



2001

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Abdelsayed, V., Ibrahim, Y., Rusyniak, M., et al. Fluoroalcohols as nucleating agents in supersaturated vapors: Efficient clustering with water in the vapor phase. *The Journal of Chemical Physics* 115, 2897 (2001). Copyright © 2001 AIP Publishing LLC.

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Fluoroalcohols as nucleating agents in supersaturated vapors: Efficient clustering with water in the vapor phase

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(Received 4 April 2001; accepted 26 June 2001)

Fluoroalcohols in small concentrations in the vapor phase display striking enhancing effects on homogeneous nucleation of supersaturated aliphatic alcohols, and on the formation of water clusters by supersonic expansion. The enhanced nucleation effects are attributed to the surfactant properties of fluoroalcohols, which lower the surface tension of the growing droplets, and therefore lower the barrier to nucleation. © 2001 American Institute of Physics. [DOI: 10.1063/1.1394937]

Nucleation is one of the most ubiquitous and important phenomena in science and technology. It plays a decisive role in materials science and metallurgy, crystal, aerosol formation, natural gas hydrates, atmospheric science, and cosmochemistry.^{1–3} Vapor phase homogeneous nucleation involves the decay of the supersaturated vapor by the spontaneous occurrence of thermal fluctuations through the formation of nuclei or embryonic droplets of the liquid phase.^{1–3} Droplets that are larger than a critical size grow, and thus the stable liquid phase results. Because of the dependence of the barrier height for homogeneous nucleation on the cube of the surface tension of the condensing liquid, it is expected that incorporation of substances that exhibit properties of surfactants into the condensing droplets can dramatically enhance the rate of nucleation from the vapor phase. Recent studies have suggested that fluorocarbons at low concentrations in the gas phase exhibit properties of surfactants by essentially reducing the surface tension of organic and inorganic liquids.⁴ Motivated by these results, we have investigated whether the presence of fluoroalcohols in the gas phase can influence the rate of homogeneous nucleation from a supersaturated vapor, and whether the fluoroalcohols exhibit higher affinities than aliphatic alcohols for the clustering water molecules in the vapor phase.

In this communication, we present the results, which indicate that the addition of fluoroalcohols at low concentrations to a supersaturated vapor changes the composition of the condensation nuclei in a way that enhances the nucleation process. Furthermore, we demonstrate that fluoroalcohols have a much higher tendency to cluster water molecules than the corresponding aliphatic alcohols.

Two experimental methods have been used. The first involves measuring the homogeneous nucleation rate of a supersaturated vapor of an aliphatic alcohol in the presence of a small concentration of the fluoroalcohol within a thermal diffusion cloud chamber (DCC). In the second method we compare the extent of clustering produced from a supersonic expansion of water vapor containing a small concentration of the fluoroalcohol with that produced by a similar expansion

of water vapor containing the corresponding aliphatic alcohol.

Detailed description of the DCC and the principles of its operation are given elsewhere.^{5–7} This chamber is used to measure (i) the temperature dependence of the critical supersaturation corresponding to the onset of nucleation (rate of 1 drop/cm³/s), and (ii) the isothermal nucleation rate as a function of supersaturation. The rate of nucleation is determined by observing the forward scattering of light from drops falling through a horizontal He–Ne laser beam positioned near the middle of the chamber. A photomultiplier positioned to detect the forward-scattered light, a counting circuit, and a computer are used to measure the rate of nucleation within a well-defined volume.

Binary ethanol–water (E–W) and trifluoroethanol–water (TFE–W) clusters are generated by pulsed adiabatic expansion in a supersonic cluster beam apparatus.^{8,9} The essential elements of the apparatus are jet and beam chambers coupled to a coaxial quadrupole mass spectrometer. During operation a saturated ethanol–water vapor mixture is formed by flowing ultrahigh-purity He at a pressure of 2–4 atmospheres through two separate temperature controlled reservoirs filled with ethanol and water. The vapor mixture is then expanded through a conical nozzle in pulses of $\approx 200 \mu\text{s}$ duration at repetition rates of 6–10 Hz. The cluster beam is ionized by electron impact and the amplified signal from a particle multiplier is processed to sample at arrival times appropriate for the detected ions.

