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Supplementary material to:

Mutual diffusion governed by kinetics and thermodynamics in the partially miscible mixture methanol + cyclohexane

by

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A Molar excess volume

The molar excess volume v^{E} was calculated from the measured specific mixture density ρ_m by

$$v^{\mathrm{E}} = \sum_{i=1}^{2} x_i M_i \left(\frac{1}{\rho_m} - \frac{1}{\rho_{m,i}^0} \right) , \tag{1}$$

where M_i is the molar weight and $\rho_{m,i}^0$ is the specific density of the pure component i.

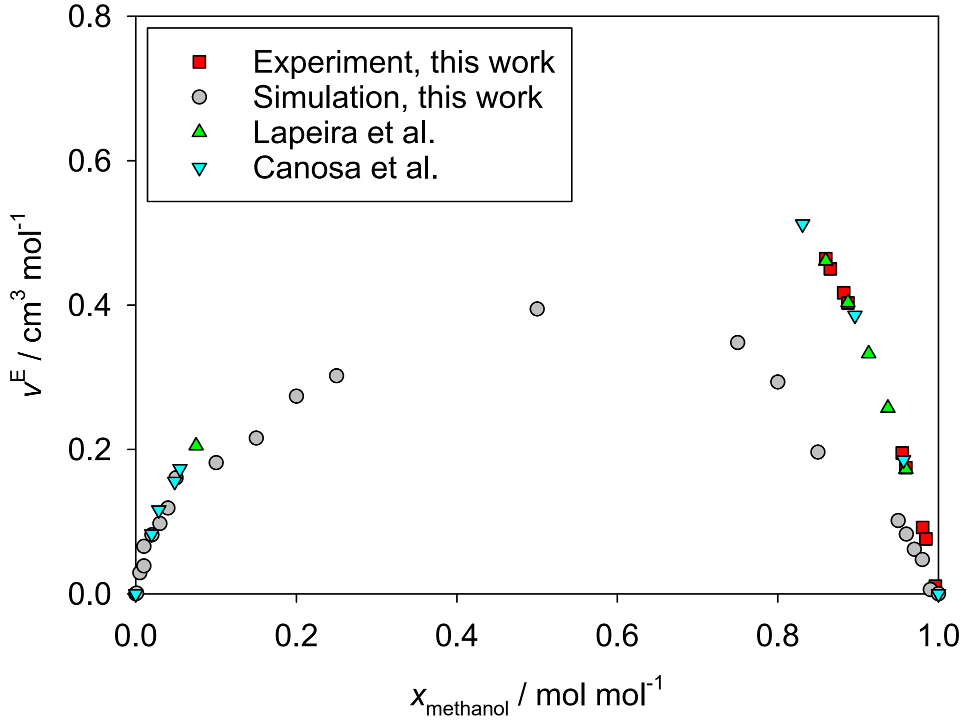

Fig. 1: Excess molar volume of methanol + cyclohexane at 298.15 K and 0.1 MPa compared to experimental data from the literature [1,2].

B Shear viscosity

Simulation

The shear viscosity η can be obtained from equilibrium molecular dynamics simulations by means of the correlation function of the off-diagonal elements of the stress tensor J_p^{xy}

$$\eta = \frac{1}{Vk_BT}\int_0^\infty dt\,\left\langle J_p^{xy}(t)\cdot J_p^{xy}(0)\right\rangle, \tag{2}$$

where V is the total volume. The component J_p^{xy} of the microscopic stress tensor $\mathbf{J}_p$ is given by[3]

$$J_p^{xy} = \sum_{k=1}^{N} m_k v_k^x v_k^y - \frac{1}{2}\sum_{k=1}^{N}\sum_{l\neq k}^{N} r_{kl}^x \frac{\partial u(r_{kl})}{\partial r_{kl}^y}. \tag{3}$$

Here, k and l denote different molecules of any species. The upper indices x and y stand for the spatial vector components, e.g. for velocity v_k^x or site-site distance r_{kl}^x. Five independent terms of the stress tensor, i.e. J_p^{xy}, J_p^{xz}, J_p^{yz}, $(J_p^{xx}-J_p^{yy})/2$ and $(J_p^{yy}-J_p^{zz})/2$, were considered to improve statistics[4].

