

**Effect of Sodium Dodecyl Sulphate on the Photoinduced Electron Transfer Reactions of Ruthenium(II)-Polypyridyl Complexes with Polyphenols**

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Email: [gallengraj@gmail.com](mailto:gallengraj@gmail.com)Accepted on 12<sup>th</sup> April 2014**ABSTRACT**

*Photoinduced electron transfer between the excited state Ru(II)-polypyridyl complexes and polyphenols (p-coumaric acid and ferulic acid) has been investigated in sodium dodecyl sulphate at pH 11 using luminescent quenching technique. The dynamic nature of quenching is confirmed from the ground state absorption studies. The observed quenching rate constant ( $k_q$ ) values are sensitive to the nature of the ligand, medium and the structure of the quenchers. The electron transfer rate is low in sodium dodecyl sulphate compared to that in aqueous medium may be due to the operation of predominant electrostatic interaction over the hydrophobic interaction of the cationic complexes with the anionic micelle. The reductive quenching of Ru(II)-polypyridyl complexes by phenolate ions has been confirmed from transient absorption spectra.*

**Keywords:** Ru(II)-polypyridyl complex, Electron transfer, Dynamic quenching, Electrostatic interaction.

**INTRODUCTION**

Surface active agents or the surfactants are molecules that have a hydrophilic head group and a hydrophobic tail group. The head group may be either a cationic, anionic, neutral or even a zwitter-ionic. In a dilute solution, these surfactants behave like a simple salt solution, while at higher concentrations of the surfactants they interact together and deviate far from the properties of salt solution. The intermolecular interactions arising either due to the electrostatic or polar-polar interactions lead to the aggregation of surfactants. Above a particular concentration, known as the critical micellar concentration (CMC), they form the micelles. The CMC depends on the nature of surfactant as well as the solvent. The study of micellar solutions is of interest both from the point of view of basic research and applications of surfactants.

The understanding of electron transfer has been a long-standing goal in the active research area due to its important role in many industrial, chemical and biological processes [1,2]. Recent emphasis in this area has been centered on the dynamical aspect of solvent influences as well as on influences of microenvironment on this process. In recent years the photoinduced electron transfer (PET) has been found to be a well known triggering process in various physical, chemical and biological systems [1]. Photo

induced electron transfer reactions in surfactant solutions are potentially important for efficient energy conversion and storage because surfactant micelles help to achieve the separation of the photoproducts by hydrophilic-hydrophobic interactions of the products with the micellar interface [3,4].

The Ru(II)-polypyridyl complexes ( $[\text{Ru}(\text{NN})_3]^{2+}$ ) have been extensively used as probes in micellar media and the photophysical properties like emission maximum, excited state lifetime and emission quantum yield vary enormously with the nature of the surfactant and concentration. Furthermore the presence of micelle significantly affects the kinetics of chemical reactions. The kinetics of micellar solution is governed by electrostatic and hydrophobic interactions between micelles and reactants. The interaction of micelle with any one of the reaction species will affect the reaction rate. The present study concentrates on the quenching behavior of  $[\text{Ru}(\text{NN})_3]^{2+}$  complexes with *p*-coumaric acid and ferulic acid in sodium dodecyl sulphate (SDS) at pH 11. The electronic absorption spectra validate the dynamic nature of quenching that takes place in these PET reactions. The effect of SDS on the quenching of  $[\text{Ru}(\text{NN})_3]^{2+}$  complexes with phenols by luminescent quenching technique is more helpful in understanding the role of electrostatic interactions apart from the hydrophobic interactions. In order to know the role of SDS in this PET reaction, the observed results are compared with the results obtained from aqueous medium at pH 11. The transient absorption spectra confirm the electron transfer nature of  $[\text{Ru}(\text{NN})_3]^{2+}$  complexes with *p*-coumaric acid and ferulic acid in SDS at pH 11.

