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SOLVATION OF THE ELECTRON IN ALCOHOLS STUDIED USING THE ARGONNE PICOSECOND PULSE RADIOLYSIS STEM

by

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SOLVATION OF THE ELECTRON IN ALCOHOLS STUDIED USING THE ARGONNE PICOSECOND PULSE RADIOLYSIS SYSTEM

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INTRODUCTION

A large advance in the resolution of pulse radiolysis occurred when John Hunt and coworkers designed and built their stroboscopic pulse radiolysis system [1]. With this system they were able to measure the reactions of solvated electrons [2], dry electrons [3] and solvation times of electrons in alcohols from 20 psec to 350 psec [4]. They also showed that the models then existing describing spur processes were quantitatively incorrect [5].

When it was proposed that the Argonne linac be bunched [6], that is, have almost all (greater than 90%) of the charge be in one single fine structure pulse, we wanted to design a system which would make a maximum use of the linac pulse. After considering several alternatives we decided to make use of the technique pioneered by Hunt and coworkers. The technique required considerable modification since we are working with a single fine structure pulse, while Hunt used a train of pulses. This allows us to look over a time range of 3.8 nsec instead of 350 psec, although the time resolution is not as good as that of Hunt [7].

I will describe the system and its application towards understanding solvation processes in polar liquids. The problem of the solvation of the electron in water and polar liquids has elicited a great deal of experimental and theoretical work and has up to the present resisted complete elucidation [8]. We have been studying solvation processes in alcohols and alcohol-alkane solutions. Solvation is a complex process which depends on the microscopic structure of the fluid [9]; therefore, solvation studies in alcohols as a function of temperature or as a function of the concentration of the alcohol must take into account the structure of the fluid being studied.

The role of the alkane is to break up the clusters formed in the alcohol in a controlled fashion. These mixtures have been heavily studied by other techniques [10] which give an idea of the structure of the alcohol molecule clusters when the alcohol has been diluted by an alkane. We will discuss n-butanol-hexane and t-butanol-hexane systems and use these systems as a basis for our discussion.

It might be presumptuous to consider the dynamics of electron solvation when the static solvated electron is not totally understood. The spectrum of the hydrated electron has not yet been satisfactorily calculated and recently it has been proposed that the hydrated electron might be better described as a solvated H_2O^- molecule [11] rather than as an electron roughly equally associated with several water molecules as had been thought before. However, in understanding the mechanism, at least partially, of the solvation process, one can limit the final states and therefore exclude certain possible final states. Presolvated electron reactions (reactions which occur before electron solvation) are of great interest [3,12-14] and understanding the mechanism can be facilitated by understanding the solvation process; for if a particular state of the electron does not exist in the solvation process, it cannot be the state of the electron from which the presolvated electron reacts.

EXPERIMENTAL

In Table I, we list the parameters of the Toronto linac, the Argonne linac, and the proposed modification of the Argonne linac (expected to be brought on line in 1979).

TABLE I

	Charge/ Pulse	Satellite	Pulse Width	Spacing	Energy
Toronto	.2 nc	n/a	10 ps	350 ps	40 MeV
Argonne present	7 nc	5-10%	24-28 ps	770 ps	20 MeV
Argonne (1979 prop) (Spiral cavity)	14 nc	0%	24-30 ps	770 ps	20 MeV

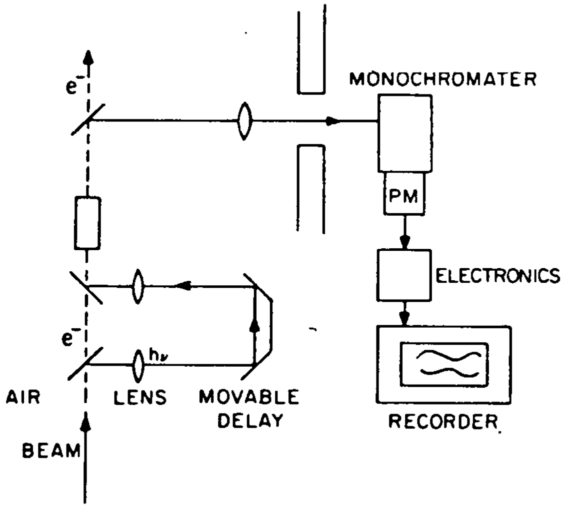


Fig. 1. Diagram of the stroboscopic pulse radiolysis system of J. W. Hunt [1].

