

**SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIRECCIÓN DE NUEVAS CREACIONES**

2020
Bogotá D.C.,

Abogado
Luis Felipe Castillo Gibsone

ASUNTO	Radicación	07 137 504
	Trámite	011
	Evento	379
	Actuación	519
	Oficio	1 0886
	Folios	4

Patente de Invención
Vía Nacional
Vía PCT (Fase Nacional)



Patente de Modelo de Utilidad



Cap.I



Cap. II



No. Solicitud Internacional PCT/MX2005/000092
Fecha de Presentación Internacional 13/Octubre/2005

Como resultado del Examen de Fondo realizado, con fundamento en el Artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se comunica:

1. Documentos estudiados

Descripción:	Folios 8 a 23	28/Diciembre/2007
	Folios 63 a 76	28/Diciembre/2007
Reivindicaciones:	Folios 24 a 30	28/Diciembre/2007
	Folios 41 a 43	13/Marzo/2008
	Folios 77 a 79	02/Junio/2010
Prioridad:	MX GT/a/2005/000006	09/Junio/2005

2. Análisis de la Prioridad

Se acepta la reivindicación de Prioridad porque esta solicitud fue presentada dentro del plazo establecido (Art. 9 D 486) y su contenido técnico corresponde con el de la prioridad reivindicada.

3. Objeto de la invención

Título de la solicitud: "Método fotoelectroquímico para la separación del agua en hidrógeno y oxígeno, utilizando como elemento central electrificante las melaninas, sus análogos, sus análogos, sus precursores o sus derivados".

Expediente 07 137504 1er Art 45

El problema planteado en esta solicitud es la necesidad de nuevos métodos de obtención de energía alterna, particularmente procesos fotoelectroquímicos, por medio de los cuales se obtiene la generación de átomos de hidrógeno y oxígeno.

Para resolver este problema técnico la solicitud en estudio proporciona un método de obtención de energía eléctrica y agua, a temperatura ambiente y utilizando luz natural o artificial como única fuente de energía, para dar lugar a la partición de la molécula de agua, obteniéndose átomos de hidrógeno y oxígeno y volviéndolos a unir, además de obtener electrones de alta energía.

El objeto de la presente Solicitud se relaciona con la Clasificación Internacional de Patentes (CIP): C 25 B 1/04

4. Reivindicaciones relativas a un uso o a un segundo uso (Art 14 y 21 D 486)

El uso de las reivindicaciones 1 – 3 y 5 – 9 no es patentable, de acuerdo con el Art 14. Puesto que se menciona el uso de las melaninas, precursores, derivados, entre otros para el proceso fotoelectroquímico.

Además en el estado de la técnica se conoce un documento que podrían llevar a emplear las melaninas en la producción de energía eléctrica, tal como lo es el artículo "Light induced production of hydrogen from water by catalysis with ruthenium melanoidins" INTERNATIONAL JOURNAL OF HYDROGEN ENERGY (vol. 25, 2000, pages 733-737), enseña unas Ru-melanoidinas, que podrían ser una variante de las melaninas, como un sistema de producción de hidrógeno; el documento patente

5. De la Solicitud de Patente

Reivindicaciones (Art 30 D 486, Art 22 PCT)

El capítulo reivindicatorio no se encuentra bien caracterizado por sus características técnicas esenciales, puesto que una reivindicación tiene una forma estructural que consiste en "preámbulo-enlace gramatical-parte característica; donde el preámbulo indica cual es el objeto de la invención, que suele coincidir con el título de la invención (aparato, proceso, composición, etc.) y las características técnicas conocidas en el estado de la técnica. El enlace gramatical puede ser del tipo: "caracterizado por", "que comprende", "que consiste en" y la parte característica indica las características técnicas nuevas que se desean proteger." (Guía para examen de solicitudes de patente de invención y modelo de utilidad. Superintendencia de Industria y Comercio. Bogotá, 2011). Se le requiere al solicitante que teniendo en cuenta lo mencionado modifique el capítulo reivindicatorio teniendo en cuenta el solicitante debe definir específicamente la materia y el alcance de la invención a través de las características técnicas esenciales que se encuentren enteramente soportadas en la descripción.

Además se debe tener en cuenta que si se quiere reivindicar un procedimiento o un método este debe definirse por una serie de etapas o secuencia de pasos lógicos, si se trata de una composición debe definirse en términos de sus

componentes y proporciones o si lo que se quiere definir es un producto se debe mencionar entidades físicas tales como: objeto, sustancia, composición, sistema, etc.

