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Luminescence quenching of uranyl ion adsorbed in nafion membrane by alcohols and vinyl monomers

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Abstract

The luminescence quenching of $^*UO_2^{2+}$ ion adsorbed in hydrated Nafion membrane by methanol, ethanol, 2-propanol, 2-propen-1-ol (allyl alcohol), acrylic acid, methacrylic acid, vinyl acetic acid, and vinyl acetate are studied and compared with experiments with reactants in homogeneous aqueous solution. The luminescence quenching rate constants are enhanced in Nafion by a factor of about 3 and 7.5 for alcohols and vinyl monomers, respectively. The increase in reactivity is ascribed to a combination of favorable partition of the organic compounds in the Nafion membrane and cage effect that reduces the rate of dissociation of bimolecular complexes in the mechanism of the photo-oxidation processes involving $^*UO_2^{2+}$ ion and the organic compounds.

Keywords: Luminescence; Excited-state reactions; Photo-oxidation; Membranes; Photo-catalysis

1. Introduction

The photophysical and photochemical properties of uranyl ion in solution, including excited-state redox reactions with several types of compounds, have been studied extensively [1,2]. Among several types of organic and inorganic compounds, the photo-induced reactions of uranyl ion with alcohols [3–9], phenols [10,11], carboxylic acids [12], alkenes [13–17], *N*-heteroaromatics [18], dialkyl sulfides [19], organosulfur, organohalogen and organometal species [20], cyanometallates [21], metal–carbonyls [22], and metal ions [23] illustrate the variety of systems that have been investigated. The reaction of $^*UO_2^{2+}$ with an aliphatic alcohol is described by a mechanism involving α-hydrogen atom abstraction producing aldehyde from primary alcohol and ketone from secondary alcohol [6]. The photochemical reaction of $^*UO_2^{2+}$ with carboxylic acid usually leads to an oxidative decarboxylation, where the photo-reactivity depends on the type of carboxylic acid involved, being low for linear aliphatic and high for cycloalkane and aromatic carboxylic acids [12]. Unsaturated compounds like alkenes were found to exhibit high luminescence quenching of $^*UO_2^{2+}$ with rate constants approaching diffusion control [12,13]. The photochemical mechanism seems to occur via exciplex formation with possible electron-transfer reaction generating radicals [14]. This effect has been explored in the reaction of $^*UO_2^{2+}$ with vinyl monomer like acrylamide to initiate the polymerization process [24].

Most of the photochemical studies have been performed in homogeneous aqueous and solvent mixtures [1,2]. However, $^*UO_2^{2+}$ is an active photochemical species which may be incorporated in different materials from inorganic solids to polymers [2]. It is also a potential photophysical probe for studying micro-heterogeneous systems forming by surfactants, polymer and colloids in solution [25]. In these different media, the physical and chemical quenching of $^*UO_2^{2+}$ by organic compounds is a less explored area. In this sense, the luminescence quenching of $^*UO_2^{2+}$ adsorbed in Nafion acid membrane by aliphatic alcohols (methanol, ethanol, 2-propanol and allyl alcohol) and vinyl monomers (acrylic acid, methacrylic acid, vinyl acetic acid, and vinyl acetate) are studied and compared with the same experiments with the reactants in aqueous solution. Hydrated Nafion has a characteristic morphology in which the sulfonic acid groups, by partial dissociation, form ionic clusters surrounding water nanodroplets. The clusters of diameter of 40–60 Å are randomly distributed throughout the polymer chain phase, and are eventually interconnected by channels of about 8–10 Å. Thus, the Nafion structure resembles a random network of interconnected reverse micelles [26].

Some of the possible advantages of the use of polyelectrolyte supports are easy recovery of the uranyl ion from the

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reaction media, surface photocatalysis, and concentration effects in oxidative photoreaction of organic compounds.

2. Experimental

Uranyl(VI) sulphate (Alfa products) and the alcohols (methanol, ethanol, 2-propanol with HPLC degree from MERK) were used as received. Allyl alcohol and the vinyl monomers (acrylic acid, methacrylic acid, vinyl acetic acid, and vinyl acetate) from Aldrich, were used after removing their inhibitors by standard treatments. Nafion-117 hydrogen ion form membrane (Aldrich, 1100 EW) was carefully cleaned by a two-steps treatment [27]. First, the membrane was immersed in 5% of boiling hydrogen peroxide for 30 min, and then rinsed with hot water several times. This step was performed three times. In the second step, the membrane was disposed into 0.5 M aqueous solution of H_2SO_4 at 60 °C during 1 h, removed from it, rinsed several times with hot water, and kept in aqueous acid media.

