INFLUENCE OF VISCOSOUS MEDIA ON CHARGE TRANSFER REACTIONS

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The influence of viscous H₂O-Dextran media on two charge transfer reactions has been investigated using laser photolysis coupled with pico and nanosecond time resolved absorption spectroscopy. In the first case, a charge-transfer reaction from a solute (potassium ferrocyanide) to the solvent was studied and the electron solvation dynamics was followed. A solvation time delay, depending on the polymer concentration, is observed which indicates that electrons remain quasi-free for longer periods in these media.

In the second case, the quenching process of the triplet state of an excited metallo porphyrin(ZnP₄⁺) by an electron acceptor, methylviologen chloride (MV₂⁺, 2 Cl⁻) is studied. The measured triplet quenching rate constant values decrease with increasing dextran concentration, but remain higher than those calculated, taking into account a simple viscosity effect. This result is explained in terms of a competition between a decay of the diffusion rate constants of (ZnP₄⁺)* and MV₂⁺ due to a viscosity effect and an enhanced cage effect around the ions (ZnP₄++*, MV₂+). Once formed, this last effect favours the charge transfer reaction.

1. INTRODUCTION

The hydrodynamic properties of aqueous solutions of dextran, a polymer of biological interest, are interesting in many
respects. It is known, for example, that the dextran solutions may be used as a blood plasma substitute and it is therefore of a great interest to understand the influence of such biological structured media on chemical reactions in comparison with organized media such as micelles and polyelectrolytes. Free and solvated electrons, or excited molecules are the species usually generated upon the irradiation of a given medium, and their reducing or oxidizing properties are often used to induce chemical reactions. The influence of the local environment, especially in structured media can strongly influence the physical properties and reactivity of such species. In the present work, we report the study of the influence of viscous aqueous dextran media on two charge transfer reactions leading in the first case to the formation of solvated electrons, and in the second case to organic ions with a great reducing power.

Part. I

The mechanism of electron injection, localization and solvation in non polar and polar media have been extensively investigated. It has been shown that the method of electron injection (by direct ionization of a molecule in a pure liquid\textsuperscript{1-2} or from photodetachment or photoionization of a solute ion or neutral molecule\textsuperscript{3-4}, as well as the life time of the intermediate ionizing or detaching level\textsuperscript{5} and the nature and structure of the liquids, strongly influence the temporal evolution of the solvation process.

For linear primary alcohols (from methanol to hexadecanol), a class of liquids in which solvated electron spectroscopic properties are very similar, Kenney-Wallace
and Jonah 6 have established a correlation between the electron solvation time $\tau_s$ and the dielectric relaxation time corresponding to the relaxation of the alcohol monomer molecules when submitted to a weak external and uniform electric field, $\tau_2$. In order to explain this correlation, an electron solvation mechanism has been proposed in which the excess electrons are first trapped by small preexisting cluster molecules. The strong local electric field is then weakened and screened by the layer of cluster molecules and the induced rotation of the dipole monomers outside the cluster can be treated by weak field conditions. However, with H$_2$O as a solvating medium, a large discrepancy between $\tau_s$ ($<0.1-0.3$ ps) 7 and the dielectric relaxation time has been found and explained in terms of the existence of deep trapping sites composed of hydrogen bonded cluster molecules.

In a previous nanosecond pulse radiolysis study of electron solvation in viscous aqueous dextran solutions, we have found that the presence of the large dextran molecules (polyose with a molecular weight of $\sim 10^5$) at a concentration above 43 weight %, alters the aqueous molecular structure and leads to a drastic decrease of the hydrated electron yield 8. As this decrease corresponds to a break in the dielectric relaxation time of water molecules, one might expect that the water dipole rotation would be hindered and hence the solvation time of electrons at picosecond time scale would be longer.

With the aim of checking this assumption, we decided to study the electron solvation dynamics in the viscous aqueous dextran solutions following the charge transfer reaction from the 266 nm UV excited potassium ferrocyanide to the solvent, using laser photolysis coupled with picose-
cond time resolved absorption spectroscopy.

**Experimental**

The dextran (Serva, RFA) aqueous solutions were prepared in triply distilled water. Potassium ferrocyanide solutions having concentrations varying from $7.5 \times 10^{-3} \text{M}$ to $10^{-2} \text{M}$ were used.

