

# Effect of solubilization in micelles on the kinetics of electron transfer photoreactions and redox properties of reactants. Quenching of $\text{RuL}_6^{2+}$ luminescence in SDS micelles

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## Abstract

The oxidative luminescence quenching of tris(2,2'-bipyridyl)ruthenium(II) ( $\text{RuL}_6^{2+}$ ) by various quenchers (quinones and nitroaromatic compounds) was investigated in homogeneous (organic and aqueous) solutions and in sodium dodecylsulphate (SDS) micelles to reveal the effects of the local microenvironment on the energy of electron transfer and on the reorganization energy of the reaction. Analysis of the reaction kinetics in micellar solutions showed that, in systems in which the redox potential of the quencher  $E_{1/2}(\text{Q}/\text{Q}^-) < 1.5$  V, "internal" quenching was observed, i.e. reaction of  $^*\text{RuL}_6^{2+}$  with a quencher molecule solubilized inside a micelle. In these systems, true intramicellar quenching rate constants were obtained, and the electron transfer reactions in micelles were compared with those in homogeneous solutions. In SDS micelles, the Gibbs energy of electron transfer  $\Delta G_{et}$  was close to that observed in water; however, the spectral properties of  $\text{RuL}_6^{2+}$  and the value of the limiting diffusion rate constant were typical of media with medium polarity and high viscosity. This suggests a considerable reorganization of the local microenvironment of the  $\text{RuL}_6^{2+}$  complex and quencher during the electron transfer reaction and a specific effect of surrounding water molecules on the reaction kinetics.

**Keywords:** Micelles; Electron transfer; Redox properties; Quenching; Luminescence

## 1. Introduction

The specific effect of the local microenvironment on the kinetics of electron transfer reactions and the redox properties of reactants are of principal importance in numerous reactions in organized molecular systems, including redox processes in biomembranes, biological photosynthesis, etc. The rate constants of electron transfer reactions, according to conventional models, depend on the Gibbs energy of electron transfer (thermodynamic factor) and on the medium and internal reorganization energy (kinetic factor) [1,2]. To analyse the effects of solubilization in micelles on both of these factors, we studied the rate constants of tris(2,2'-bipyridyl)ruthenium(II) ( $\text{RuL}_6^{2+}$ ) luminescence quenching by electron acceptors with various reduction potentials in sodium dodecylsulphate (SDS) micelles in comparison with homogeneous organic and aqueous solutions. We chose these systems because of the very

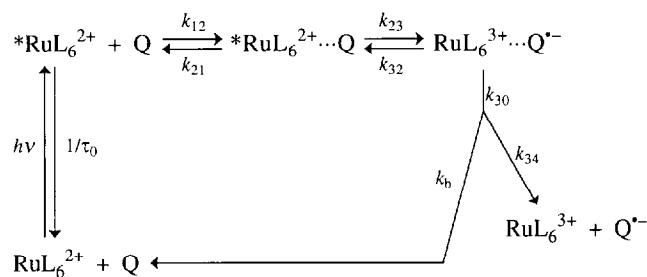
large difference in the redox potentials of  $\text{RuL}_6^{2+}$  and quenchers (quinones and nitroaromatic compounds) between aqueous and organic solvents [3].  $\text{RuL}_6^{2+}$  is solubilized in SDS micelles and located in the surface region [4].

The kinetics of electron transfer processes in microheterogeneous systems has been studied in detail [5–26]. Much attention has been paid to the reactions of the  $\text{RuL}_6^{2+}$  complex [14,16,18–20,24,27–31]. In most of these studies, the kinetic properties were discussed in terms of pseudo-unimolecular quenching. Since the aim of this work was to compare the electron transfer reactions in micelles and homogeneous media, a formal approach was developed to obtain the bimolecular quenching rate constants in micelles, paying attention to two different limiting steps of the quenching: intramicellar reaction ("internal quenching") and diffusion of the quencher towards and into micelles ("external quenching"). In most previous publications, the dependence of the electron transfer rate constants on the Gibbs energy of electron transfer has been discussed

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for pseudo-unimolecular rate constants of intramicellar quenching [7,13,18,20,28,29,31] (which includes implicitly the local concentration of the quencher in the micelles), or the bimolecular rate constants obtained have been found to be close to the diffusion rate constants [31,32]. To obtain the true bimolecular rate constants of intramicellar quenching of  $\text{RuL}_6^{2+}$  luminescence and to compare them with the analogous bimolecular quenching rate constants in homogeneous aqueous and organic solutions, we studied the dependence of the  $\text{RuL}_6^{2+}$  luminescence decay on the quencher and micelle concentrations.

The quenching of  $\text{RuL}_6^{2+}$  luminescence in acetonitrile by a wide range of donors and acceptors has been investigated previously [2,33,34], and has been discussed within the framework of a well-known general kinetic scheme (Scheme 1), proposed for electron transfer processes in homogeneous solutions [35,36] (as well as for excited organic molecules and coordination compounds).



Scheme 1.

$k_{12}$  and  $k_{21}$  are the forward and back diffusion rate constants,  $k_{23}$  and  $k_{32}$  are the forward and back electron transfer reaction rate constants,  $k_{30} = k_b + k_{34}$  and  $k_{34}$  and  $k_b$  are the rate constants of ion pair dissociation and recombination respectively.

The general expression for the quenching rate constant, obtained from this scheme

$$k_q = k_{12} / [1 + (1 + k_{32}/k_{30})k_{21}/k_{23}] \quad (1)$$

may be simplified depending on the relationship between  $k_{21}$  and  $k_{23}$  and  $k_{32}$  and  $k_{30}$ . The approximate expression for  $k_q$  depends on the kind of equilibrium established during the course of the reaction, i.e. either between the reactants and their encounter complex, or between the reactants and the radical ion pair formed as a result of electron transfer. In the first case (when  $k_{21} \ll k_{23}/(1 + k_{32}/k_{30})$ )

$$k_q \approx k_{12}$$

In the second case (when  $k_{21} \gg k_{23}/(1 + k_{32}/k_{30})$ ) either  $k_{30} \gg k_{32}$  and

$$k_q = K_{12}k_{23}, \text{ where } K_{12} = k_{12}/k_{21} \quad (2)$$

or  $k_{30} \ll k_{32}$  and

$$k_q = K_{23}K_{30}k_{30}, \text{ where } K_{23} = k_{23}/k_{32} \quad (3)$$

We investigated the  $\text{RuL}_6^{2+}$  luminescence quenching by various electron acceptors in SDS micelles, and found effects of both the viscosity and local polarity of the microenvironment on the quenching rate constants and redox potentials of the reactants. We studied and analysed the kinetics of  $\text{RuL}_6^{2+}$  luminescence in the presence of various quencher concentrations to obtain true quenching rate constants inside the micellar phase.

A kinetic analysis of some peculiarities of electron transfer processes in micelles is given in the Appendix, which provides the possibility to obtain the true quenching rate constants in the micellar phase for a series of electron acceptors with various reduction potentials and reveals the effects of the micellar phase on the diffusion rate constants, redox potentials of the reactants and activation barrier of electron transfer. The mobility of the reactants is found to be typical for the interior of a micelle, but the redox potential shift is close to that of the aqueous phase rather than that of the relatively less polar micellar interior.

## 2. Experimental section

### 2.1. Materials

SDS (SERVA) was used as received. Nitro-substituted aromatic compounds were recrystallized; quinones were sublimated. Ethanol was used without further purification. All solutions were prepared in either distilled or deionized water.

### 2.2. Apparatus

A Specord M40 spectrophotometer and a Perkin-Elmer LS50 spectrofluorometer were used for stationary measurements. Fluorescence lifetimes were determined with a time-correlated, single-photon-counting instrument (exciting light pulse decay time, about 1 ns).

### 2.3. Procedure

Quenching rate constants ( $k_q$ ) and equilibrium distribution coefficients of the quenchers between the micelles and the bulk phase ( $\rho$ ) were obtained from the measurement of the  $\text{RuL}_6^{2+}$  luminescence lifetimes at various quencher and micelle concentrations. Solutions of SDS in water of a desired concentration were sonicated for 10 min at 35 °C; solutions of luminophore and quencher were prepared from these micellar solutions and sonicated for 5 min at the same

temperature. Solutions for experimental measurements were prepared by mixing these solutions and the micellar solution to obtain the desired quencher concentration. Before measurements, all the solutions were thermostatically controlled at 35 °C for at least 30 min. The concentrations of luminophore and quencher were controlled spectrophotometrically.

Quenching rate constants were determined from luminescence lifetime measurements. In this case, the concurrent absorption of excitation light by the quencher could be neglected. For lifetime measurements, a glass filter, with a broad transmission bandwidth in the wavelength range 400–500 nm, was used. Registration was carried out using a monochromator (600–620 nm). Each measurement was carried out during equal time intervals (30 min) in a thermostatically controlled cell, and was corrected for the background noise measured in the cuvette with the same SDS concentration for the same time. The decay curves obtained were computed using the program STATGRAF for exponential decay, or a deconvolution procedure for non-exponential decay.

For the calculation of  $\varphi_0/\varphi$  values the concurrent absorption by some quenchers at the excitation wavelength had to be taken into account. In this case, we multiplied the measured luminescence intensities by  $10^{\Delta D/2}$ , where  $\Delta D$  is the difference between the optical densities of solutions with and without quencher at the excitation wavelength.