Cada una de las reivindicaciones esta definidas por el uso de las melaninas, lo cual no es una característica técnica que defina la invención y además el uso no es patentable.

En la reivindicación 1 se menciona una serie de argumentos, ya mencionados en la descripción tales como, cual es el problema a solucionar y porque se realiza la invención, argumentos que no se deben mencionar en las reivindicaciones puesto que no son características esenciales que definan la invención.

La reivindicación 4 define un aparato pero este no esta definido por un diseño, naturaleza, su construcción y funcionamiento, además dicho aparato no se encuentra debidamente sustentado en la descripción ni tampoco en las realizaciones preferidas ya que estas se refieren fundamentalmente a pequeños ensayos donde las melaninas generan una corriente eléctrica pero no se menciona dicho aparato o cual es su funcionamiento, ni principalmente que se genere energía eléctrica, objeto de la invencion. El solicitante debe definir específicamente la materia y el alcance de la invención a través de las características técnicas esenciales que se encuentren enteramente soportadas en la descripción.

6. Unidad de invención(Art 25 D 486)

Esta oficina encuentra dos Grupos Inventivos los cuales están definidos por las siguientes características **esenciales**:

Grupo 1º: método fotoelectroquímico, empleando melaninas (reivindicaciones 1 – 3 y 5 – 9)

Grupo 2º: aparato para el proceso fotoelectroquímico o de producción de energía (reivindicación 4)

Los grupos mencionados anteriormente no presentan un concepto común inventivo puesto que el primer grupo es un método para fotoelectroquímico, mientras que el segundo grupo es un aparato, por lo tanto tendrían un problema técnico diferente a resolver, por lo que la presente solicitud no tiene unidad de invención.

Se sugiere presentar las Solicitudes Divisionales que considere necesarias, ó limitar la solicitud inicial a una sola invención, eliminando de ella las otras invenciones.

7. Conclusión

En cumplimiento del artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le indica que debe dar respuesta dentro del término desesenta (60) días contados a partir de la fecha de notificación de la presente comunicación. En caso de no dar respuesta al presente requerimiento, o si a

pesar de la respuesta subsistieran los impedimentos para la concesión, se denegará la patente.

Se invita al solicitante se sirva indicar, si así lo considera, su renuncia al término faltante y presentarla por escrito

Notifíquese el presente oficio conforme a lo dispuesto en el numeral 5.2, literal e), del capítulo quinto del título primero de la Circular Única No. 10 de 2001.



JOSÉ LUIS SALAZAR LÓPEZ

Director de Nuevas Creaciones (C)

El anterior requerimiento fue notificado por fijación en lista, de fecha

22 JUN. 2012

Elaborado por: Mayra Alejandra Quintero
Revisado por: Gloria Jacqueline Alfonso

ocef



Light induced production of hydrogen from water by catalysis with ruthenium melanoidins

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Abstract

A ruthenium containing melanoidin (a condensation product of amino acids and carbohydrates) was found to photocatalyze hydrogen production from water under light irradiation with $\lambda < 320$ nm, in the presence of EDTA as an electron donor and methyl viologen as an electron relay. Tracer experiments indicate that the hydrogen evolved originates from water. The bimolecular quenching constant for the quenching of melanoidin fluorescence by methyl viologen is large ($k_q \sim 10^9$) suggesting a diffusion controlled reaction rate. The small Stern–Volmer constant ($K_{sv} \sim 10$) indicates an inefficient electron transfer between the excited melanoidin and the methyl viologen, perhaps due to the difficulties in removing O_2 from the polymer. The Ru-melanoidin photocatalyst is stable under prolonged irradiation times and, due to its insolubility in water, is suitable for recycling. © 2000 International Association for Hydrogen Energy. Published by Elsevier Science Ltd. All rights reserved.

1. Introduction

A promising system for the production of hydrogen is the photosensitized reduction of water to hydrogen. The reaction is carried out in the presence of a photosensitizer, a sacrificial electron donor, an electron relay and a catalyst for H_2 evolution. Ruthenium tris (2,2'-bipyridine) complexes [1–4], metal porphyrins [5] and various organic dyes [1,6,7] act as photosensitizers when methyl viologen [1,3,5,6,8,9] or viologen derivatives [3,7,8] are used as electron relays and EDTA, amines [1], H_2S or cysteine [8] represent the sacrificial electron donor. The most efficient catalysts are based on colloidal Pt [12–15]. We have explored the possible

use of ruthenium melanoidin as a novel substitute for the Ru-bipyridyl complex.