## MATERIALS AND METHODS

$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ , ligands (2,2'-bipyridine (bpy), 4,4'-dimethyl-2,2'-bipyridine (dmbpy), 4,4'-di-*tert*-butyl-2,2'-bipyridine (dtbpy)) and the quenchers (*p*-coumaric acid and ferulic acid) were procured from Sigma-Aldrich. HPLC grade solvents were used throughout the study for the synthesis of complex as well as for quenching studies. The double distilled deionized water was used for the quenching studies. The three  $[\text{Ru}(\text{NN})_3]^{2+}$  complexes { where NN = 2,2'-bipyridine (bpy), 4,4'-dimethyl-2,2'-bipyridine (dmbpy), 4,4'-di-*tert*-butyl-2,2'-bipyridine (dtbpy)} were synthesized by reacting  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  with the corresponding ligands according to the procedure previously described [5,6]. The chloride salt of  $[\text{Ru}(\text{bpy})_3]^{2+}$  complex was treated with sodium tetrafluoroborate to get the  $\text{BF}_4^-$  salt  $[\text{Ru}(\text{bpy})_3](\text{BF}_4)_2$ . Samples of the  $[\text{Ru}(\text{NN})_3]^{2+}$  complexes, as well as the quenchers in aqueous and SDS media at pH 11 were freshly prepared for each measurement. Absorption spectra were measured using SYSTRONICS 2203 double beam spectrophotometer. The emission spectra were recorded using ELICO SL 174 spectrofluorometer. All the sample solutions used for the emission and excited state lifetime measurements were deaerated for about 30 min by dry nitrogen gas purging keeping the solutions in cold water to ensure that there is no change in volume of the solution. All the spectral measurements were carried out at 293 K. Excited state lifetime was made with laser flash photolysis technique. Transient spectra were obtained by a point-to-point technique, monitoring the absorbance changes ( $\Delta A$ ) after the flash at intervals of 10 nm over the spectral range 300 - 700 nm, averaging at least 30 decays at each wavelength.

The structure of the ligands and the quenchers used in the present study are shown in **Fig. 1**. The photochemical reduction of  $[\text{Ru}(\text{NN})_3]^{2+}$  complexes with various concentrations ( $2 \times 10^{-4}$  -  $1.4 \times 10^{-3}$  M) of polyphenols in SDS (0.01M) at pH 11 has been studied. Phenolate ions of *p*-coumaric acid and ferulic acid for the quenching studies were prepared by mixing the corresponding phenols with NaOH and the pH of the solutions were maintained at 11 to confirm that the quenchers were present as phenolate ions. The change of emission intensity of  $[\text{Ru}(\text{NN})_3]^{2+}$  with change of [Q] measured at 293 K is shown in **Fig. 2**. The quenching rate constant ( $k_q$ ) for the reactions were determined from the Stern-Volmer equation using emission intensity data.

$$I_0/I = 1 + k_q \tau [Q]$$

Where  $I_0$  and  $I$  are the emission intensities in the absence and presence of quencher respectively and  $\tau$  is the emission lifetime of Ru (II) complexes in the absence of quencher. Stern-Volmer plot for the PET reaction of  $[\text{Ru}(\text{NN})_3]^{2+}$  complexes with polyphenol is shown in **Fig. 3**.