### 3. Results

#### 3.1. Kinetics of $\text{RuL}_6^{2+}$ luminescence decay

We studied the kinetics of  $\text{RuL}_6^{2+}$  luminescence decay in homogeneous and micellar solutions in the absence and presence of various quenchers. The luminescence decay of  $\text{RuL}_6^{2+}$  in alcohol solutions is exponential in both the absence and presence of quenchers (Fig. 1). The lifetime of  $^*\text{RuL}_6^{2+}$  in the presence of oxygen is 240 ns. Apparent values of the quenching rate constant  $k_q$ , determined by the Stern–Volmer equation from a linear plot of  $\tau_0/\tau$  vs.  $[\text{Q}]$

$$\tau_0/\tau = 1 + k_q \tau_0 [\text{Q}] \quad (4)$$

depend on the reduction potential  $E_{1/2}(\text{Q}/\text{Q}^{\cdot-})$  of the quencher (Table 1). This confirms that quenching in these systems follows the electron transfer mechanism. Similar dependences have been obtained previously for the quenching of  $^*\text{RuL}_6^{2+}$  by various donors and acceptors in other solvents [1,2,26,33,34].

In all micellar solutions (except for the system in which duroquinone is used as quencher), the luminescence decay of  $\text{RuL}_6^{2+}$  is exponential. The lifetimes in solutions of different samples of SDS in the absence

of quenchers (in the presence of oxygen) vary in the range 330–420 ns (probably due to uncontrolled impurities in SDS). In each set of experiments, samples of SDS with identical  $\tau_0$  values were used. Exponential decay in the absence and presence of quenchers provides evidence for the kinetic equivalence of all  $^*\text{RuL}_6^{2+}$  ions in the micellar systems in the time range under study (greater than 10 ns).

Plots of  $\varphi_0/\varphi$  and  $\tau_0/\tau$  vs.  $[\text{Q}]_0$  (Fig. 2) for systems containing toluquinone and 1,3-dinitrobenzene do not coincide in homogeneous and micellar solutions. However, in ethanol solutions, the  $\varphi_0/\varphi$  plot is linear and the  $\tau_0/\tau$  plot is sublinear. In contrast, in micellar solutions, the plot of  $\varphi_0/\varphi$  vs.  $[\text{Q}]_0$  deviates from linearity (superlinear) and the plot of  $\tau_0/\tau$  is linear. This provides evidence (see Appendix, Eqs. (A9) and (A10)) of the establishment of an equilibrium in the excited state between the reactants and the radical ion pair in ethanol ( $k_{32} \gg k_{30}$ ). The same equilibrium was shown in Ref. [2] to be established in acetonitrile. For acceptors with  $E_{1/2}(\text{Q}/\text{Q}^{\cdot-}) < -1.0$  V, the luminescence quantum yields were not measured in ethanol. Nevertheless, the deviations of the  $\tau_0/\tau$  plot from linearity at high quencher concentrations, observed in some cases, and the results obtained in Ref. [2] indicate that equilibrium is established in the excited state between the reactants and radical ion pairs, when an acceptor with  $E_{1/2}(\text{Q}/\text{Q}^{\cdot-}) < -1.0$  V is used in homogeneous systems.

For all investigated SDS micellar solutions, a plot of  $\tau_0/\tau$  vs. the total concentration of the quencher in solution ( $[\text{Q}]_0$ ) is linear (Fig. 3). Therefore (see Appendix, Eq. (A6))  $k_{30} \gg k_{32}$ .

For the investigated systems in SDS micelles,  $\varphi_0/\varphi$  plots coincide with  $\tau_0/\tau$  plots for all quenchers with  $E_{1/2}(\text{Q}/\text{Q}^{\cdot-}) > -1.0$  V. Such a coincidence can only be observed in the case of “internal” quenching (see Appendix) in the absence of static quenching and when  $k_{30} \gg k_{23}$  (Eqs. (A8)–(A11), (A15)). For “external” quenching,  $\varphi_0/\varphi$  and  $\tau_0/\tau$  plots must differ by  $e^{\langle n \rangle}$ , where  $\langle n \rangle$  is the mean number of quencher molecules per micelle (Eqs. (A15) and (A17)). For the quencher concentrations used,  $\langle n \rangle$  varies in the range 0.5–4 and  $e^{\langle n \rangle}$  varies in the range 1.6–55. So, in all systems with  $E_{1/2}(\text{Q}/\text{Q}^{\cdot-}) > -1.0$  V, “internal” quenching with  $k_{30} \gg k_{23}$  is observed.

As shown above, in SDS solutions,  $k_{30} \gg k_{32}$ . The cause of the difference between the  $\varphi_0/\varphi$  and  $\tau_0/\tau$  plots in the systems containing quenchers having reduction potentials of less than  $-1.0$  V may be either the formation of a ground state complex or “external” quenching. According to the slower decrease in the experimental values of  $\varphi\tau_0/\varphi_0\tau$  in comparison with the fraction of micelles which do not contain quencher molecules  $P_0(n=0)$ , calculated using Eq. (A4) (Fig. 4), the contribution of “external” quenching to the total quenching in the investigated systems must be rather

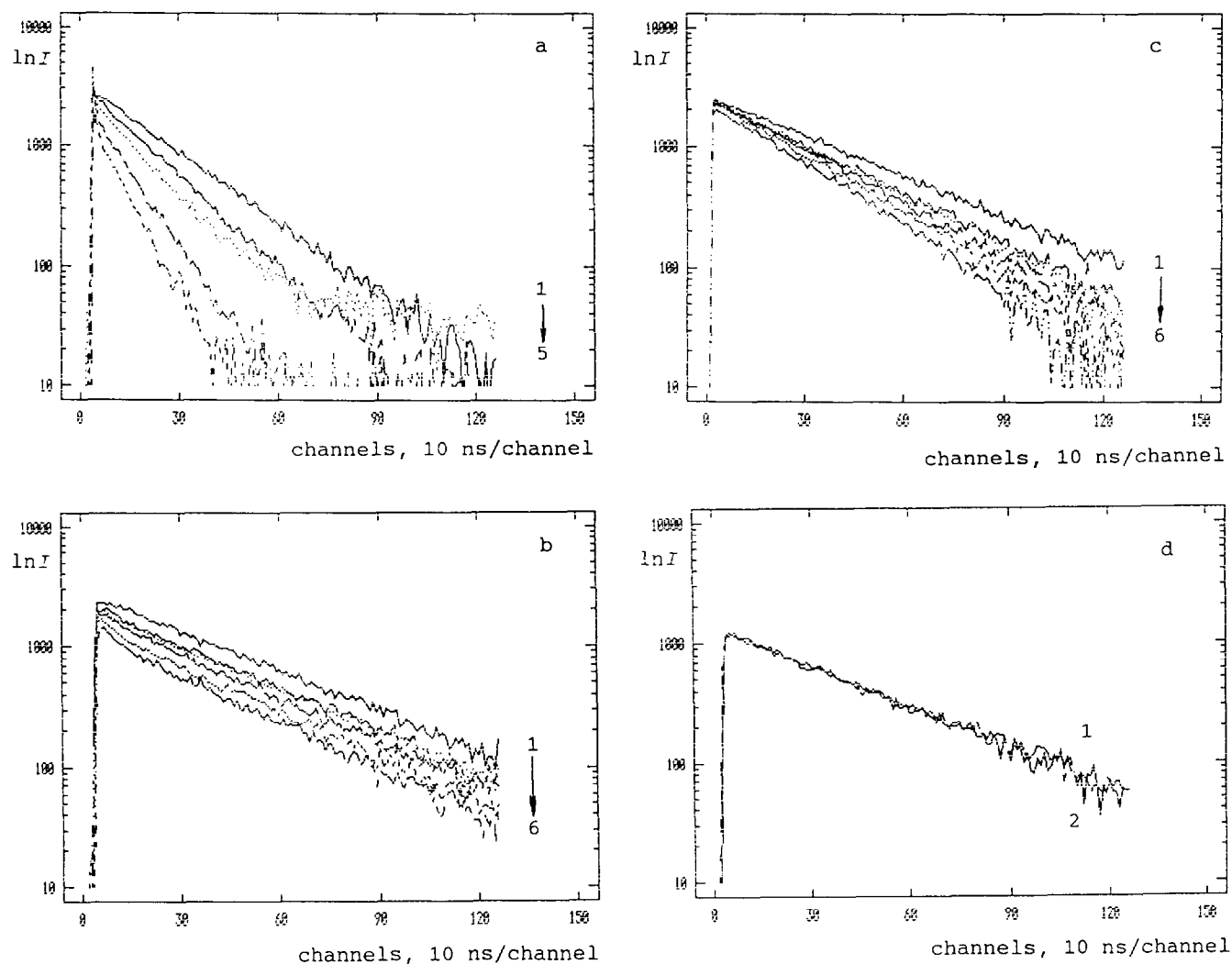


Fig. 1.  $\text{RuL}_6^{2+}$  luminescence decay curves in the presence of: (a) duroquinone in ethanol:  $[\text{Q}]_0 = 0$  M (1);  $0.69 \times 10^{-3}$  M (2);  $1.38 \times 10^{-3}$  M (3);  $2.75 \times 10^{-3}$  M (4);  $4.13 \times 10^{-3}$  M (5); (b) duroquinone in 0.4 M solution of SDS:  $[\text{Q}]_0 = 0$  M (1);  $0.85 \times 10^{-3}$  M (2);  $1.28 \times 10^{-3}$  M (3);  $1.71 \times 10^{-3}$  M (4);  $2.14 \times 10^{-3}$  M (5);  $2.56 \times 10^{-3}$  M (6); (c) 4-fluoronitrobenzene in 0.17 M solution of SDS:  $[\text{Q}]_0 = 0$  M (1);  $0.84 \times 10^{-3}$  M (2);  $1.26 \times 10^{-3}$  M (3);  $1.61 \times 10^{-3}$  M (4);  $2.11 \times 10^{-3}$  M (5);  $2.53 \times 10^{-3}$  M (6); (d) benzophenone in 0.4 M solution of SDS:  $[\text{Q}]_0 = 0$  M (1);  $4.5 \times 10^{-2}$  M (2).