The experimental set up for the picosecond absorption study is shown in fig. (1)

![Figure 1: Experimental set up of the time resolved absorption spectroscopy](image)

Briefly, the 27 ps duration pulse was extracted from a train of 7 pulses delivered by a Quantel Nd-YAG laser and the frequency doubled. A dielectric coated mirror deflects the 1064 nm pulse and transmits $\sim 90\%$ of the 532 nm pulse which is again frequency doubled. The exciting beam (266 nm, 0.8 - 1.2 mJ) is then focused into a 1 mm diameter entrance of the sample cell (C) of 1 mm thickness. The analyzing beam is a 630 nm stimulated Raman line generated by focu-
sing the residual 532 nm pulse into a quartz cell of 4 cm path length containing dimethylsulfoxide (Merk). The analyzing beam is then focused into the same entrance of the sample cell and the exit beam (I) focused through an optical fiber of 5 m length into a photodiode (rise time < 200 ps) and the signal visualized on a Tektronix 7912 oscilloscope screen. Before entering the sample cell, the analyzing beam is splitted, and I₀ used as a reference is focused into the same photodiode.

The optical density values of the transient absorbing species formed during the excitation of the sample were determined from the Io/I intensity ratio values measured in the absence and in the presence of the exciting beam. An optical delay allowed the determination of the time axis origin between the exciting and analyzing beam, following the photobleaching at 630 nm of Pinacyanol chloride (OD = 0,4 at 532 nm) in isopropanol excited at 532 nm. The time after which the photobleaching was a half of its maximum was defined as the origin of the time axis. The aqueous potassium ferrocyanide solution in the absence and in the presence of various dextran concentrations were excited with the 266 nm beam and the electron solvation dynamics followed spectroscopically at two wavelengths 630 and 1064 nm.

Results and discussions

The normalized curves of the transient absorbances at λ = 630 nm of solvated electrons as a function of the delay time between the exciting and an analyzing beam are shown in fig (2). The time after which the absorbance was a half of the plateau was defined as the rise time of the hydrated electron absorbance.
The value for an aqueous solution of potassium ferrocyanide in the absence of dextran was $28 \pm 2$ ps. Since the formation time of hydrated electrons is known to be very fast (less than 0.3 ps) this result is quite surprising. Taking into account the frequency dependent retardation of a light pulse through different media for the exciting and analyzing beam, cannot account for this large discrepancy. A similar result has been found by Miyasaka et al.\textsuperscript{2} for neat H$_2$O and has been interpreted in terms of a multiphotonic H$_2$O excitation process within the pulse width. Since their experimental conditions (pulse width $\approx$ 20 ps fwhm and 0.5 - 0.7 mJ output power focussed into a spot of 2 mm diameter) are very similar to ours, one can not rule out at the present time the existence of the multiphotonic excitation of water. This result is of no consequence as regards to the following results since in the presence of dextran

Figure 2 : The absorbance rise time of solvated electrons.
the experimental conditions are unchanged.

In the presence of the polymer, the rise time of the hydrated electron absorbance in the visible region at the same wavelength ($\lambda = 630$ nm) increases with increasing dextran concentration: (fig (2) and table (I)). On the other hand, the rise time of the transient absorbances of hydrated electrons measured at $\lambda = 1064$ nm are instantaneous in the absence as well as in the presence of dextran (fig. 2). We therefore attribute the instantaneous absorbance rise time in the near infrared region to the absorption in the very early stage of quasi free electrons localized in shallow-traps composed of free water cluster molecules. The following step of the electron solvation dynamics would be the reorganization of the medium about the cluster which finally leads to the long lived solvated species absorbing in the visible region. Thus, in the visible region, the dependence of both the solvation time delay and the dielectric relaxation time of water upon the dextran concentration can be interpreted as follows. As the dextran concentration increases, the hydration process of the polymer leads to a decrease in the freely rotating water molecule concentration and to an enhanced formation of "perturbed" water molecules attached to the polymer. A consequence of this is that the induced rotation of the water dipole monomers outside the cluster becomes more and more difficult with increasing dextran concentration, and it takes a longer time for the electron to deepen its trap and become solvated. This interpretation is also consistent with the break observed in the dielectric properties of water molecules for dextran-concentration above 43 % weight, which has been interpreted in terms of
an increase in the "perturbed" water concentration at the expense of the freely rotating molecules. A 450 fs electron hydration risetime has been reported in anionic aqueous micelles and interpreted in terms of microviscosity change of the electron boundary layer. Hence it would seem that the presence of structured media such as micelles cannot induce so large a microviscosity change as found for polymers.

