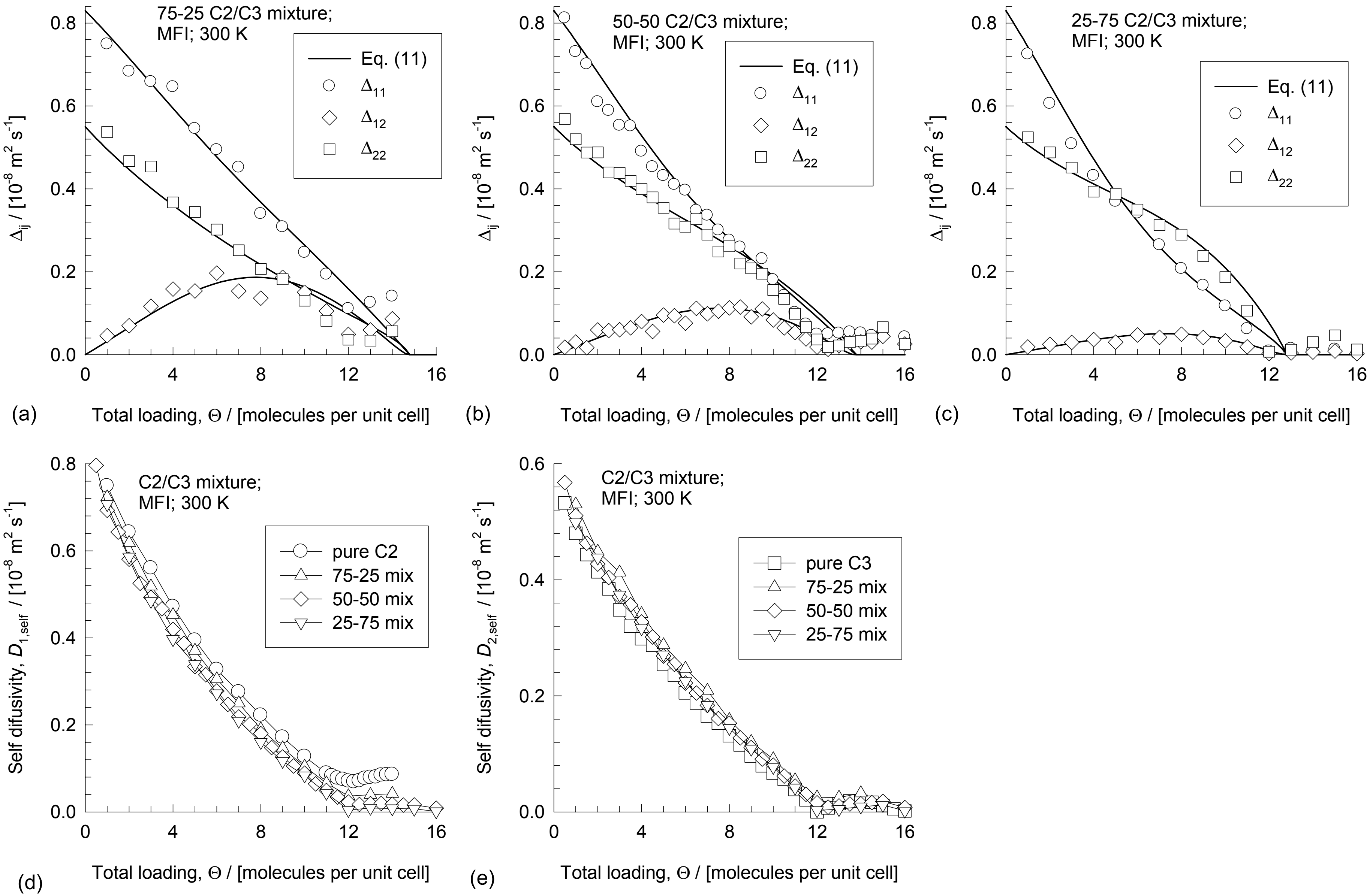
FAU; 300 K; C1/C2/C3/nC4 equimolar quaternary; varying loadings



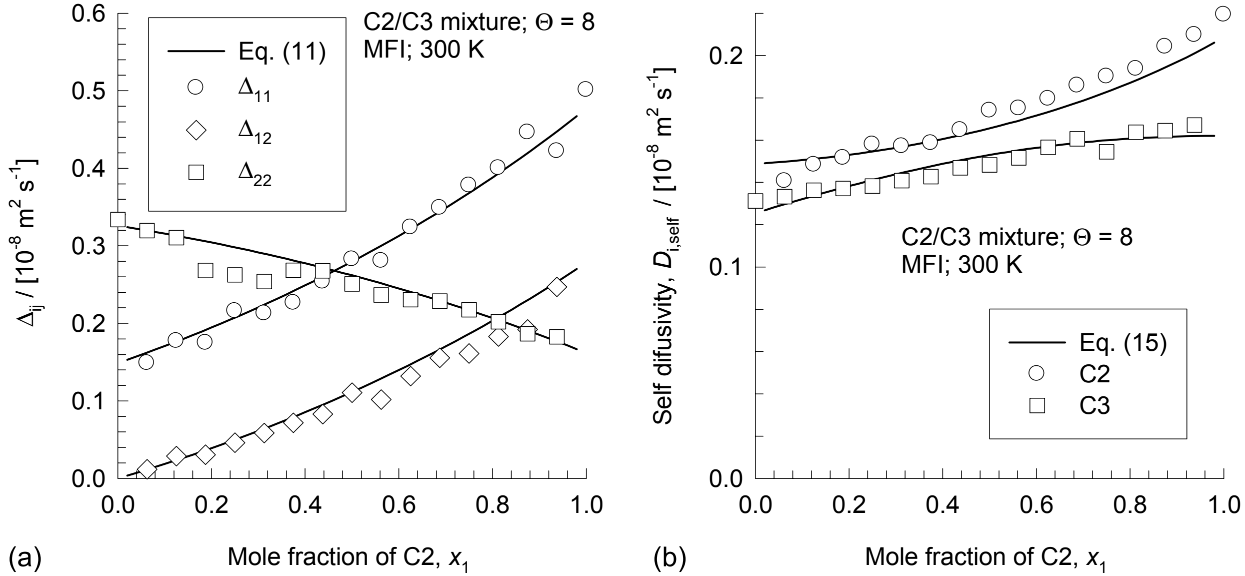
MFI; 300 K; pure component isotherms and diffusion data for C1, C2 and C3



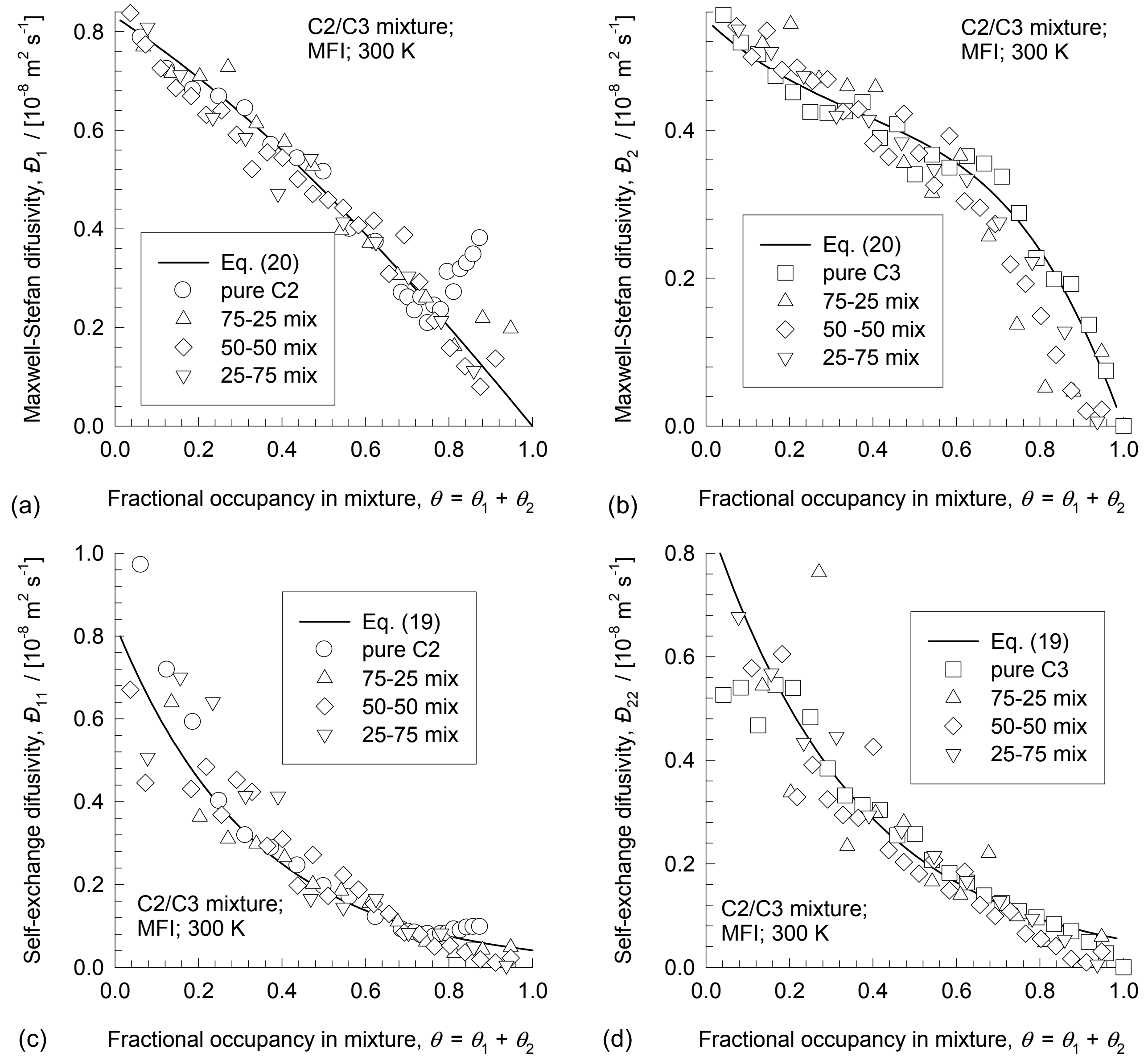
MFI; 300 K; C2/C3 75-25, 50-50, 25-75 mix; varying loadings