small (rate constant of dynamic quenching is slightly higher than the true rate constant of “internal” quenching). The formation of a ground state complex in micellar solutions has been observed in other systems [25,38–40]. Its formation in the case of paraquat cation quenching has been observed spectrophotometrically [40]. It should be noted that the ground state complex can be observed in micellar solutions at much lower total concentrations of quencher compared with homogeneous solutions because the quencher is concentrated in the micellar phase due to solubilization. The true constants of ground state complex formation in micelles  $K_C$  are calculated using Eq. (A11) (Table 1).

In the case of toluquinone, the values of the dynamic quenching rate constants are surprisingly high for both “external” and “internal” quenching; they are significantly higher than  $k_{\text{diff}}$ , calculated from the diffusion

coefficients [40,41] for both micellar ( $1.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ) and water ( $4.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) phases. At present we cannot explain this observation.

The quenching of  $^*\text{RuL}_6^{2+}$  by benzophenone is not observed in micellar solution (luminescence quantum yield and lifetime constant at all quencher concentrations used) (Fig. 1). To estimate the upper limit of  $k_q$ , it is necessary to know the distribution coefficient ( $\rho$ ) of the quencher between the micellar and bulk phases. However, in this system, and in that containing duroquinone, where the luminescence decay in the presence of quencher is non-exponential, the value of  $\rho$  cannot be found from luminescence measurements. Nevertheless, it can be estimated from the value of the distribution coefficient between water and hexane ( $\rho'$ ) measured spectrophotometrically. For some of the quenchers (nitro derivatives), the values of  $\rho'$  obtained are ap-

Table 1

Gibbs energies of excited state electron transfer calculated from the redox potentials in acetonitrile ( $\Delta G_{et}^{an}$ ) and aqueous ( $\Delta G_{et}^w$ ) solution, rate constants of  $*RuL_6^{2+}$  quenching in acetonitrile ( $k_q^{an}$ ), ethanol ( $k_q^e$ ), water ( $k_q^w$ ) and SDS micelles ("internal" ( $k_q^{in}$ ) and "external" ( $k_q^{ext}$ ) quenching rate constants) equilibrium constants of ground state complex formation ( $K_C$ ) in SDS micelles and equilibrium distribution coefficients of quenchers between micellar and water phases ( $\rho$ ) and in the system hexane–water ( $\rho'$ )

| Quencher ( $E_{1/2}(Q/Q^-)$ vs. SCE)      | $\Delta G_{et}^{an}$<br>(kJ mol $^{-1}$ ) | $k_q^{an}$<br>(M $^{-1}$ s $^{-1}$ ) | $k_q^e$<br>(M $^{-1}$ s $^{-1}$ ) | $k_q^w$<br>(M $^{-1}$ s $^{-1}$ ) | $K_C$<br>(M $^{-1}$ ) | $\rho$ | $\rho'$ | $\Delta G_{et}^w$<br>(kJ mol $^{-1}$ ) | $k_q^w$<br>(M $^{-1}$ s $^{-1}$ ) |
|---|---|--------------------------------------|-----------------------------------|-----------------------------------|-----------------------|--------|---------|--|-----------------------------------|
| Toluquinone (-0.57) <sup>a</sup>          | -34.6 <sup>a</sup>                        | $9.0 \times 10^9$                    | $4.0 \times 10^9$                 | $2.2 \times 10^9$                 | 9                     | 30     | -       | -108.5                                 | $3.5 \times 10^9$                 |
| Duroquinone (-0.84) <sup>a</sup>          | -10.6 <sup>a</sup>                        | $3.8 \times 10^9$                    | $1.8 \times 10^9$                 | -                                 | -                     | (100)  | 10      | -91.2                                  | $4.4 \times 10^9$                 |
| 1,3-Dinitrobenzene (-0.81) <sup>a</sup>   | -4.8 <sup>a</sup>                         | $1.7 \times 10^9$                    | $1.4 \times 10^9$                 | $9.9 \times 10^7$                 | 13                    | 160    | 15      | -75.8                                  | -                                 |
| 3-Nitrobenzaldehyde (-1.02) <sup>a</sup>  | 6.7 <sup>a</sup>                          | $4.1 \times 10^7$                    | $1.0 \times 10^8$                 | $6.9 \times 10^7$                 | 1                     | 40     | 2       | -73.0                                  | -                                 |
| 4-Chloronitrobenzene (-1.06) <sup>a</sup> | 10.6 <sup>a</sup>                         | $7.8 \times 10^6$                    | $6.6 \times 10^7$                 | $5.6 \times 10^7$                 | -                     | 540    | 100     | -66.2 <sup>b</sup>                     | -                                 |
| 4-Fluoronitrobenzene (-1.13) <sup>a</sup> | 17.3 <sup>a</sup>                         | $7.2 \times 10^5$                    | $2.4 \times 10^7$                 | $3.0 \times 10^7$                 | -                     | 30     | -       | -61.4 <sup>b</sup>                     | -                                 |
| 4-Nitrotoluene (-1.21) <sup>a</sup>       | 30.7 <sup>a</sup>                         | -                                    | $5.7 \times 10^6$                 | $2.4 \times 10^7$                 | -                     | 50     | -       | -41.3                                  | -                                 |
| 4-Nitroanisole (-1.27) <sup>a</sup>       | 31.7 <sup>a</sup>                         | -                                    | $< 8 \times 10^5$                 | $2.5 \times 10^7$                 | -                     | 400    | -       | -66.2                                  | $4.2 \times 10^9$                 |
| Quinaldic acid (-1.70) <sup>c</sup>       | 73 <sup>b</sup>                           | -                                    | -                                 | $7.4 \times 10^8$                 | -                     | (5000) | 500     | -17.3                                  | $2.0 \times 10^9$                 |
| Benzophenone (-2.07) <sup>c</sup>         | 108 <sup>b</sup>                          | -                                    | $< 5 \times 10^6$                 | $< 1 \times 10^4$                 | -                     | -      | -       | 11.1                                   | $1.0 \times 10^7$                 |
| Acetophenone (-2.11) <sup>c</sup>         | 112 <sup>b</sup>                          | -                                    | -                                 | -                                 | -                     | -      | -       | 17.9                                   | -                                 |

<sup>a</sup> In acetonitrile [1,2].

<sup>b</sup> Values calculated from half-wave potentials, given by formulae  $E_{1/2} = -1.45 + 0.84$  for water and  $E_{1/2} = -1.85 + 0.644A$  for acetonitrile ( $A$  is the electron affinity in the gas phase) [37].

<sup>c</sup> Values estimated from electrochemical potentials in water [3]; accuracy of calculation of quenching rate constants was about 20%. SCE, saturated calomel electrode.

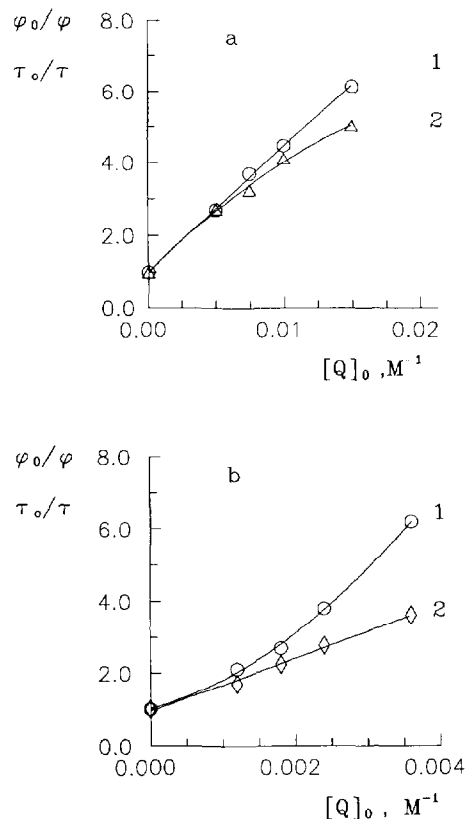


Fig. 2. Dependence of the  $RuL_6^{2+}$  luminescence quantum yield ( $\phi_0/\phi$ ) (1) and the  $RuL_6^{2+}$  luminescence lifetime ( $\tau_0/\tau$ ) (2) on 1,3-dinitrobenzene concentration in ethanol (a) and in a 0.2 M solution of SDS (b).

proximately one order lower than those obtained for micelles ( $\rho$ ) (Table 1). Different values of the distribution coefficients, obtained by different methods, have been observed previously for naphthalene derivatives [42]. Nevertheless, it can be concluded from the estimated values of  $\rho$  ( $\rho > 10^2$ ) that at least a large part of the quencher is solubilized inside the micelle. The limiting values of  $k_q$  were estimated by Eq. (A13) (Table 1).