Melanoidins are ill defined heteropolycondensates which are formed through condensation of aldehydes with amines. This condensation is frequently referred to as the Maillard or browning reaction [16,17]. The most characteristic type of reaction is that between sugars and amino acids or proteins [18] which is probably one of the most ubiquitous reactions in nature, extending from its occurrence in living organisms through the food industry into being used as one of the models for the formation of sedimentary and soil organic matter of the humic substances type [19–21].

2. Materials and methods

The Ru-melanoidin was prepared by heating at $90^\circ C$ for 96 h a solution of 1 M L-lysine, 1 M D-glucose, 0.1 M Na_2CO_3 and 0.05 M $RuCl_3$. The insoluble mela-

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noidin polymer was recovered by centrifugation and purified by dialysis against distilled water followed by lyophilization. The Ru content of the melanoidin was 2.3% by weight (analysis by emission spectrography). Methyl viologen, Na₂EDTA and all other chemicals were used without further purification. The Carbowax 20 M protected colloidal platinum catalyst was prepared according to the literature [10].

The visible-UV absorption spectrum of the Ru-melanoidin was run as a 0.1 mg ml⁻¹ solution in water (particle size <1 µm) on a Kontron Uvikon-810 spectrophotometer. All the melanoidin solutions were filtered through 0.45 µm filters prior to the spectrophotometric measurements. The excitation and emission fluorescence spectra were run on 0.001 mg ml⁻¹ solution in water in a Perkin-Elmer MPF-44E fluorescence spectrophotometer. The excitation spectra were obtained by 360 nm xenon flash lamp. The spectra were monitored at 550 nm for the emission and corrected for the spectral output of the xenon lamp. The photolysis experiments were conducted in 100 ml Pyrex tubes, either under vacuum or under argon; 40 ml of the unfiltered solution were irradiated with an Osram HBO 200W mercury lamp from a distance of 30 cm. The light was filtered through a 2.5 cm path length cell filled with 200 g l⁻¹ CuSO₄. The light transmission of the solution filter was smaller than 10% at wavelength below 310 nm and above 610 nm. The gas chromatographic analyses of the produced hydrogen were carried out on a Perkin-Elmer Sigma 2B gas chromatograph fitted with a 5 Å molecular sieve column and a thermal conductivity detector. Nitrogen was used as a carrier gas. The hydrogen was sampled

from the gas phase above the solution using a 0.5 ml gas-tight syringe and 0.1 ml was directly injected into the GC.

3. Results and discussions

The UV-visible absorption spectrum of the Ru-melanoidin (Fig. 1) is typical for melanoidins and related materials such as humic polymers, by the absence of any characteristic absorption maxima. The light absorption increases monotonously with frequency which is interpreted as being an additional evidence for the idea that melanoidins are not distinct chemical entities but rather a complex mixture of various components. The fluorescence excitation spectrum (Fig. 2), which closely resembles the absorption spectrum, further confirms that hypothesis. The small peaks appearing at 311, 313 and 318 nm are probably artifacts due to the correction for the spectral output of the xenon lamp rather than authentic excitation maxima.

The absence of a distinct absorption maximum in the Ru-melanoidin spectrum makes the use of monochromatic light in the photochemical experiments unnecessary; consequently the irradiations were conducted with light comprising a large part of the visible and the UV range down to 310 nm. After approximately 10 min irradiation, a deaerated solution containing 4.5×10^{-2} M EDTA, 2×10^{-3} M methyl viologen and a suspension of 0.1 mg ml⁻¹ melanoidin ($= 2.3 \times 10^{-5}$ M Ru) begins to develop the blue color characteristic of methyl viologen radical cation (MV^{•+}). The initial reaction rate for the photoreduction (as measured from the slope of the change in absorbance peak at 600 nm) was 0.014 micromoles methyl viologen ml⁻¹ min⁻¹ (Fig. 3).

Because of the difficulties involved in the estimation of the amount of light scattered by the insoluble melanoidin as well as in the actinometry of a wide spectral range as the one used by us in the light irradiation experiments, no measurements of the photochemical yield were made.

