Dynamics and Microstructures of Nicotine/Water Binary Mixtures Near the Lower Critical Solution Temperature

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Supporting Information

I. OHD-OKE time constants

The OHD-OKE time constants, τ, were plotted as a function of nicotine concentration at each temperature in Figure 3. The values of τ are given in Table S1.

Table S1. OHD-OKE time constants of nicotine/water mixtures at various concentrations and temperatures

T (°C)	τ (ps)							
	x_{nic}=1	x_{nic}=0.9	x_{nic}=0.6	x_{nic}=0.5	x_{nic}=0.4	x_{nic}=0.3	x_{nic}=0.1	x_{nic}=0.006
15.5	101±2	139 ± 9	255 ± 12	366 ± 10	805 ± 27	767±49	493±23	74 ± 5
30.0	55 ± 2	69 ± 6	127 ± 9	152 ± 7	323 ± 6	280 ± 9	194 ± 9	43 ± 3
44.9	36 ± 1	49 ± 4	83 ± 3	98 ± 5	135 ± 6	131 ± 4	107 ± 2	31 ± 3
59.8	28 ± 1	35 ± 3	51 ± 3	53 ± 2	65 ± 2	63 ± 6	73 ± 4	22 ± 1
74.6	22.3±0.2	26 ± 4	32 ± 1	34 ± 2	39 ± 1	40 ± 1	--	16 ± 2
97.5	16.0±0.3	18 ± 2	19 ± 1	21 ± 1	24 ± 2	--	--	11 ± 1

II. Bulk viscosities of nicotine/water binary mixtures at various temperatures

The viscosity of nicotine/water binary mixtures is highly water dependent, particularly as temperature is lowered below the LCST. Viscosities were measured at ten concentrations from ~10 ºC up to the phase separation point and up to ~100ºC in infinitely miscible samples. The viscosities at the OHD-OKE experimental temperatures are given in Table S2.

Table S2. Viscosity (cP) of nicotine/water mixtures at various concentrations and temperatures

T (°C)	χ_{nic}=1	χ_{nic}=0.9	χ_{nic}=0.8	χ_{nic}=0.7	χ_{nic}=0.6	χ_{nic}=0.5	χ_{nic}=0.4	χ_{nic}=0.3	χ_{nic}=0.1	χ_{nic}=0.006
15.5	5.5	3.6	8.0	8.9	12.0	27.5	50.8	39.9	14.9	1.49
30.0	3.6	2.0	4.8	4.5	5.8	11.1	17.3	14.2	7.1	1.33
44.9	2.5	1.3	3.5	2.8	3.1	5.0	5.8	6.2	4.1	1.15
59.8	1.9	0.59	2.9	2.1	2.0	2.8	2.0	3.4	2.6	0.95
74.6	1.5	0.77	2.5	1.8	1.5	2.0	0.76	2.0	1.8	0.75
97.5	1.1	0.63	2.2	1.7	1.2	1.6	0.22	--	--	0.23

[a]Viscosity error is ~1%.

III. First-principles calculations and atomistic simulations

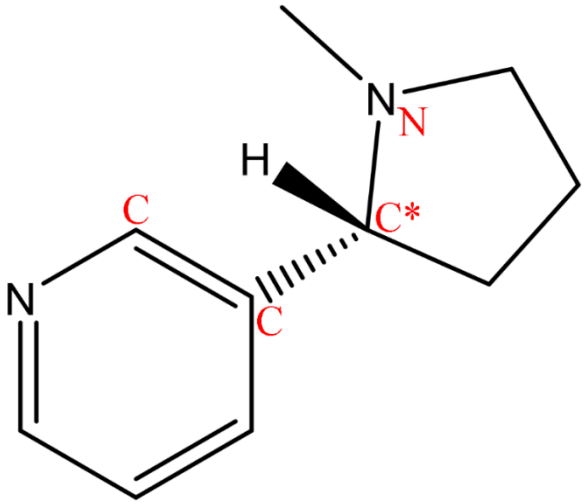

Figure S1. Definition of N-C*-C-C dihedral angle between two ring planes in nicotine molecule.

