Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

for

Hydrogen bonding in DPD:

Application to low molecular weight alcohol-water mixtures

Gokhan Kacar [a, b, c] and Gijsbertus de With [a*]*

[a] Laboratory of Materials and Interface Chemistry, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Eindhoven, The Netherlands

[b] Dutch Polymer Institute (DPI), P.O. Box 902, 5600 AX Eindhoven, The Netherlands

[c] Department of Genetics and Bioengineering, Faculty of Engineering, Trakya University, 22030, Edirne, Turkey

Corresponding authors:

* E-mail: gokhankacar@trakya.edu.tr

* E-mail: g.dewith@tue.nl

Morse parameters

The concentrations of alcohols in the mixtures we simulated are different than they are reported in reference [1]. Therefore, we first calculate the $E_{\text{H-bond}}$ for the reported concentrations from Eq. 1 in the manuscript and then interpolated to the concentration of our interest. The interpolation is straightforward as there is a linear relationship between the reported concentrations and the derived $E_{\text{H-bond}}$. In the simulations, we use the concentrations tabulated as 'Calculated' and the corresponding D_0s.

Table S1. D_0 values calculated for Methanol-Water mixture for different concentrations.

Derived from reference [1]				Calculated	
x_{alcohol}	E_{pot} [kJ/mol]	$E_{\text{H-bond}}$ [kJ/mol]	$E_{\text{H-bond}}$ [$k_{\text{B}}T$]	x_{alcohol}	D_0 [$k_{\text{B}}T$]
0.00	–41.37	–	–	0.00	–
0.06	–39.79	11.50	4.65	0.10	5.06
0.12	–37.99	13.30	5.37	0.20	6.33
0.19	–35.93	15.36	6.20	0.30	7.46
0.27	–33.64	17.65	7.13	0.39	8.68
0.36	–31.04	20.25	8.18	0.51	10.07
0.46	–28.09	23.20	9.37	0.59	11.12
0.57	–24.65	26.64	10.76	0.69	12.41
0.69	–20.66	30.63	12.37	0.84	14.20
0.83	–15.86	35.43	14.31	0.93	15.31
1.00	–9.92	–	–	1.00	–

Table S2. D_0 values calculated for Ethanol-Water mixture for different concentrations.

Derived from reference [1]				Calculated	
$x_{alcohol}$	E_{pot} [kJ/mol]	$E_{H\text{-}bond}$ [kJ/mol]	$E_{H\text{-}bond}$ [k_BT]	$x_{alcohol}$	D_0 [k_BT]
0.00	–41.37	–	–	0.00	–
0.04	–40.70	19.31	7.80	0.10	8.22
0.09	–39.84	20.17	8.15	0.20	9.14
0.14	–38.77	21.24	8.58	0.30	9.97
0.21	–37.46	22.55	9.11	0.39	10.85
0.28	–35.81	24.20	9.77	0.51	11.86
0.37	–33.84	26.17	10.57	0.59	12.62
0.48	–31.41	28.60	11.55	0.69	13.56
0.61	–28.33	31.68	12.79	0.84	14.86
0.78	–24.31	35.70	14.42	0.93	15.66
1.00	–18.64	–	–	1.00	–

Table S3. D_0 values calculated for 1-Propanol-Water mixture for different concentrations.

Derived from reference [1]				Calculated	
$x_{alcohol}$	E_{pot} [kJ/mol]	$E_{H\text{-}bond}$ [kJ/mol]	$E_{H\text{-}bond}$ [k_BT]	$x_{alcohol}$	D_0 [k_BT]
0.00	–41.37	–	–	0.00	–
0.03	-40.69	16.18	6.53	0.10	7.21
0.07	–39.81	17.06	6.89	0.20	8.28
0.11	–38.71	18.16	7.33	0.30	9.23
0.17	–37.38	19.49	7.87	0.39	10.25
0.23	–35.73	21.14	8.54	0.51	11.42
0.31	–33.66	23.21	9.37	0.59	12.3
0.41	–31.05	25.82	10.43	0.69	13.38
0.55	–27.55	29.32	11.84	0.84	14.88
0.73	–22.78	34.09	13.77	0.93	15.82
1.00	–15.50	–	–	1.00	–