According to the classical nucleation theory (CNT), the rate of homogeneous nucleation from a supersaturated vapor is given by³

$$J = (a/\rho)(2N_A^3 \sigma M/P)^{1/2} (S P_e/RT)^2 \exp(-W^*/RT), \quad (1)$$

where J is the rate of nucleation ($\text{cm}^{-3} \text{s}^{-1}$), a is a sticking coefficient and is set equal to 1, ρ is the liquid density, N_A is Avogadro's number, σ is the flat surface tension of the liquid, M is the molecular weight, S is the supersaturation ratio

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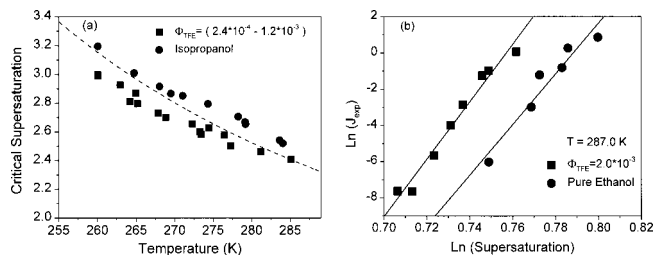


FIG. 1. (a) Temperature dependence of the critical supersaturation of isopropanol in the presence and absence of small concentrations (2×10^{-4} to 1×10^{-3} mole fraction) of TFE in the vapor phase. The total pressure (He+isopropanol+TFE) in these experiments ranges from 448 to 542 torr. (b) Isothermal nucleation rates of supersaturated ethanol in the presence and absence of TFE as indicated. The total pressures in the ethanol/He and ethanol/TFE/He experiments are 726 and 747 torr, respectively.

(P/P_e) where P is the pressure of the vapor, and P_e is the equilibrium or “saturation” vapor pressure at the temperature of the vapor T , and R is the gas constant. The central quantity in the rate equation is the barrier height W^* that is given by

$$W^* = 16\pi N_A M^2 \sigma^3 / 3(\rho RT \ln S)^2. \quad (2)$$

Because of the dependence of the barrier height on the cube of the surface tension, any small reduction of the surface tension should result in large enhancement of the nucleation rate.

Figure 1(a) displays the temperature dependence of the critical supersaturation of isopropanol in the presence and absence of a small concentration of TFE (2×10^{-4} to 1×10^{-3} mole fraction in the vapor). The critical supersaturation is defined as the supersaturation required for a nucleation rate of 1–3 drops/cm³/s. The dashed line in Fig. 1(a) presents the prediction of the CNT for the temperature dependence of the critical supersaturation of isopropanol. It is clear that the addition of a small concentration of TFE in the vapor phase reduces the critical supersaturation of isopropanol significantly and thus increases the rate of nucleation. It should be noted that only a small change in the supersaturation results in a large change in the rate of nucleation because of the exponential dependence of the rate on supersaturation. Figure 1(b) illustrates the effects of adding small concentrations of TFE on the measured isothermal nucleation rate of supersaturated ethanol vapor. The range of TFE vapor concentrations arises from the estimated vapor pressure of TFE in the alcohol solutions at the temperatures of upper and lower plates of the DCC. It is clear that the addition of a small concentration of TFE to the supersaturated ethanol vapor leads to a significant enhancement of the nucleation rate. This effect can be explained by the surface enrichment phenomenon observed in the binary nucleation of aliphatic alcohol–water vapors, where enhancement of the surface composition with the lower surface tension component occurs.^{10,11} In the fluoroalcohol–water systems, the surface enrichment effect is expected to be much more pronounced than in the aliphatic alcohol–water systems. Therefore, the enhancement effect in the present study is observed at very small vapor concentrations of TFE. The nucleation results are consistent with the effect of reducing the surface tension of water and ethanol observed in the pres-

ence of fluorocarbon vapor at room temperature.⁴ For example, a 6% reduction in the surface tension of ethanol has been measured in the presence of TFE vapor.⁴ Note that a 6% reduction in the surface tension leads to a 17% reduction in the barrier height for nucleation according to Eq. (2). This significant reduction in the nucleation barrier results in pronounced increase in the nucleation rate. It should be noted that some of the enhancement effect might come from a change in the free energy associated with the bulk term due to the difference in chemical potentials between the supersaturated vapor and the liquid. However, because of the small concentrations of TFE used in the nucleation experiments, the bulk term is expected to have a smaller contribution to the enhancement effect. We also note that the enhancement effect is more pronounced at small vapor concentrations of the fluoroalcohol. We are currently measuring the binary nucleation rates of ethanol and TFE over the entire composition range in order to establish the difference between the typical binary enhancement in the nucleation rate and the observed surfactant induced nucleation effect.