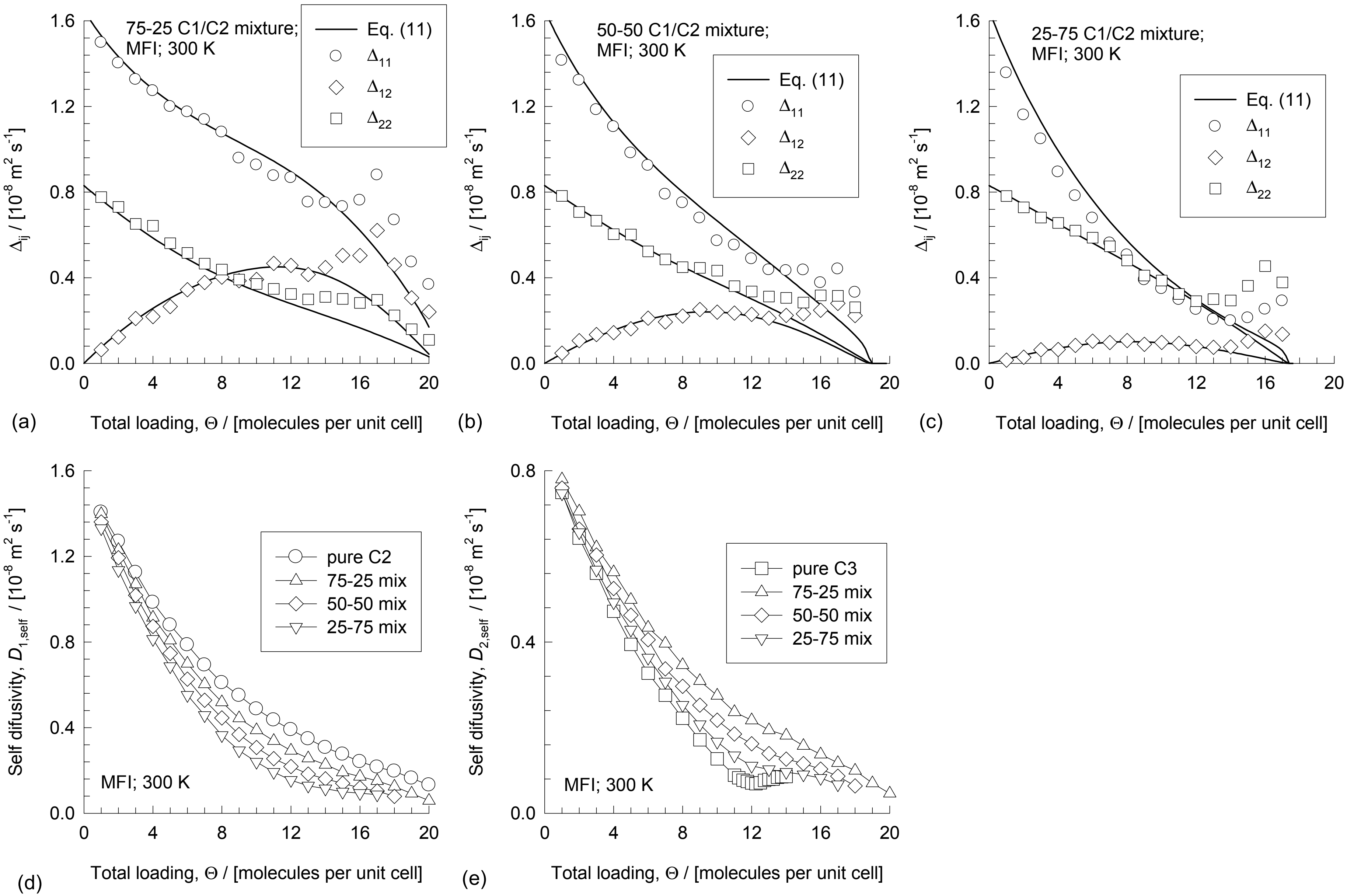
MFI; 300 K; C2/C3 binary; Θ = 8; varying compositions



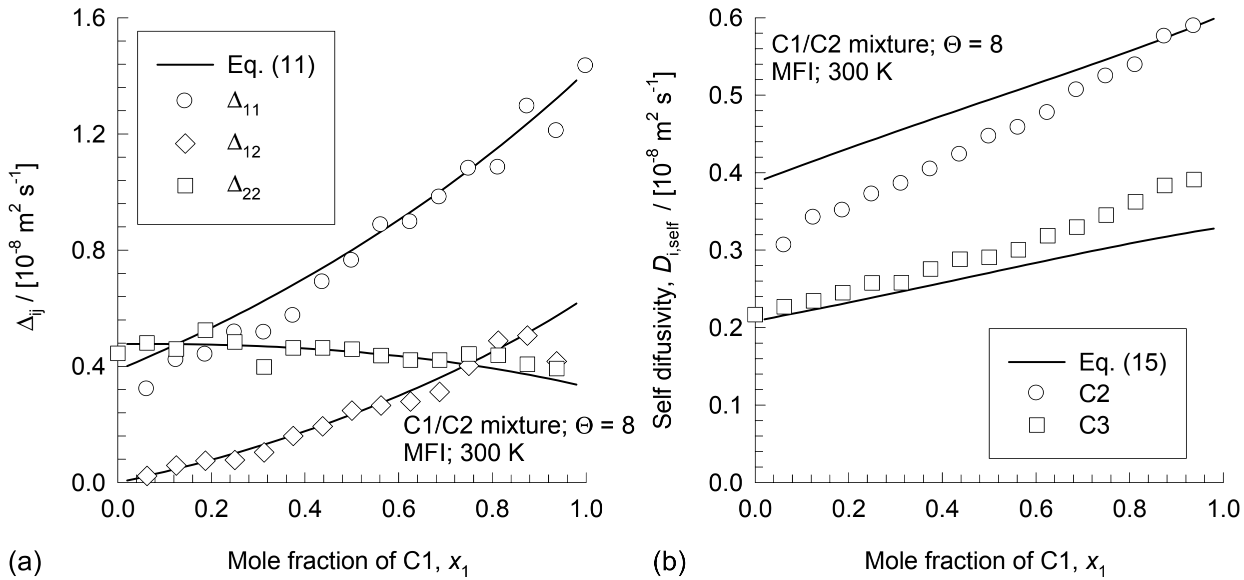
MFI; 300 K; C2/C3 75-25, 50-50, 25-75 binary mixtures; Data on $Đ_i$ and $Đ_{ii}$ backed out from MD simulations