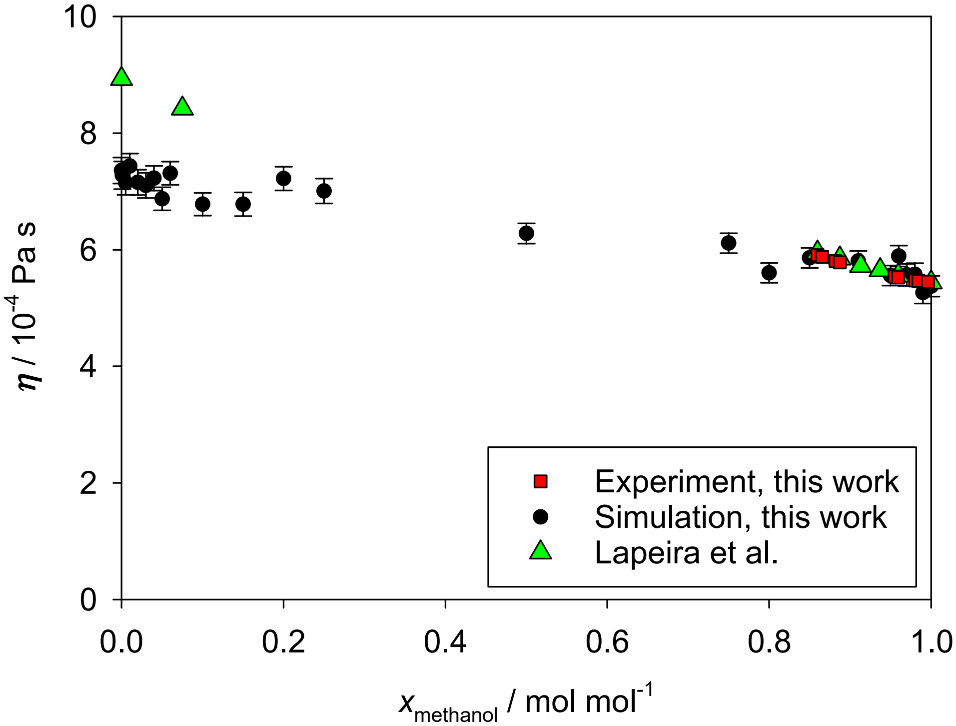

Fig. 2: Shear viscosity of methanol + cyclohexane at 298.15 K and 0.1 MPa compared to experimental data from the literature[1].

C Thermodynamic relations

Chemical potential

The chemical potential μ_i of component i in a binary mixture is defined as the partial derivative of the Gibbs energy with respect to the mole number n_i at constant temperature T, pressure p and mole number of the second component n_j

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j} . \tag{4}$$

It can be subdivided into three parts

$$\mu_i = \mu_i^0 + RT\ln(x_i) + RT\ln(\gamma_i)\,, \tag{5}$$

with the chemical potential of the pure component μ_i^0, the mole fraction x_i and the activity coefficient γ_i.

Gibbs energy

The molar Gibbs energy at constant temperature and pressure is

$$\begin{aligned} g = G/n &= \sum_i x_i\mu_i\,, \\ &= \sum_i x_i\mu_i^0 + RT\sum_i x_i\ln(x_i) + RT\sum_i x_i\ln(\gamma_i) = \sum_i x_i\mu_i^0 + RT\sum_i x_i\ln(x_i\gamma_i)\,, \\ &= g^{\text{ideal},0} + g^{\text{ideal,mix}} + g^{\text{E}} = g^{\text{ideal},0} + g^{\text{mix}}\,. \end{aligned} \tag{6}$$

Liquid-liquid equilibrium

In addition to thermal and mechanical equilibrium, the chemical equilibrium condition for two phases I and II must hold for all components i at the binodal

$$\begin{gathered} \mu_i^{(I)} = \mu_i^{(II)}\,, \\ (x_i\gamma_i)^{(I)} = (x_i\gamma_i)^{(II)}\,, \\ \left(\frac{\partial g^{\text{mix}}}{\partial x_i}\right)_{T,p}^{(I)} = \left(\frac{\partial g^{\text{mix}}}{\partial x_i}\right)_{T,p}^{(II)} . \end{gathered} \tag{7}$$

Fig. 3 shows the mole fraction dependence of the activities $a_i = x_i\gamma_i$, molar Gibbs energy of mixing g^{mix} and thermodynamic factor Γ of a partially miscible liquid mixture at constant temperature and pressure. The binodal condition is fulfilled in Fig. 3 at the compositions marked by the outer limits of the light gray areas, which indicate the metastable region. Stability ceases to exist at the spinodal, where

$$\begin{gathered} \left(\frac{\partial \mu_i}{\partial x_i}\right)_{T,p} = 0\,, \\ \left(\frac{\partial \ln(x_i\gamma_i)}{\partial x_i}\right)_{T,p} = 0\,, \end{gathered}$$

$$\left(\frac{\partial^2 g^{\text{mix}}}{\partial x_i^2}\right)_{T,p} = 0\,, \tag{8}$$

which is fulfilled in Fig. 3 at the compositions marked by the outer limits of the dark gray area, which indicates the unstable region. The thermodynamic factor Γ is zero at the spinodal compositions.

