

## 論文の内容の要旨

論文題目     The temperature dependent absorption spectra  
                  and yields of solvated electrons in alcohols  
                  (アルコール中の溶媒和電子の吸収スペクトル、収量に対する温  
                  度効果の研究)

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In this work, we measured the absorption spectra in primary alcohols, at elevated temperature with fixed pressure, by using nanosecond electron pulse radiolysis technique. Including above data, a compilation of currently available experimental data on the energy of absorption maximum ( $E_{\max}$ ) of solvated electrons changed with temperature in monohydric alcohols, diols and triol is presented. The molecular structure effect, including OH numbers, OH position and carbon chain length, are investigated. And then, the optical absorption spectra of the solvated electron ( $e_{\text{sol}}^-$ ) in sub- and supercritical methanol and ethanol are measured by electron pulse radiolysis and laser photolysis techniques, at temperatures in the range of 220-270 °C. The effect of addition of a small amount of water to the alcohol on the optical absorption energy of  $e_{\text{sol}}^-$  is also investigated. Then we measured the time dependent  $G(e_{\text{sol}}^-)$  in water and methanol at elevated temperatures by using both scavenging method (indirect method) and picosecond pulse radiolysis (direct method).

### 1. Introduction

In the last two decades, there has been an increased interest in the supercritical fluids (SCFs). Besides its important contribution to the fundamental chemistry, SCFs has drawn interest because of its innovative role in a variety of chemical processes and technological applications, such as the synthesis of new materials and the destruction of hazardous wastes. It is well known that supercritical fluids (SCF) possess many peculiar and desirable characters, and it is possible to control the reaction rate and the selectivity sensitively by changing temperature and pressure. In particular, the nature of SCF is that the density can be varied continuously at constant temperature over a wide range using only small changes in the applied pressure. However, the density is in fact microscopically inhomogeneous and there is clustering structure. The studies of the density and solvent structure effects are thus important.

And fundamental research on the solvated electron in alcohols is of importance in deep understanding of dynamics of solvation process and solvent structures, as well as subsequently developing applications in many industrial arenas.

Some behaviors of the solvated electrons in supercritical fluids of alcohols, including their absorption spectra, decay kinetics and yields after their production by use of pulse radiolysis and/or laser photolysis methods, are studied in this work.

The purpose of this study is to investigate the temperature and structure of the solvent

effects on the energy of maximum absorption ( $E_{\max}$ ), the density effect on the  $E_{\max}$  in sub- and supercritical solvent, and the yield of solvated electron at different times and temperatures.

## 2. Experimental

In this work, a method of nanosecond pulse radiolysis, picosecond pulse radiolysis and/or laser photolysis combined with absorption spectroscopy, have been used for measurement of the time-resolved absorption spectrum of the transient species which produced by irradiation of the sample with high energy electron beam or ultraviolet laser beam. And the transient absorption spectroscopic method has an advantage that; it enables us to measure signals deriving from the short-lived species in the solution; as like solvated electrons in this work. We combined the advantage of pulse radiolysis for producing the solvated electrons in alcohols with a high efficiency, and that of transient absorption spectrum for measuring the low concentration short-lived species in liquids with a high sensitivity.

Two different high-temperature and high-pressure (HTHP) cells (Taiatsu Techno<sup>®</sup>) were used in pulse radiolysis and laser photolysis experiments, coupled with a linear electron accelerator (nanosecond or picosecond) or a KrF excimer laser (Lambda Physik, Compex 102; pulse duration: 20 ns;  $\lambda = 248$  nm), respectively, at the Nuclear Professional School of The University of Tokyo.

## 3. Solvated electrons at elevated temperatures in different alcohols

Jay-Gerin et al. compared available experimental data on some physicochemical properties of solvated electrons in 99 pure polar solvents at room temperature, and Krebs et al. discussed the correlation between mobility and the absorption spectra of solvated electron in polar solvents. However there is not simple correlation between the physicochemical properties of solvents and the position of the absorption spectrum of solvated electron, which indicate that it is governed by solvent molecular structure. Further investigation has shown that the absorption spectra of solvated electron are also dependent on the temperature and the pressure, which suggests a charge transfer to solvent (CTTS) state for their absorption band.

In this work, we measured the absorption spectra of solvated electrons in methanol, ethanol, butanol, pentanol, hexanol, octanol from room temperature to higher temperatures. We fixed pressure at 20 MPa in methanol and ethanol, and at 15 MPa in butanol, pentanol, hexanol and octanol. For methanol we changed temperature from room temperature (22 °C) to supercritical condition (270 °C). And the absorption spectra of solvated electrons in ethanol, butanol, pentanol, hexanol and octanol are measured from 22 to 230, 22 to 175, 22 to 200, 22 to 175, and 50 to 150 °C, respectively. For all the investigated alcohols,  $E_{\max}$  will have a red-shift with increasing temperature.

Including above data, a compilation of currently available experimental data on the energy of absorption maximum of solvated electrons changed with temperature in monohydric alcohols, diols and triol is presented. The molecular structure effect, including OH numbers, OH position and carbon chain length, are investigated. For the primary alcohols with same OH group number and position (at the end of chain), the temperature coefficient increases with increasing chain length. For the alcohols with same chain length and OH numbers, temperature coefficient is larger for the symmetric alcohols than the asymmetric ones.  $E_{\max}$  will be larger in the alcohol which has more OH groups at all the temperatures.

#### 4. Temperature and density effects on the absorption maximum of solvated electrons in sub- and supercritical methanol and ethanol

Alcohols form an interesting class of liquids in which to investigate the factors influencing the formation and stabilization of electrons in fluids. Considering the structure of methanol is very like that of water (methanol, the simplest alcohol, may be considered as “methylated water”), one methyl group just replacing one H atom, it is reasonable to assume that density dependent behaviors similar to those observed for water also exist in sub- and supercritical methanol and ethanol .

