Pulse Radiolysis Studies of Solvated Electrons in Supercritical Ethane with Methanol as Cosolvent[†]

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Pulse radiolysis has been used to study the solvated electron in supercritical ethane with methanol as a cosolvent. These measurements give information about the liquid structure of the cosolvent in these systems. The results show that at temperatures below 110 °C, there are high local concentrations of alcohol molecules (clusters), which are capable of solvating an electron. The agglomeration number of methanol clusters depends on mole fraction of alcohol at a fixed temperature. Addition of salts increases the size of methanol clusters.

Introduction

Supercritical fluids have been suggested as reaction media for many synthetic (and destructive) processes. The desirable characteristics are many—among them are ease of separation, high mobilities so that reactions can take place quickly, and the ability to alter the reaction medium easily by changing pressure and temperature. Unfortunately, the ease of separability may mean low solubility for many reactants. To overcome solubility limitations, cosolvents are often used. Depending on the cosolvent−solvent combination, the cosolvent may not be distributed homogeneously and there will be transient high, localized concentration of the cosolvent. We shall refer to these regions as clusters; this is not meant to imply that the regions have a fixed or specific structure. The reactivity between a molecule in a cluster and a molecule in the bulk of the solution may well depend on the size of the enclosing cluster. The reaction between molecules in different clusters may also be considerably different than the reaction between molecules in the bulk of the solution.

Work has been done that makes use of the ability of cosolvents to increase the yield of photochemically activated bimolecular reactions by confining the reactants to a smaller reaction volume. In those experiments, the two reactants were isolated in butanol or acetonitrile clusters in supercritical CO_2 and then exposed to photolytic light.[1,2] This enabled the synthesis to be done with limited concentrations of reactants and thus conserve expensive starting materials.

Experiments at Argonne and elsewhere have used cosolvent and/or reversed micelles systems to generate small, potentially catalytic metallic particles.[3−6] In our studies, silver perchlorate was dissolved in methanol and then reacted with solvated electrons in sc-C_2H_6.[3] By controlling the mole fraction of the methanol and pressure of ethane, we were able to produce small metallic silver particles with a narrow size distribution (diameter less than 10 nm).

The experiments cited above have made use of the fact that the cosolvent distribution in supercritical fluids is not homogeneous. To facilitate such uses of cosolvent systems, it is necessary to understand the structure of the local inhomogeneities in supercritical fluids. Clearly the structure of such clusters is dynamic. For that reason, we use techniques that can probe the dynamic nature of the system. One probe that has been used in the past is the solvated electron in alcohol clusters.[7−11] The electron will attach to alcohol clusters in mixed solvent systems. Spectral shifts, electron mobilities, and kinetics have suggested that the alcohol clusters do not substantially change after the initial rotational relaxation. This appears to be a characteristic of the electron attachment. Fast anion creation does display a growth in the size of the cluster. The time dependence and spectral characteristics of the electron were measured as a function of alcohol concentration in mixtures of alcohol−alkanes. With supercritical fluids it is possible to measure the concentration dependence and the mole fraction dependence separately, something that could not be studied previously.

In this paper we describe a measurement of the characteristics of alcohol clusters in supercritical ethane. We also discuss how the inclusion of a reactant in a cluster can alter the reactivity. The size of the alcohol clusters in the methanol−ethane cosolvent system is probed by measuring the solvated electron spectrum as a function of temperature, pressure, and alcohol concentration. The reactivity of clustered species is measured in reaction of solvated electrons with solvated silver cations in the methanol−ethane cosolvent system.

We use the phrases "methanol clusters" or "clusters" to refer to a local small aggregation of methanol molecules. It is not meant to imply that there is a specific structure.

Experimental Section

Materials. All chemicals were of the highest purity commercially available and were used as purchased. The C_2H_6 (99.95%) was purchased from AGA. The gas was passed through a filter (Pall Gaskleen, GLPV2SIVMM4) for purification. A clear decrease in the lifetime of the electron was observed if the filter was not used.

