INFLUENCE OF VISCOUS MEDIA ON CHARGE TRANSFER REACTIONS

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The influence of viscous H_2O-Dextran media on two char-
ge transfer reactions has been investigated using laser
photolysis coupled with pico and nanosecond time resol-
ved 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 concen-
tration, 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(ZnP^{4+}) by an elec-
tron acceptor, methylviologen chloride (MV^{2+}, 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 (ZnP^{4+})* and MV^{2+}
due to a viscosity effect and an enhanced cage effect
around the ions (ZnP^{4+*}, MV^{2+}). 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 solu-
tions may be used as a blood plasma susbstitute 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 irra-
diation 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 extensive-
ly investigated. It has been shown that the method of elec-
tron injection (by direct ionization of a molecule in a
pure liquid[1-2]   or from photodetachment or photoioniza-
tion of a solute ion or neutral molecule[3-4],   as well as
the life time of the intermediate ionizing or detaching
level [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 hexade-
canol), 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 τ_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, τ_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_2O as a solvating medium, a large discrepancy between
τ_s (<0.1- 0.3ps)[3,7] and the dielectric relaxation time has been
found and explained in terms of the existence of deep trap-
ping 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 concentra-
tion above 43 weight %, alters the aqueous molecular struc-
ture 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-

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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 10^{-3}M to 10^{-2}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

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 ∿ 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 mn 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 I_o 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 defi-
ned 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 spectros-
copically 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 elec-
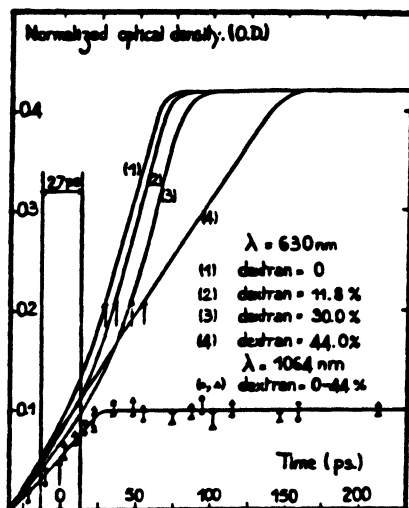tron absorbance.

Figure 2 : The absorbance rise time of solvated electrons.

The value for an aqueous solution of potassium ferrocya-
nide 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[2]   for
neat H_2O and has been interpreted in terms of a multi-
photonic H_2O excitation process within the pulse width. Since
their experimental conditions (pulse width $\tilde{}$ 20 ps fwhm and
0,5 - 0,7 mJ outout 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 excita-
tion of water. This result is of no consequence as regards
to the following results since in the presence of dextran

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 (λ = 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 λ = 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 [8-9]. A
450 fs electron hydration risetime has been reported in
anionic aqueous micelles and interpreted in terms of mi-
croviscosity change of the electron boundary layer[7].
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[8]
and which might correspond to a greater trapping ener-
gy. 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
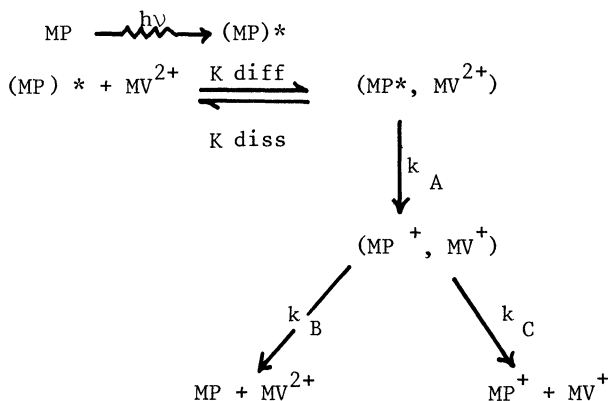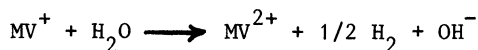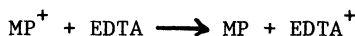relaxation time of water (Table I)