Table S3. Atomistic simulation system compositions for binary nicotine-water mixtures. The simulation box lengths and liquid densities for these binary mixtures were obtained at 333 K.

x_{nic}	No. of nicotine	No. of water	Total atoms	Box length (nm)	Liquid density (g/cm^3)
0.01	60	5940	19380	5.8944	0.9506
0.10	360	3240	19080	5.8618	0.9556
0.15	450	2550	19350	5.9068	0.9589
0.30	600	1400	19800	5.9515	0.9644
0.40	640	960	19520	5.9120	0.9671
0.50	680	680	19720	5.9413	0.9699
0.60	690	460	19320	5.8939	0.9735
0.75	720	240	19440	5.8926	0.9773
0.90	720	80	18960	5.8405	0.9813
1.00	750	0	19500	5.8774	0.9851

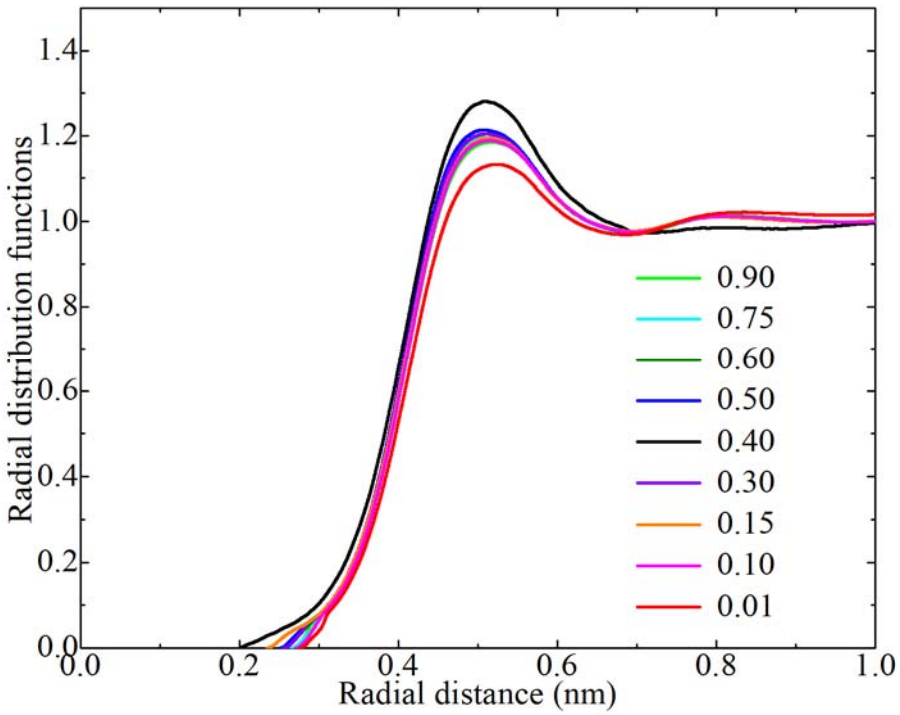

Figure S2. The $N_{pyrrolidino}$-H_{water} RDF plots in nicotine/water mixtures with various nicotine mole fractions (x_{nic}) at 333 K.

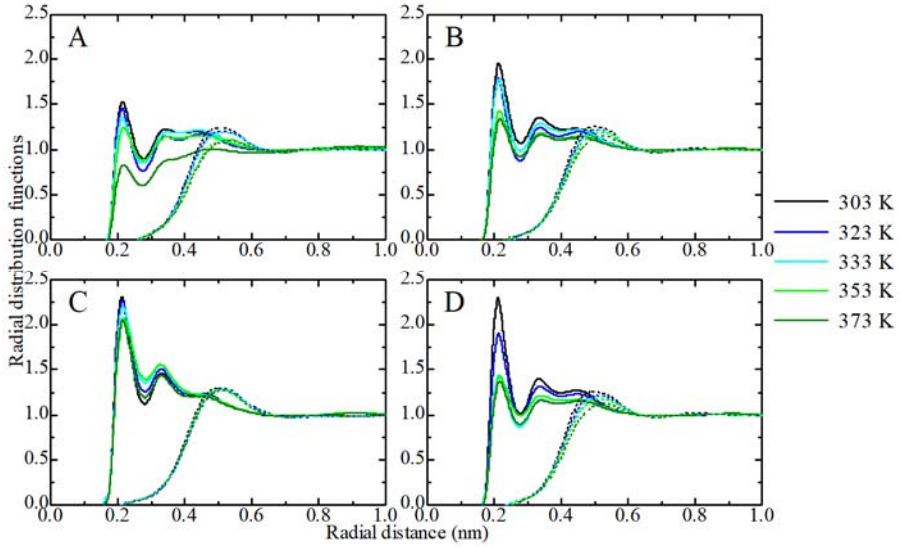

Figure S3. The $N_{pyridine}$-H_{water} (solid lines) and $N_{pyrrolidino}$-H_{water} (short-dashed lines) RDF plots in nicotine/water mixtures with nicotine concentration (x_{nic}) of (A) 0.90, (B) 0.60, (C) 0.40, and (D) 0.15, at different temperatures.