For dextran concentration equal to 44%, a nanosecond time resolved photolysis experiment allowed us to observe a slight blue shift (from 1.7 to 1.8 eV) consistent with that observed in our previous pulse radiolysis experiments and which might correspond to a greater trapping energy. This result could also explain why the time delay of the solvated electron absorbance rise time grew faster as a function of dextran concentration than did the dielectric relaxation time of water (Table I).

**TABLE I**

| Dextran Wt% | e− rise time (10^-12 s) | Viscosity (P) | τ H2O (10^-12 s) | delay (10^-12 s) |
|-------------|------------------------|--------------|-----------------|-----------------|
| 0           | 28 ± 2 ps              | 0.01         | 7.5             | 0               |
| 11.8 %      | 35.5 ± 1.5             | 0.3          | 8.1             | 7.5             |
| 30 %        | 45.5 ± 2.0             | 2.2          | 11.2            | 17.5            |
| 44          | 54 ± 3                 | 32.0         | 16.0            | 26.0            |
| 45 %        | 55 ± 1.5               | 38.0         | 16.5            | 27.0            |
This study provides direct evidence for the changes in the structural properties of the aqueous media. Hence, the electrons created either by pulsed radiolysis or photolysis can be used as an efficient microscopic probe of both the local structure and the molecular dynamics of liquids.

Part. II

Most studies on laser induced charge transfer reactions devoted to the search for efficient photosensitisers for the transformation of solar energy, are focused on the photochemistry of tris (bipyridine) ruthenium II compounds\textsuperscript{1} metalloporphyrins, chlorins and phtalocyanines\textsuperscript{2}. Some charged metalloporphyrins (MP) have been found to be particularly effective photosensitisers when methyl viologen (MV\textsuperscript{2+}) is used as an electron relay and ethylene diamine-tetraacetate (EDTA) as a sacrificial donor, and lead to high quantum yield of H\textsubscript{2} production\textsuperscript{3-4}. The well established mechanism for this overall reaction is the following

\[
\begin{align*}
\text{MP} & \xrightarrow{h\nu} (\text{MP})^* \\
(\text{MP})^* + \text{MV}^2+ & \xrightarrow{K \text{ diff}} (\text{MP}^*, \text{MV}^2+) \\
(\text{MP}^*, \text{MV}^2+) & \xrightarrow{K \text{ diss}} \text{MP}^+ + \text{MV}^2+ \\
\text{MP}^+ + \text{MV}^2+ & \xrightarrow{k_B} \text{MP}^+ + \text{MV}^+ \\
\text{MP}^+ + \text{MV}^+ & \xrightarrow{k_C} \text{MP}^+ + \text{MV}^+ \\
\end{align*}
\]
$\text{MP}^+ + \text{EDTA} \rightarrow \text{MP} + \text{EDTA}^+$

$\text{EDTA}^+ \rightarrow \text{products}$

$\text{MV}^+ + \text{H}_2\text{O} \rightarrow \text{MV}^{2+} + 1/2 \text{H}_2 + \text{OH}^-$

A crucial step in the formation of $\text{H}_2$ is the charge separation process of the ion pair ($\text{MP}^+$, $\text{MV}^+$). Many attempts have been made to optimize the dissociation of the ion pair and minimize the back reaction. By changing the nature of the substituted porphyrins (positively or negatively charged), Richoux et al.\(^3\) have shown the dependence between the charge separation efficiency and the attractive or repulsive coulombic field between the porphyrins and $\text{MV}^{2+}$. Heterogeneous media such as charged micelles or polyelectrolytes have also been used with the aim of enhancing the dissociation of the ion pair.\(^5-6\) In the solid state, with $\text{Ru(bpy)}_3^{2+}$ and $\text{MV}^{2+}$ adsorbed on cellulose, the $\text{MV}^+$ species produced upon irradiation was found to be especially stable even in the presence of oxygen.\(^7\) In rigid media, the possibility of hindering the motion of the oxidised and reduced species seemed to decrease the probability of the back reaction. Thus, the aqueous solutions of dextran for which the viscosity can be varied from 0.01 to 50 poises, from a liquid to a gel-like phase, appear to be suitable media for this kind of study.

In the present work, we report the effect of high viscosity and structuration of the medium upon the quenching process of the triplet state of an excited metalloporphyrin ($\text{ZnP}^{4+}$) by $\text{MV}^{2+}$, and the charge separation process following
the charge transfer reaction. The laser induced processes are followed by nanosecond time resolved absorption spectroscopy.