The enhancement effect is expected to be much stronger for the nucleation of supersaturated water vapor since a 66% reduction in the surface tension of water has been observed in the presence of TFE vapor.⁴ Nucleation experiments of supersaturated water vapor in the DCC require special treatments of the chamber plates because water does not wet the top metal plate of the chamber. Preliminary visual experiments using wet Kim wipes to cover the top plate of the DCC have shown that a catastrophic increase in the number of water droplets occurs when the TFE/He vapor mixture is introduced to the supersaturated water vapor in the DCC. Experiments with surface modified plates are in progress in order to measure the isothermal nucleation rates of supersaturated water vapor in the presence of variable concentrations of TFE.

Figure 2 displays the mass spectra of the resulting ethanol–water (EW) and TFE–water (TW) clusters generated by the supersonic expansion of the corresponding vapor mixture in He. In the ethanol–water system, protonated clusters of the form $H^+E_nW_m$ with $m=1$ and 2 are observed only at $n \geq 7$. This is in agreement with previous work on aliphatic alcohol–water clusters.⁹ In contrast, in the TFE–water system, protonated clusters of the form $H^+T_nW_m$ are observed starting from $n=1$ and with $m=1-8$. It should be noted that the water/ethanol ratio (1:1) is higher than the water/TFE ratio (1:4) in the pre-expansion mixtures. This indicates that the extent of clustering of water around TFE molecules is much higher than that of water around ethanol molecules. This behavior is illustrated in Figs. 3(a) and 3(b), which exhibit comparisons of the normalized relative intensities of $H^+T_nW_m$ and $H^+E_nW_m$ clusters. It should be noted that while the addition of a few water molecules is only observed on large ethanol clusters ($n \geq 7$), the monomer TFE and its small as well as large clusters tend to add a significant number of water molecules (up to 8). Figure 3(c) compares the relative intensities of the $H^+T_nW_m$ and $H^+E_nW_m$ clusters. It is clear from Fig. 3(c) that the sum of the ion intensities of the water containing ions represents more than 50% of the total ion intensity in the TFE–W sys-

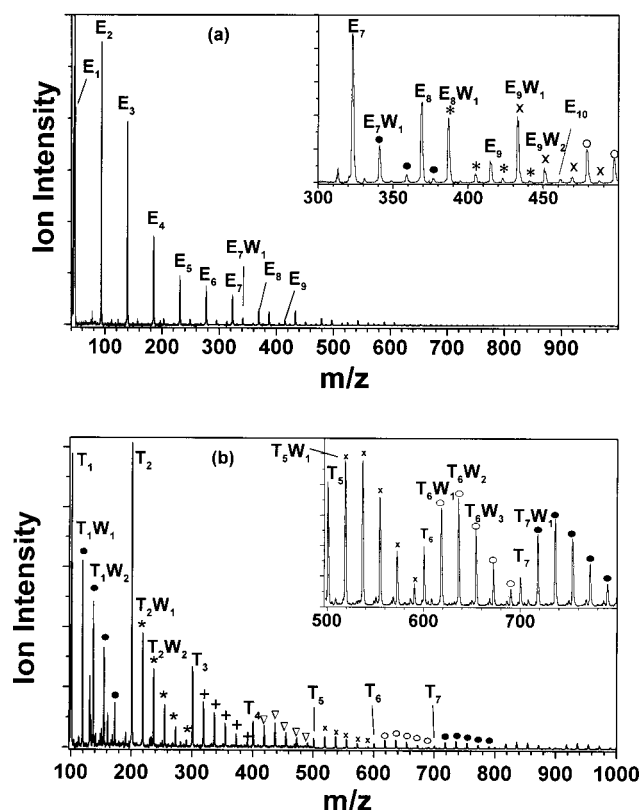


FIG. 2. Mass spectra of (a) ethanol/water ($E_n W_m$) and (b) trifluoroethanol (TFE)/water ($T_n W_m$) clusters. The ethanol/water and the trifluoroethanol/water ratios are 1.0 and 0.25 in the pre-expansion mixtures.