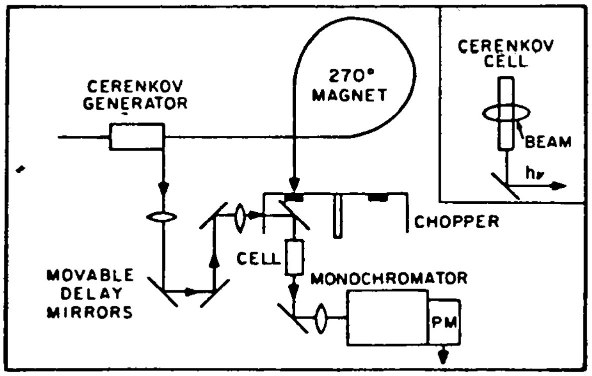


Fig. 2. Diagram of Argonne picosecond pulse radiolysis system.

In Fig. 1 we show the experimental system designed by Hunt [1]. In this system the light is Cerenkov radiation generated by the electron beam passing through air. It is delayed by an optical delay line and rejoins the electron beam at the cell. Thus the light generated by a fine structure pulse of the linac is used to monitor the absorption created by a later electron pulse. The time resolution is determined by the width of the light pulse since that is the only time one is observing the system. The time resolution does not require a fast detector; one need only measure the total intensity of the light transmitted to effectively measure the transmittance of the sample at the time of the flash

With our single fine structure linac pulses two changes were necessary [15]. First, since there is a single fine structure linac pulse the electrons must be delayed, otherwise, the analyzing light cannot reach the cell before the electron pulse. The second problem is that the energy of the linac pulse is insufficient to generate Cerenkov radiation in air. In Fig. 2 we show a diagram of our system. The electrons are delayed by using a 270° magnet and the analyzing light is generated using xenon gas which has a higher refractive index than does air. This system has the advantage that one is not limited to working between fine structure pulses but can measure over a time scale as wide as one can delay the light (in our case, 3.8 nsec; the limit is set by the length of the optical delay line). However, we have had to give up some time resolution and some beam in using this technique. We lose time resolution because all electrons do not have the same energy and they will therefore take different paths around the 270° magnet and will stretch the pulse [7]. In addition, misadjusting the entrance angle of the beam into the magnet will broaden the pulse. The optical analyzing pulse will be 25-30 psec wide while the best pulse one can obtain at the radiation point is 35 psec [7]. Some beam is lost since the beam used to generate the Cerenkov light (≈ 30-50% of the beam) cannot be used for radiolysis because the energy of the beam will be degraded and it will be lost in the magnet. The pulse directly out of the linac can be reduced to 20-25 psec by decreasing the current, but this will not improve the time resolution substantially because of the spreading due to the magnet [7].

The light pulses are detected using R818 photomultiplier where 4 or 5 dynodes are used or a C7253G, a 5 stage variant of the 1P28. Gain of the tube can vary depending on how close together pulses are, the critical time being .5 to 5 nsec. The noise on the signal is due to shot noise. A Tennelec 162 charge sensitive preamplifier is used to measure the charge from a single light pulse. Corrections are made to the absorption signal by analog signal processing modules for Cerenkov light generated in the sample cell and for changes in analyzing light intensity arising from changing the length of the optical delay line [15]. The resulting signal is digitized and averaged using a voltage to frequency converter and a multichannel analyzer in the multiscaling mode. The analyzer is stepped in synchronism with the movement of the optical delay line. After scanning the analyzer and optical delay line to their extremes, the data are transferred to a central computer. Several scans of the optical delay line can be made and the results averaged at the end of the run. This data acquisition method has several advantages. The use of the voltage to frequency converter gives a large dynamic range so that one can work with a transmission signal directly rather than having to offset the transmission signal. Also, by accumulating the various sweeps separately one can discard those with artifacts due to beam fluctuations or flow fluctuations and can check for changes in the signal as a function of the time of irradiation. However, since the computer is isolated from the raw data, it cannot check for loss of beam or for excessive signal fluctuations due to beam fluctuations or (more commonly) bubbles occurring in the flow system.

Since the intensity of the light signals detected changes sharply as a function of wavelength due to changes in the optical system, the wavelength dependence of the light and the response characteristics of the photodetector, a circuit was added to hold the analyzing light constant by inserting a set of fingers of variable transmittance directly before the monochromator slits. These fingers are controlled by a stepping motor which is driven by a circuit shown in Fig. 3.