Experimental

The synthesis and purification of water soluble Zn derivative of 5, 10, 15, 20 tetra (N methylpyridinium 3-yl) porphyrin (ZnP$_{4}^{4+}$) has been previously reported$^{8}$. Methyl viologen chloride (Sigma) was used as supplied. The aqueous solutions of dextran were prepared with tridistilled water, and the concentrations of porphyrin and MV$_{2}^{2+}$ were varied respectively from $10^{-5}$ to $2.10^{-4}$ M and $10^{-3}$ M to $2.10^{-2}$ M.

The nanosecond absorption spectroscopy set up has been described elsewhere$^{8}$. Briefly, the 532 nm exciting laser pulse (from a Nd YAG) has a 6 ns f.w.h.m. duration and its energy output (up to $\approx 600$ mJ) was varied from 5 to 7 mJ in this study. The analyzing light perpendicular to the laser beam in the sample cell, coming from a Xe source (400 W), is dispersed in a M 25 Huet monochromator and analyzed by a Hamamatsu R928 T photomultiplier and a Tektronix 7834 memory oscilloscope. Appropriate filters were used to avoid second order diffraction contributions. Optical densities of irradiated solutions (normalized to a constant dose) were measured as a function of time at each wavelength studied.

Results and discussions

Excitation at 532 nm of aqueous solutions of dextran (up to 47 % weight does not lead to the formation of any transient absorbing species in the 350-780 nm domain. Air
free aqueous solutions of porphyrin were then excited at 532 nm in the absence and in the presence of various dextran concentrations. In all cases, the differential absorption spectrum, shows the characteristic profile of excited porphyrins, which results from a ground state bleaching in the UV domain and a triplet absorption in the visible part. The life time of the porphyrin triplet state, determined at its maximum absorption ($\lambda = 470$ nm) depends on the dextran concentration (table II).

The decay kinetics of the triplet state of the excited ZnP$^4+$ ($T_{ZnP}^4+$) are pseudo first order in all cases.

The charge transfer process from $T_{ZnP}^4+$ to MV$^{2+}$ was studied as a function of MV$^{2+}$ concentration ($2 \times 10^{-4}$ M - $2 \times 10^{-2}$ M) for various solutions containing a constant ZnP$^4+$ concentration ($5 \times 10^{-5}$ - $8 \times 10^{-5}$ M) and different concentrations of dextran (6 to 47 weight %). The decay kinetics of $T_{ZnP}^4+$ determined at 470 nm are first order for all the systems. The $T_{ZnP}^4+$ decay rate ($K$), calculated for each system, is a linear function of MV$^{2+}$ concentration over the whole MV$^{2+}$ concentration range studied (up to $2 \times 10^{-2}$ M).

$$K = K_0 + k_q[MV^{2+}]$$

where $K_0$ is the $T_{ZnP}^4+$ decay rate in the absence of MV$^{2+}$, and $k_q$, the bimolecular quenching rate constant of $T_{ZnP}^4+$ in the presence of MV$^{2+}$.

In aqueous solution of porphyrin, a non linear dependence of $K$ upon MV$^{2+}$ was found for MV$^{2+}$ concentration above $\approx 5 \times 10^{-3}$ M. A similar result has been obtained by Leroux et al. for the same porphyrin and explained in terms of the ionic strength effect of the solution. The presence of
dextran molecules in aqueous solutions of porphyrin seems to suppress this effect as $K$ is a linear function of $[\text{MV}^2+]$ up to $2\times10^{-2}$ M for all the studied dextran concentrations.

From the proposed mechanistic scheme (I), it is seen that

$$k_q = \frac{K_{\text{diff}} K_A}{K_{\text{diss}} + K_A}$$

depends not only on the diffusion rate constants of $\text{T}^{4+}$ and $\text{MV}^2+$ ($k_{\text{diff}}$) but also on the dissociation rate constant of the ion pair ($\text{T}^{4+}, \text{MV}^2+$). The values of $k_q$ calculated from the slope of $K = f [\text{MV}^2+]$, were plotted as a function of dextran concentration (fig. 3)

Fig. 3: $k_q$ as a function of the dextran concentration

It is seen that $k_q$ remains constant for 0 to 6 dextran % by weight but decreases above this. This decrease might be explained in terms of the $k_{\text{diff}}$ rate constant depen-
dence upon the dextran concentration, due to the viscosity of the solutions becoming very high with increasing dextran concentration.