tem. However, in the E–W system, this sum represents less than 5% of the total ion intensity of the system. This reflects the stronger TFE–water interaction as compared to ethanol–water interaction, probably due to the electronegativity and the electron withdrawing effects of the fluorine atoms.

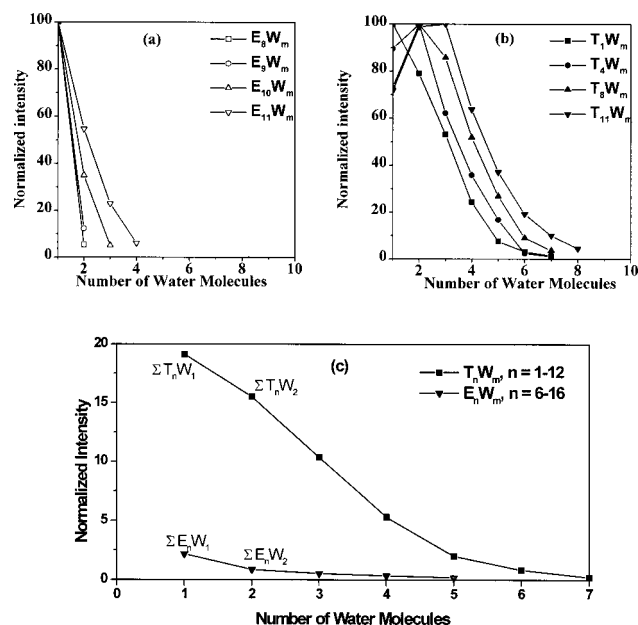


FIG. 3. Normalized ion intensity of (a) ethanol/water ($E_n W_m$) and (b) TFE/water ($T_n W_m$) clusters. (c) Comparison of the total ion intensities of the water containing clusters in $E_n W_m$ and $T_n W_m$ systems. The ion intensities are calculated from the mass spectra shown in Fig. 2.

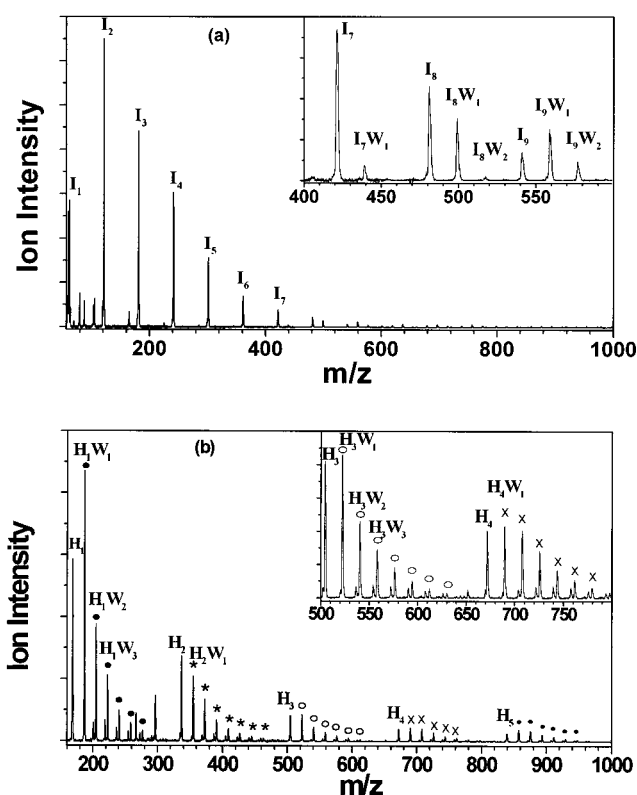


FIG. 4. Mass spectra of (a) isopropanol/water ($I_n W_m$) and (b) hexafluoro-2-propanol/water ($H_n W_m$) clusters. The isopropanol/water and the hexafluoro-2-propanol/water ratios are 0.14 and 0.60 in the pre-expansion mixtures.