In order to ascertain whether there is a direct reaction between the photoexcited melanoidin and methyl viologen, measurements of the quenching of melanoidin fluorescence in the presence of methyl viologen (MV²⁺) were made. The fluorescence decay curve was deconvoluted assuming a bi-exponential decay with a root mean square deviation (RMS) of 8.8×10^{-3} . A mono-exponential decay was found to lead to a less accurate fitting with a RMS of 41.5×10^{-3} . The possibility that the decay is composed of more than two exponential curves cannot be ruled out, but the experimental noise level makes impossible the testing of this hypothesis. Assuming a bi-exponential decay,

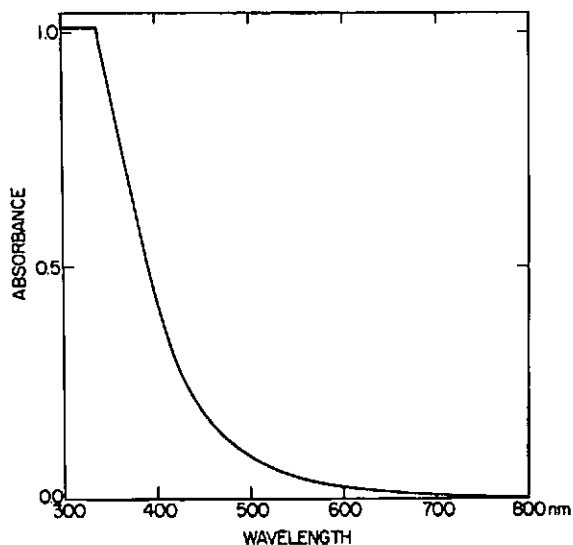


Fig. 1. Visible-UV absorption spectrum of the Ru-melanoidin.

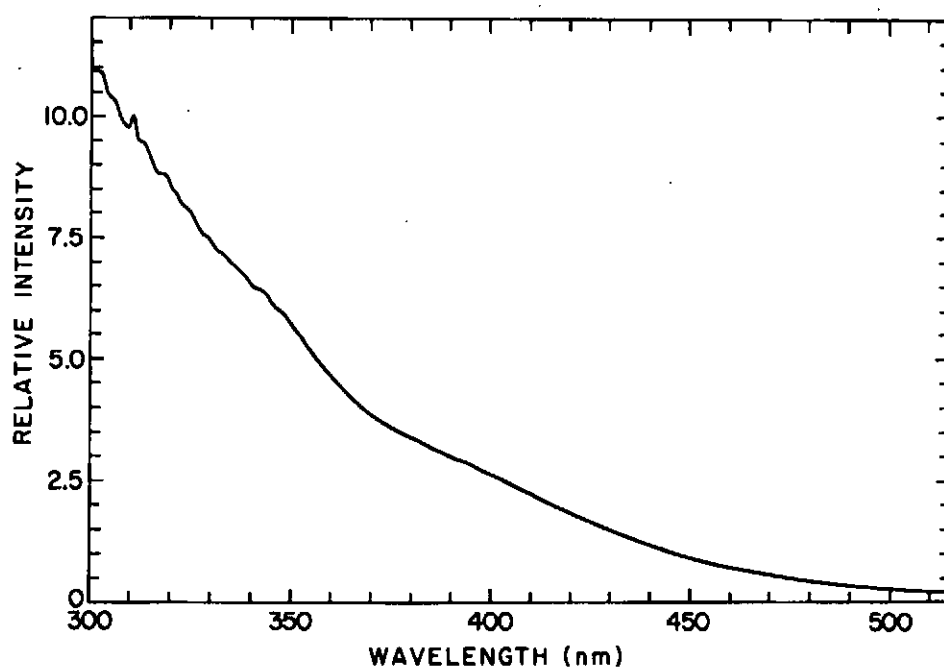


Fig. 2. The corrected fluorescence excitation spectrum of the Ru-melanoidin.