With the aim of checking this, a theoretical value of $k_q$ was calculated, taking into account a simple viscosity effect (table II)

**TABLE II**

| Dextran wt % | viscosity (P) | $\tau(T_{ZnP}^{4+})$ ms | $k_q$(exp.) $10^6 s^{-1}$ | $k_q$(calc) $10^6 s^{-1}$ |
|--------------|---------------|--------------------------|---------------------------|---------------------------|
| 0            | 0,01          | 1,9 $\pm$ 0.1            | 2,0 $\pm$ 0,05            | 2,0                       |
| 6            | 0,18          | 0,85 $\pm$ 0.05          | 2,0 $\pm$ 0,05            | 0,11                      |
| 20           | 0,47          | 0,79 $\pm$ 0.05          | 1,4 $\pm$ 0,05            | 0,043                     |
| 42           | 23            | 1,3 $\pm$ 0.1            | 0,42 $\pm$ 0,05           | 0,0009                    |
| 45           | 38            | 1,43 $\pm$ 0.1           | 0,19 $\pm$ 0,05           | 0,0005                    |
| 47           | 50            | 1,52 $\pm$ 0.1           | 0,19 $\pm$ 0,05           | 0,0004                    |

The plot of $k_q$ (calc) as a function of dextran concentration, shows a large decrease of $k_q$ compared with the experimental findings. We attribute this discrepancy to a competition between a decay of the diffusion rate-constant arising from a viscosity effect (macroscopic property of the medium) and an enhanced cage effect around the ion pair ($^{T}ZnP^{4+}$, $MV^{2+}$) due to microscopic environment, the latter effect slowing down the dissociation reaction and thus favoring the charge transfer reaction.

In the light of the present study, it is seen that the use of very viscous and structured media, is able to enhance the charge transfer process and leads to longer lived
MV\(^+\) species. These results are promising especially when one knows that the reduction of water to \(\text{H}_2\) cannot be carried out without the presence of a sacrificial electron donor. A steady state photolysis study of these media is under investigation in order to understand the efficiency of such a system in the solar energy conversion process.

REFERENCES (Part. I)

1. D.N. Nikogosyan, D.A. Angelov, Chem. Phys. Letters 77, 208, (1981)
2. H. Miyasaka, H. Masuhara, N. Mataga, Chem. Phys. Letters, 98, 277 (1983)
3. J.H. Wiesenfeld, E.P. Ippe, Chem. Phys. Letters 73, 47 (1980).
4. P.M. Rentzepis, R.P. Jones, J. Jortner, J. Chem. Phys. 59, 766, (1973)
5. J.C. Mialocq, J. Sutton, P. Goujon, Il Nuovo Cimento, Vol 63 B, 317, 1981.
6. G.A. Kenney-Wallace, Can. J. Chem., 55, 2009, (1977)
   G.A. Kenney-Wallace, C.D. Jonah, J. Phys. Chem., 86, 2572, (1982).
7. Y. Gauduel, A. Migus, J.L. Martin, A. Antonetti, Chem. Phys. Letters, 108, 319, (1984)
8. A.M. Koulkes-Pujo, T.H. Tran-Thi, Rad. Phys. Chem. 26, 201, (1985)
9. E. Wolf, Thèse, Université Paris XI, (1981).

REFERENCES (Part. II)

1. B.H. Milosavljevic, J.K. Thomas, J. Phys. Chem., 87, 616, (1983) and references therein
2. A. Harriman, G. Porter, A. Wilowska, J. Chem. Soc. Faraday. Trans. 2, 80, 19] (1984) and references therein
3. M.C. Richoux, A. Harriman, J. Chem. Soc. Faraday Trans. 1, 78, 1873, (1982).
4. R.H. Felton, in The porphyrins (Academic Press, London, 1978), vol. V, part C, p. 53
5. M.A.J. Rodgers, J.C. Becker, J. Phys. Chem., 84, 2762, 1980
6. R.E. Sassoon, Z. Aizenshtat, J. Rabani, J. Phys. Chem., 89, 1182 (1985) and references therein
7. M. Kaneko, A. Yamada, Photochem. Photobiol., 33, 793, (1981)
8. D. Le Roux, J.C. Mialocq, O. Anitoff, G. Folcher, J. Chem. Soc. Faraday. Trans. 2, 80, 909, (1984).
   D. Le Roux, Thèse, Université Pierre et Marie Curie, (1983).