The scaling function α

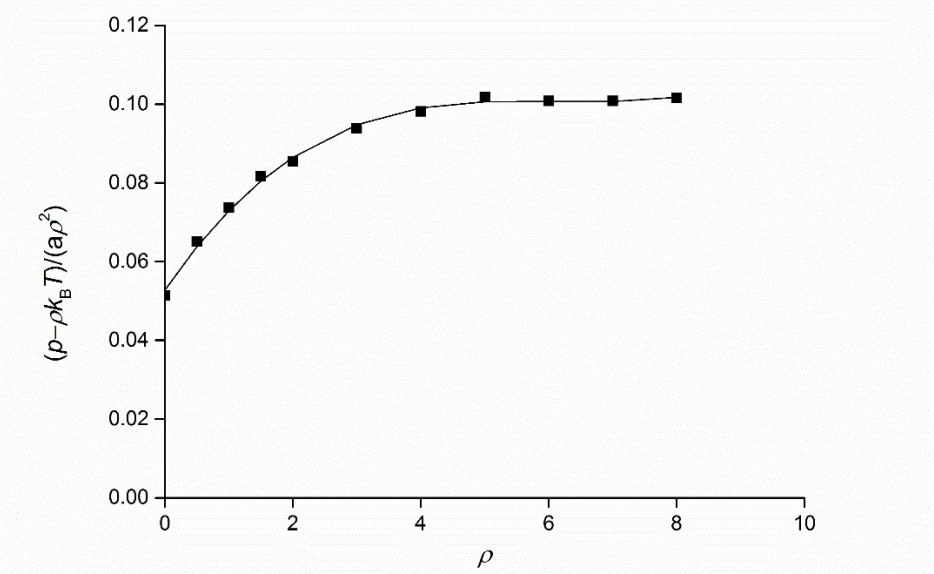

Figure S1. Fig. 4 of Groot and Warrens original work (■) in which the data points are fitted a third order polynomial (–) $(p-\rho k_B T)/(a\rho^2) = p_1\rho^3 + p_2\rho^2 + p_3\rho + p_4$ with parameters $p_1 = 0.0002131, p_2 = -0.003917, p_3 = 0.02381, p_4 = 0.05282$.

Parameterization of conservative interactions

For the coarse-graining, we consider every molecule representing Methanol, Ethanol, 1-Propanol or Water as a single bead. The physical parameters of the beads and calculated DPD interactions are given in Table S4.

Table S4. Liquid state properties of beads used in simulations with mass density $\rho_{m,i}$, Molecular weight M_W, number density $\rho_{i,\text{pure}}$, solubility parameter δ, like-like interaction a_{ii}, and interactions of bead i with water $a_{i\text{-water}}$.

Type of Bead	$\rho_{m,i}$ [g/cm^3]	M_W [g/mol]	$\rho_{i,\text{pure}} = \rho_{m,i}/M_W$ [Å^{-3}]	δ [(J/cm^3)$^{0.5}$]	a_{ii} [k_BT]	$a_{i\text{-water}}$ [k_BT]
Methanol (M)	0.787	32.04	0.0148	29.61	177.44	73.27
Ethanol (E)	0.784	46.07	0.0103	26.49	409.71	107.58
1-Propanol (P)	0.799	60.09	0.0080	24.53	729.59	143.03
Water (W)	1.000	18.02	0.0334	47.00	25.00	25.00

References

1. Wensink, E. J. W.; Hoffmann, A. C.; van Maaren, P. J.; van der Spoel, D. Dynamic properties of water/alcohol mixtures studied by computer simulation. *J. Chem. Phys.* **2003,** *119* (14), 7308-7317.