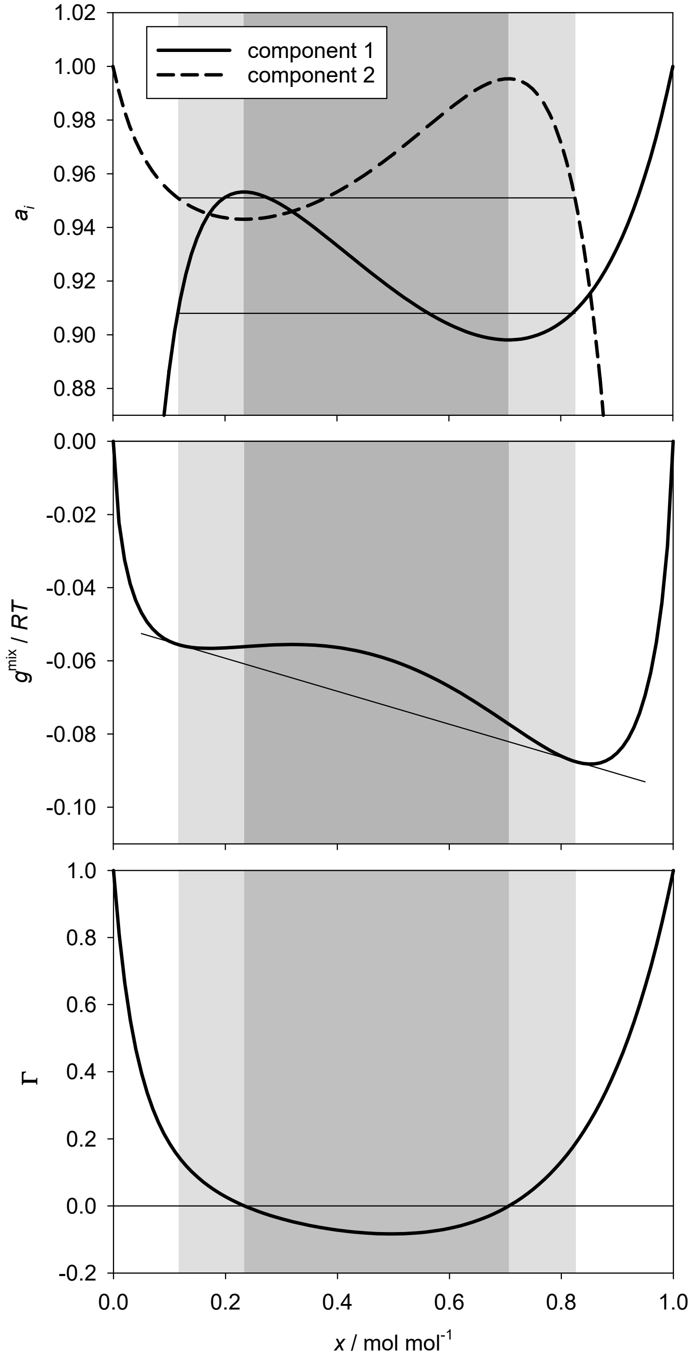

Fig. 3: Mole fraction dependence of activities (top), molar Gibbs energy of mixing (center) and thermodynamic factor (bottom) of a system with liquid-liquid equilibrium at constant temperature and pressure.

D Comparison of excess Gibbs energy models

Five excess Gibbs energy g^E models were assessed for their ability to describe the composition dependent activity coefficients in the mixture methanol and cyclohexane: Van Laar, Margules, NRTL, UNIQUAC and a modified Wilson model. Initially, all models were fitted to experimental LLE data, resulting in an adequate reproduction of the binodal curve. The spinodal curve predicted by this set of models shows a moderate variance, cf. Fig. 4. However, all models significantly underestimate the activity coefficients at infinite dilution (ACID), especially for methanol, cf. Fig. 5. Note that the upper critical temperature is not accurately met by several models. Because the modified Wilson model showed the best results for the ACID it was used for subsequent calculations of the Fick diffusion coefficient.

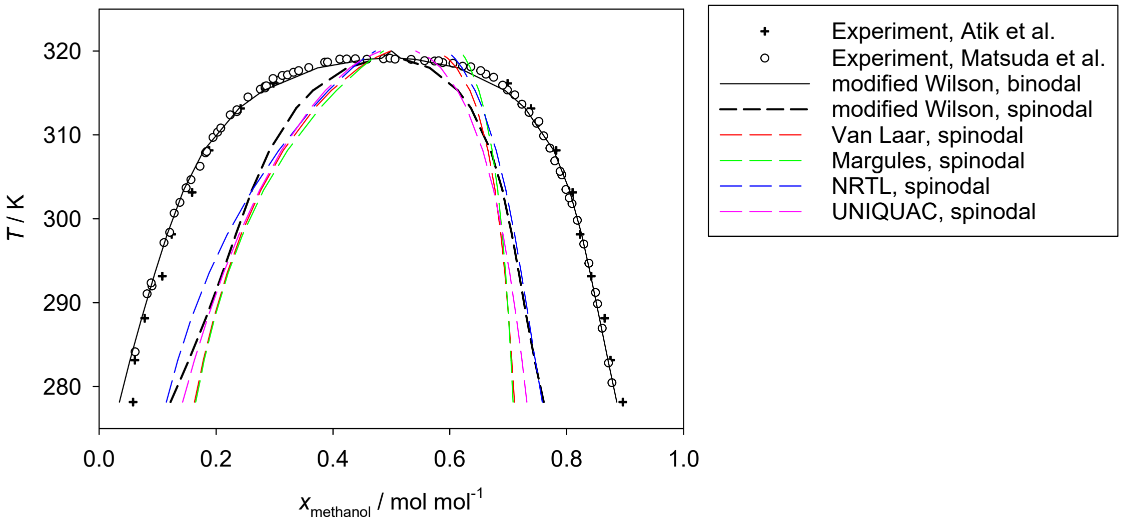

Fig. 4: Temperature dependent liquid-liquid equilibrium of methanol + cyclohexane at 0.1 MPa. Experimental data for the binodal[5,6] and spinodal curves calculated with five g^E models fitted to experimental LLE data are shown.