Methods. Experiments were performed in a stainless steel high-pressure cell with an optical path of 5 cm and effective volume of 12.5 cm^3. Two suprasil windows (1 cm thick) were mounted to the cell using Teflon O-rings. Experiments were done over the temperature range 80−110 °C. The temperature was monitored and controlled using an Omega Model CN 1001

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RTD controller. Pressure in the cell was adjusted using a high-pressure piston pump and monitored with a Cole-Parmer digital pressure meter (model 7350-38). The experimental arrangements were similar to those described previously.[12,13]

Pulse radiolysis experiments were performed using the Argonne 20 MeV linear accelerator with 4 ns electron pulses. Transient species were detected optically. Interference filters (bandwidth 10 or 40 nm) and a silicon photodiode (EG&G, FND 100) were used as optical detectors. The electron pulses were collinear with the analyzing light beam, but in the opposite direction.

The dose in the cell was measured using aerated solutions of thiocyanate and hexacyanoferrate(II).[14,15] Details are published elsewhere.[13] The average dose absorbed in a sample was 27.5ρ Gy, where ρ is density of sc-C_2H_6 in g/cm^3. The density of sc-C_2H_6 was taken from the *PVT* relationship calculated using the BWR equation.[16] The effect of cosolvent was not taken into account for calculation of absorbed doses.

Neat methanol was purged with nitrogen prior to use. Solutions of the salts in methanol were prepared and deaerated immediately before using. The desired volume of neat methanol or solution was added to the previously evacuated cell at working temperature (80−110 °C) under the flow of ethane using an injector (Rheodyne, model 7030). The cell was then finally filled and pressurized with C_2H_6.

Results and Discussion

A pulse of high-energy electrons was used to ionize the ethane. The electrons that escape geminate recombination can be detected spectroscopically if solvated in alcohols.[17] Experiments on the spectrum of the solvated electron were carried out both as a function of temperature and pressure of methanol−ethane system. We found that at about 333 K, we were able to measure the absorption from the solvated electron at the times of nanoseconds to microseconds after the pulse. However on a time scale between 1 ms and 1 s, the solution scattered the analyzing light. After about 2−3 min, the solution became clear again and we were able to make measurements. We did not study this phenomenon. We found that at higher temperatures, this difficulty did not occur. We were unable to find data in the literature for the phase equilibria for the ethane−methanol system at 353 °C. For this reason we attempted to use our experimental data to establish that we had a single-phase system. We carried out experiments at higher mole fractions than reported in this paper and found that the both the spectrum of the electron and its decay kinetics were altered at the higher alcohol concentrations. This result shows that we could increase the alcohol concentrations above those reported in the present publication. We also found th tat the system remained optically clear for all of the systems studied (other than the 333 K results discussed above). For these reasons we feel that we are studying a single-phase system.

In Figure 1, we display the decay of the electron at three different pressures. The concentration of the methanol is the same for all three traces; however the mole fraction changes. These decays will be a factor of 3 to 4 faster if the ethane is not purified using the "Gaskleen" filter. The decay gets faster as the ethane pressure increases. We also have seen that the decay is faster if the concentration of methanol is decreased at constant total pressure.

In Figure 2a, the spectra of the electron at different pressures of ethane are presented. The maxima are normalized. In this experiment the amount of the methanol added was kept constant. Thus the concentration of methanol remains constant, while the mole fraction decreases as the pressure goes up. The results show a steady increase in the amount of absorption in the red; however the blue side of the spectrum remains approximately constant. The wavelength of the spectral maximum does seem to increase as the pressure increases; however, this can primarily be accounted for by the increase in the red side of the spectrum. In Figure 2b we display the two spectra at the same mole fraction but different densities. These two spectra overlap very well.

