Electronic Supplementary Information

A Comprehensive Physico-chemical Study on the Molecular Structure Effects of Sulfonated Polyamide Thin-film Composite

Jiahui Hu,[a] Yang Liu,[a] Xingzhong Cao,[b] Peng Zhang,[b] Junfeng Zheng,[a] Meng Li,[a] Xuan Zhang*[a] and Lianjun Wang *[a]

a Jiangsu Key Laboratory of Chemical Pollution Control and Resources Reuse, School of Environmental and Biological Engineering, Nanjing University of Science & Technology, Nanjing 210094, China;

b Multidiscipline Research Center, Institute of High Energy Physics, CAS, Beijing China.

Corresponding Author:

xuanzhang@mail.njust.edu.cn (Xuan Zhang), Tel./fax: +86-25-84315916

wanglj@mail.njust.edu.cn (Lianjun Wang)

Simulation Details.

A bead is defined essentially in terms of the chemical constitution of the system. The bead is a representation that conserves aspects from the initial structure. The pair repulsion parameters, a_{mn}, were calculated between each pair of molecular structures. The calculation of these parameters is related to Groot's approximation[1] that utilized Flory-Huggins parameter χ_{mn} to determine the maximum repulsion between the particle pair *m* and *n*, Equation (1).

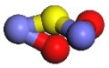
$$a_{mn} = a_{mm} + 3.27\chi_{mn} \qquad for\ \rho = 3 \tag{1}$$

The term a_{mm} is the self-repulsion interaction that is derived from the compressibility of pure water (a_{mm} = 75 k_BT/ρ = 25, with k_BT=1 and ρ = 3). In this work Flory-Huggins parameters χ_{mn} were determined by cohesive energy density (CED) at 298 K via molecular dynamics (MD) simulation.

The second method involves the calculation of the Flory-Huggins parameter by an approximation using solubility parameters (δ_m) of the pure components. The CED is simply the cohesive energy per unit of volume. The solubility parameters of pure systems are obtained from atomistic simulations such as MD. In particular, for our case study, MD methodology includes the construction of three periodic boundary cells, each one containing 20 molecules of corresponding substance, methanesulfonic acid. The CED was obtained by performing with a successive steps involving a first NVT ensemble at *T*=298 K, second NVT ensemble at P=0.006 GPa, *T*=298 K and the last NVT ensemble molecular dynamics simulations at *T*=298 K. Berendsen's barostat with decay constant 0.1 ps and Nose's thermostat *Q* ratio 1 were used to control pressure

and temperature, respectively. The system is MD-relaxed during 1 x 10^5 simulations steps using a time step of 1 fs. Configurations were then collected every 2500 steps until completing configurations. The CED is calculated as the average of the CED from 40 output configurations. During the whole MD simulation, COMPASS force field was used for the calculation of the Flory-Huggins χ_{mn}. COMPASS is a general all-atom force field for atomistic simulation of common organic molecules and polymers, developed by using state of the art ab initio and empirical parametrization techniques, and it has been validated for a wide variety of systems. In our calculations we used the charge assignment by the force field for the interatomic interactions.

Table S1 Coarse-grained structure for the involved components.

Solvent	Molecules	Bead type	Molecular structure	Coarse-grained structure	Solubility parameter $(J\ cm^{-3})^{1/2}$
Water	H_2O	W			47.9 [a]
Aniline	C_6H_5N	A			21.4 [a]
Methanesulfonic acid	CH_3SO_3H	S			45.5 [b]
Diphenyl ether	$C_6H_5OC_6H_5$	E			20.9 [a]
n-Hexane	C_6H_{14}	H			14.9 [a]
Benzene	C_6H_6	B			18.6 [a]
Acetyl chloride	CH_3COCl	C			19.4 [a]

a) Obtained from ref;[2]

b) Obtained from cohesive energy density (CED) result.[3]

Table S2 The input repulsion (reduced) parameters for the interacting beads.

	W	A	S	H	B	C	E
W	25.00						
A	97.00	25.00					
S	25.42	84.41	25.00				
H	162.30	31.43	142.82	25.00			
B	111.78	25.99	97.95	27.06	25.00		
C	96.55	25.45	84.81	27.79	25.07	25.00	
E	134.71	25.04	115.99	32.21	25.93	25.36	25.00

Table S3 The calculated stoichiometry for ODADS and BDSA with C_{TMC} fixed at 0.10% (w/v).

ODADS % (w/v)	Calculated stoichiometry [a]	R [b] %	BDSA % (w/v)	Calculated stoichiometry [a]	R [b] %
0.3	2.21	65.93	0.5	3.85	52.2
0.5	3.68	90.36	0.7	5.40	86.5
0.8	5.89	98.10	0.85	6.56	90.9
1.0	7.37	98.54	1.0	7.71	95.4
-	-	-	1.2	9.25	91.0

a) The stoichiometry refers to the functionality;

b) Rejection to Na_2SO_4 of 1.0 g L^{-1}.

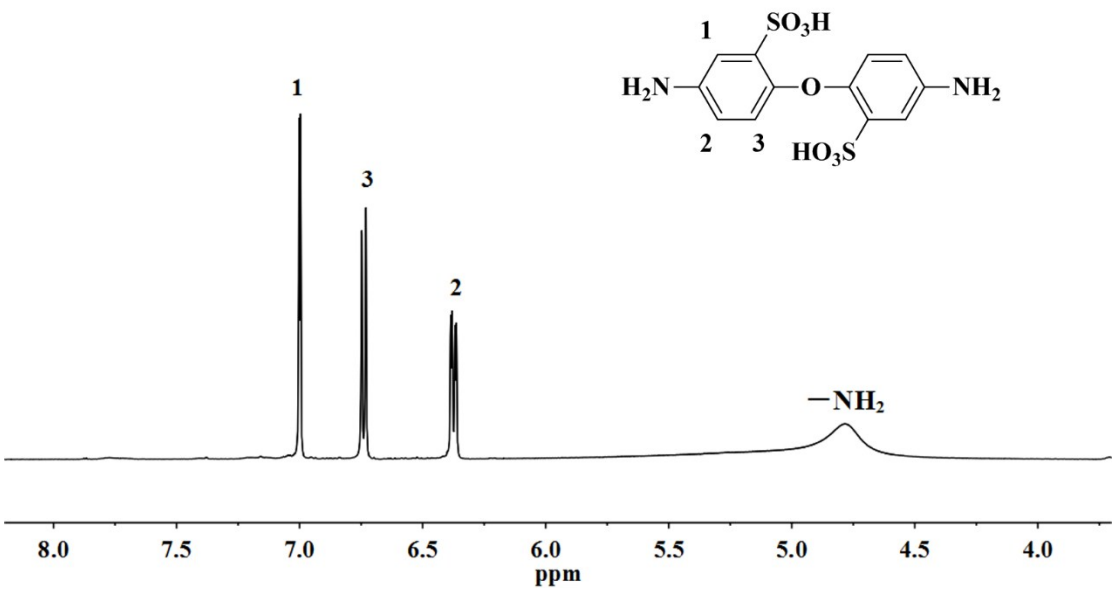


Fig. S1. ^{1}H NMR spectrum of ODADS.

References

1. R. D. Groot and P. B. Warren, *J. Chem. Phys.*, 1997, **107**, 4423−4435.

2. C. M. Hansen, Hansen Solubility Parameters A User's Handbook, second ed., *Taylor and Francis*, Boca Raton, 2007.

3. J. H. Hu, Z. W. Lv, Y. Z. Xu, X. Zhang and L. J. Wang, *J. Membr. Sci.*, 2016, **505**, 119-129.