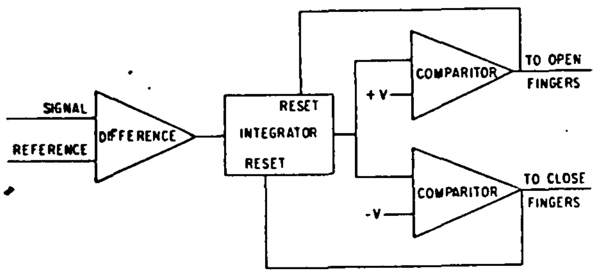


Fig. 3. Logic diagram for controller to keep the intensity of light constant.

Typical data acquisition times range from six minutes for signals with 30% absorption (the hydrated electron at 600 nm) to an hour for absorption of 1%. The wavelength range is 250-750 nm; the lower wavelength limit is due to the loss of light on reflection; the upper wavelength limit is due to the monochromator. Full scale times are .475, .95, 1.9 and 3.8 nsec.

Risetime is difficult to state unambiguously since the risetime depends on what sort of phenomena one is observing. The risetime is due to the pulse width of the light and the linac and the dephasing of the electron and light beam in the cell. The dephasing comes from the fact that light travels in water at a speed of approximately .7 the speed of light in vacuum while the electron travels within .03% of the speed of light in a vacuum. This will lead to a risetime of approximately 20 psec [1]. However, if one compares the signal of interest to a signal in which a very short risetime is expected (for instance, the absorption of the solvated electron in water), one can extract the risetime of the signal of interest by difference. An example is shown in Fig. 4 [16]. Thus the risetime will limit the first time at which one can measure a full absorption but not the rate of change. This would not be true for an electronic risetime but is true for the optical sampling risetime done in this experiment.

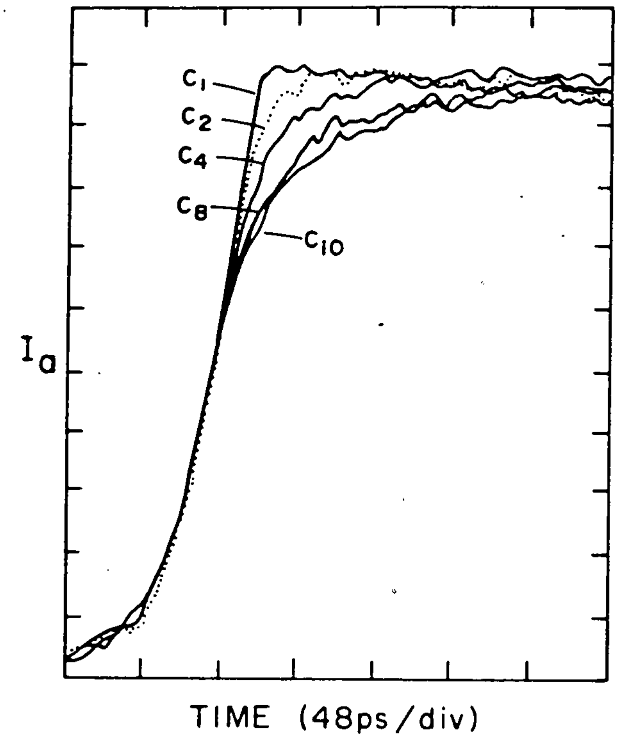
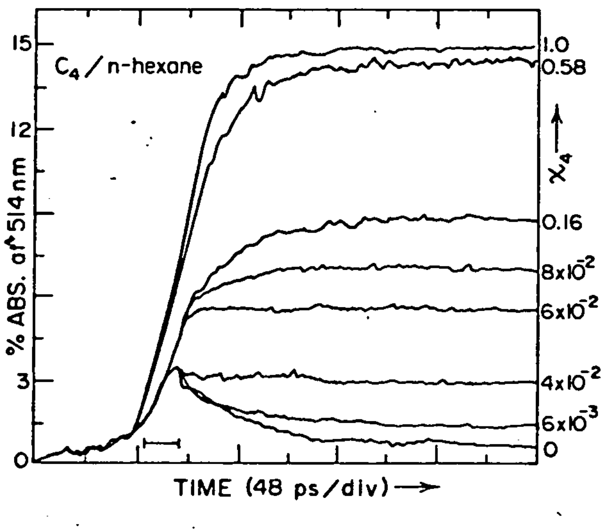


Fig. 4. Absorption of the solvated electron as a function of time at 500 nm for neat alcohols.

RESULTS AND DISCUSSION

To obtain an idea of the solvation process in alcohol we measured the change in the absorption of the electron at 500 nm. The results are shown in Fig. 4. From these data the time constant for solvation process was determined and this time constant is the same as was measured by Hunt for the decay of an absorption at 1300 nm for ethanol and propanol [4]. These times were very similar to the τ_2 values for the alcohols where τ_2 is the rotational relaxation time of the alcohol where no hydrogen bonds are broken [4,15].