There have been experimental measurements and molecular dynamics simulations of the cluster size as a function of pressure for the methanol−ethane and methanol−CO_2 systems.[18,19] In

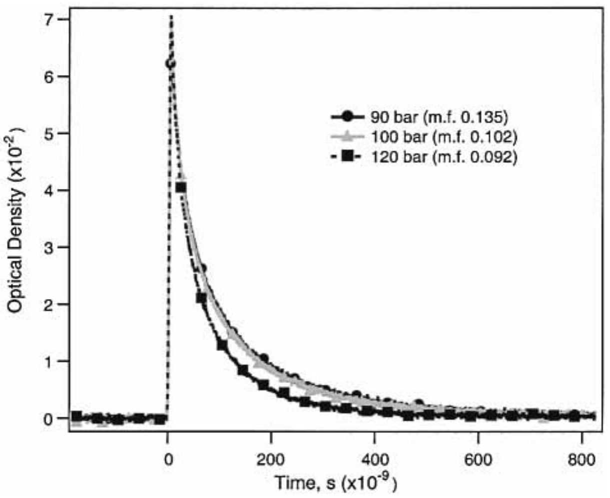

Figure 1. Time profiles of the solvated electron signal at 650 nm in solutions of 0.79 M methanol in sc-ethane at 80 °C at 90, 100, and 120 bar. The mole fractions of the methanol for the three pressures are given in the figure legend.

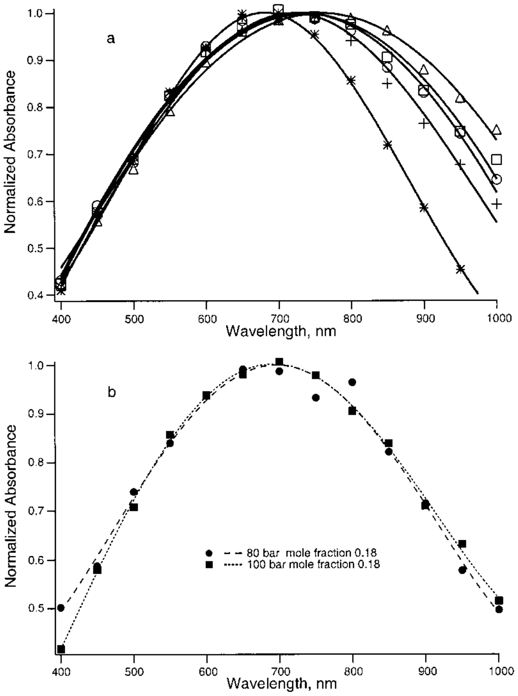

Figure 2. (a)The spectrum of the solvated electron in 0.79 M methanol in ethane at 80 °C as a function of pressure: (+) 70 bar, (○) 80 bar, (□) 100 bar, and (△) 120 bar. All spectra are normalized to give the same maximum. The spectrum of solvated electron in neat methanol (∗) at 86 °C. (b) The spectrum of the electron at 80 (●) and 100 (■) bar at 0.18 mole fraction. The spectra were measured 18 ns after the pulse.

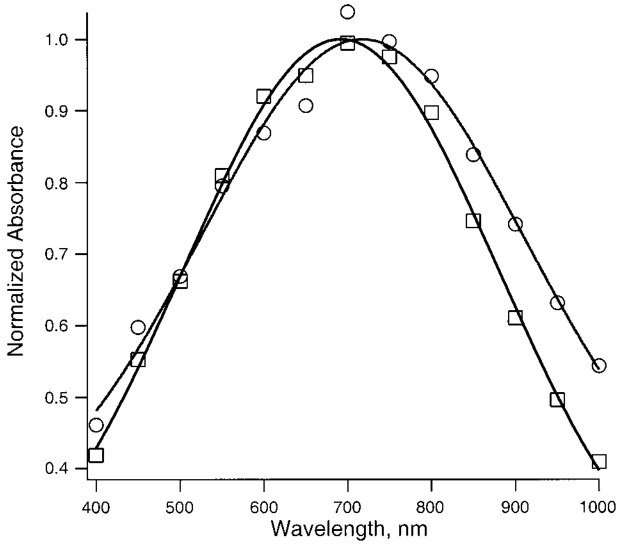

Figure 3. Spectrum of the electron in methanol−ethane (○), and in 0.6 M $NaClO_4$ in methanol−ethane (□). Concentration of methanol in ethane is 0.79 M. Pressure is 120 bar. Spectra were taken 45 ns after pulse.