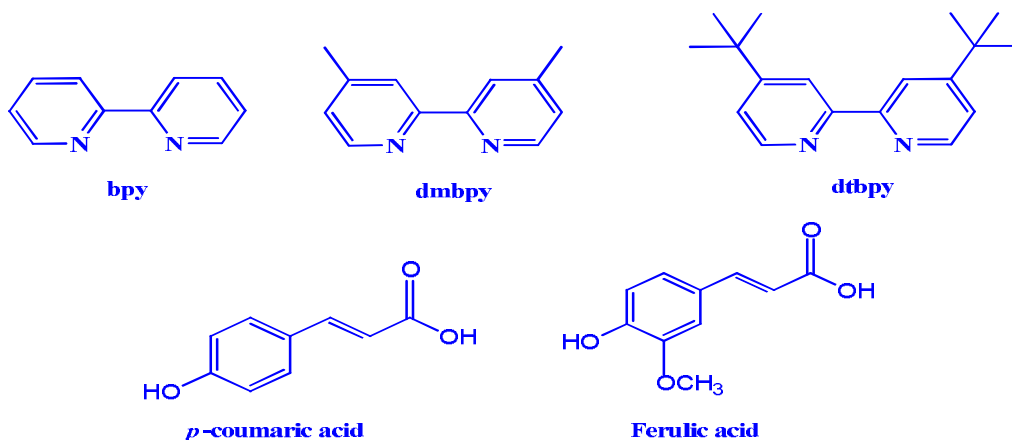


Fig. 1 Structure of the ligands and the quenchers

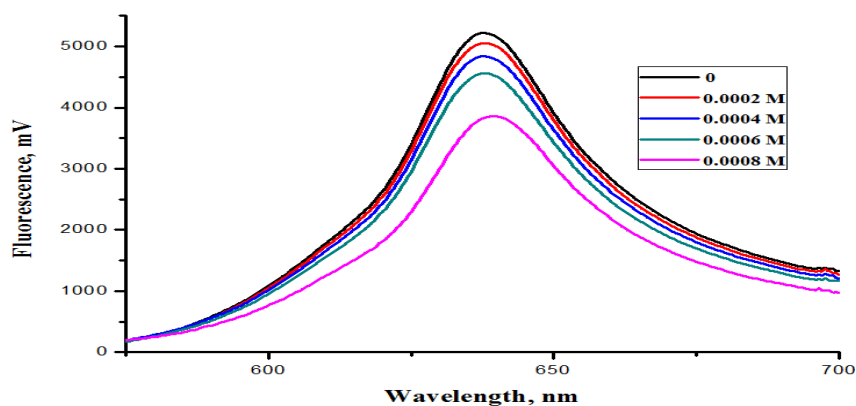


Fig.2 The change in emission intensity of  $^*[Ru(dmbpy)_3]^{2+}$  with *p*-coumaric acid ( $2 \times 10^{-4}$  -  $8 \times 10^{-4}$  M) of different concentrations in SDS at pH 11

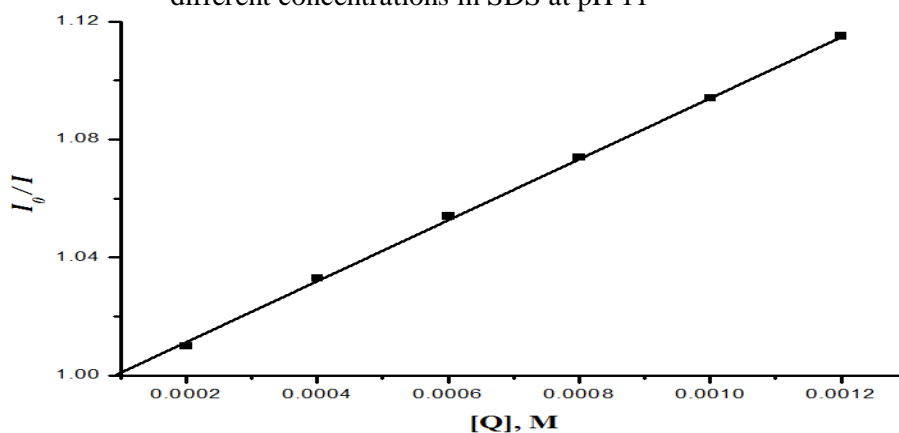


Fig.3 Stern-Volmer plot for the reductive quenching of  $^*[Ru(dmbpy)_3]^{2+}$  with ferulic acid in SDS at pH 11

## RESULTS AND DISCUSSION

The absorption and emission spectral data, the excited state lifetime ( $\tau$ ) of the Ru(II) complexes in aqueous medium and in SDS at pH 11 measured, are collected in **Table 1**. The lifetime of the Ru(II)-polypyridyl complexes in SDS are longer than those in aqueous solution, mainly due to electrostatic interactions of cationic Ru(II) complexes with the surface of the anionic micelle. Because of this binding, the excited state complex will be shielded to some extent from the exposure of the solvent water molecules. The bimolecular quenching rate constant ( $k_q$ ) for the reductive quenching of three Ru(II) complexes  $^*[Ru(bpy)_3]^{2+}$ ,  $^*[Ru(dmbpy)_3]^{2+}$  and  $^*[Ru(dtbp)_3]^{2+}$  with the phenolate ions of *p*-coumaric acid and ferulic acid at pH 11 in aqueous and SDS media are given in **Table 2**.