The uranyl ion was incorporated into swelled Nafion by keeping the membrane for about 48 h immersed in 10^{-3} M aqueous solution of uranyl sulfate. After loading and prior to spectroscopic measurements, the membranes were rinsed with Milli-Q water. The optical density of the membranes at the maximum of the absorption spectrum of the uranyl ion (418 nm) was lower than 0.1. In the luminescence measurements, the 1 cm × 2 cm thick membrane containing the luminescence uranyl was disposed in front face configuration and placed diagonally in a quartz cuvette filled with 3 ml aerated water. The luminescence quenchers were added via micro-syringe to the sample cuvette, and their concentrations refer to the analytical value in the whole volume. After each quencher addition, the solution was stirred for 15 min in dark room prior to spectroscopic measurements. In the comparative results obtained in the aqueous samples without the membrane, the uranyl concentration was 10^{-3} M.

Absorption measurements were performed on a Hitachi U-2000 spectrophotometer. Corrected steady-state luminescence spectra were recorded on a CD-900 Edinburgh luminescence spectrometer. Decays were measured with the same spectrometer with samples excited at 418 nm by the equipment flash lamp. Average lifetimes were determined from biexponential fitting of the luminescence decays. All measurements were taken in air-equilibrated condition at 298 K. The luminescence rate constants were determined from the Stern–Volmer plot of the relative luminescence intensity,

$$\frac{I_0}{I} = 1 + k_q \langle \tau_0 \rangle [Q] \tag{1}$$

taking the measured average lifetime $\langle \tau_0 \rangle$ of the uranyl in water and adsorbed in Nafion membrane, as given below. The average lifetime was calculated using,

$$\langle \tau_0 \rangle = \frac{a_1 \tau_1^2 + a_2 \tau_2^2}{a_1 \tau_1 + a_2 \tau_2} \tag{2}$$

where a_i and τ_i are the normalized amplitude and decay time, respectively.

3. Results and discussion

The luminescence decays of uranyl sulphate in water (pH ≈ 3) and adsorbed into Nafion acid form membrane were measured in the absence of added organic quencher. In both the cases, the decays were biexponential (decay components are given in Table 1). The average lifetime of the $^*UO_2{}^{2+}$ ion in aqueous solution found in this work (5.6 μs) is close to the reported values in similar condition [5]. It does not differ appreciable from the average value found in Nafion membrane (6.1 μs). The two lifetime components measured here from biexponential fitting are similar to the values of 1.7 and 7.7 μs (pH in the range of 3–3.5) from Park et al. [28], 1.35 and 8.3 μs (pH = 3.0) from Formosinho and Miguel [29], and 1.3 and 5.3 μs (pH = 1.9) from Deschaux and Marcantonatos [30].

Although the decay parameters of uranyl in aqueous and in Nafion are similar, the emission spectra have some differences. In Nafion, the emission spectrum has a better resolution of five bands, while in aqueous solution there are less resolution and only three bands and a shoulder are recovered. In Nafion, the position (in nm) and relative intensity of the bands are: 491 (1.00), 513 (1.18), 536 (0.73), 562 (0.33) and 590 nm (0.11). In the measurements in aqueous solution, values in 490 (1.00), 511 (1.13), 532 (0.69), and a shoulder in 558 nm (0.29) are observed.

The biexponential character of the decay of uranyl has been discussed based on the reversible-crossing model [29] or using the exciplex-formation kinetics [30–32]. An additional effect is the occurrence of partial hydrolysis of uranyl sulphate in water at pH > 3.0. If hydrolysis occurs, then the dual luminescence would have contributions from excited aqua and hydrolyzed ions, $^*UO_2{}^{2+}$ and$^*(UO_2)_2(OH)_2{}^{2+}$, respectively, that could be present in the solution [28,32]. An alternative interpretation of the biexponential kinetics of the luminescence decay has been the assumption of an acid–base dissociation of uranyl in the excited state [33,34]. This interpretation has overcome the reversible-crossing model [34].