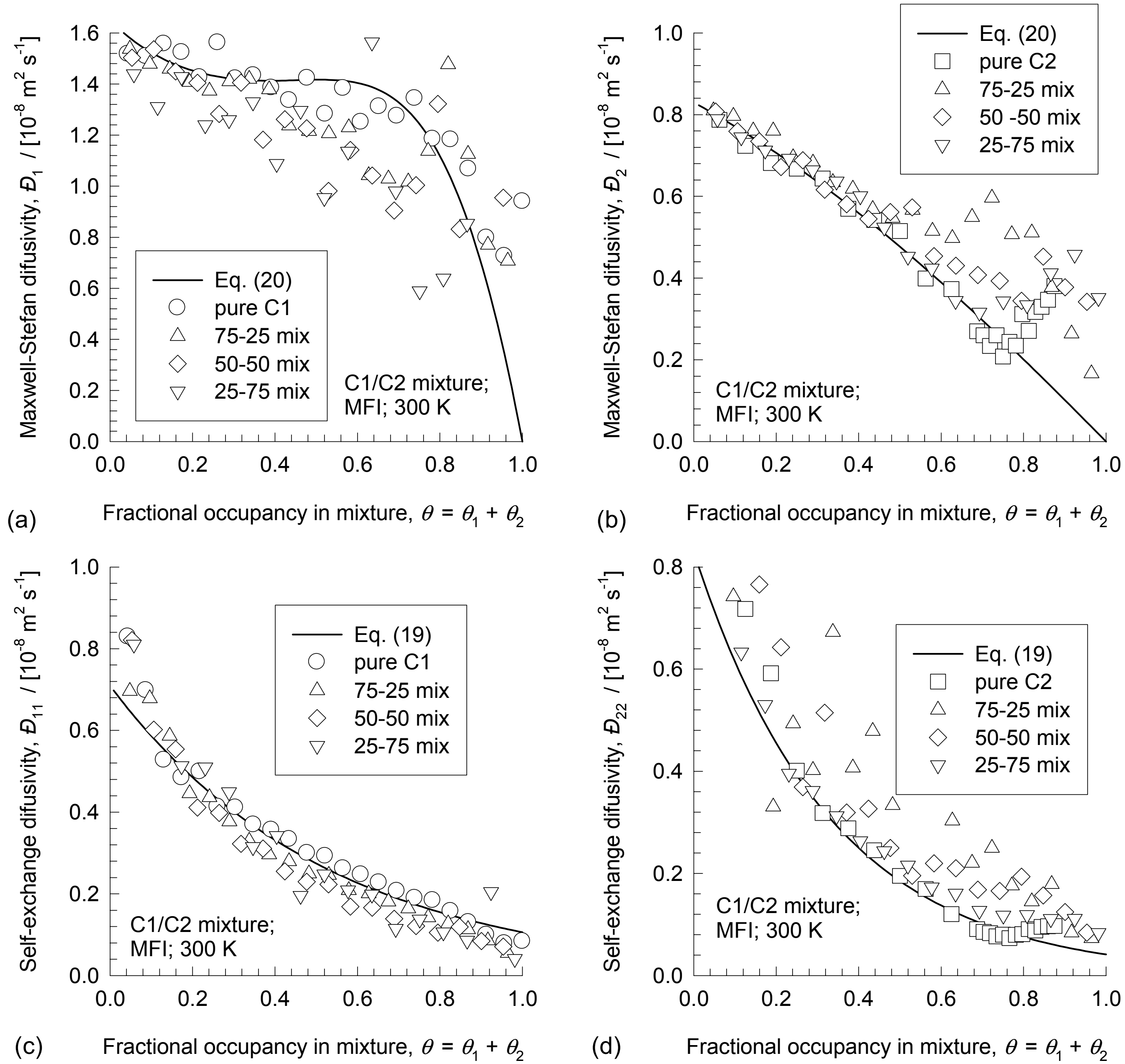
MFI; 300 K; C1/C2 75-25, 50-50, 25-75 mix; varying loadings



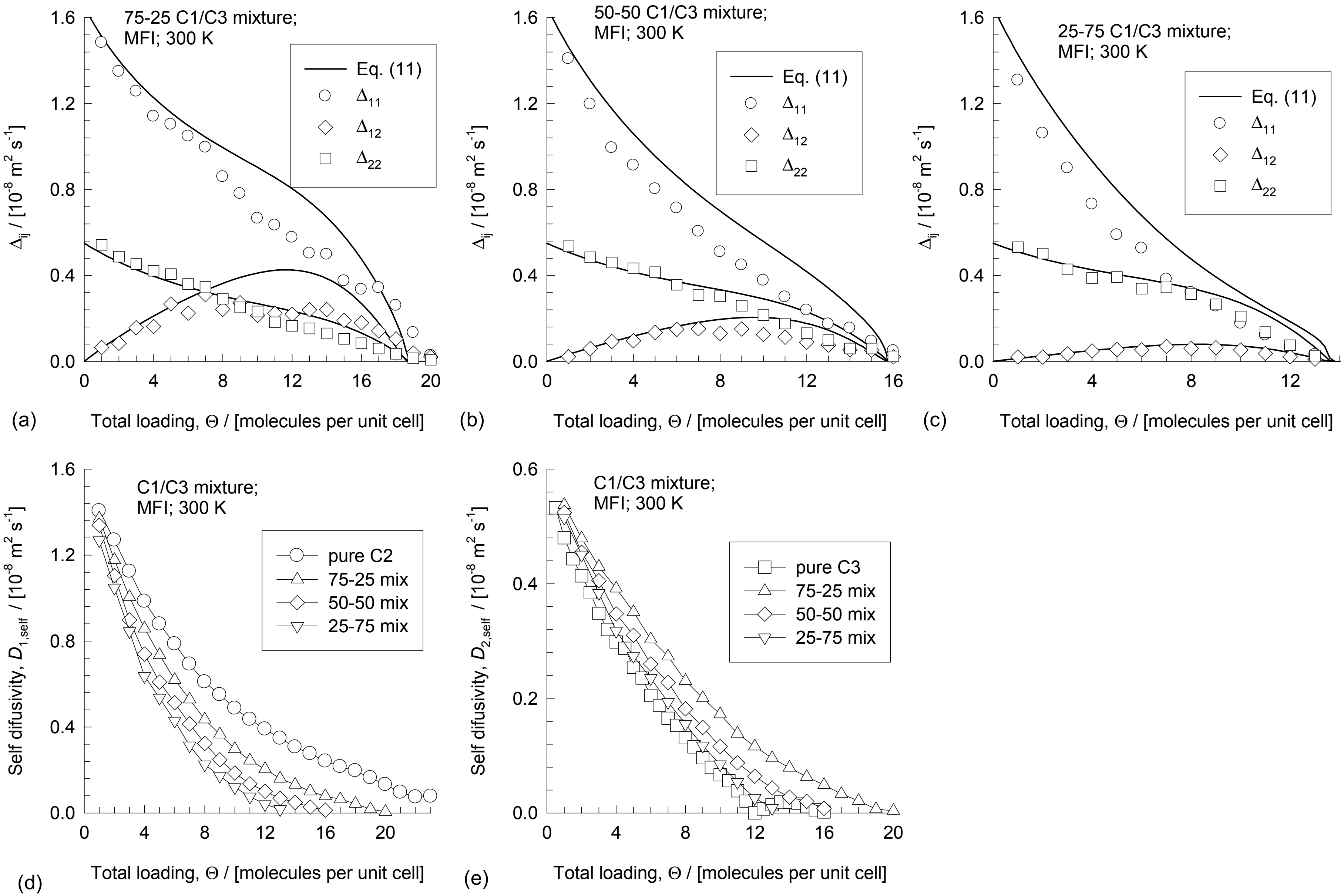
MFI; 300 K; C1/C2 binary; Θ = 8; varying compositions



