

D₂O-H₂O Condensation in Supersonic Nozzles: I. Experiments

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Abstract. Pressure trace measurements and small angle neutron scattering (SANS) were used to probe the binary condensation of D₂O-H₂O mixtures in a supersonic nozzle. Each expansion started from the same initial pressure (carrier gas and condensible vapor) and temperature. The partial pressures of D₂O and H₂O were adjusted so that the onset of condensation always occurred at the same position in the nozzle. Under these conditions, the total pressure of condensible at onset varied linearly between the pressures of the pure components. Furthermore, the partial pressure at onset for pure H₂O was 29-34% higher than that for pure D₂O. The SANS scattering signals also varied systematically with the mixture composition. As the mixtures became progressively richer in H₂O, the scattering intensity dropped rapidly because the scattering length of H₂O is much smaller in magnitude and of opposite sign to that of D₂O. Further analysis of the scattering spectra showed that the particle size of the aerosol was increasing as the mixtures became more water rich. The increase in particle size was consistent with the increase in condensible molar flowrate needed to maintain onset at a fixed position in the nozzle as the mixture becomes richer in H₂O.

INTRODUCTION

Water is the most important fluid for life. Water condensation occurs in many natural and industrial processes including cloud formation, power generation and turbomechanical flows. Condensation of water in nozzles has been studied for over 50 years¹, and experiments range from those studying pure stream condensation^{2,3} to the more dilute systems^{3,4} described here. Another way to enhance our understanding of the behavior of this important substance is to conduct experiments using light water, H₂O, heavy water, D₂O, and their intermediate mixtures. In this paper we describe the results of our D₂O-H₂O binary condensation studies in which we combine conventional pressure trace measurements⁵ with aerosol SANS measurements^{6,7}

EXPERIMENTAL

A schematic diagram of the equipment used to conduct the pressure trace and the SANS experiments is illustrated in Fig. 1. The key components of the apparatus include⁵ the carrier gas generator, the condensible vapor generators and the supersonic nozzle. In the nozzle, a mixed gas stream consisting of N₂(g) with ~2 mol%

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condensible expands and cools. The supersaturation of the condensible vapor increases until a point is reached where rapid particle formation and growth deplete the vapor and reduce the supersaturation to close to 1. Under typical operating conditions^{6,7} the resulting aerosol has a number concentration N on the order of 10^{11} cm^{-3} , an average particle radius $\langle r \rangle$ in the range of 5 to 12 nm, and a relative polydispersity of about 20-25%. Conventional investigations of particle formation in the nozzle have focused on measuring the deviation of a state variable (pressure or density) for the expansion containing a condensible vapor from that observed for the expansion of the carrier gas alone. In our experiments we measure the static pressure as a function of position, and define the onset of condensation as that point in the nozzle where the temperature of the condensing flow curve is 0.5 K higher than the temperature of the (hypothetical) isentropic expansion of the mixed gas stream. Once the onset behavior of the aerosol is well characterized, we can use SANS to directly measure the parameters of the corresponding size distributions.

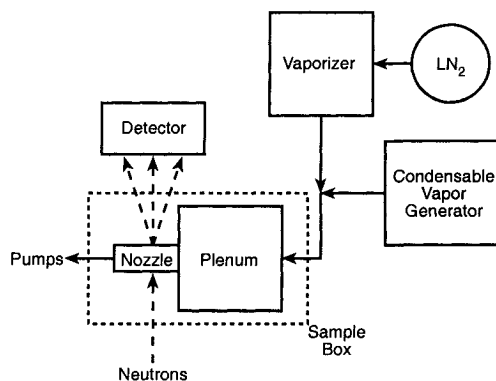


FIGURE 1. The experimental setup as it is used at NIST. To measure the axial pressure profile, a thin static pressure probe traverses the nozzle from 2-3 cm upstream to about 8-9 cm downstream of the throat. For the SANS experiments the pressure probe is removed.

To examine binary condensation in the nozzle, we first fix the total pressure p_0 and the temperature T_0 in the plenum, and then measure the static pressure profiles for different flowrates of one binary mixture. For each mixture, the values of pressure and temperature at onset define a straight line on a plot of $\ln p$ versus T . The mixture composition is then changed, and the process is repeated for other mixture compositions including the pure components. From the onset lines ($\ln p$ vs T) generated this way we are able to define the partial pressure of each species required to maintain onset at constant temperature. When the experiments begin with the same value of T_0 , constant onset temperature corresponds to a fixed position in the nozzle. Figure 2 summarizes the pressures required to maintain onset at 231 K for D_2O , H_2O , and four intermediate mixtures.