### 3.2. Calculations of the true quenching rate constants

To calculate the true quenching rate constants in micelles from the apparent Stern–Volmer constants, we need to know the rate-determining factor of quenching and the local concentration of the quencher in the micellar phase. This was done by measuring the Stern–Volmer constants in micellar solutions at various SDS concentrations (Eqs. (A13) and (A14), Fig. 3).

### 3.3. Calculations of the Gibbs energy of electron transfer

The Gibbs energy change of the forward electron transfer step  $\Delta G_{et}$  can be calculated [1] from the

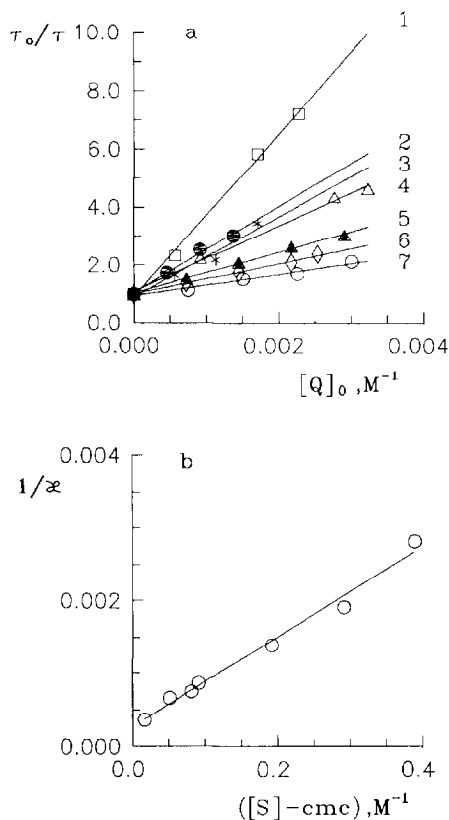


Fig. 3. (a) Dependence of the  $\text{RuL}_6^{2+}$  luminescence lifetime ( $\tau_0/\tau$ ) on the total quencher concentration for various concentrations of SDS: 1, 0.045 M; 2, 0.06 M; 3, 0.09 M; 4, 0.1 M; 5, 0.2 M; 6, 0.3 M; 7, 0.4 M. (b) Dependence of the apparent quenching constant ( $1/\kappa$ ) on the SDS concentration for the quenching of  $^*\text{RuL}_6^{2+}$  by 1,3-dinitrobenzene.

reduction potential of the acceptor ( $E_{1/2}(\text{Q}/\text{Q}^{\cdot-})$ ), the oxidation potential of the donor ( $E_{1/2}(\text{RuL}_6^{3+}/\text{RuL}_6^{2+})$ ) and the excited state energy of the luminophore ( $E^*(\text{RuL}_6^{2+})$ )

$$\Delta G_{\text{et}} = FE_{1/2}(\text{D}^+/\text{D}) - FE_{1/2}(\text{A}/\text{A}^-) - E^*(\text{D}) - w_r + w_p \quad (5)$$

where  $F$  is the Faraday number and  $w_r$  and  $w_p$  are the electrostatic work necessary to bring two product ions or two reactants together to the close contact distance respectively. Since all the quenchers used are neutral molecules,  $w_r$  is zero. When the quenching of  $\text{RuL}_6^{2+}$  luminescence was studied in acetonitrile [1,2,33,34],  $\Delta G_{\text{et}}^{\text{an}}$  was calculated by Eq. (5), using the electrochemical potentials of the reactants measured in acetonitrile, and  $w_p$  was calculated from

$$w_p = (z_a z_b e^2 / \epsilon d) / (1 + \beta d \mu^{1/2}) \quad (6)$$

where  $z_a$  and  $z_b$  are the charge numbers of the two product ions,  $\epsilon$  is the static dielectric constant of the medium,  $d$  is the sum of the radii of donor and acceptor,  $\mu$  is the ionic strength of the medium and  $\beta = (8\pi N_A e / 1000 \epsilon k_B T)$ . For the investigated systems in acetonitrile

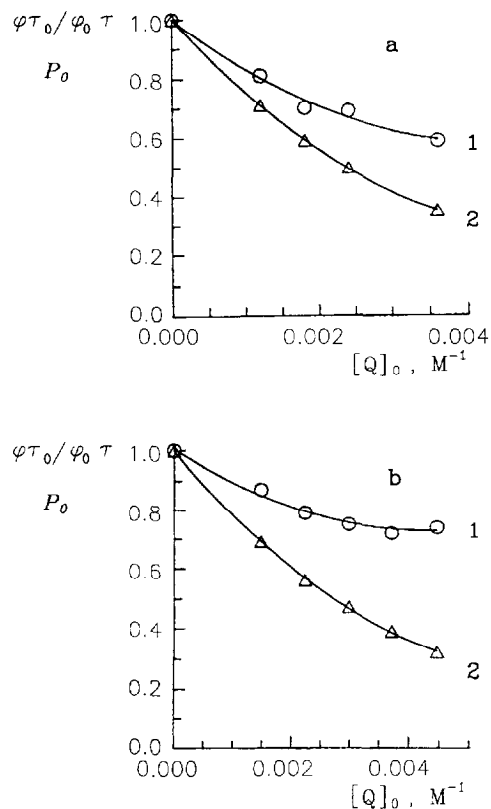


Fig. 4. Dependence of  $\varphi\tau_0/\varphi_0\tau$  (1) and  $P_0$  (2) (Eq. (A4)) on quencher concentration for 1,3-dinitrobenzene (a) and toluquinone (b) in a 0.2 M solution of SDS.

[2],  $\mu = 0$ ,  $z_a = +3$ ,  $z_b = -1$ ,  $d = 1.09$  nm,  $\epsilon = 37.5$  and  $w_p = -13.4$  kJ mol $^{-1}$ .

We used the  $\Delta G_{\text{et}}^{\text{an}}$  values, calculated for acetonitrile, as the universal scale for all investigated systems including micelles.

#### 3.4. Dependence of the rate constants of electron transfer on the Gibbs energy change of electron transfer

When the transition state theory is applied, the rate constants of elementary reactions  $k_{ij}$  (where  $ij = 23, 32, 30$ ) can be written as

$$k_{ij} = (\kappa_i k_B T / h) \exp(-\Delta G_{ij}^{\ddagger} / RT) \quad (7)$$

$\kappa_i$  is the electronic transmission coefficient and  $\Delta G_{ij}^{\ddagger}$  are the Gibbs energies of the corresponding reactions. The equilibrium constant can be represented as  $K_{23} = \exp(-\Delta G_{23}/RT)$ .

The quenching rate constants can be expressed in different ways, depending on the  $k_{30}/k_{32}$  ratio. When  $k_{30} \gg k_{32}$

$$k_q = k_{12} / [1 + k_{21} \nu_{23}^{-1} \exp(\Delta G_{23}^{\ddagger} / RT)] \quad (8)$$

When  $k_{30} \ll k_{32}$

$$k_q = k_{12} / \{1 + k_{21} [\nu_{23}^{-1} \exp(\Delta G_{23}^*/RT) + k_{30}^{-1} \exp(\Delta G_{23}/RT)]\} \quad (9)$$

where  $\nu_{23}$  is the frequency factor of  $k_{23}$  and  $\Delta G_{23} \approx \Delta G_{et}$ .

The dependence of the activation energy on the Gibbs energy of electron transfer  $\Delta G_{23}$  can be described by the empirical Weller equation [35]

$$\Delta G_{23}^* = \Delta G_{23}/2 + [(\Delta G_0^*)^2 + (\Delta G_{23}/2)^2]^{1/2} \quad (10)$$

or by the theoretical Marcus equation [43]

$$\Delta G_{23}^* = (\lambda/4)(1 + \Delta G_{23}/\lambda)^2 \quad (11)$$

where  $\Delta G_0^* = \lambda/4$  is an activation parameter corresponding to  $\Delta G_{23} = 0$  and  $\lambda$  represents the sum of the inner- and outer-sphere reorganization energies. Eqs. (10) and (11) give similar plots for  $\Delta G_{23}^*$  vs.  $\Delta G_{23}$  in the range  $-30 < \Delta G_{23} < +30$  kJ mol<sup>-1</sup> (however, Eq. (11) predicts a decrease in the rate constants at high negative values of  $\Delta G_{23}$ , which occurs only in special cases).

A comparison of the relationship between  $k_q$  and  $\Delta G_{23}$  in acetonitrile, ethanol, water and micelles (Fig. 5) shows that there are three solvent-dependent parameters: (1) the diffusion limit ( $k_{12}$ ), determined by the rate constants at highly negative values of  $\Delta G_{et}^{an}$ ; (2) the shift along the  $\Delta G_{et}^{an}$  axis ( $\delta$ ) determined mainly by points at positive values of  $\Delta G_{et}^{an}$ ; (3) the curvature in the transition region between the horizontal and inclined branches of the relationship (at  $\Delta G_{23}$  close to zero). As noted above, we used the  $\Delta G_{et}^{an}$  values for

acetonitrile, calculated by Eq. (5), as the universal  $\Delta G_{23}$  scale for all investigated systems.