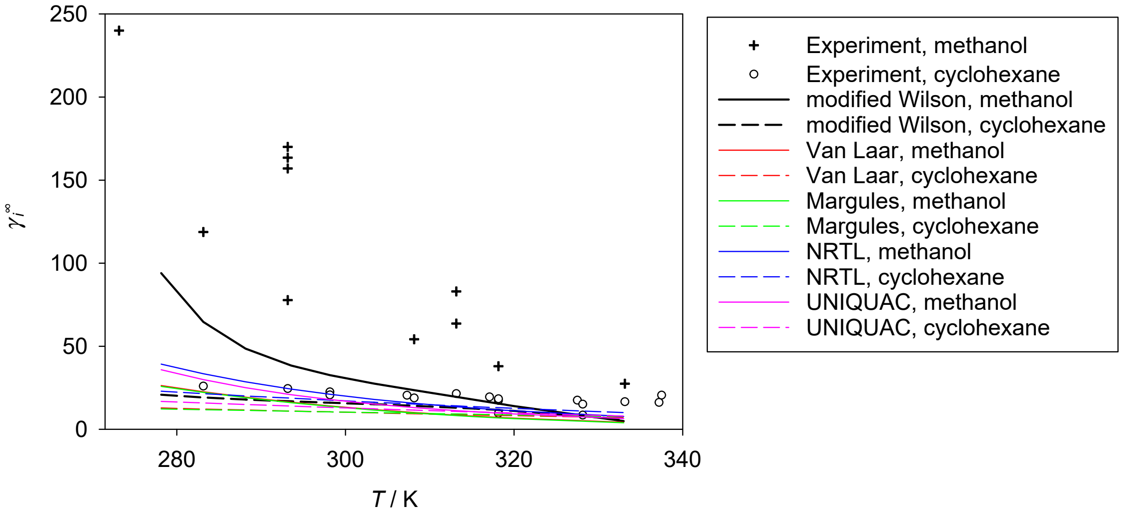

Fig. 5: Temperature dependent activity coefficients at infinite dilution at 0.1 MPa. Experimental data[7–15] and calculated data with five g^E models are shown.

E Hydrogen bonding statistics and simulation snapshots

Hydrogen bonding statistics

Hydrogen bonding statistics were obtained by molecular simulation on the basis of geometric criteria. Following Haughney et al.[16], two methanol molecules are considered as hydrogen bonded when the distance between an oxygen (acceptor) site and a hydrogen (donor) site of two molecules is below 2.6 Å, the distance between the oxygen (acceptor) sites is less than 3.5 Å and the angle between the acceptor acceptor axis and the acceptor donor axis of one molecule is below 30°.

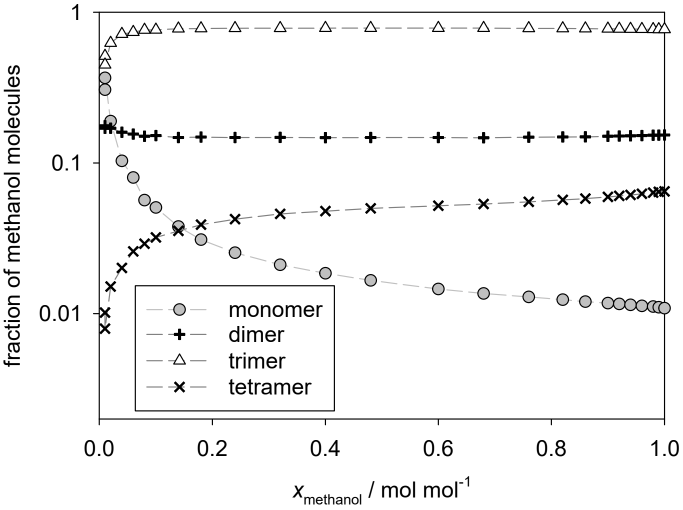

Fig. 6: Fractions of methanol molecules in different association states due to hydrogen bonding in the mixture methanol + cyclohexane at 298.15 K and 0.1 MPa.

Simulation snapshots

The simulation snapshots in Fig. 7 indicate that the methanol molecules do not only constitute dimers to tetramers through hydrogen bonding, but also form larger clusters depending on the methanol concentration.