**Table 1** Absorption and emission spectral data and excited state lifetime of  $[Ru(NN)_3]^{2+}$  complexes in aqueous and SDS media at pH 11

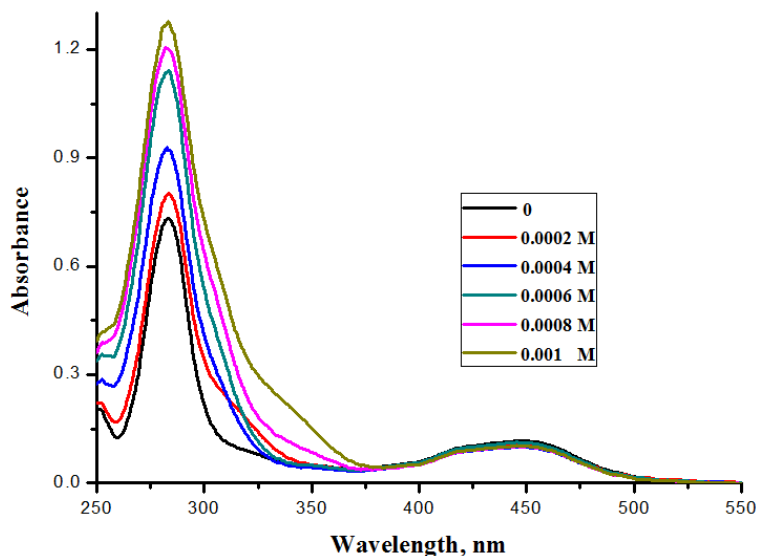
| Complex              | Absorption maximum (nm) |     | Emission maximum (nm) |     | Excited state lifetime (ns) |     |
|----------------------|-------------------------|-----|-----------------------|-----|-----------------------------|-----|
|                      | Aqueous                 | SDS | Aqueous               | SDS | Aqueous                     | SDS |
| $[Ru(bpy)_3]^{2+}$   | 451                     | 445 | 612                   | 628 | 614                         | 740 |
| $[Ru(dmbpy)_3]^{2+}$ | 457                     | 450 | 625                   | 639 | 380                         | 530 |
| $[Ru(dtbp)_3]^{2+}$  | 457                     | 456 | 626                   | 633 | 510                         | 760 |

**Table 2** Quenching rate constant,  $k_q$  ( $M^{-1}s^{-1}$ ) for  $^*[Ru(NN)_3]^{2+}$  with phenolate ions in the aqueous and SDS medium at pH 11

| Quencher                | $[Ru(bpy)_3]^{2+}$ |                   | $[Ru(dmbpy)_3]^{2+}$ |                   | $[Ru(dtbp)_3]^{2+}$ |                   |
|-------------------------|--------------------|-------------------|----------------------|-------------------|---------------------|-------------------|
|                         | Aqueous            | SDS               | Aqueous              | SDS               | Aqueous             | SDS               |
| Phenol                  | $4.6 \times 10^8$  | $5.4 \times 10^7$ | $3.1 \times 10^8$    | $4.3 \times 10^7$ | $2.3 \times 10^8$   | $2.6 \times 10^7$ |
| <i>p</i> -coumaric acid | $5.7 \times 10^8$  | $6.6 \times 10^7$ | $4.1 \times 10^8$    | $5.2 \times 10^7$ | $3.1 \times 10^8$   | $3.9 \times 10^7$ |
| Ferulic acid            | $1.7 \times 10^9$  | $3.8 \times 10^8$ | $1.2 \times 10^9$    | $1.9 \times 10^8$ | $9.4 \times 10^8$   | $1.0 \times 10^8$ |