Considering the morphology of hydrated Nafion membrane, uranyl ion should be adsorbed in the interfacial domain of the water pool as represented in Fig. 1 and, therefore, it will be associated to the $SO_3{}^-$ ions. The low pH of the acid Nafion membrane should avoid the hydrolysis,

Table 1
Decay time components and normalized amplitudes obtained from biexponential fitting of the luminescence decay of uranyl in water and in Nafion membrane

Medium	τ_1 (μs)	τ_2 (μs)	$\langle \tau_0 \rangle$ (μs)
H_2O, pH = 3.0	1.26 (0.69)	7.33 (0.31)	5.6
Nafion H^+ form	1.84 (0.58)	7.60 (0.42)	6.1

T = 298 K.

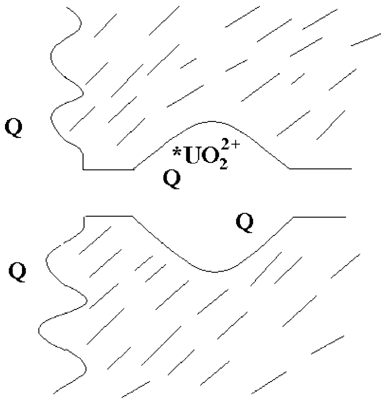


Fig. 1. Schematic picture of the Nafion membrane with uranyl ion bound to its water interface and in the presence of hydrophilic quenchers (Q).

Table 2
Luminescence quenching rate constant of $^*UO_2^{2+}$ ion by aliphatic alcohols and vinyl monomers in water and in Nafion membrane

Quencher	k_q ($M^{-1}\,s^{-1}$) in water	k_q ($M^{-1}\,s^{-1}$) in Nafion	Ratio
Methanol	4.9×10^6	1.3×10^7	2.7
Ethanol	7.1×10^6	2.4×10^7	3.4
2-Propanol	2.6×10^7	6.7×10^7	2.6
2-Propen-1-ol	2.1×10^8	6.2×10^8	2.9
Acrylic acid	2.8×10^7	2.1×10^8	7.5
Vinyl acetic acid	1.1×10^8	6.2×10^8	5.6
Vinyl acetate	9.7×10^7	9.3×10^8	9.6
Methacrylic acid	2.7×10^8	NA	–

$T = 298\,K$; NA, no quenching observed.

but the ion pairing of uranyl with SO_3^- occurs. These two factors explain the enhancement of the vibrational structure in the emission spectrum observed in Nafion. On the other hand, the nature of the biexponential decay in Nafion would result from the presence of $^*UO_2^{2+}$ and$^*UO_2^{2+}(SO_3^-)_2$, where the strong ion pair species accounts in great part for the longer decay component observed. In aqueous solution at pH 3.0, a certain fraction of uranyl ions forms complexes with sulfate, which manifest themselves in the appearance of the long-lived component of the luminescence decay [33]. In addition, hydrolysis will be more effective in aqueous media at pH = 3 and, therefore, the long-lived component would also have a contribution from the emission of the hydrolyzed species as discussed.

Uranyl luminescence in Nafion is readily quenched by aliphatic alcohols and by vinyl monomers. A typical result of the decrease of the luminescence intensity upon addition of the quencher (2-propanol) is shown in Fig. 2. The inset of Fig. 2 is the Stern–Volmer plot that enables the calculation of the average quenching rate constant (k_q) using Eq. (1). The values of k_q obtained in water and in Nafion are listed in Table 2 for comparison purposes. The values found in water for the aliphatic alcohols resemble reported data [6,15]. The largest value found for allyl alcohol would be a result of the C=C group effect in the α-hydrogen abstraction mechanism. Unsaturated compounds like the vinyl monomers employed have slightly higher k_q values when compared with the values for aliphatic alcohols. The operative quenching mechanism could be the deactivation via exciplex formation plus a reactive step (H-atom abstraction) like that occurring with alkenes [15,17] (vide infra, Scheme 1), but the presence of carboxylic acid group does not preclude the possibility of oxidative decarboxylation [12].