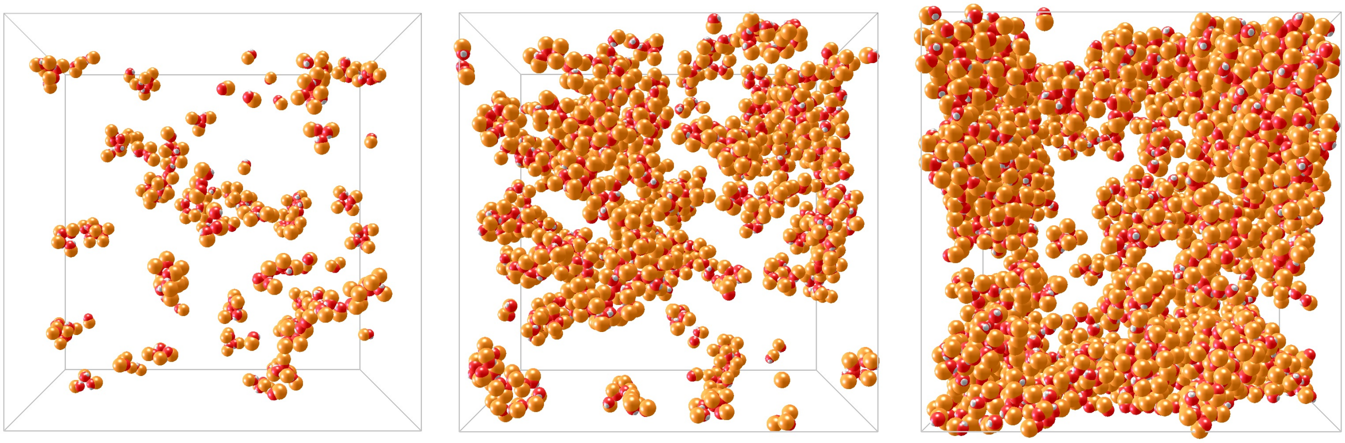

Fig. 7: Simulation snapshots of methanol + cyclohexane at 298.15 K and 0.1 MPa for methanol mole fractions of 0.05, 0.2 and 0.5 mol mol^{-1}. Cyclohexane molecules are not visible, while methanol molecules are fully depicted.

F Chemical potentials from Monte Carlo simulation

Chemical potentials were computed by thermodynamic integration[17,18] in the isobaric-isothermal (NpT) ensemble by Monte Carlo simulation. With these simulations the configurational part of the reduced chemical potentials $\tilde{\mu}_i = \mu_i^*/(RT)$ was obtained. The activity coefficients can be calculated from these data by

$$\ln \gamma_i = \tilde{\mu}_i - \tilde{\mu}_i^0 - \ln x_i\,, \tag{9}$$

where $\tilde{\mu}_i^0$ is the chemical potential of pure component i at the same temperature and pressure.

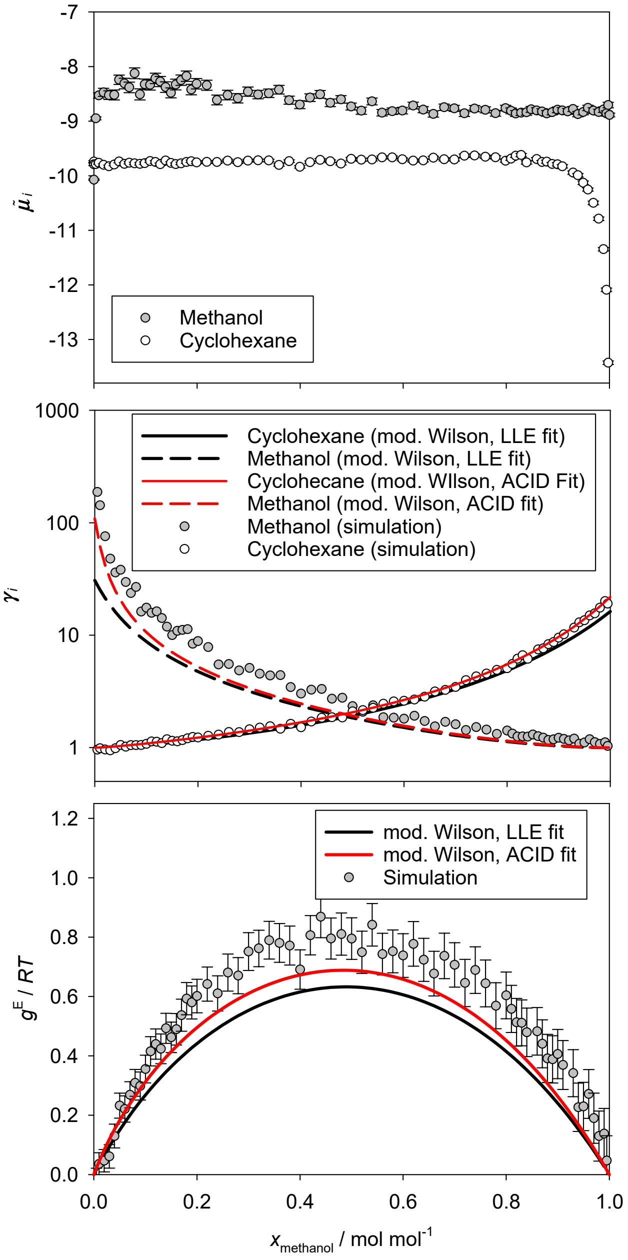

Fig. 8: Chemical potentials, activity coefficients and excess Gibbs energy of methanol + cyclohexane at 298.15 K and 0.1 MPa from simulation compared to the modified Wilson model based on parameters fitted to experimental LLE data or experimental ACID data.