IV. Additional COSY spectra

The COSY spectra for x_{nic}=0.9 and x_{nic}=0.4 were presented in Figure 11 in the main text. Additional COSY spectra are shown in Figure S4 below. The COSY spectrum for x_{nic}=0.8 (panel A) shows no intermolecular cross peaks between water and nicotine. This is similar to what was observed for x_{nic}=0.9 in the main text. The spectra for x_{nic}=0.6 (panel B) and x_{nic}=0.1 (panel C) show intermolecular cross peaks. This is similar to the COSY spectrum for x_{nic}=0.4 that was presented in the main text.

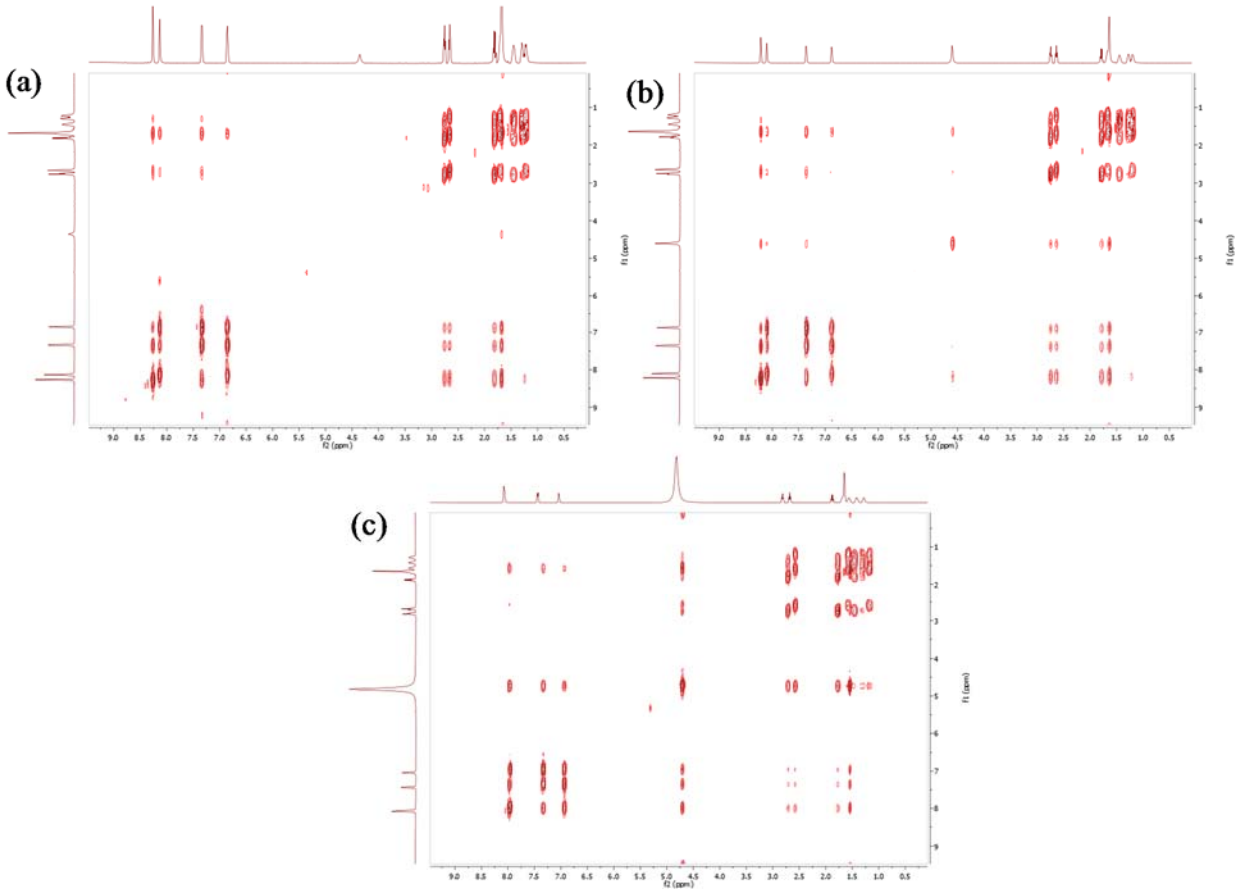

Figure S4. COSY spectra of nicotine/water binary mixtures at various concentrations (A) x_{nic}=0.8, (B) x_{nic}=0.6, and (C) x_{nic}=0.1.