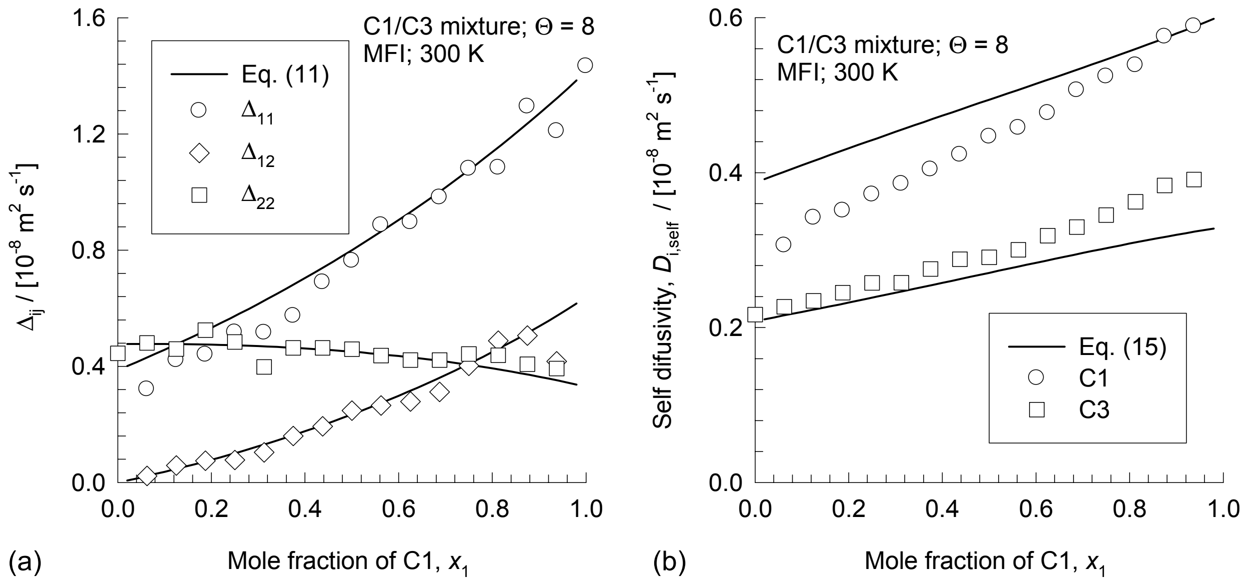
MFI; 300 K; C1/C2 75-25, 50-50, 25-75 binary mixtures; Data on $Đ_i$ and $Đ_{ii}$ backed out from MD simulations



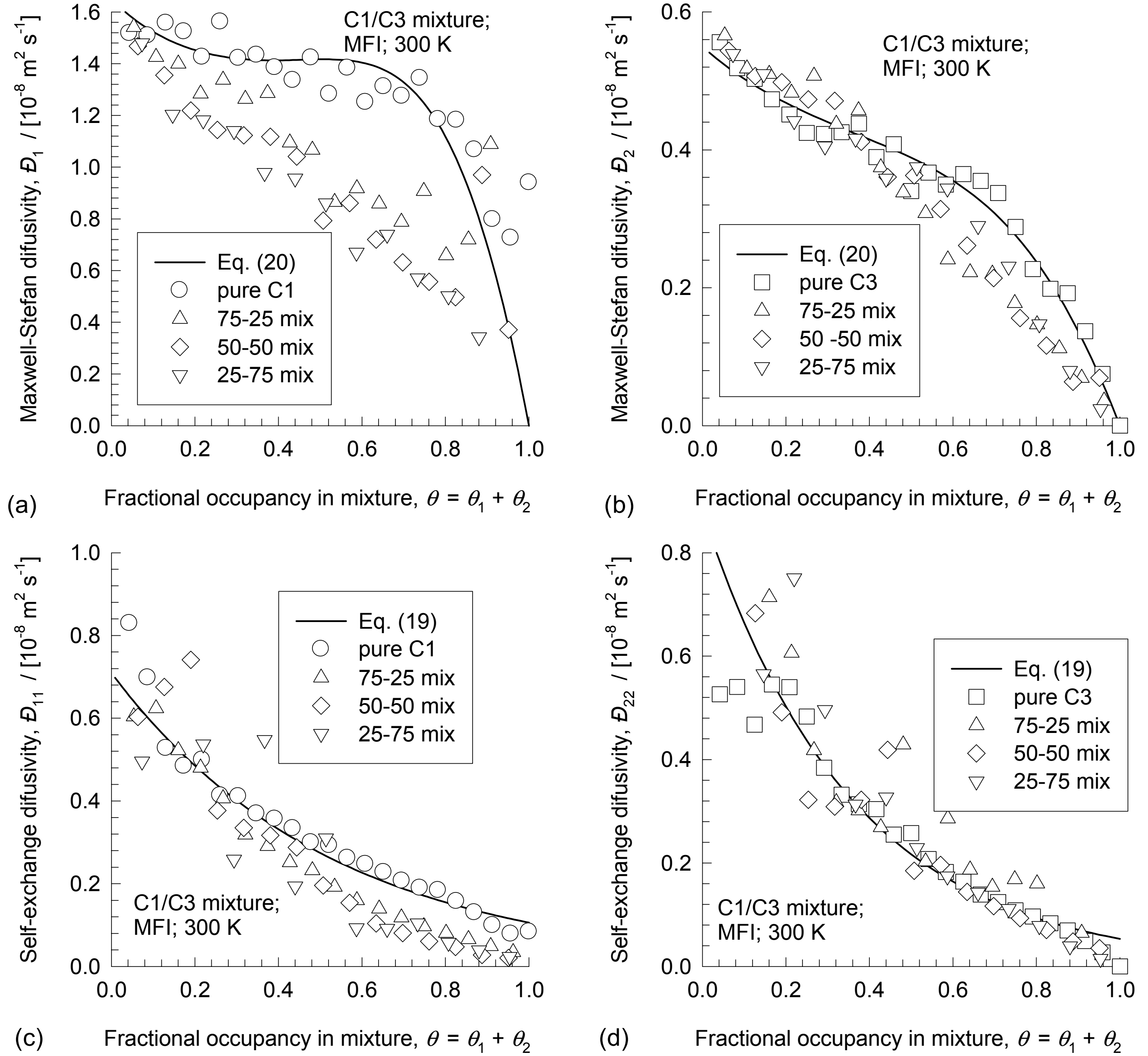
MFI; 300 K; C1/C3 75-25, 50-50, 25-75 mix; varying loadings



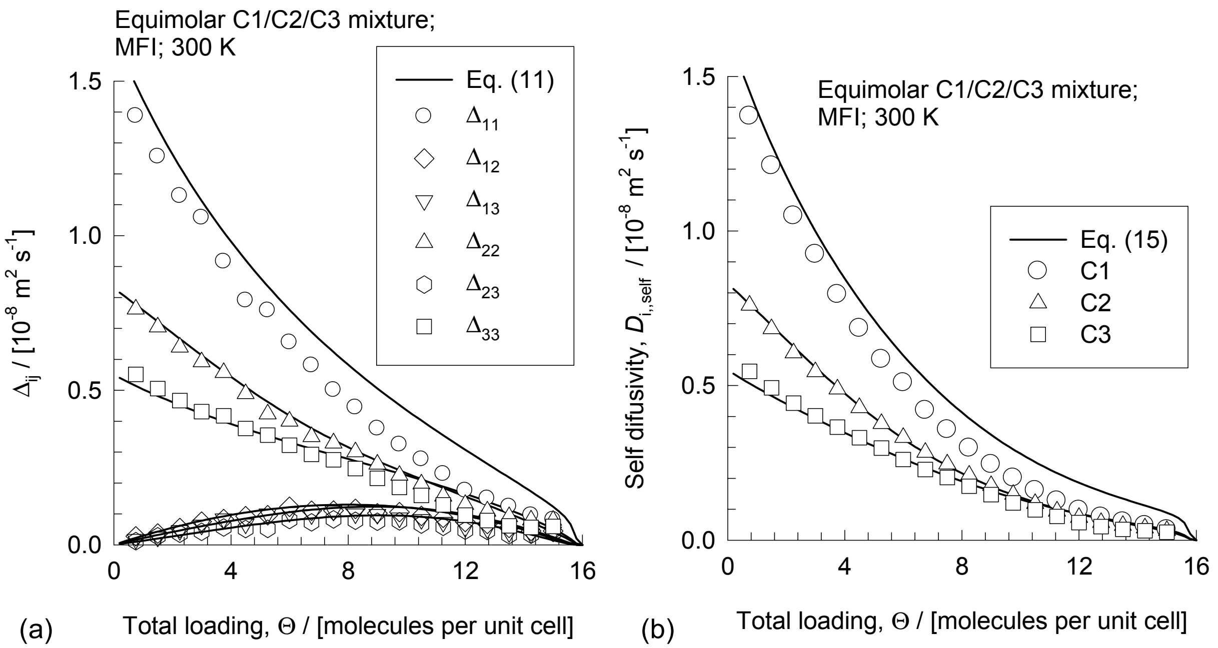
MFI; 300 K; C1/C3 binary; Θ = 8; varying compositions