The shift along the  $\Delta G_{et}^{an}$  axis, denoted by parameter  $\delta$ , has a positive value for acetonitrile and negative values for all the other solvents, increasing in magnitude from ethanol to SDS micelles and water (Table 2). In SDS and water solutions,  $\delta$  appears to be significantly higher (approximately 100 kJ mol<sup>-1</sup>) than in organic solvents, although the diffusion rate constant in micellar solutions corresponds to a medium with high viscosity. The change in the electrochemical potentials of both RuL<sub>6</sub><sup>2+</sup> and the investigated electron acceptors in water compared with acetonitrile results in a decrease in  $\Delta G_{et}$  by about 100 kJ mol<sup>-1</sup>. The reasons for this change will be discussed later. Thus  $\Delta G_{23}$  for the investigated systems in SDS micelles is close to  $\Delta G_{et}$  in water solution.

In order to analyse the influence of the different solvent properties on the quenching rate constants, the experimental relationships between  $k_q$  and  $\Delta G_{et}^{an}$  were approximated by Eqs. (10)–(12)

$$k_q \approx k_{12} / [1 + b \exp(\{\Delta G/2 + [(\Delta G_0^*)^2 + (\Delta G/2)^2]^{1/2}\}/RT)] \quad (12)$$

where  $\Delta G = \Delta G_{et}^{an} + \delta$ , and the parameters  $\Delta G_0^*$  and  $\delta$  were fitted (coefficient  $b = k_{21} \nu_{23}^{-1}$  was assumed to be equal to 0.01 [34]). Parameter  $\delta$  formally allows for a change in  $\Delta G_{23}$  in a given solvent compared with  $\Delta G_{et}^{an}$ . The reasonable scatter of the experimental data (Fig. 5) indicates that the approximation of a roughly constant “shift” of the redox potentials of the quenchers for the given solvents (for example, between acetonitrile, ethanol and water) is adequate. It should be noted that  $\delta$  includes not only the true change in  $\Delta G_{23}$  in a given medium compared with acetonitrile ( $\Delta \Delta G$ ), but also the rate constants  $k_{21}$  and  $k_{30}$  or  $k_{21}$  and  $\nu_{23}$ . If  $k_{30} \ll k_{32}$  and  $k_{21} k_{32} / k_{23} k_{30} \gg 1$ , then

$$\ln k_q \approx \ln k_{12} - [\Delta G + RT \ln(k_{21}/k_{30})]/RT \quad (13)$$

and

$$\delta = \Delta \Delta G + RT \ln(k_{21}/k_{30}) \quad (14)$$

If  $k_{30} \ll k_{32}$  and  $k_{21} \gg k_{23}$ , then in the  $\Delta G_{et} \gg \Delta G_0^*$  limit

$$\delta = \Delta \Delta G + RT \ln(k_{21}/\nu_{23}) \quad (15)$$

Experimental difficulties, associated with the selection of weak acceptors as quenchers which could be solubilized in micelles, did not allow us to obtain many points on the  $\log k_q$  vs.  $\Delta G_{et}^{an}$  relationship in the kinetic region. For quinaldic acid, whose quenching rate constant in the micellar phase has the lowest value, the electrochemical potential in acetonitrile is not known, and a direct calculation of  $\Delta G_{et}^{an}$  in acetonitrile is impossible. However, using the  $E_{1/2}$  value of quinaldic

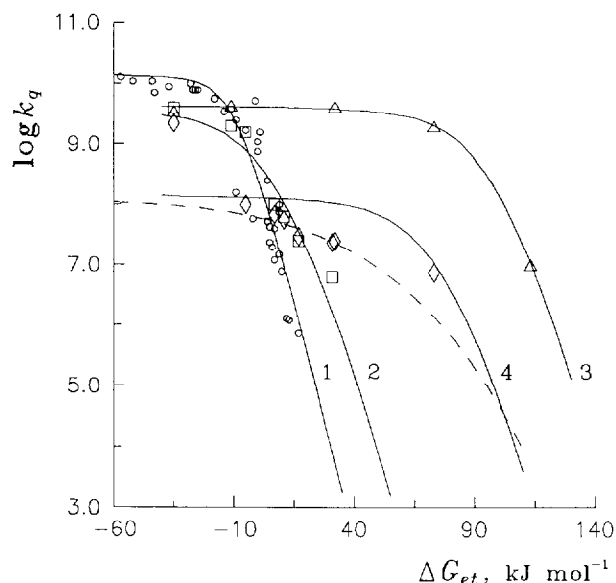


Fig. 5. Dependence of the quenching rate constants on the Gibbs energy of electron transfer ( $\Delta G_{et}^{an}$ ), calculated from the redox potentials of the reactants in acetonitrile (Eq. (5)), for the quenching of RuL<sub>6</sub><sup>2+</sup> luminescence by electron acceptors: O, acetonitrile [1,2]; □, ethanol; △, water; ◇, SDS micelles. The full curves indicate the fitting in terms of Eq. (12). The broken curve for SDS micelles corresponds to the fitting of  $\delta$  with fixed  $\Delta G_0^*$ .

Table 2  
Diffusion rate constants ( $k_{12}$ ) and parameters  $\Delta G_0^*$  and  $\delta$  (see text, Eq. (12)) in various media

| System  | Medium       | $k_{12}$<br>( $M^{-1} s^{-1}$ ) | $\Delta G_0^*$<br>( $kJ mol^{-1}$ )              | $\delta$<br>( $kJ mol^{-1}$ )    | Ref. |
|---|--------------|---------------------------------|--|----------------------------------|------|
| RuL <sub>6</sub> <sup>2+</sup> + electron acceptors                   | Acetonitrile | $1.5 \times 10^{10}$            | $14 \pm 3$<br>17.8 <sup>a</sup>                  | $+12 \pm 3$<br>–                 | [1]  |
|   | Ethanol      | $4.0 \times 10^9$               | $24 \pm 2$                                       | $-19 \pm 4$                      |      |
|   | Water        | $4.4 \times 10^9$               | $23 \pm 1$                                       | $-107 \pm 2$                     |      |
|   | SDS micelles | $1.5 \times 10^8$               | (24) <sup>b</sup><br>( $40 \pm 5$ ) <sup>c</sup> | $-88 \pm 4$<br>( $-120 \pm 30$ ) |      |
| RuL <sub>6</sub> <sup>2+</sup> + methylviologens                      | Water        |                                 | 22   | –                                | [44] |
| Pyrene,<br>N-ethylcarbazole,<br>N-methylphenothiazine +<br>metal ions | Water        |                                 | 25   | –                                | [32] |
|   | SDS micelles |                                 | 54   | –                                | [32] |

<sup>a</sup> Data from Ref. [1], recalculated by Eq. [12]).

<sup>b</sup> Data obtained by fitting of both parameters.

<sup>c</sup> Data obtained by fitting of  $\delta$  with fixed  $\Delta G_0^*$ .

acid in water ( $-0.86$  V) [3], we can estimate the  $\Delta G_{et}^{an}$  value in acetonitrile ( $40$   $kJ mol^{-1}$  or more). It should be noted that a different mechanism of quenching by quinaldic acid (e.g. energy transfer) is highly improbable since the lowest excited state of the RuL<sub>6</sub><sup>2+</sup> complex has a lower energy ( $2.1$  eV) than the T<sub>1</sub> level of quinoline derivatives ( $2.7$  eV) [45].

#### 4. Discussion

The data presented in Table 2 and Fig. 5 can be used to analyse the effects of the medium on the diffusion rate constants, the difference between redox potentials of the reactants (related to parameter  $\delta$ ) and the activation energy of electron transfer in homogeneous solutions and SDS micelles. In spite of the low accuracy of determination of the last two parameters in SDS micelles, because of the lack of a sufficient number of experimental points in the kinetic region ( $k_{12} < k_q < 10^7$   $M^{-1} s^{-1}$ ), several conclusions could be drawn.

##### 4.1. Change in the diffusion rate constant $k_{12}$

The decrease in the upper limit of the quenching rate constant ( $k_{12}$ ) (at  $\Delta G_{et} \ll 0$ ) in ethanol, water and SDS micelles compared with acetonitrile is consistent with the difference in the viscosity of these media ( $1.0$ ,  $1.1$  and  $0.3$  cP for ethanol, water and acetonitrile respectively [46], and  $30$  cP for SDS micelles [41]). Therefore the mechanism of quenching of \*RuL<sub>6</sub><sup>2+</sup> involves the diffusion of the reactants inside the micelle.

##### 4.2. Change in the redox potential difference

The value of parameter  $\delta$  in acetonitrile coincides with  $w_p$ , used for the calculation of  $\Delta G_{et}^{an}$  by Eq. (5) from redox potential data, but has the opposite sign. This indicates that the experimental value of  $w_p$  in acetonitrile is close to zero.