V. Linear Fits and Residuals for Figures 6A and 6B

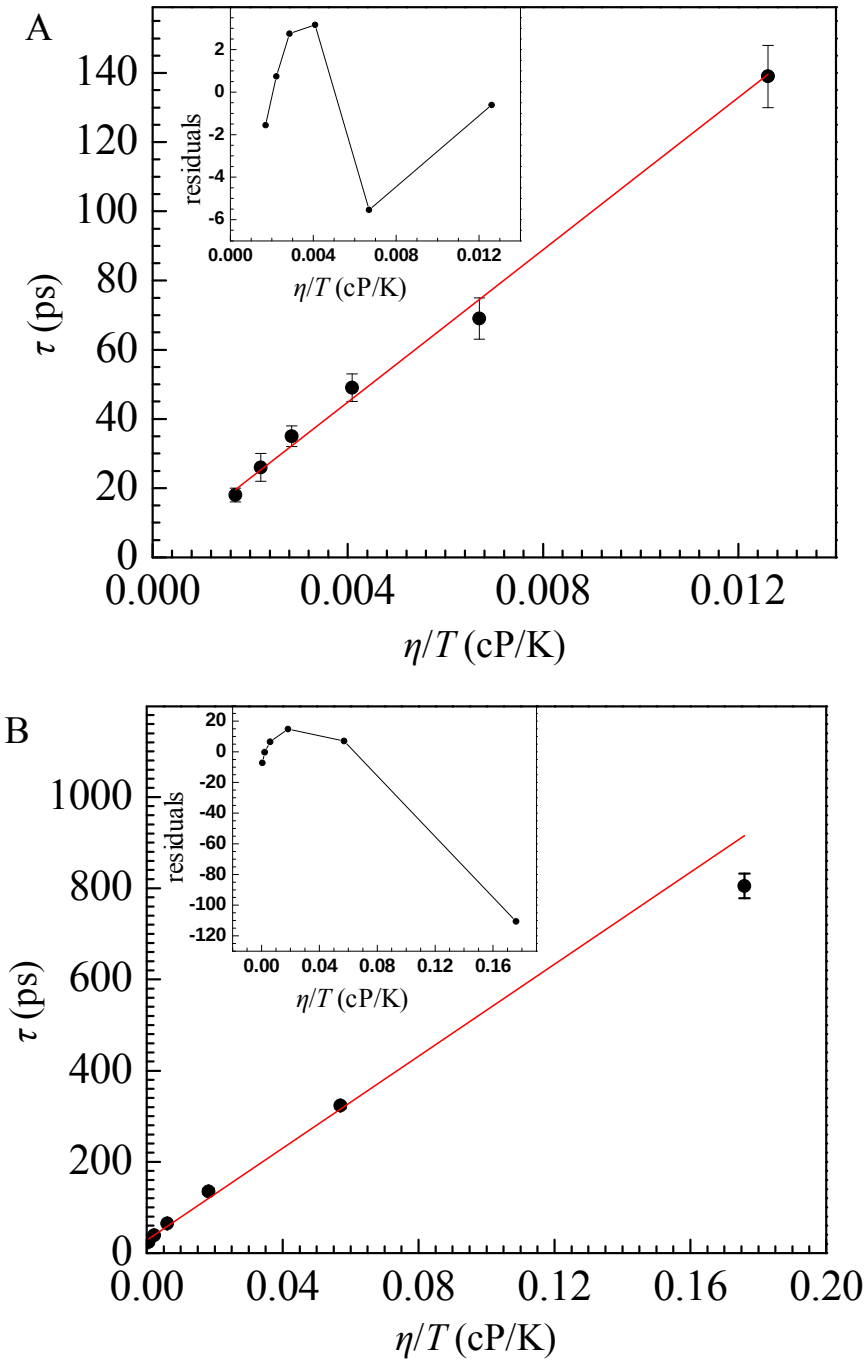

Figure S5. Linear fits to the data in Figures 6A and 6B and the residuals to the fits. It is possible to fit the data with a line, but the residuals show systematic deviations, which indicate that a line is not the correct functional form for the data. A deviation from linearity shows that the data are not hydrodynamic, which supported by the material presented in Sections III B and III C.