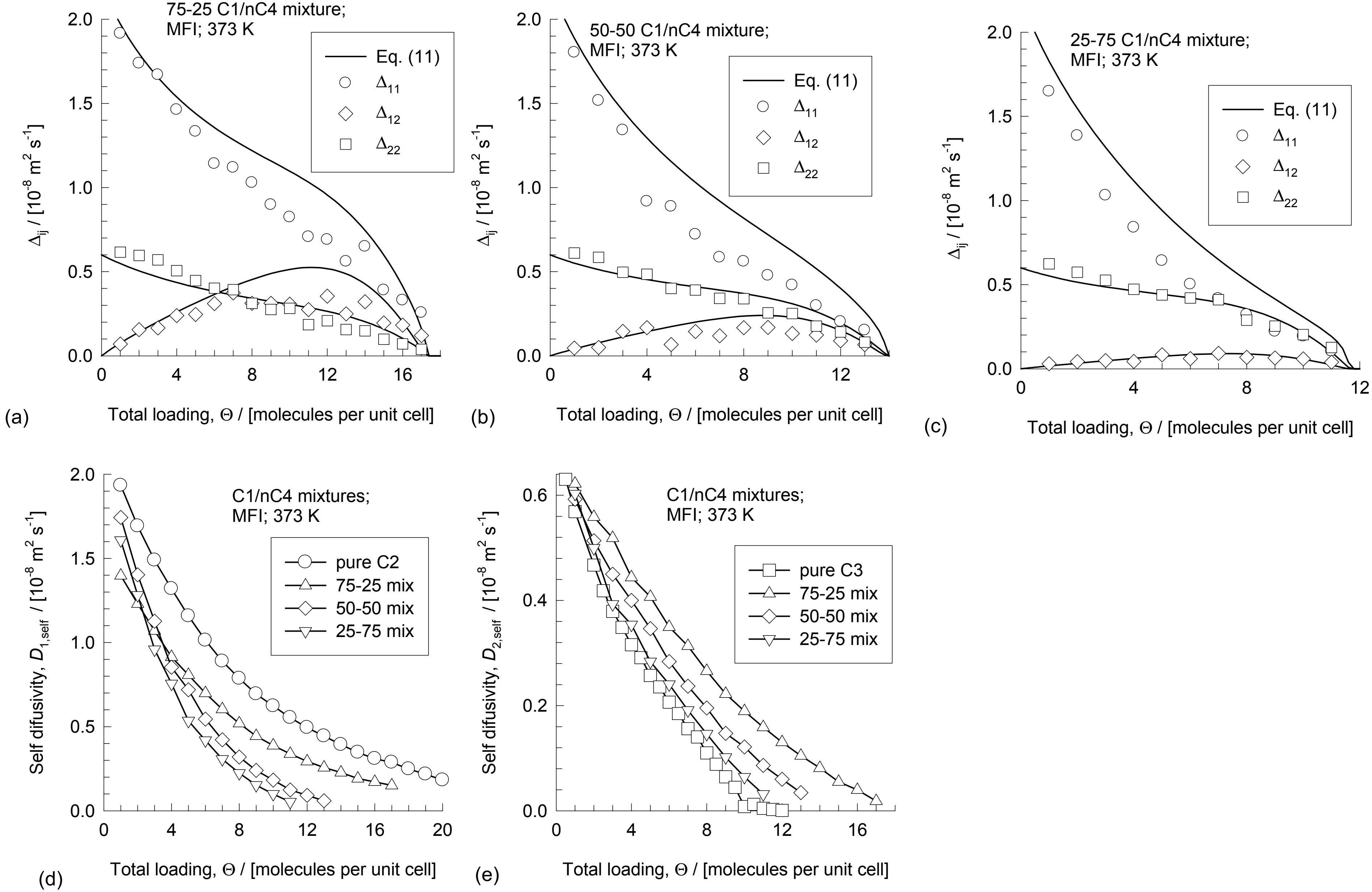
MFI; 300 K; C1/C3 75-25, 50-50, 25-75 binary mixtures; Data on $Đ_i$ and $Đ_{ii}$ backed out from MD simulations



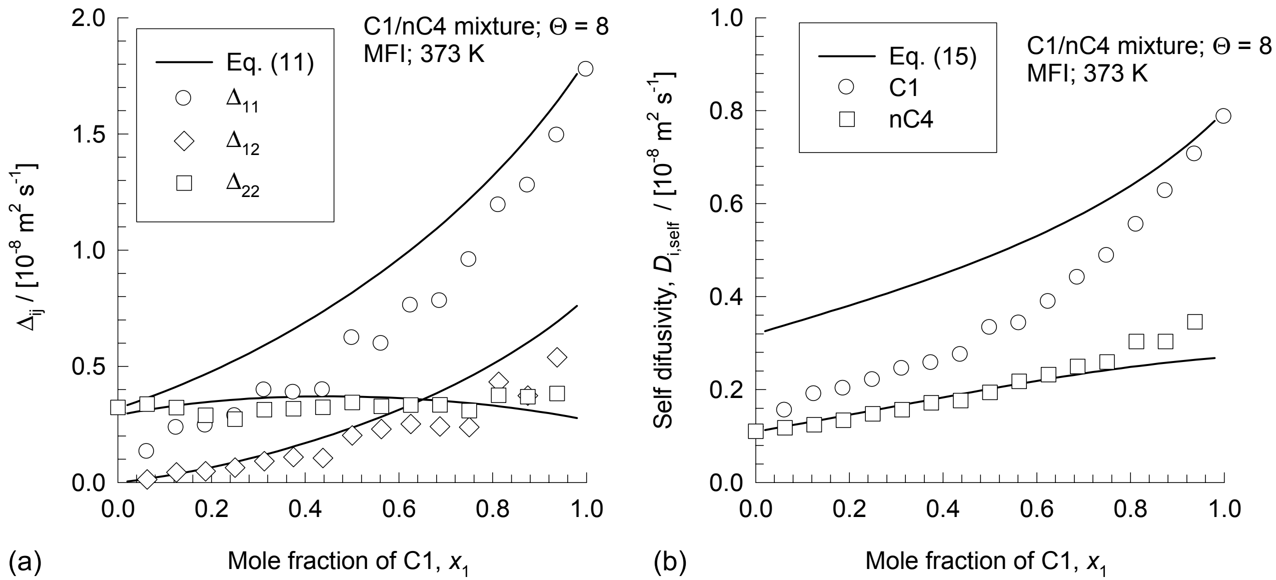
MFI; 300 K; C1/C2/C3 equimolar ternary mix; varying loadings