The decrease in  $\delta$  in ethanol may be caused by two factors: (1) a change in  $\Delta G_{et}$ ; (2) an increase in  $k_{30}$  and a transformation of the quenching mechanism to irreversible radical ion pair formation ( $k_{32} \ll k_{30}$ ). However, for such a profound change in  $\delta$  ( $-26$   $kJ mol^{-1}$  compared with acetonitrile),  $k_{30}$  would be greater than  $10^{10}$   $s^{-1}$ , which is unreal. The non-linear plot of  $\tau_0/\tau$  vs. quencher concentration in the investigated systems in ethanol indicates that this stage of the reaction is reversible. Therefore the decrease in  $\delta$  originates from the change in  $\Delta G_{et}$  ( $\delta \approx \Delta \Delta G_{et}$ ).

In water,  $\delta$  appears to be significantly higher than in organic solvents. The experimental values of the redox potentials of both RuL<sub>6</sub><sup>2+</sup> and the investigated electron acceptors differ significantly in water and acetonitrile, although the difference in  $w_p$ , calculated (Eq. (6)) from the difference in the dielectric constants of the medium ( $\epsilon = 37.5$  and  $78$  for acetonitrile and water [46] respectively) is much smaller ( $-13.4$  and  $-6.7$   $kJ mol^{-1}$  respectively). The experimental value of the RuL<sub>6</sub><sup>2+</sup> oxidation potential decreases from  $1.29$  V to  $1.03$  V (vs. SCE) on going from acetonitrile to water [47], and the reduction potentials of the quenchers [3] increase by  $0.65$ – $0.92$  V. The relatively narrow range of the difference between the reduction potentials of the electron acceptors in acetonitrile and aqueous solutions indicates that it is possible to assume that the “shift” in the redox potentials of various compounds of a similar kind between the two given solvents is



roughly constant in the first approximation. Thus the significant difference between the redox potentials in water and organic solvents (even protic solvents) indicates the importance of the specific solvation in aqueous solutions for both the ruthenium complex and organic quenchers. The nature of these specific solvent effects is not investigated in this paper. However, these effects may be used to reveal the peculiarities of electron transfer reactions in organized molecular systems. The changes in the electrochemical potentials result in a very strong (0.91–1.18 V) decrease in the difference ( $E_{1/2}(\text{RuL}_6^{3+}/\text{RuL}_6^{2+}) - E_{1/2}(\text{Q}/\text{Q}^-)$ ). The values of  $\Delta G_{\text{et}}$  (Table 1), calculated from experimental redox potentials, are approximately 90–110 kJ mol<sup>-1</sup> lower in water ( $\Delta G_{\text{et}}^{\text{w}}$ ) than in acetonitrile ( $\Delta G_{\text{et}}^{\text{an}}$ ). The significant difference in  $\Delta G_{\text{et}}$  between water and other solutions is confirmed by the values of the quenching rate constants in these solvents. Thus for 4-nitroanisole in water,  $k_{\text{q}}$  is  $4.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , whereas in acetonitrile and ethanol, it is less than  $10^6 \text{ M}^{-1} \text{ s}^{-1}$ .

In SDS micelles, the observed value of  $\delta$  was found to be about 90 kJ mol<sup>-1</sup>. This large value of  $\delta$  cannot be explained by an increase in  $k_{30}$ . However, this value is close to the value of  $\delta$  in aqueous solution, and to the change in the difference between the redox potentials of  $\text{RuL}_6^{2+}$  [47] and the electron acceptors in water [3] compared with the other solvents. A relatively small alteration of  $\Delta G_{\text{et}}$  originates from the difference between the energies of the excited states of  $\text{RuL}_6^{2+}$  in SDS relative to homogeneous solutions. The luminescence spectra of  $\text{RuL}_6^{2+}$  in acetonitrile, water and ethanol are similar ( $\lambda_{\text{max}} = 608\text{--}610 \text{ nm}$ ), but in SDS solutions the spectrum is shifted to longer wavelengths ( $\lambda_{\text{max}} = 628 \text{ nm}$ ). For  $E^*(\text{RuL}_6^{2+})$ , we used the energy corresponding to the inflexion point at the short-wavelength band of the emission spectrum. For acetonitrile, water and ethanol,  $E^*(\text{RuL}_6^{2+}) = 209 \text{ kJ mol}^{-1}$ , and for SDS micelles, it equals  $200 \text{ kJ mol}^{-1}$ . This causes a decrease in  $\Delta G_{\text{et}}$  in micellar solutions by more than  $9 \text{ kJ mol}^{-1}$  relative to acetonitrile. Thus  $\Delta G_{23}$  for the investigated systems in SDS micelles is close to  $\Delta G_{\text{et}}$  in aqueous solution.

#### 4.3. Change in $\Delta G_0^*$

The values of  $\Delta G_0^*$  for ethanol, water and SDS micellar solutions are similar and close to literature data for water (Table 2).

We obtained a slightly lower value of  $\Delta G_0^*$  ( $-14 \text{ kJ mol}^{-1}$ ) for acetonitrile than calculated in Ref. [1] ( $-17.8 \text{ kJ mol}^{-1}$ ) from the same data, because we varied both parameters ( $\Delta G_0^*$  and  $\delta$ ) instead of only one parameter ( $\Delta G_0^*$ ) in Ref. [1]. The lower value of  $\Delta G_0^*$  may be attributed to the shift along the  $\Delta G_{\text{et}}$

axis due to the formal interrelationship between  $\Delta G_0^*$  and  $\delta$ . It can be seen (Eq. (12)) that, in the kinetic region, when  $k_{\text{q}} \ll k_{12}$  and the values of  $\Delta G_{\text{et}}$  and  $k_{\text{q}}$  are fixed

$$\Delta G = \Delta G_{\text{et}}^{\text{an}} + \delta = \beta - (\Delta G_0^*)^2/\beta \quad (16)$$

where  $\beta = -2.3RT[\log(k_{\text{q}}/k_{12}) + \log b]$ . The accuracy of the determination of  $\Delta G_0^*$  is rather low, but the fitted value of  $\delta$  is hardly affected by  $\Delta G_0^*$  when  $k_{\text{q}}/k_{12} < 10^{-2}$ . When the  $\Delta G_0^*$  value is varied from 10 to  $20 \text{ kJ mol}^{-1}$ , the value of  $\Delta G_{\text{et}}$  at a given  $k_{\text{q}}$  value varies from 20 to  $7 \text{ kJ mol}^{-1}$ . Since the parameters  $\Delta G_0^*$  and  $\delta$  are mutually correlated, and the number of experimental points in the transition region is too small, we used two methods of fitting: (1) fitting at fixed  $\Delta G_0^*$ , which was taken to be equal to the value obtained for aqueous solutions; (2) fitting of both parameters. In the second case, the inaccuracy in the determination of  $\delta$  is larger (Table 2).

The value of  $\Delta G_0^*$  for SDS solution, obtained in Ref. [32], is greater than our value ( $54 \text{ kJ mol}^{-1}$ ). This difference may be attributed to the fact that, in Ref. [32], only one parameter ( $\Delta G_0^*$ ) was fitted ignoring the possible change in  $\Delta G_{\text{et}}$ , and apparent rather than true quenching rate constants were used.

#### 4.4. Comparison of medium effects in SDS micelles

As noted above,  $\Delta G_{23}$  in SDS micelles, for the investigated systems, is close to  $\Delta G_{\text{et}}$  in aqueous solution and indicates a polar microenvironment of the reactants. However, at the same time, the spectral properties of  $\text{RuL}_6^{2+}$  in SDS solutions (emission maximum, halfwidth of the emission band [4]) and the value of the limiting diffusion rate constant are typical of high-viscosity media (i.e. micelle interior with a low polarity).

This contradiction points to a considerable reorganization of the local microenvironment and a specific effect of water molecules (probably water cluster formation) during the reaction of  $^*\text{RuL}_6^{2+}$  with electron acceptors in micelles. The value of  $\Delta G_{23}$  must be strongly dependent on the local microenvironment of the  $^*\text{RuL}_6^{2+}$  and electron acceptor molecules. It has been shown by the magnitude of the  $\text{D}_2\text{O}/\text{H}_2\text{O}$  isotope effect on the lifetimes of Ru and Os complexes in water and micellar solutions that approximately 30% of the ligand surface of  $\text{RuL}_6^{2+}$  localized in micelles is accessible to water molecules [16]. Other data [48,49] also indicate that  $\text{RuL}_6^{2+}$  is localized in the outer sphere of micelles.

The hydrated ion pair formed by electron transfer must dissociate rapidly ( $k_{30} > 10^{10} \text{ s}^{-1}$ ) [34], and its formation must be irreversible ( $k_{30} \gg k_{32}$ ).

## 5. Conclusions

We have investigated the oxidative luminescence quenching of  $\text{RuL}_6^{2+}$  by various quenchers (quinones and nitroaromatic compounds) in homogeneous (organic and aqueous) solutions and SDS micelles.  $\text{RuL}_6^{2+}$  luminescence decay in micellar solutions, for most of the investigated systems, is exponential, enabling the quenching rate constants and distribution coefficients of the quenchers to be obtained. An analysis of the reaction kinetics in micellar solutions has shown that, in systems in which the redox potential of the quencher  $E_{1/2}(\text{Q}/\text{Q}^-) < 1.5$  V, internal quenching is observed, i.e. reaction of  $^*\text{RuL}_6^{2+}$  with a quencher molecule solubilized inside a micelle. In these systems, true intramicellar quenching rate constants were obtained, enabling the electron transfer reactions in micelles and homogeneous solutions to be compared.