G Darken relation from velocity correlation functions

The Darken relation for the Maxwell-Stefan (MS) diffusion coefficient can be derived from velocity correlation functions. As discussed in the article, the MS coefficient $Đ$ was computed in this work from[19]

$$Đ = \frac{x_j}{x_i}\Lambda_{ii} + \frac{x_i}{x_j}\Lambda_{jj} - \Lambda_{ij} - \Lambda_{ji}\,, \tag{10}$$

with

$$\Lambda_{ij} = \frac{1}{3N}\int_0^\infty \left\langle \sum_{k=1}^{N_i} \mathbf{v}_i^k(0) \cdot \sum_{l=1}^{N_j} \mathbf{v}_j^l(t) \right\rangle \mathrm{d}t\,. \tag{11}$$

The phenomenological coefficients Λ_{ij} contain the velocity cross-correlations for particles of different species i and j. On the other hand, the coefficients Λ_{ii} can be expanded to two types of terms: the auto-correlation functions, which correlate the velocity of one particle with itself, and cross-correlation functions between different particles belonging to the same species i. Considering this, the MS coefficient can be rewritten as[20–22]

$$Đ = x_i D_j^a + x_j D_i^a + x_i x_j (D_{ii}^c + D_{jj}^c - D_{ij}^c - D_{ji}^c)\,. \tag{12}$$

Superscript a denotes auto-correlations of individual particles and these coefficients coincide with the intra-diffusion coefficients, i.e. $D_i = D_i^a$. Superscript c denotes cross-correlations between different particles. There are two types of cross-correlations: between different particles of the same species, denoted by lower indices ii and jj, and correlations between particles of different species, denoted by lower indices ij and ji, where $D_{ij}^c = D_{ji}^c$. Neglecting the cross-correlations entirely leads to the Darken relation

$$Đ = x_i D_j + x_j D_j\,. \tag{13}$$

It can be concluded that the Darken relation is valid for mixtures where the velocity of single molecules is only correlated to itself, which is fulfilled e.g. in the case of gases when molecules hardly interact with each other general. The Darken relation is also valid when the different cross-correlations cancel each other out, e.g. in a nearly ideal liquid (or solid) mixture of very similar molecules.

H Numerical simulation data

Table 1: Simulation results for molar density ρ, intradiffusion coefficients D_i and Maxwell-Stefan diffusion coefficient *Đ* in methanol + cyclohexane at 0.1 MPa.

x_1	ρ	err	D_1	err	D_2	err	*Đ*	err
mol mol^{-1}	mol l^{-1}		10^{-9}m^{2}s^{-1}		10^{-9}m^{2}s^{-1}		10^{-9}m^{2}s^{-1}	
T = 293.55 K								
0.000	9.2728	0.0003			1.457	0.002		
0.001	9.2769	0.0000	2.919	0.067	1.458	0.002	3.11	0.15
0.005	9.2984	0.0000	2.374	0.029	1.464	0.002	3.75	0.18
0.010	9.3263	0.0004	2.002	0.020	1.468	0.002	4.70	0.22
0.020	9.3821	0.0004	1.782	0.014	1.469	0.002	5.05	0.23
0.030	9.4402	0.0004	1.731	0.011	1.476	0.002	5.47	0.26
0.040	9.4992	0.0004	1.682	0.010	1.484	0.002	6.32	0.31
0.050	9.5589	0.0004	1.638	0.009	1.487	0.002	5.69	0.29
0.060	9.6192	0.0002	1.610	0.008	1.490	0.002	6.05	0.28
0.100	9.8676	0.0005	1.594	0.006	1.502	0.002	6.31	0.31
0.150	10.1995	0.0004	1.602	0.005	1.518	0.002	6.92	0.33
0.200	10.5604	0.0005	1.617	0.005	1.535	0.002	8.10	0.38
0.250	10.9533	0.0006	1.643	0.005	1.538	0.002	10.17	0.47
0.500	13.3866	0.0000	1.770	0.004	1.638	0.003	12.17	0.55
0.750	17.2878	0.0000	1.923	0.003	1.771	0.004	7.04	0.30
0.799	18.4190	0.0011	1.929	0.004	1.799	0.004	6.07	0.27
0.850	19.6178	0.0000	1.980	0.003	1.844	0.004	4.52	0.19
0.910	21.3601	0.0007	2.065	0.003	1.923	0.005	2.98	0.12
0.951	22.7354	0.0008	2.135	0.004	1.960	0.007	2.43	0.12
0.960	23.0793	0.0012	2.150	0.004	1.942	0.007	2.38	0.11
0.970	23.4508	0.0014	2.170	0.004	1.981	0.008	2.36	0.10
0.980	23.8420	0.0016	2.189	0.003	1.952	0.010	2.08	0.10
0.990	24.2529	0.0013	2.218	0.004	1.958	0.014	2.18	0.10
1.000	24.6802	0.0014	2.240	0.004				
T = 298.15 K								
0.000	9.2189	0.0003			1.568	0.002		
0.001	9.2246	0.0003	3.150	0.077	1.568	0.002	3.72	0.18
0.005	9.2452	0.0003	2.497	0.031	1.572	0.002	4.65	0.22
0.010	9.2734	0.0003	2.174	0.021	1.576	0.002	4.93	0.22
0.020	9.3296	0.0003	1.937	0.015	1.585	0.002	5.03	0.25
0.030	9.3875	0.0003	1.863	0.012	1.589	0.002	5.73	0.26
0.040	9.4462	0.0003	1.830	0.010	1.594	0.002	6.07	0.27
0.050	9.5050	0.0003	1.790	0.009	1.599	0.002	6.35	0.29
0.060	9.5627	0.0002	1.789	0.008	1.609	0.002	7.34	0.32
0.100	9.8149	0.0004	1.720	0.007	1.619	0.002	7.10	0.33
0.150	10.1486	0.0004	1.726	0.006	1.638	0.002	9.21	0.40
0.200	10.5031	0.0004	1.751	0.005	1.659	0.002	10.10	0.44
0.250	10.8869	0.0005	1.756	0.005	1.660	0.003	9.53	0.45
0.500	13.3289	0.0006	1.903	0.004	1.758	0.003	11.37	0.49
0.750	17.2244	0.0007	2.051	0.003	1.894	0.004	6.95	0.28
0.800	18.3089	0.0009	2.074	0.003	1.915	0.004	5.41	0.23

