Anion Solvation in Alcohols

Charles D. Jonah, Zhang Xujia, and Yi Lin
Chemistry Division
Argonne National Laboratory
Argonne, IL 60439, USA

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This submitted manuscript has been authored by a contractor of the U. S. Government under contract No. W-31-109-ENG-38. Accordingly, the U. S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution or allow others to do so, for U.S. Government purposes.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER
Anion Solvation in Alcohols

Charles D. Jonah, Zhang Xujia, and Yi Lin
Chemistry Division
Argonne National Laboratory
Argonne, IL 60439, USA

Abstract: Anion solvation is measured in alcohols using pump-probe pulse radiolysis and the activation energy of solvation is determined. Solvation of an anion appears to be different than excited state solvation. The continuum dielectric model does not appear to explain the results.

Keywords: solvation, radiation chemistry, anions

Introduction: The role of the solvent in chemistry has long been an important subject of study. The solvent can act by removing energy from a reactant, trapping the reacting compounds and by accommodating to the creation of a charged entity in solution. Early work has probed the role of the solvent in altering the electronic energy levels of molecules by observing the shift of absorption or emission spectra (solvato-chromatic effect). Recently it has been possible to determine the dynamics of the response of the solvent to the alteration of the charge of a molecules. Systems that have been studied include the solvated electron [1-7] and excited states (recent reviews include [8,9]). These measurements provided considerable information about the solvation mechanism. However in chemical reactions, ions, rather than dipoles (excited states) are often formed. We felt that the solvation of an anion might well be different than the solvation of an excited state. Based on work of Marignier et al.[10], and Ichikawa et al.[11] we began a study of the solvation of anions in alcohols and anions[12,13]

In all of the solvation kinetics experiments, either the electron, an excited state, or an anion, the species that is solvated is created very quickly. The optical spectrum (either emission or absorption) is measured as a function of time. From these measurements the solvation time is determined. Our experiments on anion solvation make use of a probe molecule, benzophenone, in alcohols. The benzophenone reacts with the “dry electron” and the benzophenone anion is formed very quickly. The absorption spectrum of the anion is in the red. As a function of time, the absorption spectrum of the anion shifts towards the blue, which is attributed to the solvation of the anion. Our studies have been done in alcohols because an alcohol will mimic many of the processes that can occur in aqueous solution but with slower solvation times. However because of the complex dielectric relaxation behavior of alcohols [14], it is not easy to determine the microscopic motions that are important in solvation. To assist us in understanding solvation mechanisms, we have carried out experiments as a function of alcohol length, alcohol type (primary and secondary) and temperature and have carried out theoretical calculations.

Experimental: The experimental apparatus has been described in detail previously.[15] The Argonne stroboscopic pulse radiolysis system was used for the measurement of the kinetics and spectra. The approximate time resolution of the system is 30 ps and was determined from the
formation of the hydrated electron in water at 600 nm. Low temperature experiments were done by cooling the solutions by passing them through a coil that is immersed in dry ice-acetone. The temperature was controlled by rewarming the solution as it exits the cooling coil.

Benzophenone (specified as 99+% and the alcohols were used as received. The samples were degassed by bubbling with argon. No interference from the absorption of the solvated electron could be observed.

Results and Discussion: The spectra typically shift from having a maximum at 710 nm at early times to a maximum of about 625-630 nm after complete solvation. We find that the spectrum of the fully solvated anion is the same in all primary alcohols. However the spectrum of the completely solvated anion in 2-octanol is approximately 35 nm red-shifted from the spectrum of 1-octanol. This result clearly shows that the structure of the alcohol affects the amount of solvation. This result is in clear conflict with a theory of a continuum fluid. In a continuum dielectric fluid, the solvation energy will be dependent on the density of dipoles. However as we have seen, the spectrum of the solvated benzophenone is the same for all primary alcohols, where the dipole density varies by about a factor of three from propan'ol to decanol. In addition, the spectrum of the anion is considerably different between 1-octanol and 2-octanol, where the dipole density is the same.

These results can be compared with the solvation kinetics determined for the electron in alcohols and for excited states (Figure 1). To allow a simple comparison, we plot the measured solvation time vs. the longitudinal solvation time, a measure of the speed of response of the fluid. These results clearly show that solvation is different between excited states and anions, and that anions are much more similar to the solvated electron.

To probe the possible microscopic mechanisms of anion solvation, experiments were carried out as a
function of temperature. Because the different processes will have different activation energies, these experiments have the potential to determine what are the microscopic processes that are occurring. Figure 2 shows the solvation of the benzophenone in 1-propanol, 2-propanol and 1-octanol. The activation energy was determined to be 22 kJ/mole for the anion in 1-propanol and 1-butanol and 16 kJ/mole for 2-propanol. These energies are very similar to the hydrogen bond energies for the solvents [16]. These activation energies are larger than the activation energy for dipole solvation in the same alcohols [8].

Conclusion: We have shown that pulse radiolysis can be used to measure anion solvation. The results show that anion solvation is much faster at room temperature than is the solvation of dipoles; however at lower temperatures, the kinetics of dipole solvation are faster due to the lower activation energy for dipole solvation. We have shown that a continuum picture is not appropriate for anion solvation and we suggest that anion solvation is dominated by local structure. Low temperature experiments suggest that hydrogen bond breaking in the solvent is important in solvation.

References:
† Work performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Science, US-DOE under contract number W-31-109-ENG-38.