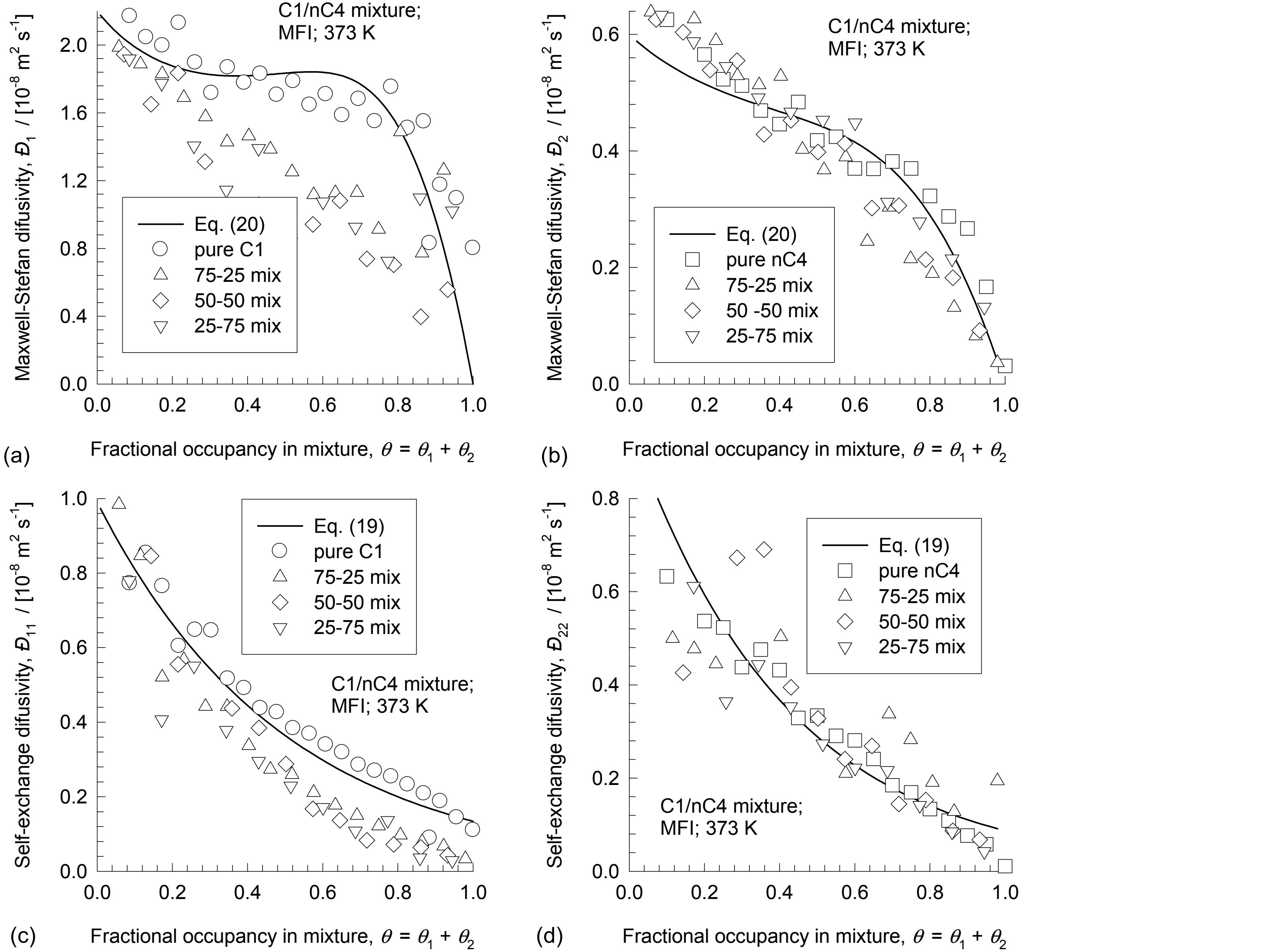
MFI; 373 K; C1/nC4 75-25, 50-50, 25-75 mix; varying loadings



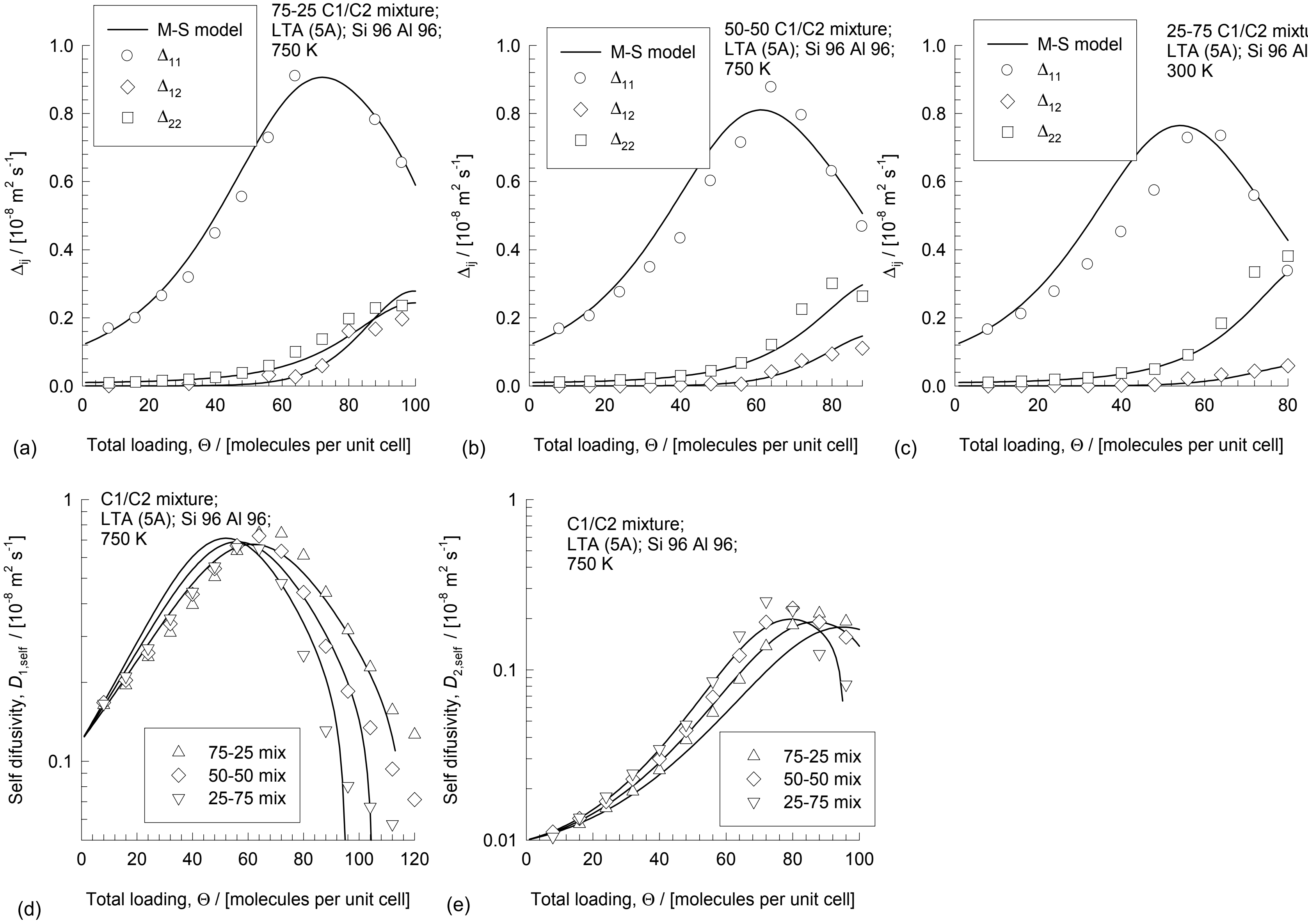
MFI; 373 K; C1/nC4 binary; Θ = 8; varying compositions



MFI; 373 K; C1/nC4 75-25, 50-50, 25-75 binary mixtures; Data on $Đ_i$ and $Đ_{ii}$ backed out from MD simulations