Work by Baxendale [17] has shown that at very low concentrations of alcohol in alkanes the electron forms a complex with a cluster of alcohol molecules and that the most probable size of this cluster is two alcohols. The species formed is not the solvated electron since the characteristic spectrum of the solvated electron is absent, and the conductivity of the species is far above that of the solvated electron.



The kinetics of the change of the absorption at 514 nm as a function of alcohol concentration are shown in Fig. 5. The kinetics are the same at 16 M% and 58 M% alcohol [18] which means the species necessary to solvate the electron are present at 16 M% and are not greatly changed at 58 M%. The kinetics are not quite the same as one sees in pure alcohol. At about 75 M% the kinetics are the same as in the pure alcohol.

Fig. 5. Absorption of the solvated electron at 500 nm as a function of mole fraction n-butanol.

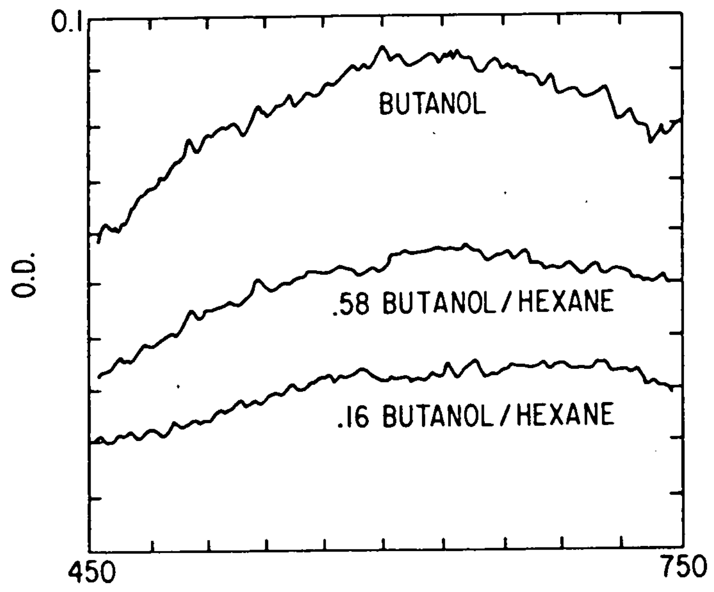


Fig. 6. Absorption spectra of the solvated electron 3 nsec after the pulse.

In Fig. 6 we show the spectra of the solvated electron at three different concentrations of alcohol in hexane. The similarity of the spectra shows that the same final state of the electron is being formed. Figure 7 shows the concentration dependence of the absorption of the electron at the various concentrations. Since we are looking at almost the same species in all concentrations it is clear that we are increasing the concentration of solvated electrons and the increase occurs because we are increasing the number of sites at which the electron can solvate. Since the kinetics remain the same, it is not an increased probability of aggregation from the increased concentration of alcohol present but an increased number of solvation sites. Previous work by Weinstein and Firestone [19] and by Baxendale [17] confirm that there is little or no aggregation after the initial solvation. Therefore, one can say that solvation occurs from structures existing in the fluid.

If we accept that the preformed structure of the fluid is important, the concentration dependence will be different for different alcohols and also for an alcohol in different hydrocarbons. For instance, if one were to use a secondary or a tertiary alcohol instead of a primary alcohol one would expect to require more alcohol before the clustering would be sufficient to allow solvation. In Table II we give comparative data for n-butanol, 2-decanol and t-butanol necessary to affect the processes occurring in the pure alkane and the concentration necessary to give the kinetics of a fully solvated electron. In Fig. 8 we show the concentration-dependent kinetics for t-butanol, similar to the data shown in Fig. 5. Note that much more alcohol is needed for the t-butanol in comparison to the n-butanol. The solvation time is seen to be quite slow in t-butanol. This is not just a viscosity effect