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Table 1 – continued from previous page

x_1	ρ	err	D_1	err	D_2	err	$Ð$	err
mol mol^{-1}	mol l^{-1}		10^{-9}m^{2}s^{-1}		10^{-9}m^{2}s^{-1}		10^{-9}m^{2}s^{-1}	
0.850	19.5554	0.0009	2.135	0.004	1.943	0.004	4.29	0.19
0.910	21.2301	0.0007	2.255	0.003	2.062	0.005	3.40	0.14
0.950	22.5869	0.0011	2.330	0.004	2.103	0.007	2.66	0.12
0.960	22.9475	0.0012	2.356	0.004	2.116	0.008	2.52	0.11
0.970	23.3209	0.0012	2.367	0.004	2.151	0.010	2.46	0.11
0.980	23.7028	0.0013	2.400	0.004	2.143	0.011	2.41	0.11
0.990	24.1134	0.0013	2.415	0.004	2.136	0.016	2.14	0.10
1.000	24.5170	0.0012	2.447	0.004				
T = 303.38 K								
0.000	9.1583	0.0003			1.709	0.003		
0.001	9.1628	0.0000	3.474	0.075	1.701	0.002	3.63	0.17
0.005	9.1823	0.0000	2.871	0.036	1.709	0.002	4.31	0.20
0.010	9.2094	0.0004	2.533	0.023	1.720	0.003	5.29	0.25
0.020	9.2653	0.0004	2.150	0.016	1.720	0.002	6.02	0.28
0.030	9.3233	0.0004	2.068	0.013	1.729	0.002	6.07	0.28
0.040	9.3794	0.0004	2.005	0.012	1.737	0.002	5.97	0.29
0.050	9.4390	0.0004	1.957	0.010	1.733	0.003	6.81	0.34
0.060	9.4988	0.0002	1.940	0.009	1.744	0.002	6.74	0.29
0.100	9.7435	0.0004	1.889	0.007	1.764	0.002	7.60	0.34
0.150	10.0723	0.0005	1.899	0.006	1.781	0.003	8.78	0.39
0.200	10.4227	0.0006	1.910	0.006	1.793	0.003	10.21	0.47
0.250	10.8172	0.0006	1.918	0.005	1.794	0.003	10.42	0.48
0.500	13.2123	0.0000	2.088	0.004	1.919	0.003	12.27	0.52
0.751	17.1049	0.0006	2.254	0.004	2.065	0.004	6.42	0.29
0.790	17.9511	0.0006	2.287	0.004	2.090	0.005	5.80	0.26
0.850	19.3600	0.0000	2.379	0.004	2.175	0.005	5.14	0.22
0.910	21.0882	0.0000	2.478	0.004	2.240	0.006	3.49	0.14
0.950	22.4319	0.0013	2.550	0.004	2.277	0.008	2.87	0.13
0.960	22.7978	0.0012	2.584	0.004	2.290	0.009	2.72	0.13
0.970	23.1670	0.0014	2.603	0.004	2.304	0.009	2.46	0.11
0.980	23.5592	0.0017	2.639	0.004	2.339	0.012	2.54	0.12
0.990	23.9660	0.0014	2.663	0.004	2.347	0.016	2.62	0.11
1.000	24.3869	0.0015	2.690	0.004				
T = 313.21 K								
0.000	9.0419	0.0004			1.975	0.003		
0.001	9.0468	0.0000	3.970	0.084	1.975	0.003	4.14	0.18
0.005	9.0666	0.0000	3.720	0.037	1.982	0.003	4.80	0.20
0.010	9.0932	0.0004	2.983	0.026	1.988	0.003	5.77	0.27
0.020	9.1478	0.0004	2.666	0.019	1.994	0.003	6.66	0.30
0.030	9.2029	0.0004	2.475	0.015	2.004	0.003	7.14	0.31
0.040	9.2593	0.0004	2.400	0.013	2.008	0.003	7.23	0.35
0.050	9.3188	0.0004	2.341	0.011	2.020	0.003	8.26	0.37
0.060	9.3765	0.0002	2.313	0.011	2.022	0.003	8.18	0.37
0.100	9.6184	0.0005	2.254	0.008	2.044	0.003	8.57	0.40
0.150	9.9411	0.0005	2.253	0.007	2.069	0.003	11.38	0.49
0.200	10.2873	0.0005	2.249	0.006	2.087	0.003	12.23	0.50