LTA; 750 K; C1/C2 75-25, 50-50, 25-75 mix; varying loadings



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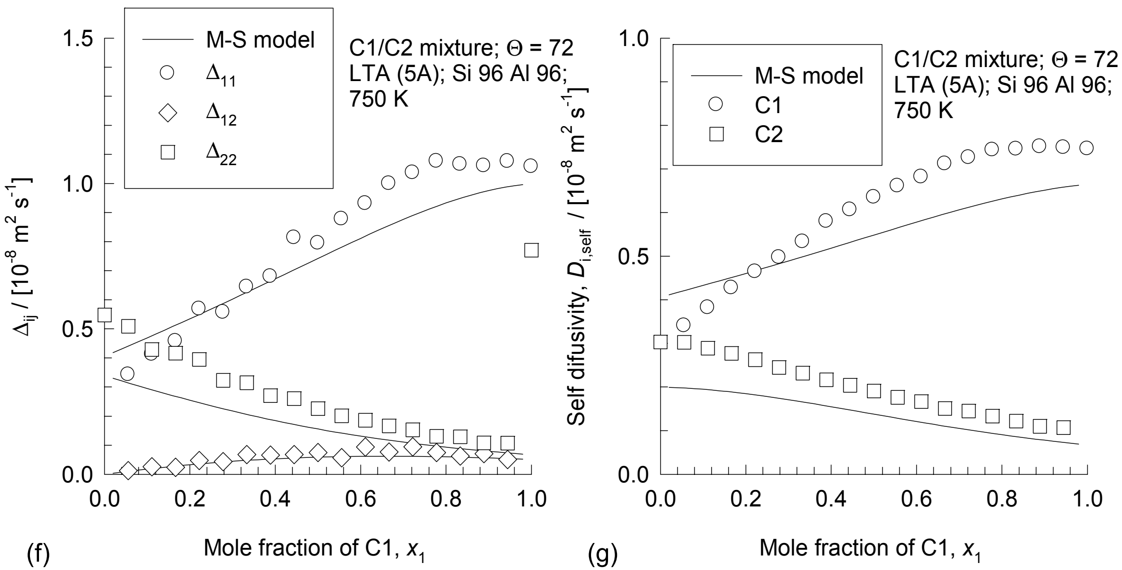
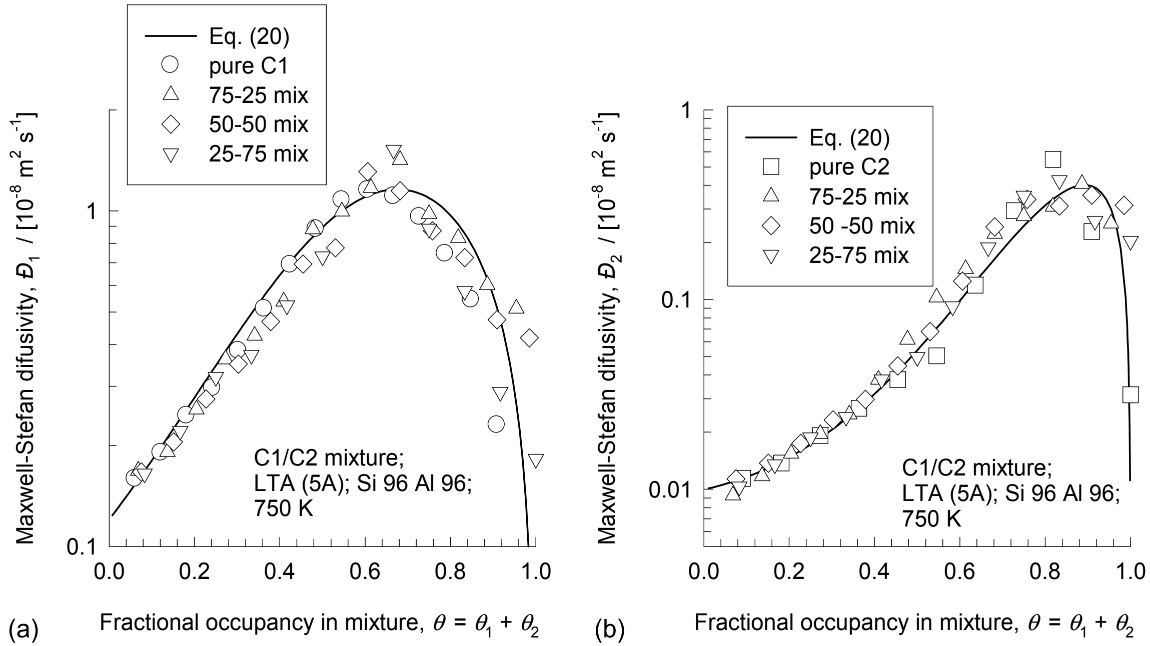
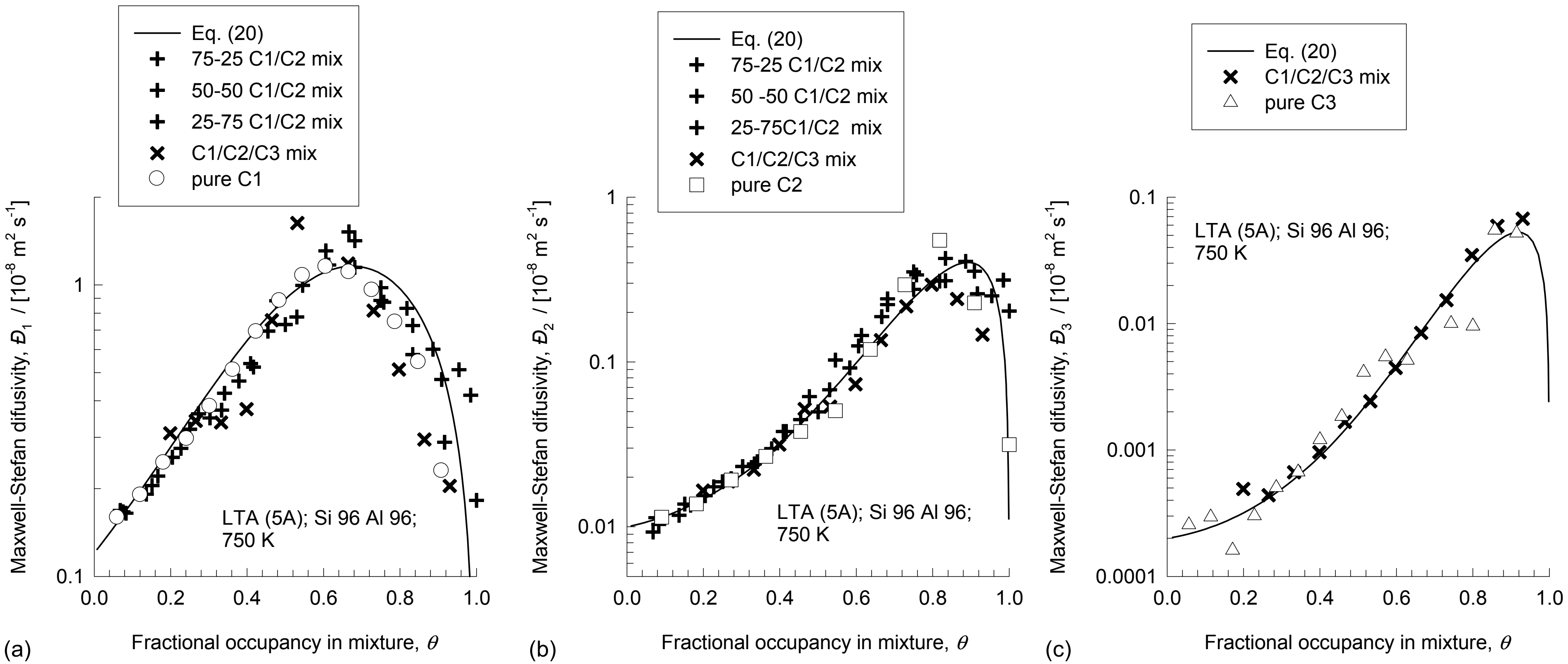


LTA; 750 K; C1/C2 75-25, 50-50, 25-75 binary mixtures; Data on $Đ_i$ backed out from MD simulations



LTA; 750 K; C1/C2/C3 equimolar ternary mixtures; Data on $Đ_i$ backed out from MD simulations



The plusses denote binary mixture data, the crosses denote equimolar ternary mixture data

Appendix B: M-S vs Onsager formulations

The Maxwell-Stefan (M-S) diffusion equations are[1-4]:

$$-\rho \frac{\theta_i}{k_B T}\nabla \mu_i = \sum_{\substack{j=1\\ j\neq i}}^{n} \frac{\Theta_j \mathbf{N}_i - \Theta_i \mathbf{N}_j}{\Theta_{i,sat}\Theta_{j,sat}Đ_{ij}} + \frac{\mathbf{N}_i}{\Theta_{i,sat}Đ_i}; \quad i = 1,...n \tag{1}$$

where $\mathbf{N}_i$ is the flux of species *i* expressed say in molecules per square meter per second, ρ is the zeolite density expressed as the number of unit cells per cubic meter, Θ_i is the loading in molecules per unit cell, $\Theta_{i,sat}$ represents the saturation loading of species *i*, *n* is the total number of diffusing species, μ_i is the chemical potential expressed in Joules per molecule and k_B is the Boltzmann constant. In Eq.(1) the fractional occupancies θ_i are defined by

$$\theta_i \equiv \Theta_i / \Theta_{i,sat} \quad i = 1,2,...n \tag{2}$$

Equation (1) *defines* two types of M-S diffusivities: $Đ_i$ and $Đ_{ij}$. If we have only a single sorbed component, then only one $Đ_i$ is needed, and in this case $Đ_i$ is equivalent to the single component "corrected" diffusivity[5]. In the case of mixture diffusion, the $Đ_i$ depend, in general, on the loading of all sorbed species, so $Đ_i = Đ_i(\Theta_1, \Theta_2, ...\Theta_n)$. The binary exchange coefficients $Đ_{ij}$ reflect *correlation* effects in mixture diffusion[6]. For mixture diffusion the $Đ_{ij}$ tends to slow down the more mobile species and speed up the relatively sluggish ones. A lower value of the exchange coefficient $Đ_{ij}$ implies a *stronger* correlation effect. When $Đ_{ij} \to \infty$, correlation effects vanish.