The absorption spectra of the  $[Ru(bpy)_3]^{2+}$ ,  $[Ru(dmbpy)_3]^{2+}$  and  $[Ru(dtbp)_3]^{2+}$  complexes with the incremental addition of *p*-coumaric acid and ferulic acid in SDS (0.01 M) at pH 11 (**Fig. 4**) show no changes in the MLCT absorption maxima of the complexes signifying the dynamic nature of quenching. The Stern-Volmer plots for the emission intensity data (**Fig. 3**) are linear for these photoredox systems indicating that, dynamic quenching is the predominant process and the contribution from static quenching is negligible in *p*-coumaric acid and ferulic acid. The *p*-coumaric acid has two ionizable-OH groups, the  $pK_a$  values are 4.5 (carboxylic acid) and 9.5 (phenolic-OH) whereas the  $pK_a$  values of ferulic acid are 4.6 and 9.4 [7,8]. The  $pK_a$  values of the quenchers taken in the present study are less than that on the pH of the medium (pH 11), hence they undergo PET reactions with the  $^*[Ru(NN)_3]^{2+}$  complexes in SDS medium. The bond dissociation energy of *p*-coumaric acid and ferulic acid are 84.9 and 83.5 Kcal/mol [9]. The bond dissociation energy of ferulic acid is slightly lower than that of *p*-coumaric acid, shows that ferulic acid forms its phenoxyl radical more easily than *p*-coumaric acid. The presence of electron donating  $-OCH_3$  group *ortho*- to the phenolic group in ferulic acid provides additional stabilization of the ferulate radical compared to the phenoxyl radical of *p*-coumaric acid. Hence the quenching efficiency of ferulic acid is

more compared to that of *p*-coumaric acid in aqueous and SDS media. Thus the nature of the substituent present in the quencher affects the bimolecular rate constant.

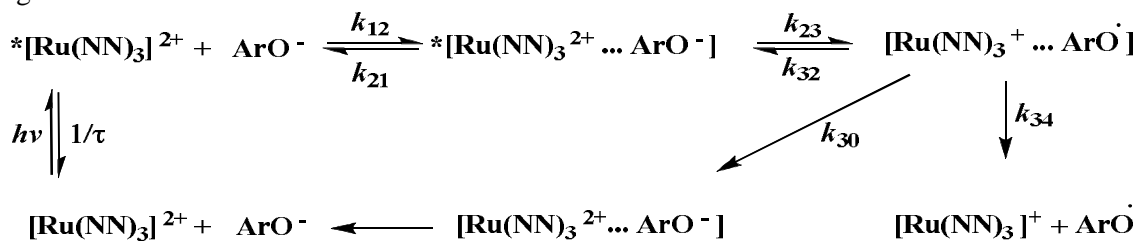


**Fig. 4** Absorption spectra of  $[\text{Ru}(\text{bpy})_3]^{2+}$  with incremental addition of *p*-coumaric acid ( $2 \times 10^{-4}$  -  $1.0 \times 10^{-3}$  M) in SDS at pH 11

For the sake of comparison of the quenching efficiencies of the polyphenols with these complexes, we have done this luminescent study with phenol also and the results are discussed here. Phenol shows least  $k_q$  for all the three complexes in both media. Miedlar and Das reported this type of least  $k_q$  value for phenol in the photoredox reactions of  $[\text{Ru}(\text{bpy})_3]^{2+}$  complex [10]. The  $k_q$  (**Table 2**) clearly shows that for all the phenolate ions, anionic micelle retards the ET process and the magnitude of retardation varies with the nature of the substituent in the phenolate ions. The reason for this lowering is due to the binding of the cationic complexes to the anionic micelle mainly through electrostatic interactions apart from the hydrophobic interactions. The  $k_q$  values drop off from  $[\text{Ru}(\text{bpy})_3]^{2+}$  to  $[\text{Ru}(\text{dtbpy})_3]^{2+}$  with the quenchers in aqueous and SDS medium because of the existence of bulky hydrophobic groups in the 4,4' position of 2,2'-bipyridine. The increase in the hydrophobic nature of the ligands in  $[\text{Ru}(\text{dmbpy})_3]^{2+}$  and  $[\text{Ru}(\text{dtbpy})_3]^{2+}$ , lowers the  $k_q$  to some extent compared to  $[\text{Ru}(\text{bpy})_3]^{2+}$  complex. Similar trend has been already reported for the photoredox reactions of  $[\text{Ru}(\text{NN})_3]^{2+}$  complexes with phenol and 2, 6-di-substituted phenols in aprotic and protic media [11,12]. Thus, the retardation of  $k_q$  obtained here in SDS can be rationalized with the assumption that  $[\text{Ru}(\text{NN})_3]^{2+}$  ions are associated with SDS leaving phenolate ion ( $\text{ArO}^-$ ) in aqueous phase. In addition to the electrostatic interaction of the complex with the micelle, hydrophobic interaction of the bipyridine ligand with the micelle also prevents the complex for quenching process. Hence the availability of the sensitizer for quenching process is less in SDS compared to aqueous medium, which retards the quenching efficiencies of the PET reactions in SDS. Thus the rate constant of this reaction in microheterogeneous medium (SDS) are largely affected than in the aqueous medium owing to the predominance of strong electrostatic interaction between the cationic complexes with the anionic micelle.