those studies it was found that the cluster sizes decreased at higher pressures for the same concentration of methanol. Those results correspond well to the experimental results that we see. As methanol cluster size decreases, one would expect the spectrum of the electron to shift toward the red because the electron will be less well solvated. This is indeed what we observe. We suspect that the breadth of the band is due to nonhomogeneous broadening, i.e., the bandwidth is made up of many different absorption bands, each due to a different size cluster. As the pressure of sc-C_2H_6 increases, more small methanol clusters are formed and so the spectra of these species are red-shifted.

Unfortunately, we were unable to compare directly the results of the simulations and measurements of electron-cluster size as a function of density to assign the spectra to different cluster sizes, because our measurements were at higher temperature (for the reason discussed above) than the literature results. If we compare our results to the alcohol−alkane results that were obtained with normal liquids, we can estimate that the red-shifted species arises most probably from clusters of 4−5 alcohol molecules.[8−10] We also measured the kinetics and found that they were independent of wavelength, showing that there is no increase in the cluster size at times greater than about 10 ns. It also suggests that the reactivity of the solvated electrons is independent of the cluster size or that the clusters redistribute quickly to retain the equilibrium distribution.

Figure 3 shows the role of adding a salt, $NaClO_4$, to the solution. The spectrum in the presence of the salt is blue-shifted from the spectrum in the absence of the salt. In addition, there is only a slight shift in the spectrum as a function of pressure. This is not surprising because highly polar salt will act to increase the size of the clusters and thus shift the spectrum toward the blue. Supporting this suggestion is the comparison to the solvated electron spectrum in the methanol salt solution. The electron spectrum in the methanol−ethane−salt spectrum is much closer to the spectrum in the comparable methanol−salt solution than is the case for the system without the salt. This suggests that the cluster is larger in the presence salt because the spectrum is closer to the liquid spectrum. This assumption is certainly reasonable because it is well-known that there are large density fluctuations in the presence of a solute.

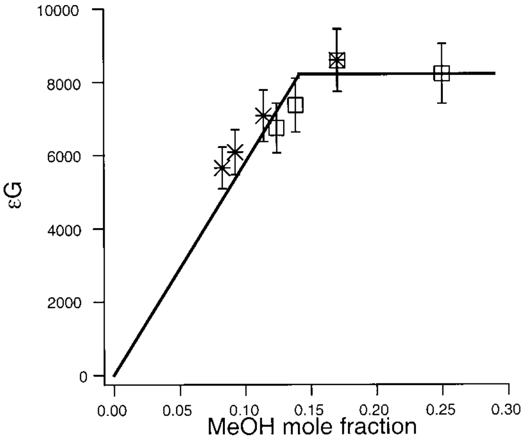

Figure 4. *G*ϵ for the electron as a function of methanol mole fraction in supercritical ethane at 80 °C. The measurements were made 18 ns after the pulse. Concentrations of methanol are (∗) 0.79 M, and (□) 1.19 M.

When the pressure is increased, the stronger forces that exist with the salt will hold the cluster together and the greater amount of methanol in the cluster would mean that a small loss of alcohol would make little difference to the spectrum. Thus, the increase in pressure does not lead to a large decrease in the size of the cluster.

In Figure 4, we present the *G*ϵ of electrons versus mole fraction of alcohol. The *G* is the yield of solvated electron (number of molecules per 100 eV absorbed energy), and ϵ is the optical absorption coefficient at the maximum. Interestingly enough, the results show that the yield increases linearly as a function of mole fraction. Once the mole fraction reaches 0.13, *G*ϵ is then constant. If we assume that the optical absorption coefficient is approximately constant, these data suggest that the yield of electrons is constant if the mole fraction of the alcohol is greater than approximately 0.13. The assumption for an approximately constant ϵ is reasonable because the spectrum shifts but retains the same shape. The behavior in yield is the same as that which had been previously observed in mixtures of normal liquids *n*-butanol in *n*-hexane.[8] Even the mole fraction where the signal plateau is about the same as that observed previously and is independent of the pressure or concentration of methanol. This plateau shows that at about 0.13 mole fraction, the concentration of alcohol clusters is sufficiently high so that virtually all of the injected electrons will solvate before they have a chance to react.