TABLE I

Dextran Wt%	e_s^- rise time $(10^{-12} s)$	Viscosity (P)	$\tau\ H_2O$ $(10^{-12}\ s)$	delay $(10^{-12} s)$
0	28 ± 2 ps	0,01	7,5	0
11,8 %	$35,5 \pm 1,5$	0,3	8,1	7,5
30 %	$45,5 \pm 2,0$	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[1]
metalloporphyrins, chlorins and phtalocyanines[2].
Some charged metalloporphyrins (MP) have been found to be
particularly effective photosensitisers when methyl violo-
gen (MV^{2+}) is used as an electron relay and ethylene diami-
ne-tetraacetate (EDTA) as a sacrificial donor, and lead
to high quantum yield of H_2 production[3-4] . The well
established mechanism for this overall reaction is the
following

$$MP \xrightarrow{h\nu} (MP)*$$

$$(MP)* + MV^{2+} \underset{K\ diss}{\overset{K\ diff}{\rightleftharpoons}} (MP*,\ MV^{2+})$$

$$\downarrow k_A$$

$$(MP^+,\ MV^+)$$

$$\swarrow k_B \qquad\qquad \searrow k_C$$

$$MP + MV^{2+} \qquad\qquad MP^+ + MV^+$$

$$MP^+ + EDTA \longrightarrow MP + EDTA^+$$

$$EDTA^+ \longrightarrow products$$

$$MV^+ + H_2O \longrightarrow MV^{2+} + 1/2\ H_2 + OH^-$$

A crucial step in the formation of H_2 is the charge separa-
tion process of the ion pair (MP^+, 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 MV^{2+}. Heteroge-
neous 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 $Ru\ (bpy)_3^{2+}$
and MV^{2+} adsorbed on cellulose, the 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 visco-
sity 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 vis-
cosity and structuration of the medium upon the quenching
process of the triplet state of an excited metalloporphyrin
(ZnP^{4+}) by MV^{2+}, and the charge separation process following

the charge transfer reaction. The laser induced processes
are followed by nanosecond time resolved absorption spec-
troscopy.

Experimental

The synthesis and purification of water soluble Zn
derivative of 5, 10, 15, 20 tetra (N methylpyridinium 3-yl)
porphyrin (ZnP^{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+} 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 $\sim$ 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 irra-
diated solutions (normalized to a constant dose) were mea-
sured 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 dex-
tran concentrations. In all cases, the differential absorp-
tion 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 [8] . The life time of the porphyrin
triplet state, determined at its maximum absorption
(λ = 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 (2.10^{-4} M –
$2 \; 10^{-2}$ M) for various solutions containing a constant ZnP^{4+}
concentration (5.10^{-5} – $8 \; 10^{-5}$ 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 $2 \; 10^{-2}$ M).

$$K = K_o + kq \left[MV^{2+} \right]$$

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

In aqueous solution of porphyrin, a non linear depen-
dence of K upon MV^{2+} was found for MV^{2+} concentration above
$\sim 5 \; 10^{-3}$ M. A similar result has been obtained by Leroux et
al. [8]   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
$[MV^{2+}]$ up to $2\ 10^{-2}$ M for all the studied dextran concentra-
tions.

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

$$kq = \frac{K_{diff}\ K_A}{K_{diss} + K_A}$$

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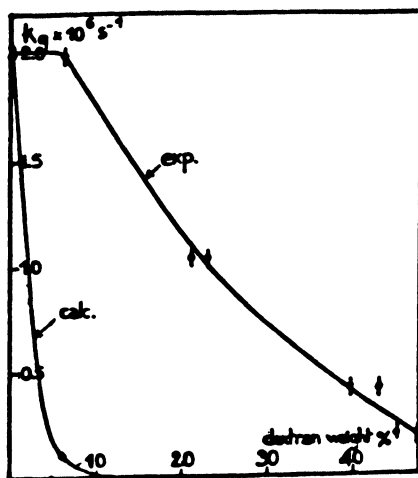a function of dextran concentration (fig. 3)

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

It is seen that kq remains constant for 0 to 6 dextran
% by weight but decreases above this. This decrease might
be explained in terms of the k 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
kq was calculated, taking into account a simple viscosity
effect (table II)

TABLE II

Dextran Wt %	viscosity (P)	$\tau(^T\text{ZnP}^{4+})$ ms	kq(exp.) 10^6s^{-1}	kq(calc) 10^6s^{-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 kq (calc) as a function of dextran concen-
tration, shows a large decrease of k_q (calc.) compared with
the experimental findings. We attribute this discrepancy
to a competition between a decay of the diffusion rate-cons-
tant arising from a viscosity effect (macroscopic property
of the medium) and an enhanced cage effect around the ion
pair $(^T\text{ZnP}^{4+}, \text{MV}^{2+})$ 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 enhan-
ce 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 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. Ippen, 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. Koulkès-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).