A distinguishing feature of the investigated systems ( $^*\text{RuL}_6^{2+}$  + electron acceptor) is the large difference between the electrochemical potentials of the reactants in organic solvents and aqueous solutions. This results in a significant decrease in the Gibbs energy of electron transfer  $\Delta G_{\text{et}}$  in aqueous solutions relative to acetonitrile, which is confirmed by the quenching rate constants obtained. In SDS micelles, the  $\Delta G_{\text{et}}$  values are similar to those in water, although the spectral properties of  $\text{RuL}_6^{2+}$  and the value of the limiting diffusion rate constant are typical of media with medium polarity and high viscosity. This suggests a considerable reorganization of the local microenvironment of the  $\text{RuL}_6^{2+}$  complex and quencher (probably water cluster formation) during electron transfer and a specific effect of the surrounding water molecules on the reaction kinetics. Thus solubilization in the micellar phase enables the local concentrations and mobility of the reactants to be changed while retaining their effective redox potentials in water solution.

### Appendix: Determination of the true quenching rate constants inside micelles

A good analysis of the mechanism of  $\text{RuL}_6^{2+}$  luminescence quenching is given by Miyashita et al. [28,29], Turro and coworkers [6,8] and others [15,17,19,25,31]. However, for a correct determination of the true bimolecular rate constants of luminescence quenching inside micelles, we had to develop a more detailed analysis of the luminescence quenching kinetics in micellar solutions for monoexponential luminescence decay.

Several problems arise when determining the true quenching rate constants in micellar systems [15,19,20].

(1) Single or multi-exponential luminescence decay.

(2) Static quenching and establishment of an equilibrium in the excited state.

(3) The elucidation of the rate-determining factor of quenching in micelles.

(4) Calculation of the true quenching rate constants from the apparent quenching rate constants obtained experimentally at particular concentrations of the surfactant.

There are two kinetic types of photoreaction in micelles and other microheterogeneous systems related to the different relationships between the reaction rate and the rate of relaxation of the reactant distribution between the particles of the microphase (such as micelles or vesicles). The first type occurs when the exchange rate of the reactant between the micelles or between the micelles and the bulk phase is higher than the decay rate of the luminophore excited state. This results in an averaging of the number of reactant molecules over all the micelles and first-order kinetics of excited molecule decay. In this case, the pseudophase model of reaction kinetics can be used [9,19,20]. The quencher distribution between the micelles and the bulk water phase is characterized by the distribution coefficient  $\rho$

$$\rho = [\text{Q}]_{\text{m}}/[\text{Q}]_{\text{v}} \quad (\text{A1})$$

where  $[\text{Q}]_{\text{m}}$  and  $[\text{Q}]_{\text{v}}$  are the quencher concentrations in micellar and water phases and

$$[\text{Q}]_{\text{m}} = [\text{Q}]_{\text{o}}/[1/\rho + v_{\text{m}}([\text{S}] - \text{cmc})] \quad (\text{A2})$$

where  $[\text{Q}]_{\text{o}}$  is the total concentration of the quencher in micellar solution,  $v_{\text{m}}$  is the surfactant molar volume,  $[\text{S}]$  is the molar concentration of the surfactant and cmc is the critical micelle concentration. A microscopic approach to the multistage chemical equilibrium of the quencher between micelles [20] gives a similar expression, using  $K_{\text{b}} = \rho v_{\text{m}} z$ , where  $K_{\text{b}}$  is the binding constant of the quencher molecule with the micelles and  $z$  is the aggregation number (for SDS [21],  $v_{\text{m}} = 0.3 \text{ M}^{-1}$  and  $z = 62$ ).

The second kinetic type occurs when the exchange rate of reactant molecules between the micelles or between the micelles and the bulk phase is significantly slower than the decay rate of the excited molecules, and a discrete distribution of reactant molecules between micelles must be considered. In this case, different numbers of quencher molecules are present in different micelles, and the kinetic curve of excited molecule decay is the sum of the decay curves for a number of first-order reactions, corresponding to different local quencher concentrations, i.e. the luminescence decay is non-exponential [19]. A microscopic approach leads to a Poisson distribution of quencher molecules between micelles [20]. The probability  $P_n$  of finding a number  $n$  of quencher molecules in a given micelle is

$$P_n = \langle n \rangle^n e^{-\langle n \rangle} / n! \quad (\text{A3})$$

where  $\langle n \rangle = [Q]_0 / (1/\rho v_m z + [M])$  is the mean number of molecules of Q per micelle and  $[M]$  is the concentration of micelles ( $[M] = ([S] - \text{cmc})/z$ ). The fraction of micelles containing no quencher Q is given by

$$P_0 = e^{-\langle n \rangle} \quad (\text{A4})$$

#### Ground state complex formation and equilibrium in the excited state

In some of the systems investigated (in both homogeneous and micellar solutions), the dependence of the luminescence quantum yields ( $\varphi_0/\varphi$ ) of the  $\text{RuL}_6^{2+}$  complex on the quencher concentration does not coincide with that of the luminescence decay lifetimes ( $\tau_0/\tau$ ). There may be two reasons for this: (1) the formation of a complex in the ground state (static quenching); (2) the establishment of an equilibrium in the excited state. They may be distinguished by different dependences of  $\varphi$  and  $\tau$  on the concentration of the quencher. For static quenching

$$\varphi_0/\varphi = (1 + K_C[Q])(1 + k_q \tau_0[Q]) \quad (\text{A5})$$

$$\tau_0/\tau = 1 + k_q \tau_0[Q] \quad (\text{A6})$$

$$\varphi_0 \tau / \varphi \tau_0 = 1 + K_C[Q] \quad (\text{A7})$$

where  $K_C$  is the equilibrium constant of ground state complex formation. In general, in addition to ground state complex formation, an equilibrium is established in the excited state between the reactants and the radical ion pair

$$\varphi_0/\varphi = (1 + K_{12}K_{23}k_{30}\tau_0[Q])(1 + K_C[Q]) \quad (\text{A8})$$

$$\tau_0/\tau = (1 + K_{12}K_{23}k_{30}\tau_0[Q]) / (1 + K_{12}K_{23}[Q]) \quad (\text{A9})$$

$$\begin{aligned} \varphi_0 \tau / \varphi \tau_0 &= (1 + K_{12}K_{23}[Q])(1 + K_C[Q]) \\ &\approx 1 + (K_{12}K_{23} + K_C)[Q] \end{aligned} \quad (\text{A10})$$

When a ground state complex is formed, the plot of  $\varphi_0/\varphi$  vs.  $[Q]$  shows positive deviations from linearity (superlinear) and the  $\tau_0/\tau$  plot is linear (Eqs. (A5) and (A6)). If a ground state complex is not formed, the  $\varphi_0/\varphi$  plot is linear. A plot of  $\tau_0/\tau$  shows negative deviations from linearity (sublinear) when equilibrium is established in the excited state (Eq. (A9)). The sum of the ground state complex formation constant and the equilibrium constant in the excited state can be obtained from the plot of  $\varphi_0 \tau / \varphi \tau_0$  vs.  $[Q]$  (Eq. (A10)).

#### Elucidation of the rate-determining factor of quenching in micelles

The quenching rate constants obtained by Eq. (A6) depend on the rate-determining factor of quenching (in terms of formal kinetics). Exponential luminescence decay in the presence of a quencher may be observed in micellar solutions in two cases.

(1) The rate of quenching is determined by the rate of interaction of the excited molecule with the quencher inside the micelle ( $k_q[Q]_m \approx 1/\tau_0$ ;  $k_q \ll (k_{\text{out}} + k_e[M])$ ;  $\rho v_m([S] - \text{cmc}) \approx 1$ , where  $k_{\text{out}}$  is the exit rate constant of the quencher and  $k_e$  is the rate constant of direct intermicellar exchange of the quencher molecules). We call this “internal” quenching, i.e. reaction with the quencher molecule localized in the micelle. The rate of quenching depends on the quencher concentration inside the micelle and Eqs. (A8)–(A10) can be rewritten as

$$\begin{aligned} \varphi_0/\varphi &= (\tau_0/\tau)(1 + K_C[Q]_m) \\ &= (\tau_0/\tau)\{1 + K_C[Q]_0/[1/\rho + v_m([S] - \text{cmc})]\} \end{aligned} \quad (\text{A11})$$

$$\ln I(t) = \ln I(0) - (1 + k_q \tau_0[Q]_m)t/\tau_0 \quad (\text{A12})$$

$$\begin{aligned} \tau_0/\tau &= 1 + k_q \tau_0[Q]_0/[1/\rho + v_m([S] - \text{cmc})] \\ &= 1 + \kappa[Q]_0 \end{aligned} \quad (\text{A13})$$

$$1/\kappa = [1/\rho + v_m([S] - \text{cmc})]/k_q \tau_0 \quad (\text{A14})$$

(2) The rate of quenching is determined by the rate of entrance of the quencher into the micelle. This occurs when the intramicellar rate of quenching is very high ( $1/\tau_0 \ll k_q[Q]_m$ ;  $[Q]_v k_{\text{in}} \approx 1/\tau_0$ ;  $\rho v_m([S] - \text{cmc}) \approx 1$ ), and luminophore emission is observed almost solely from micelles which do not contain quencher molecules (similar to static quenching). All of these luminophore molecules will be quenched dynamically by every quencher molecule entering a micelle. We call this type of quenching “external” quenching. In this case, the rate of quenching depends on the quencher concentration in the bulk phase, and taking into account the possibility of ground state complex formation

$$\begin{aligned} \varphi_0/\varphi &= e^{\langle n \rangle} (\tau_0/\tau)(1 + K_C[Q]_m) \\ &= e^{\langle n \rangle} (\tau_0/\tau)\{1 + K_C[Q]_0/[1/\rho + v_m([S] - \text{cmc})]\} \end{aligned} \quad (\text{A15})$$

$$\ln I(t) = \ln I(0) - (1 + k_q^{\text{ext}} \tau_0[Q]_v)t/\tau_0 \quad (\text{A16})$$

where  $k_q^{\text{ext}}$  is the rate constant of “external” quenching. Then

$$\begin{aligned} \tau_0/\tau &= 1 + k_q^{\text{ext}} \tau_0[Q]_v \\ &= 1 + k_q^{\text{ext}} \tau_0[Q]_0/[1 + \rho v_m([S] - \text{cmc})] \\ &= 1 + \kappa[Q]_0 \end{aligned} \quad (\text{A17})$$

$$1/\kappa = [1 + \rho v_m([S] - \text{cmc})]/k_q^{\text{ext}} \tau_0 \quad (\text{A18})$$