The observed spectral characteristics of electrons in methanol−ethane systems are similar to one seen for mixtures of normal liquids.[8,9] The spectra of the electron in methanol−ethane and in *n*-butanol−hexane are all red-shifted from the spectra in the pure alcohols. In the previous work, where picosecond time resolution was available, no spectral shift was seen after the initial solvation process (of approximately 30 ps).[8,9] This showed that the measurement probed the size of alcohol clusters present in the solution at the time of electron injection. Similarly, we expect the same behavior to be true in the supercritical solution. That is, the spectrum of the electron attachment to a cluster is a good probe for the size of the alcohol clusters in a supercritical solution.

The temperature dependence of absorption spectra of the solvated electrons in alcohols has been previously studied.[20−22] In Figure 5 we show the temperature dependence of the position of absorption maxima of the solvated electron measured in methanol−supercritical ethane solution. The mole fraction of methanol was kept constant at 0.11. Figure 5 also contains values

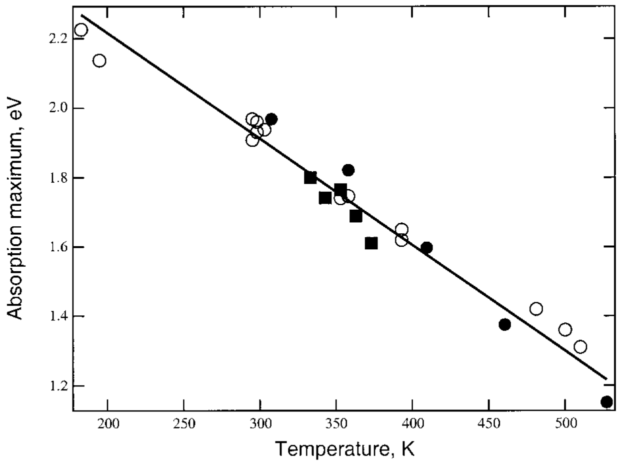

Figure 5. Temperature dependence of the absorption maxima of solvated electron in (■) methanol−ethane (0.11 mole fraction of methanol), and in neat methanol (●). The data for neat methanol (○) taken from refs 20−22 are also presented.

for neat methanol measured by us and others.[20−22] The maxima of electron absorption spectra in methanol−ethane mixture agree with the general trend observed for neat methanol, suggesting that the structure of the solvated electron in the methanol cluster depends on the temperature. At higher temperatures, the spectra shift toward the red, which suggests a more loosely structured solvated electron. What does not show up in these data is the intensity of the absorption spectrum in the supercritical ethane−methanol mixture. As the temperature rises, the spectrum becomes weaker and above 110 °C, the spectrum disappears completely. It can be seen from Figure 5 that this does not mean that the electron cannot be solvated in methanol at temperatures greater than 110 °C. This means instead that at higher temperature of methanol−ethane solutions, the concentration of methanol clusters that are large enough to solvate an electron decrease, and that above approximately 110 °C, the concentration is too low for us to observe the solvated electron. Entropy considerations would suggest that the concentration of the larger clusters would decrease as the temperature goes up. This is consistent with our idea that the electron acts as a probe of the concentration and size of clusters that are present in the methanol−ethane solution prior to irradiation. Adding to the decrease may be a shift in the equilibrium between the solvated electron and the free electron at higher temperatures. The effect of such an equilibrium has been seen previously.[10]

Alcohol−alkane solutions, whether supercritical ethane or normal liquid alkane, are very similar. This might be expected because we are considerably above the supercritical transition in ethane. Because the injection of charge caused a single-phase system to shift to a two-phase system at lower temperatures, we were unable to explore the region where supercritical fluctuation might play an important role.