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Table 1 – continued from previous page

x_1 mol mol^{-1}	ρ mol l^{-1}	err	D_1 10^{-9}m^{2}s^{-1}	err	D_2 10^{-9}m^{2}s^{-1}	err	Đ 10^{-9}m^{2}s^{-1}	err
0.250	10.6613	0.0000	2.274	0.005	2.111	0.003	11.01	0.48
0.500	13.0388	0.0000	2.454	0.005	2.229	0.003	13.25	0.54
0.740	16.6920	0.0006	2.639	0.004	2.353	0.005	8.22	0.35
0.790	17.6996	0.0006	2.737	0.005	2.435	0.005	7.49	0.33
0.840	18.8957	0.0007	2.802	0.005	2.494	0.006	5.80	0.26
0.910	20.8199	0.0008	2.955	0.005	2.602	0.007	4.16	0.18
0.950	22.1495	0.0013	3.051	0.004	2.665	0.008	3.30	0.14
0.960	22.5125	0.0013	3.085	0.005	2.677	0.009	3.28	0.14
0.970	22.8824	0.0014	3.114	0.005	2.704	0.010	2.85	0.12
0.980	23.2699	0.0015	3.148	0.005	2.722	0.013	3.09	0.13
0.990	23.6701	0.0013	3.172	0.005	2.720	0.018	2.88	0.12
1.000	24.0885	0.0014	3.208	0.005				
T = 315.31 K								
0.000	9.0175	0.0004			2.038	0.003		
0.001	9.0226	0.0000	4.093	0.086	2.037	0.003	3.98	0.19
0.005	9.0419	0.0000	3.514	0.041	2.039	0.003	4.74	0.24
0.010	9.0684	0.0004	3.140	0.027	2.043	0.003	5.77	0.25
0.020	9.1227	0.0004	2.780	0.020	2.059	0.003	7.00	0.31
0.030	9.1780	0.0004	2.620	0.015	2.063	0.003	6.82	0.31
0.040	9.2346	0.0004	2.500	0.013	2.070	0.003	7.62	0.34
0.050	9.2926	0.0004	2.438	0.012	2.077	0.003	7.75	0.34
0.060	9.3500	0.0002	2.407	0.010	2.085	0.003	8.08	0.34
0.100	9.5907	0.0004	2.307	0.009	2.106	0.003	9.04	0.44
0.150	9.9123	0.0005	2.312	0.007	2.129	0.003	9.83	0.45
0.200	10.2570	0.0005	2.340	0.006	2.157	0.003	11.46	0.52
0.250	10.6477	0.0006	2.334	0.006	2.144	0.003	12.03	0.54
0.500	13.0021	0.0000	2.544	0.005	2.293	0.004	11.83	0.52
0.750	16.8022	0.0000	2.784	0.004	2.484	0.004	8.47	0.35
0.810	18.0907	0.0006	2.863	0.004	2.549	0.005	7.05	0.29
0.850	19.0533	0.0000	2.942	0.004	2.622	0.006	5.58	0.22
0.910	20.7610	0.0008	3.061	0.004	2.682	0.007	4.06	0.17
0.950	22.0907	0.0014	3.175	0.005	2.763	0.009	3.63	0.15
0.960	22.4619	0.0014	3.184	0.005	2.735	0.010	3.16	0.14
0.970	22.8141	0.0014	3.228	0.005	2.789	0.011	3.25	0.14
0.980	23.2044	0.0015	3.258	0.005	2.787	0.013	3.13	0.13
0.990	23.6076	0.0014	3.299	0.005	2.839	0.018	3.01	0.13
1.000	24.0242	0.0013	3.326	0.005				

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