The corresponding SANS scattering spectra are illustrated in Fig. 3. Because the onset position is fixed, each gas mixture experiences the same gasdynamic history up to onset. In this almost degenerate system, one might expect that the droplets comprising the aerosol are internally well mixed, their composition is independent of

size, and the particle size distributions are essentially the same. If these assumptions are valid, the droplet composition should reflect the overall composition of the condensible mixture, the background subtracted curves should have the same shape, and the intensity should scale directly with the contrast factor corresponding to the droplet composition. In Fig. 3(b) we tested this hypothesis by finding the best fit parameters for the pure D₂O aerosol assuming a Gaussian size distribution of droplets moving⁸ at 435 m/s and fitting the data available at both sample-to-detector distances (2.9 and 1.0 m). The best fit parameters are given in Fig. 3(b). For the other mixtures we scaled the D₂O curve by the ratio of the contrast factors of the mixtures. At first glance, the data follow the expected trend reasonably well.

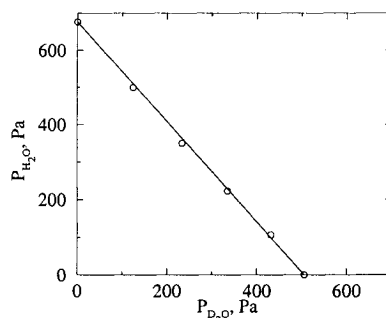


FIGURE 2. The pressures of D₂O and H₂O required to maintain onset at $T=231\text{K}$ vary linearly between the endpoints. For these experiments $T_0 = 26^\circ\text{C}$ and $p_0 = 60\text{ kPa}$.

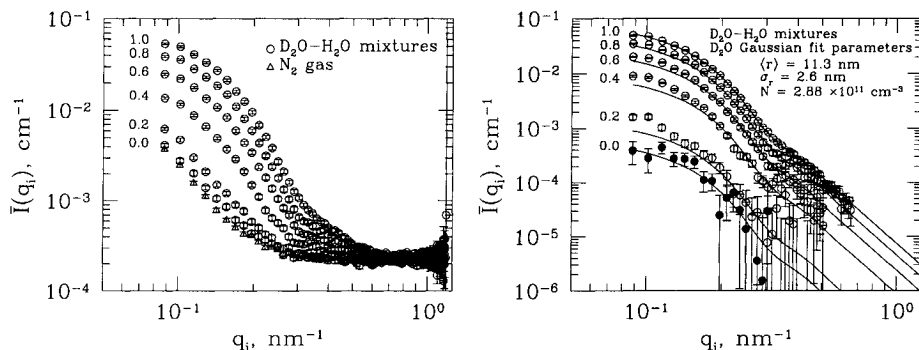


FIGURE 3. (a) The raw scattering spectra for the D₂O-H₂O aerosols and from the N₂ alone. (b) The background subtracted spectra. The corresponding mole fraction D₂O is indicated to the left of each curve. Although we were able to measure scattering from pure H₂O aerosol, the data are discounted in the remaining analysis because signal is too weak.

In the limit of $q \rightarrow 0$, the scattering intensity I_0 varies as $N \langle r^6 \rangle (b_1 x + b_2 (1-x))^2$ where b_i is the scattering length of component i and x is the mole fraction of component 1. Thus, if the assumptions stated above are correct, $\sqrt{I_0}$ should vary linearly with x . Figure 4, however, illustrates that for the mixtures $\sqrt{I_0}$ lies significantly above the solid line. Further analysis showed that the radii of gyration R_g for the mixtures were higher

(3-11%) than that for the pure D₂O aerosol. To see if the difference in droplet size can explain the observed behavior of I_0 , we scaled the values of $\sqrt{I_0}$ by $(R_g/R_{g0})^3$. The corrected curve agrees with the measured intercepts almost perfectly, suggesting that the particle formation process for D₂O and H₂O under these conditions is not very different. Furthermore, the increase in particle size is consistent with the increased molar flowrate needed to maintain onset at the desired location for the H₂O rich mixtures.

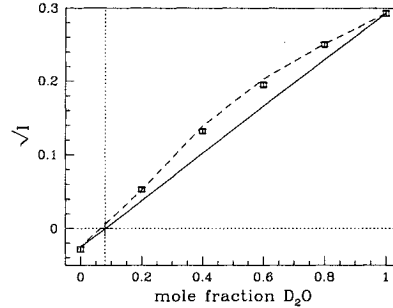


FIGURE 4. $\sqrt{I_0}$ obtained from Guinier fits to the data as a function of D₂O mole fraction. The solid line is the value of $\sqrt{I_0}$ for the pure D₂O aerosol scaled by the mixture scattering length. The short dashed lines show the location of the D₂O-H₂O null mixture. The long dashed line corrects $\sqrt{I_0}$ for the change in particle size.

In summary, the formation of D₂O-H₂O binary aerosols has been studied in a supersonic nozzle using pressure trace measurements and SANS. At this level of analysis, the composition of the droplets appears to equal that of the initial condensible vapor.

ACKNOWLEDGMENTS

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