Supplementary Information for: The Joint Effect of Surface Polarity and Concentration on the Structure and Dynamics of Acetonitrile Solution: A Molecular Dynamics Simulation Study

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(a) 

(b) 

(c) 

(d)
Figure S1 The atomic number density profiles of water oxygen with different molar fractions at surface polarity (a) $k=0.1$ (b) $k=0.2$ (c) $k=0.3$ (d) $k=0.4$ (e) $k=0.5$ (f) $k=0.6$ (g) $k=0.7$ (h) $k=0.8$ (i) $k=0.9$. 
Figure S2 The atomic number density profiles of ACN nitrogen with different molar fractions at surface polarity (a) k=0.1 (b) k=0.2 (c) k=0.3 (d) k=0.4 (e) k=0.5 (f) k=0.6
(g) $k=0.7$ (h) $k=0.8$ (i) $k=0.9$. 
Figure S3 The atomic number density profiles of ACN methyl carbon with different molar fractions at surface polarity (a) $k=0.1$ (b) $k=0.2$ (c) $k=0.3$ (d) $k=0.4$ (e) $k=0.5$ (f) $k=0.6$ (g) $k=0.7$ (h) $k=0.8$ (i) $k=0.9$.

Figure S4 The value of the first minimum on the potential of mean force (PMF) profile defined in Eq. (1) in the manuscript for (a) water (b) ACN at different surface polarities and concentrations.
Figure S5 The orientational distribution in the LS region of water dipoles with different concentrations at surface polarity (a) k=0.1 (b) k=0.2 (c) k=0.3 (d) k=0.4 (e)
k=0.5 (f) k=0.6 (g) k=0.7 (h) k=0.8 (i) k=0.9.
Figure S6 The orientational distribution in the LS region of ACN dipoles with different concentrations at surface polarity (a) $k=0.1$ (b) $k=0.2$ (c) $k=0.3$ (d) $k=0.4$ (e) $k=0.5$ (f) $k=0.6$ (g) $k=0.7$ (h) $k=0.8$ (i) $k=0.9$.

Figure S7 The rotational relaxation times for water and ACN dipoles in the bulk phase at different ACN concentrations.
Figure S8 The diffusion coefficients for water and ACN in the bulk phase at different ACN concentrations.

Figure S9 The parallel diffusion coefficients in the LS (0~5Å) region of water (a)(b) and ACN (c)(d) with different concentrations at various surface polarity.
Figure S10  The rotational relaxation times in the LS region of (a) (b): water dipole and (c) (d): ACN dipole with different concentrations at various surface polarity.
Figure S11 The parallel diffusion coefficients in the second layer (z=5~10 Å) of (a) (b): water and (c) (d): ACN with different concentrations at various surface polarity.

Translational-Rotational Decoupling

For bulk simple liquids that are above the glass transition temperature, the translational and rotational motion of particles are well described by the Stokes-Einstein and Stokes-Einstein-Debye relations\(^1\)\(^2\)

\[
D = \frac{\kappa B k_B T}{6 \pi \eta r^2} \quad (1)
\]

\[
\tau_R = \frac{4 \kappa B k_B T}{3 \eta r^2} \quad (2)
\]

where \(D\) is the diffusion coefficient, \(\tau_R\) is the rotational relaxation time, \(k_B\) is the Boltzmann constant, \(T\) is the temperature, \(\eta\) is the viscosity and \(r\) is the radius of the molecules. For bulk liquids, the value of \(D\tau_R\) is a constant only depends on \(r^2\). However, for liquids in confinement, the value \(D\tau_R\) would often deviate from constant behavior, and this is called translational-rotational decoupling\(^3\)\(^4\).

In Fig. S12, the decoupling parameter \(D\tau_R/\sigma_{||}^2/\sigma_{\perp}^2\) was calculated for water and ACN in the liquid-solid interface at different molar fractions and surface polarities. For bulk liquids, the value of this decoupling parameter would be 1. For water, all values of the decoupling parameter are significantly less than 1 (Fig. S12a), which is similar to the trend in previous work by Debenedetti and co-workers.\(^4\) This indicates that at the liquid-solid interface the translational dynamics slows down faster than the rotational dynamics, and there is a decoupling between translational and rotational dynamics. For ACN, most decoupling parameters are greater than that of water with many values greater than 1. This implies that the translational-rotational decoupling in ACN is weaker than water.
Figure S12 The decoupling parameter $D_{\parallel}/\sigma_{\text{wpp}}\sigma_{\text{wpppp}}$ of (a) water (b) ACN with different concentrations at various surface polarity.

References