Similar effects are observed in comparing the relative ion intensities of isopropanol/water (I/W) and hexafluoro-2-propanol/water clusters (HFIP/W) as shown in Figs. 4(a) and 4(b), respectively. Extensive clustering of water molecules is observed with HFIP as compared to isopropanol. Again, it is interesting that the preferential addition of water on HFIP as compared to isopropanol is observed even when the water/HFIP ratio (0.14) is smaller than the water/isopropanol ratio (0.60) in the pre-expansion mixtures. It also appears that the affinity of HFIP towards water molecules is higher than that of trifluoroethanol. This suggests that extent of interaction with water increases as the number of fluorine atoms in the alcohol molecule increases.

The cluster formation by supersonic beam expansion involves very high supersaturations and therefore, very small barriers (or no barrier at all) to nucleation. In this case, it is not appropriate to attribute the enhancement of the water clustering with fluoroalcohol to the reduction of the nucleation barrier height. However, the current results indicate that the presence of fluoroalcohol in the cluster enhances the water–water and water–fluoroalcohol interactions much more than the effects produced by the corresponding aliphatic alcohol.

The above results are in full agreement with the molecular dynamic simulation study of Kinugawa and Nakanishi.¹² Their study shows that for the hydration of fluoroalcohols, the promotion of water structure and the increase of the hydrogen bond between water molecules occur not only near the fluoroalkyl group but also even near the hydroxyl group.

The simulation results also indicate that the hydrogen bond between the OH group and water, and the interaction between the fluoroalkyl group and water become stronger as the number of F atoms in the alcohol molecule increases, owing to the electron withdrawing effect and the electronegativity of fluorine atoms. By comparing the water interaction with aliphatic and fluoroalcohols, the simulations show that the nearest neighbor interaction between water molecules near the OH group increases in the order isopropanol < trifluoroisopropanol < hexafluoroisopropanol.

It is interesting to note that the interactions of fluoroalcohols with water and hydrocarbons are responsible for several striking effects observed in aqueous peptide and protein conformations.^{13–15} For example, it is well known that TFE has a remarkable ability to induce the helical structures in peptides and to denature the native structures of proteins.^{13–15} Recently, HFIP has become widely employed as an alcohol with a much stronger effect than TFE.¹³ Studies of the solvent effect on the peptide conformation have indicated that water/hydrocarbon interactions are more favorable in pure water than in modest concentrations of fluoroalcohol–water cosolvents.^{16–18} Evidence for clusters of TFE or HFIP have been recently found in alcohol/water mixtures containing low alcohol concentrations.¹³ Such clusters provide a highly hydrophobic local environment, where microscopically, polarity decreases and hydrogen bonds are strengthened.^{13,16}

The present results indicate that the addition of trifluoroethanol at low concentrations in the vapor phase significantly increases the rate of nucleation in supersaturated ethanol and isopropanol vapors. Furthermore, the cluster study indicates that fluoroalcohols promote extensive clustering with water as compared to aliphatic alcohols. The higher affinity of fluoroalcohols toward clustering water molecules in the gas phase is consistent with the observed solvent effects on the peptide conformation in aqueous solutions. The results suggest a novel application of fluorocarbons as effective agents to control the nucleation rates of polar and non-polar substances from the vapor phase. Furthermore, the newly discovered phenomenon of surfactant-induced nucleation (SIN) in the vapor phase is of considerable interest for

practical applications. In particular, the SIN mechanism could be applied to prevent the formation of natural gas hydrates (clathrates) when small hydrocarbon gas molecules are brought into contact with water at low temperatures and high pressures.¹⁹ The strong interaction between fluoroalcohol and water molecules is expected to significantly slow down the formation kinetics of the gas hydrates, which could have a large impact on the reserved energy sources. Of course, other factors such as cost and availability need to be considered in evaluating the economical impact of the use of the fluoroalcohols as efficient retarders for the formation of natural gas clathrates.

The authors gratefully acknowledge support from NASA Microgravity Materials Science Program (Grant No. NAG8-1484).

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