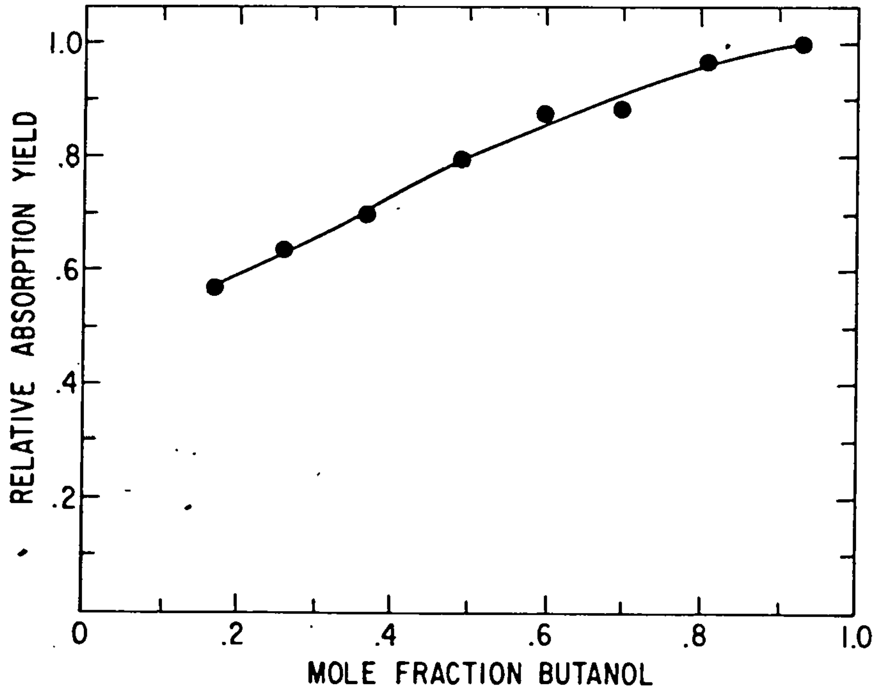


Fig. 7. Maximum absorption of the solvated electron as a function of mole fraction alcohol.

since on heating the t-butanol to 40°C the kinetics remain the same.

TABLE II

Concentration of alcohol in alkane necessary to change kinetics of the absorption process.

	To Alter Pattern of Solvent	To Reach Constant Change
n-butanol	.5 M%	15 M%
2-decanol	2-3 M%	18 M%
t-butanol	5 M%	50 M%

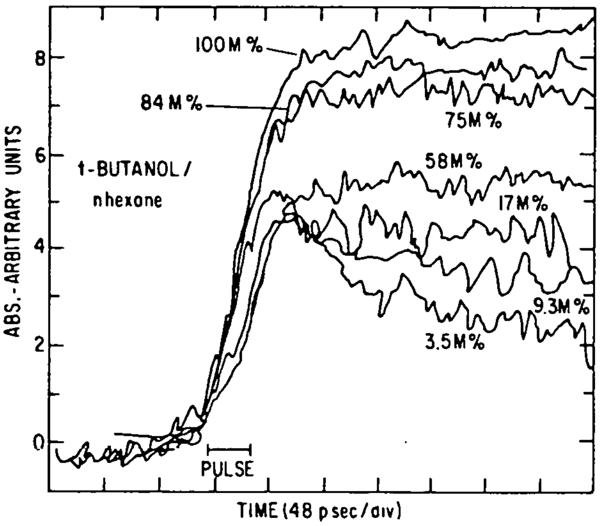


Fig. 8. Absorption of the solvated electron at 500 nm in t-butanol for different mole percent t-butanol.

These experimental results limit and/or modify the possible solvation mechanism. The polarization induced by a moving charge, which was proposed as a solvation mechanism by Schiller and Vass [20] would seem to be an unlikely mechanism since it does not make use of the preformed traps which we have shown to be quite important in the solvation process. The semicontinuum model has usually assumed that the major solvation process comes from rearrangement of the inner shell of the solvent [21]. However, the calculations assume randomly arranged alcohols and not the spatially arranged alcohol molecules which exist in the trapping site. In addition, the calculations do not consider the possibility of dielectric saturation. If the correlation between solvation time and τ_2, the non hydrogen-bonded rotation time of the alcohol, is not a coincidence, it is not clear how the hydrogen-bonded cluster relaxes in that time.

In conclusion, we have tried to give the capabilities of our pulse-radiolysis system and its application to solvation mechanisms in polar fluids. We have dealt exclusively with room temperature phenomena and the conclusions drawn may not be completely relevant at low temperatures [22,23]. Since the relaxation processes may have substantial activation energies, different processes may be dominant at low temperatures. However, in room temperature alcohols pre-existing traps are the dominant means of electron trapping. To extrapolate to water may be reasonable since water and alcohol both give similar final species. However, the existence of a second OH bond in water can lead to other structures [24].

We have not treated exhaustively the many theories of solvation due to lack of time nor have we treated what can be learned about the structure of the fluid by studying the solvation process for the same reason and since it has been treated recently [25]. However, we have shown the information which can be obtained from the picosecond pulse radiolysis system and how this information shows that the electron solvates in preformed structures in the alcohol.

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