Supporting Information

Liquid Structure and Hydrogen Bonding in Aqueous Hydroxylammonium Nitrate

Daniel D. Depew,† Ghanshyam L. Vaghjiani,*‡ Shehan M. Parmar,¶ and Joseph J. Wang†

†Department of Astronautical Engineering, University of Southern California, Los Angeles, CA 90089, United States
‡Aerospace Systems Directorate, Air Force Research Laboratory, AFRL/RQRS, Edwards Air Force Base, California 93524, United States
¶Department of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332, United States

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* Email: ghanshyam.vaghjiani@spaceforce.mil
Figure S1: Density vs. time for each NPT production simulation used to determine densities in aqueous HAN. While all equilibrated simulations showed convergence to an equilibrium density with a drift of less than 0.2% over the 48 ns run, the most concentrated solution exhibits notable low-frequency density fluctuations.
Figure S2: Histogram of NPT simulation densities in aqueous HAN. Each histogram is normalized to produce a probability distribution. Ion mole fractions increase from top left to bottom right, using the color scheme from the legend in the main text and Figure S1. A Gaussian distribution fit is overlaid on each plot. The clear Gaussian behavior in the plots indicates that the NPT simulations are well-equilibrated.
Figure S3: Site-site radial distribution functions in HAN with ion mole fraction $\chi = 0.43$ at 298 K for hydrogens H-bonding with cation oxygen $O_h$. 
Figure S4: Combined distribution functions (CDFs) in aqueous HAN at ion mole fractions \( \chi=0.05 \) (top) and \( \chi=0.77 \) (bottom) indicating the orientation of the water hydrogens in the axial lobe regions above and below a nitrate anion. The plots on the left are reproduced from Figure 7 in the text and depict the cutoffs for these lobe regions. With respect to the y-axis, a cutoff of 22° was selected for the \( \chi=0.05 \) simulation and a cutoff of 25° was selected for the \( \chi=0.77 \) simulation. In the CDFs, the horizontal axis shows the distance between the water oxygen and the nitrate nitrogen, while the vertical axis shows the N_n–O_w–H_w angle at the corresponding O_w–N_n distance. An angle of 180° indicates that the water hydrogen is pointed directly away from the nitrogen. The orange-red regions around 90° allow for the water molecule in the axial lobes to act as a hydrogen bond donor to another water already coordinated to the nitrate oxygens. This effect is enhanced at the higher ion concentration where water is less mobile in the first solvation shell.
Figure S5: Projection of water oxygen density into the plane orthogonal to the nitrate anion in HAN at ion mole fraction $\chi = 0.43$. One N–O bond is placed on the +x-axis and the projection samples a width of 1 Å on either side of the plane. Arrows indicate the average direction of the water dipole moment vector and are included in regions where $\rho_{\text{o}_w} \geq 1.5$. Larger arrows indicate a higher likelihood of orientation.
Figure S6: Water oxygen density plane projections in the hydroxylammonium cation vicinity in HAN at ion mole fraction $\chi = 0.43$. The top row aligns the cation’s $\sigma$ mirror plane to the $xy$-plane, centered at the hydroxyl oxygen with the O–N bond on the $+x$-axis. The bottom row shows the $yz$-plane looking down the O–N bond. Projections sample a width of 1 Å on either side of the respective plane. Arrows indicate the average direction of the water dipole moment vector and are included in regions where $\rho^{\omega} \geq 1.5$. Larger arrows indicate a higher likelihood of orientation.
**Figure S7:** Combined distribution functions (CDFs) used in determining Haña—Oₙ hydrogen bond criteria in the aqueous HAN system. The horizontal axis shows the distance between the water oxygen and the nitrate nitrogen, while the vertical axis shows the angle between the donor-acceptor and donor-hydrogen vectors at the corresponding Haña—Oₙ distance. A cutoff angle of 30° was selected for each mole fraction simulated.
Figure S8: Combined distribution functions (CDFs) used in determining Hₖ—Oₙ hydrogen bond criteria in the aqueous HAN system. The horizontal axis shows the distance between the water oxygen and the nitrate nitrogen, while the vertical axis shows the angle between the donor-acceptor and donor-hydrogen vectors at the corresponding Hₖ—Oₙ distance. A cutoff angle of 50° was selected for each mole fraction simulated.
Figure S9: Combined distribution functions (CDFs) used in determining $H_w$—$O_n$ hydrogen bond criteria in the aqueous HAN system. The horizontal axis shows the distance between the water oxygen and the nitrate nitrogen, while the vertical axis shows the angle between the donor-acceptor and donor-hydrogen vectors at the corresponding $H_w$—$O_n$ distance. A cutoff angle of $40^\circ$ was selected for each mole fraction simulated.
**Figure S10:** Combined distribution functions (CDFs) used in determining $H_a$—$O_w$ hydrogen bond criteria in the aqueous HAN system. The horizontal axis shows the distance between the water oxygen and the nitrate nitrogen, while the vertical axis shows the angle between the donor-acceptor and donor-hydrogen vectors at the corresponding $H_a$—$O_w$ distance. A cutoff angle of 30° was selected for each mole fraction simulated.
Figure S11: Combined distribution functions (CDFs) used in determining Hₘ—Oₜ hydrogen bond criteria in the aqueous HAN system. The horizontal axis shows the distance between the water oxygen and the nitrate nitrogen, while the vertical axis shows the angle between the donor-acceptor and donor-hydrogen vectors at the corresponding Hₘ—Oₜ distance. A cutoff angle of 30° was selected for each mole fraction simulated.
Figure S12: Combined distribution functions (CDFs) used in determining $H_w-O_w$ hydrogen bond criteria in the aqueous HAN system. The horizontal axis shows the distance between the water oxygen and the nitrate nitrogen, while the vertical axis shows the angle between the donor-acceptor and donor-hydrogen vectors at the corresponding $H_w-O_w$ distance. A cutoff angle of 35° was selected for each mole fraction simulated.
Figure S13: Snapshot of the final time step of the HAN simulation at ion mole fraction $\chi = 0.05$, omitting the water molecules for clarity. Hydrogen bonds between ions are indicated by a dashed black line. Even at this relatively low ion concentration, many small aggregates of ions are observed. Some aggregates extend across the periodic boundaries and are not fully depicted.
Figure S14: Snapshot of the final time step of the HAN simulation at ion mole fraction $\chi = 0.77$, omitting the ions for clarity. Hydrogen bonds between water molecules are indicated by a dashed black line. Aggregation of water molecules is rare at this concentration.