The clusters formed in methanol−ethane cosolvent systems can modify chemical reactivity. One example is our previous work, where we studied the conditions and possibilities to control the size of silver nanoparticles in supercritical ethane by changing the temperature and pressure.[3] As part of those measurements, we determined the rates for the reaction between solvated electrons in one cluster and silver ions in a separate cluster. The rate of decay in the presence of silver is shown by trace "b" in Figure 6. The dependence of the decay rate on silver concentration is shown in the inset. The rate constant for the reaction of a solvated electron with a silver ion is 3×10^8 M^{-1} s^{-1}. The rate for the reaction of silver ions and solvated electrons in methanol under similar conditions is about 5×10^{10} M^{-1} s^{-1} (corrected for zero ionic strength), which is 2 orders of magnitude faster than the rates found in supercritical ethane. These results clearly show that the incorporation of reactants in cosolvent clusters in supercritical solutions can lead to a decrease in the reaction rate, presumably through the development of a barrier between reactant species in different clusters.[3] To make the best use of these possibilities, it is necessary to understand the size and distribution of clusters in solvents. In the present work we have studied the role of clusters in methanol−ethane cosolvent systems.

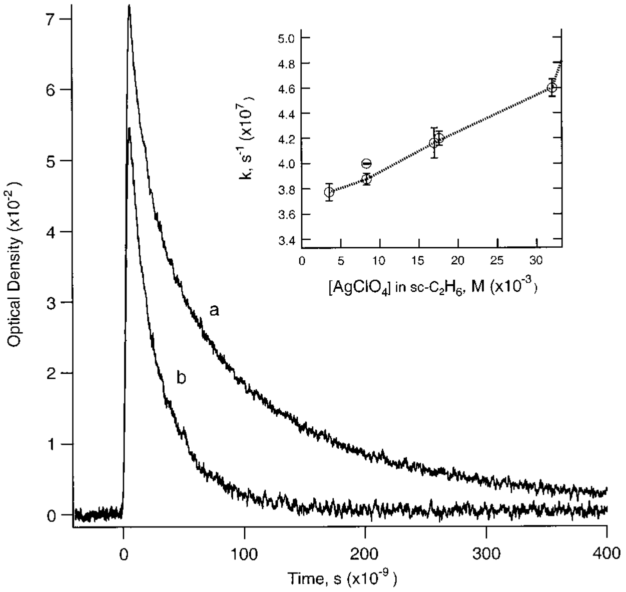

Figure 6. Time profile of solvated electron signal detected at 650 nm in a 12.5-cm^3 sc-C_2H_6 (100 bar, 80 °C) in the presence of 0.8 M methanol. (a) No silver perchlorate. (b) 0.0083 M $AgClO_4$. Inset shows the dependence of the rate of decay on the concentration of $AgClO_4$ in sc-C_2H_6.[3]

Clearly in using cosolvent systems, we are interested not only in the size of clusters in the absence of reactant molecules, but also in the presence of a third species. To this end, we have already begun the exploration of the role of methanol−ethane on the spectrum of a larger molecule (crystal violet). In the future we also plan to study different alcohols to connect with the clustering experiments that were discussed in the Introduction. We also plan to study the effects of other strongly polar cosolvents on the formation of electrons and their spectra. These experiments will be correlated with the results from molecular dynamics simulations on neat cosolvent systems.

Conclusions

In this paper, we have used the electron as a molecular probe for the structure of inhomogeneities in cosolvents in supercritical systems. These results show that the mole fraction of the alcohol rather than the concentration of the alcohol determines the size of clusters at a fixed temperature. The results suggest that at approximately 0.10 mole fraction, the size of the alcohol clusters is approximately 4−5, based on previous work.[8−10] We also find that about 110 °C, the size of the alcohol clusters in the supercritical solution decrease sufficiently so that they can no longer form solvated electrons. This means that in methanol−ethane cosolvent systems, the effect of alcohol inhomogeneities are strongly decreased at 110 °C. We have discussed the existence of a reaction barrier between species in different clusters. This barrier is sufficient to decrease reactivity by at least 2 orders of magnitude.

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