(1) In methanol: The optical absorption spectra of  $e_{\text{sol}}^-$  in sub- and supercritical methanol are measured by both electron pulse radiolysis and laser photolysis techniques, at temperatures in the range 220-270 °C. Over the density range studied ( $\sim 0.45\text{-}0.59\text{ g/cm}^3$ ), the position of  $E_{\text{max}}$  of  $e_{\text{sol}}^-$  is found to shift only slightly to the red with decreasing density. In agreement with our previous work in water, at a fixed pressure,  $E_{\text{max}}$  decreases monotonically with increasing temperature in passing through the phase transition at critical temperature ( $T_c$ ) (239.5 °C). By contrast, at a fixed density,  $E_{\text{max}}$  exhibits a minimum as the solvent passes above the critical point into the supercritical state. These behaviors are discussed in terms of microscopic arguments based on the changes that occur in the methanol properties and methanol structure in the sub- and supercritical regimes. The effect of addition of a small amount of water to the alcohol on the optical absorption energy of  $e_{\text{sol}}^-$  is also investigated.

(2) In ethanol: The optical absorption spectra of  $e_{\text{sol}}^-$  in sub- and supercritical ethanol are measured by electron pulse radiolysis technique, at temperatures in the range 220-260 °C. Over the density range studied ( $\sim 0.45\text{-}0.60\text{ g/cm}^3$ ), the position of  $E_{\text{max}}$  of  $e_{\text{sol}}^-$  is found also to shift slightly to the red with decreasing density. In agreement with in water and methanol, at a fixed pressure,  $E_{\text{max}}$  decreases monotonically with increasing temperature in passing through the phase transition at  $T_c$  (240.8 °C). However, at a fixed density,  $E_{\text{max}}$  exhibits a minimum as the solvent passes above the critical point into the supercritical state.

#### 5. Time dependent $G(e_{\text{sol}}^-)$ in water and methanol at elevated temperatures

In order to investigate the spur reaction, we can use picosecond pulse radiolysis (direct method) or nanosecond pulse radiolysis (indirect method). It is possible to trace directly the decay of transients from a few picoseconds to several nanoseconds by using picosecond pulse radiolysis. But it needs sophisticated and complicated systems, which is very expensive, so called ‘rich man’ method. The indirect method is to use a chemical (scavenger) to react with  $e_{\text{sol}}^-$  to produce a relative stable intermediate radical which can be detected by nanosecond pulse radiolysis, also be called as scavenger method or ‘poor man’ method.

(1) In water: Methyl viologen ( $MV^{2+}$ ) was used as a scavenger of hydrated electron for estimation of its yield from room temperature to 300 °C with a fixed pressure 25 MPa. By changing the concentration of  $MV^{2+}$  from 0.01 to 10 mM, the time dependent yield of hydrated electrons were estimated at different temperatures. The corresponding time were calculated by equation:  $t=(k[MV^{2+}])^{-1}$ , where  $k$  is the reaction rate of  $MV^{2+}$  and  $e_{\text{aq}}^-$ ;  $[MV^{2+}]$  is the concentration of  $MV^{2+}$ . By using picosecond pulse radiolysis method, the kinetics of hydrated electrons were measured at fixed pressure of 25 MPa from room temperature to 300 °C. The wavelengths of analysis laser light are 700 nm for room temperature, 860 nm for 150

°C, and 940 nm for above 250 °C. They are in good agreement between direct and indirect methods.

(2) In methanol: 4,4'-bipyridyl (Bpy) was used as a scavenger of hydrated electron for estimation of its yield from room temperature to 250 °C with a fixed pressure of 10 MPa. By changing the concentration of Bpy from 0.05 to 100 mM, the time dependent yield of solvated electrons were estimated at different temperatures. The corresponding time were calculated by equation:  $t=(k[\text{Bpy}])^{-1}$ , where  $k$  is the reaction rate of Bpy with ~~and~~  $e^-_{\text{aq}}$  and  $[\text{Bpy}]$  is the concentration of Bpy. The rate constant  $k$  at different temperatures were measure by change of Bpy concentration. By using picosecond pulse radiolysis method, the kinetics of solvated electrons were measured at a fixed pressure of 10 MPa below supercritical temperature and 15 MPa in 250 °C.

## 6. Conclusion

For the investigated alcohols, the  $E_{\text{max}}$  will decrease with the increasing the temperature, and the decreasing rate has the relationship with the chain length, the number and position of the OH group. Temperature effect on  $E_{\text{max}}$  will increase with increasing chain length. For the isomers, the temperature effect on symmetric one will be smaller.  $E_{\text{max}}$  will be higher with more OH groups.

In both methanol and ethanol, the temperature dependence of  $E_{\text{max}}$  in sub- and supercritical fluids (SFC) reveals that, at a fixed pressure,  $E_{\text{max}}$  decreases monotonically with increasing temperature in passing through the liquid-SCF phase transition at  $t_c$ , but exhibits a minimum at a fixed density as the fluids passes above  $T_c$  into SCF.

The yields of solvated electron in water decrease with increasing temperature up to 300 °C, monotonously, by both scavenging method and picosecond pulse radiolysis method. Below supercritical temperature, the yields of solvated electron in methanol decrease with increasing temperature up to 200 °C, monotonously, by both scavenging method and picosecond pulse radiolysis method. For scavenging method, the yield of solvated electron in methanol, at earlier time, is higher in supercritical state than that in lower temperature. And the decreasing rate of it is the fastest of all temperatures.