Equation (1) can be cast into *n*-dimensional matrix notation as

$$(\mathbf{N}) = -\rho\,[B]^{-1}\,[\Gamma](\nabla\Theta) \tag{3}$$

with the following definitions of an *n*-dimensional square matrix [*B*] with elements

$$B_{ii} = \frac{1}{Đ_i} + \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{\theta_j}{Đ_{ij}}; \quad B_{ij} = -\frac{\Theta_{i,sat}}{\Theta_{j,sat}} \frac{\theta_i}{Đ_{ij}}; \quad i, j = 1,2....n \tag{4}$$

and the matrix of thermodynamic correction factors [Γ]

$$\frac{\Theta_i}{k_B T} \nabla \mu_i = \sum_{j=1}^{n} \Gamma_{ij} \nabla \Theta_j; \quad \Gamma_{ij} \equiv \frac{\Theta_i}{\Theta_j} \frac{\partial \ln f_i}{\partial \ln \Theta_j}; \quad i, j = 1,..n \tag{5}$$

where f_i represents the fugacity of component i in the bulk fluid phase. The Γ_{ij} can be calculated from knowledge of the multicomponent sorption isotherms.

It must be noted that in the paper by Kapteijn et al.[1] and Skoulidas et al.[3], an alternative, but consistent derivation is followed for the flux relation in the form

$$(\mathbf{N}) = -\rho [\Theta_{sat}] [B^*]^{-1} [\Gamma^*] (\nabla \theta) \tag{6}$$

with the following definitions:

$$B^*_{ii} = \frac{1}{Đ_i} + \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{\theta_j}{Đ_{ij}}; \quad B^*_{ij} = -\frac{\theta_i}{Đ_{ij}}; \quad i, j = 1,2....n \tag{7}$$

$$\frac{\theta_i}{k_B T} \nabla \mu_i = \sum_{j=1}^{n} \Gamma^*_{ij} \nabla \theta_j; \quad \Gamma^*_{ij} \equiv \left(\frac{\Theta_{j,sat}}{\Theta_{i,sat}} \right) \frac{\Theta_i}{f_i} \frac{\partial f_i}{\partial \Theta_j} \equiv \frac{\theta_i}{\theta_j} \frac{\partial \ln f_i}{\partial \ln \theta_j}; \quad i, j = 1,2\ldots n \tag{8}$$

$$[\Theta_{sat}] \equiv \begin{bmatrix} \Theta_{1,sat} & 0 & 0 & 0 & 0 \\ 0 & \Theta_{2,sat} & 0 & 0 & 0 \\ 0 & 0 & \ddots & 0 & 0 \\ 0 & 0 & 0 & \ddots & 0 \\ 0 & 0 & 0 & 0 & \Theta_{n,sat} \end{bmatrix} \tag{9}$$

Using straightforward matrix algebra it is easy to show that Eqs (3) – (5) are entirely equivalent to Eqs (6) – (9). In the present paper it is more convenient to adopt the formulation given by Eqs (3) – (5).

More commonly in the literature MD simulations are used to determine the matrix of Onsager coefficients defined by

$$(\mathbf{N}) = -[L](\nabla\mu) \tag{10}$$

The units of $L_{ij}\, k_B T$ are molecules per meter per second. The elements of [L] are obtained from the MD simulations using

$$L_{ij} = \frac{1}{6Vk_BT} \lim_{\Delta t\to\infty} \frac{1}{\Delta t} \left\langle \left(\sum_{l=1}^{N_i} \left(\mathbf{r}_{l,i}(t+\Delta t) - \mathbf{r}_{l,i}(t) \right) \right) \bullet \left(\sum_{k=1}^{N_j} \left(\mathbf{r}_{k,j}(t+\Delta t) - \mathbf{r}_{k,j}(t) \right) \right) \right\rangle \tag{11}$$

In our paper we have defined the matrix [Δ]:

$$(\mathbf{N}) = -\rho \frac{[\Delta]}{k_BT} \begin{bmatrix} \Theta_1 & 0 & 0 & 0 & 0 \\ 0 & \Theta_2 & 0 & 0 & 0 \\ 0 & 0 & \ddots & 0 & 0 \\ 0 & 0 & 0 & \ddots & 0 \\ 0 & 0 & 0 & 0 & \Theta_n \end{bmatrix} (\nabla\mu) \tag{12}$$

and calculated this from MD simulations using

$$\Delta_{ij} = \frac{1}{6} \lim_{\Delta t\to\infty} \frac{1}{N_i} \frac{1}{\Delta t} \left\langle \left(\sum_{l=1}^{N_i} \left(\mathbf{r}_{l,i}(t+\Delta t) - \mathbf{r}_{l,i}(t) \right) \right) \bullet \left(\sum_{k=1}^{N_j} \left(\mathbf{r}_{k,j}(t+\Delta t) - \mathbf{r}_{k,j}(t) \right) \right) \right\rangle \tag{13}$$

where V is the volume of the simulation box.

The molecular loadings are

$$\Theta_i = \frac{N_i}{\rho V} \tag{14}$$

and so

$$\rho \Theta_i \Delta_{ij} = L_{ij} k_B T \tag{15}$$

The Onsager Reciprocal Relations $L_{ij} = L_{ji}$ imply

$$\Theta_i \Delta_{ij} = \Theta_j \Delta_{ji} \tag{16}$$

(1) Kapteijn, F.; Moulijn, J. A.; Krishna, R. *Chem. Eng. Sci.* **2000**, *55*, 2923.
(2) Krishna, R.; Baur, R. *Sep. Purif. Technol.* **2003**, *33*, 213.
(3) Skoulidas, A. I.; Sholl, D. S.; Krishna, R. *Langmuir* **2003**, *19*, 7977.

(4) Chempath, S.; Krishna, R.; Snurr, R. Q. *J. Phys. Chem. B* **2004**, *108*, 13481.
(5) Skoulidas, A. I.; Sholl, D. S. *J. Phys. Chem. B* **2001**, *105*, 3151.
(6) Kärger, J.; Vasenkov, S.; Auerbach, S. M. Diffusion in zeolites, Chapter 10. In *Handbook of Zeolite Science and Technology*; Auerbach, S. M., Carrado, K. A., Dutta, P. K., Eds.; Marcel Dekker: New York, 2003; pp 341.

Appendix C: Nomenclature

a_i	constants describing self-exchange, dimensionless
b_i	constants describing self-exchange, dimensionless
$[B]$	matrix of inverse Maxwell-Stefan coefficients, m^{-2} s
$[B^*]$	alternative definition of matrix of inverse Maxwell-Stefan coefficients, m^{-2} s
$[D]$	matrix of Fick diffusivities, m^2 s^-
$D_{i,self}$	self-diffusivity, m^2 s^{-1}
$Đ_i$	Maxwell-Stefan diffusivity of species *i* in zeolite, m^2/s
$Đ_i(0)$	zero-loading M-S diffusivity of species *i* in zeolite, m^2/s
$Đ_{ii}$	self-exchange diffusivity, m^2/s
$Đ_{ij}$	binary exchange diffusivity, m^2/s
f_i	Reed-Ehrlich parameter, dimensionless
k_B	Boltzmann constant, 1.38×10^{-23} J molecule^{-1} K^{-1}
$L_{ij}\, k_B T$	(modified) Onsager coefficients, molecule m^{-1} s^{-1}
$\mathbf{N}_i$	molecular flux of species *i*, molecules m^{-2} s^{-1}
N_i	number of molecules of species *i*, molecules
p_i	partial pressure of species *i*, Pa
t	time, s
T	absolute temperature, K
V	volume, m^3
x_i	mole fraction of species *i* in mixture, dimensionless
z	coordination number, dimensionless

Greek letters

β_i	Reed-Ehrlich parameter, dimensionless

$[\Delta]$	matrix of Maxwell-Stefan diffusivities, $m^2\ s^{-1}$
ε_i	Reed-Ehrlich parameter, dimensionless
$[\Gamma]$	matrix of thermodynamic factors, dimensionless
θ	total occupancy of mixture, dimensionless
θ_i	fractional occupancy of component *i*, dimensionless
Θ_i	molecular loading, molecules per unit cell
$\Theta_{i,sat}$	saturation loading, molecules per unit cell
μ_i	molar chemical potential, J molecule^{-1}
ρ	density, number of unit cells per m^3

Subscripts

sat	referring to saturation conditions
i,j	components in mixture

Superscripts

*	modified definitions of B_{ij} and Γ_{ij}

Vector and Matrix Notation

( )	vector
[ ]	square matrix