Eqs. (A14) and (A18) are similar, but the quenching rate constants obtained ( $k_q$  and  $k_q^{\text{ext}}$ ) have very different physical meaning. The two mechanisms cannot be distinguished by measurement of the  $\tau_0/\tau$  vs.  $[Q]_0$  plot. However, the absence of emission from luminophore molecules localized in micelles containing one or more

quencher molecules can be used to distinguish between them. In the case of “external” quenching, we should observe a behaviour resembling “static” quenching. The contribution of “static” quenching can be evaluated from a comparison of the dependence of the ratios  $\varphi\tau_0/\varphi_0\tau$  and  $I(0)/I_0(0)$  (initial intensities of the luminescence decay kinetic curves (at their maxima)) on the quencher concentration and the fraction of micelles containing no quencher (calculated from the relative concentrations of quencher and micelles by Eq. (A4))

$$\varphi\tau_0/\varphi_0\tau = I(0)/I_0(0) = e^{-\langle n \rangle} / (1 + K_C[Q]_m) \quad (\text{A19})$$

The absorbance of the quencher at the excitation wavelength must be taken into account when  $\varphi$  and  $I(0)$  are measured.

## References

- [1] C.R. Bock, J.A. Connor, A.R. Gutierrez, T.J. Meyer, D.G. Whitten, B.P. Sullivan and J.K. Nagle, *J. Am. Chem. Soc.*, **101** (1979) 4815.
- [2] H.-B. Kim, N. Kitamura, Y. Kawanishi and S. Tazuke, *J. Phys. Chem.*, **93** (1989) 5757.
- [3] D. Dobos, *Electrochemical Data*, Akademia Kiado, Budapest, 1975.
- [4] D. Meisel, M.S. Matheson and J. Rabani, *J. Am. Chem. Soc.*, **100** (1978) 117.
- [5] N.J. Turro and A. Yekta, *J. Am. Chem. Soc.*, **100** (1978) 5951.
- [6] N.J. Turro, I.V. Khudyakov and K.G. Gopidas, *Chem. Phys.*, **162** (1992) 131.
- [7] S.S. Atik and L.A. Singer, *Chem. Phys. Lett.*, **59** (1978) 519.
- [8] K.R. Gopidas, A.R. Leheny, G. Caminati, N.J. Turro and D.A. Tomalia, *J. Am. Chem. Soc.*, **113** (1991) 7335.
- [9] A. Yekta, M. Aikawa and N.J. Turro, *Chem. Phys. Lett.*, **63** (1979) 543.
- [10] J. Moroi, *J. Phys. Chem.*, **84** (1980) 2607.
- [11] F. Grieser and R. Tausch-Tremple, *J. Am. Chem. Soc.*, **102** (1980) 7258.
- [12] H.W. Ziemiecki, R. Holland and W.R. Cherry, *Chem. Phys. Lett.*, **73** (1980) 145.
- [13] J.C. Dederen, M. Van der Auweraer and F.C. De Schryver, *J. Phys. Chem.*, **85** (1981) 1981.
- [14] P.-A. Brugger, P.P. Infelta, A.M. Braun and M. Graetzel, *J. Am. Chem. Soc.*, **103** (1981) 320.
- [15] M. Van der Auweraer, C. Dederen, C. Palms-Windels and F.C. De Schryver, *J. Am. Chem. Soc.*, **104** (1982) 1800.
- [16] B.L. Hauenstein, Jr., W.J. Dressick, S.L. Buell, J.N. Demas and B.A. De Graff, *J. Am. Chem. Soc.*, **105** (1983) 4251.
- [17] G.G. Warr and F. Griser, *J. Chem. Soc., Faraday Trans. I*, **82** (1986) 1813.
- [18] G.G. Warr and F. Griser, *J. Chem. Soc., Faraday Trans. I*, **82** (1986) 1829.
- [19] K. Kalyanasundaram, *Photochemistry in Microheterogeneous Systems*, Academic Press, New York, 1987, p. 388.
- [20] M.G. Kuzmin and N.K. Zaitsev, in V.E. Kazarinov (ed.), *The Interface Structure and Electrochemical Processes at the Boundary Between Two Immiscible Liquids*, Springer-Verlag, Berlin, Heidelberg, 1987, p. 246.
- [21] J. Moroi, R. Humphry-Beker and M. Graetzel, *J. Colloid Interface Sci.*, **119** (1987) 588.
- [22] D. Fornasiero and F. Griser, *J. Chem. Soc., Faraday Trans. I*, **86** (1990) 2955.
- [23] J. Alsins and M. Almgren, *J. Phys. Chem.*, **94** (1990) 3062.
- [24] M. Wolszczak and J.K. Thomas, *Radiat. Phys. Chem.*, **38** (1991) 155.
- [25] M.H. Gehlen, M. Van der Auweraer and F.C. De Schryver, *Photochem. Photobiol.*, **54** (1991) 613.
- [26] H. Garrera, J.J. Cosa and C.M. Previtali, *J. Photochem. Photobiol. A: Chem.*, **56** (1991) 267.
- [27] V.G. Kuykendall and J.K. Thomas, *J. Phys. Chem.*, **94** (1990) 4224.
- [28] T. Miyashita, T. Murakata, J. Jamaguchi and M. Matsuda, *J. Phys. Chem.*, **89** (1985) 497.
- [29] T. Miyashita, T. Murakata and M. Matsuda, *J. Phys. Chem.*, **87** (1983) 4529.
- [30] S.M.B. Costa and A.L. Macanita, *J. Phys. Chem.*, **84** (1980) 2409.
- [31] Y. Croonen, Y. Gelade, M. Van der Zegel, M. Van der Auweraer, H. Vandendriessche, F.C. De Schryver and M. Almgren, *J. Chem. Phys.*, **87** (1983) 1426.
- [32] S. Hashimoto and J.K. Thomas, *J. Phys. Chem.*, **89** (1985) 2771.
- [33] N. Kitamura, H.-B. Kim, S. Okano and S. Tazuke, *J. Phys. Chem.*, **93** (1989) 5750.
- [34] N. Kitamura, R. Obata, H.-B. Kim and S. Tazuke, *J. Phys. Chem.*, **93** (1989) 5764.
- [35] D. Rehm and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **73** (1969) 834.
- [36] D. Rehm and A. Weller, *Isr. J. Chem.*, **8** (1970) 259.
- [37] P. Kebarle and S. Chowdhury, *Chem. Rev.*, **87** (1987) 513.
- [38] Y. Waka, K. Hamamoto and N. Mataga, *Chem. Phys. Lett.*, **53** (1978) 242.
- [39] S.S. Atik, C.L. Kwan and L.A. Singer, *J. Am. Chem. Soc.*, **101** (1979) 5696.
- [40] F.M. Martens and J.W. Verhoeven, *J. Phys. Chem.*, **85** (1981) 1773.
- [41] R. Humphry-Beker and M. Graetzel, *J. Am. Chem. Soc.*, **102** (1980) 847.
- [42] M. Gonzalez, J. Vera, E.b. Abuin and E.A. Lissi, *J. Colloid Interface Sci.*, **98** (1984) 152.
- [43] R.A. Marcus, *J. Chem. Phys.*, **24** (1956) 966.
- [44] E. Amonyal, B. Zidler, P. Keller and A. Moradpour, *Chem. Phys. Lett.*, **74** (1980) 314.
- [45] Landolt-Börnstein, *Numerical Data and Functional Relationships in Science and Technology*, Vol. 3, Group II, New Series, Springer-Verlag, Berlin, 1967, p. 416.
- [46] A. Weissberger, E.S. Proskauer, J.A. Riddik and E.E. Toops, *Organic Solvents*, Interscience, New York, 1955.
- [47] F.E. Lytle and D.M. Hercules, *Photochem. Photobiol.*, **13** (1971) 123.
- [48] J.C. Russell and D.J. Whitten, *J. Am. Chem. Soc.*, **104** (1982) 5937.
- [49] M.J. Colaneri, L. Kevan and R. Schmehl, *J. Phys. Chem.*, **93** (1989) 397.