The reductive quenching of  $[\text{Ru}(\text{NN})_3]^{2+}$  complexes by the phenolate ions of polyphenols have been confirmed from the transient absorption spectra. The band at 510 nm in the transient absorption spectra of the  $[\text{Ru}(\text{dtbpy})_3]^{2+}$  complex with  $1.0 \times 10^{-3}$  M ferulic acid (**Fig.5**) confirms the reductive nature ( $[\text{Ru}(\text{dtbpy})_3]^+$ ) of the complex. The behavior of these redox systems can be discussed by a common mechanism depicted in **scheme 1**. The reactants diffuse together to form the encounter complex at the

closest distance of approach. The electron transfer occurs in this association complex  $[\text{*Ru}(\text{NN})_3^{2+} \dots \text{ArO}^-]$  resulting in the formation of a caged pair of radicals or radical ions. The radical ions either escape from the solvent cage to give the redox products or undergo back electron transfer leading to the formation of the original reactants.



Scheme 1 Mechanism for the electron transfer quenching of  $[\text{*Ru}(\text{NN})_3]^{2+}$  with  $\text{ArO}^-$

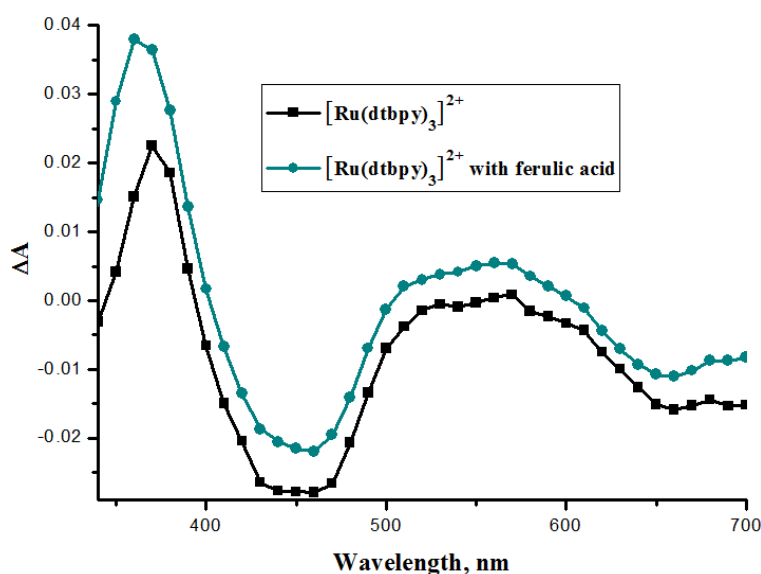


Fig. 5 Transient absorption spectra of  $[\text{Ru}(\text{dtbp})_3]^{2+}$  in the absence and presence of  $1 \times 10^{-3}$  M ferulic acid in SDS (pH 11) recorded at 300 ns

## APPLICATIONS

The study is applicable for the substituent effect and the electrostatic interactions on the electron transfer reactions of biologically important phenolate ions with the excited state Ru(II) complexes.

## CONCLUSIONS

The present study clearly establishes the effect of SDS on the luminescence quenching of  $[\text{Ru}(\text{NN})_3]^{2+}$  complexes with the polyphenols at pH 11. Absorption spectral studies confirm the dynamic nature of quenching of the  $[\text{Ru}(\text{NN})_3]^{2+}$  complexes with the polyphenols in SDS at pH 11. The  $k_q$  values are sensitive to the nature of the ligand, medium and the structure of the quenchers. SDS results in low quenching rate constant compared to that in aqueous medium at pH 11 due to the electrostatic interactions of the cationic complexes with the anionic micelle. Transient absorption spectra confirm the reductive quenching of  $[\text{Ru}(\text{NN})_3]^{2+}$  complexes by the phenolate ions of polyphenols. The study confirms the

substituent effect and the electrostatic interactions on the electron transfer reactions of biologically important phenolate ions with the excited state Ru(II) complexes.

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