An interesting point is that the luminescence quenching rate constants are considerably enhanced in Nafion when compared with the values found in water. The ratio of k_q in Nafion and in water is roughly constant for the same type of quencher, especially for alcohols (see Table 2). It seems that the enhancement of k_q does not result entirely from a high partition of the compounds to the Nafion membrane because

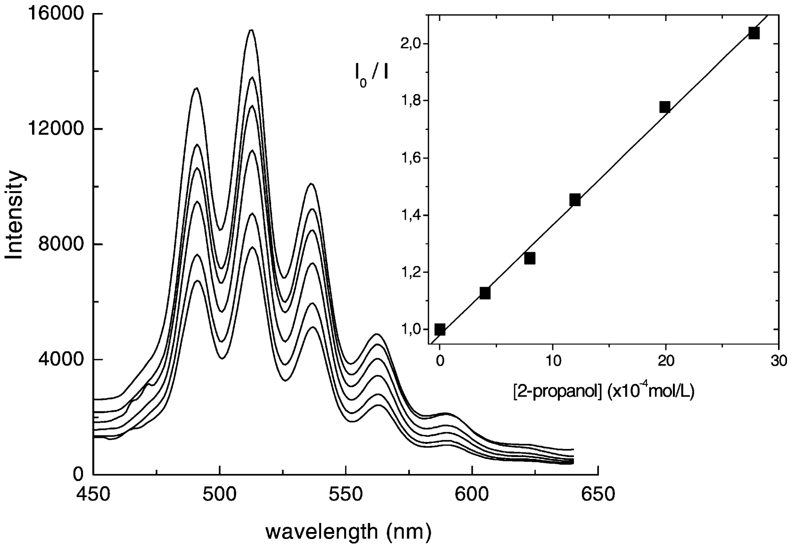
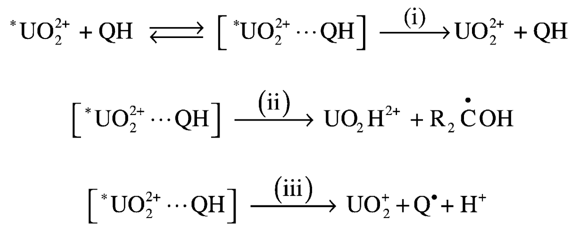


Fig. 2. Luminescence quenching of uranyl ion by 2-propanol in Nafion membrane. Inset plot is the Stern–Volmer data treatment according to Eq. (1).



$$^{*}UO_2^{2+} + QH \rightleftharpoons \left[^{*}UO_2^{2+} \cdots QH\right] \xrightarrow{(i)} UO_2^{2+} + QH$$

$$\left[^{*}UO_2^{2+} \cdots QH\right] \xrightarrow{(ii)} UO_2H^{2+} + R_2\dot{C}OH$$

$$\left[^{*}UO_2^{2+} \cdots QH\right] \xrightarrow{(iii)} UO_2^{+} + Q^{\bullet} + H^{+}$$

Scheme 1. Initial reaction processes. QH is (ii) aliphatic primary and secondary alcohols; or (iii) vinyl monomers.

the hydrophilic and hydrophobic contributions to solubility in Nafion of the polar group and the CH_n segments of the solutes are not the same for alcohols or vinyl monomers used. The high reactivity in Nafion would result from a proper confinement of the reactants in the ionic interface of the membrane. According to the reaction Scheme 1, a cage effect will promote the association and will reduce the dissociation of the bimolecular complex of uranyl and quencher, thus increasing the efficiency of the irreversible steps of (i) photophysical deactivation via exciplex, and hydrogen-atom abstraction in the case of: (ii) alcohol; or (iii) vinyl monomers and, therefore, may improve the rate of global reaction.

A second aspect that has to be taken into account to explain in part the difference in quenching rate constants in these two media is the occurrence of partial hydrolysis of uranyl sulphate in water at $pH = 3$, which may generate less photoreactive species.

Finally, methacrylic acid which quenches quite efficient the luminescence of $^{*}UO_2{}^{2+}$ in water, has no quenching capability when the uranyl ion is adsorbed in Nafion, at least in equal range of quencher concentration. This result may be ascribed to a low incorporation of the methacrylic acid inside the membrane. The small fraction adsorbed may be solubilized preferentially in the organic phase of the Nafion membrane and, therefore, the quencher is less accessible to the uranyl ion located in the aqueous interface of the membrane (see Fig. 1).

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