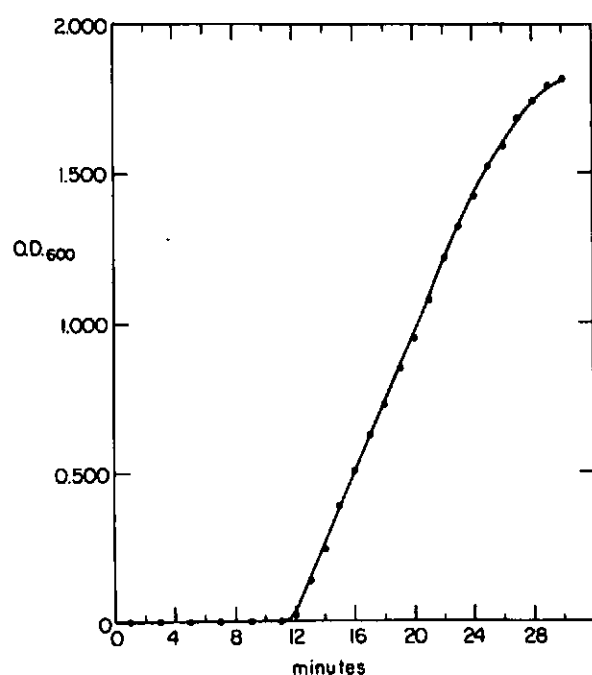


Fig. 3. Photoreduction of methyl viologen by EDTA and melanoidin.

the fluorescence lifetimes were calculated to be $t_1 = 7.3$ ns and $t_2 = 1.3$ ns (Fig. 4).

The fluorescence of melanoidin is quenched by MV. The Stern–Volmer constant K_{sv} and the bimolecular quenching constant K_q as calculated from the slopes in Fig. 5 are shown in Table 1.

The quenching constants K_q are quite large suggesting a diffusion controlled reaction. The Stern–Volmer constants point toward an inefficient electron transfer process. This is obviously due to the very short lifetime of the excited state of the melanoidin. At this point we cannot rule out the idea that traces of dissolved oxygen may be responsible for the quenching of melanoidin fluorescence. It was shown [22] that removal of oxygen from the macromolecular matrix of melanoidin is very difficult and also that oxygen is a very efficient quencher for photoexcited melanoidins. We suggest, therefore, that the K_{sv} values for quench-

Table 1

Lifetime of chromophore (ns)	K_{sv} ($l \text{ mol}^{-1}$)	$10^9 k_q$ ($l \text{ mol}^{-1} \text{ s}^{-1}$)
$t_1 = 7.3$	12.01	1.65
$t_2 = 1.3$	9.78	7.52

ing by melanoidin of methyl viologen fluorescence could be higher than reported here provided oxygen is rigorously excluded. It is possible that the lag period between beginning of irradiation and the initial appearance of MV^+ is due to reaction with oxygen.

When colloidal platinum catalyst is added to the irradiated reaction mixture the blue color disappears and hydrogen gas is evolved due to the reduction of water by MV^+ . In addition, CO_2 and formaldehyde were formed by oxidation of the EDTA⁷ [1]. When the reaction was carried out in 99.75% D_2O , the evolved gas contained (in addition to CO_2) D_2 and HD in a 3:1 ratio indicating that the source for the hydrogen is indeed D_2O . The excess of protons is probably due to isotopic exchange with the acetate buffer.

The production rate of hydrogen was measured in a 40 ml solution containing 0.1 mg ml^{-1} melanoidin, $2 \times 10^{-3} \text{ M } MV^{2+}$, $4.5 \times 10^{-2} \text{ M EDTA}$ and 10 mg l^{-1} colloidal platinum in an acetate buffer, $pH=5.0$. After a lag time of 10–20 min the hydrogen production rate (during 4 h irradiation) averaged 0.14 micromoles H_2 per min. The hydrogen production fell off with longer

irradiation time and stopped after 8–10 h. This is probably due to inactivation of the electron relay MV^{+2} by catalytic hydrogenation [11]. The melanoidin photosensitizer is not inactivated, because experiments in which the melanoidin was separated from an exhausted system and introduced into a fresh mixture showed no decrease in initial hydrogen production rates after ten consecutive transfers. Although the methyl viologen was shown to undergo direct photoreduction when irradiated with near UV light [23], we were unable to detect any hydrogen production when the Ru-melanoidin photosensitizer was absent.

Our results show that Ru containing melanoidin can act as cheap, stable and reasonably efficient photosensitizer for photocatalytic hydrogen production from water. It is also conceivable that a support mounted catalyst system would allow hydrogen production in a flow system. Search for other types of melanoidins (and perhaps natural humic compounds) coupled to the use of more stable electron relays may allow improvement in hydrogen yields and energy conversion efficiency.

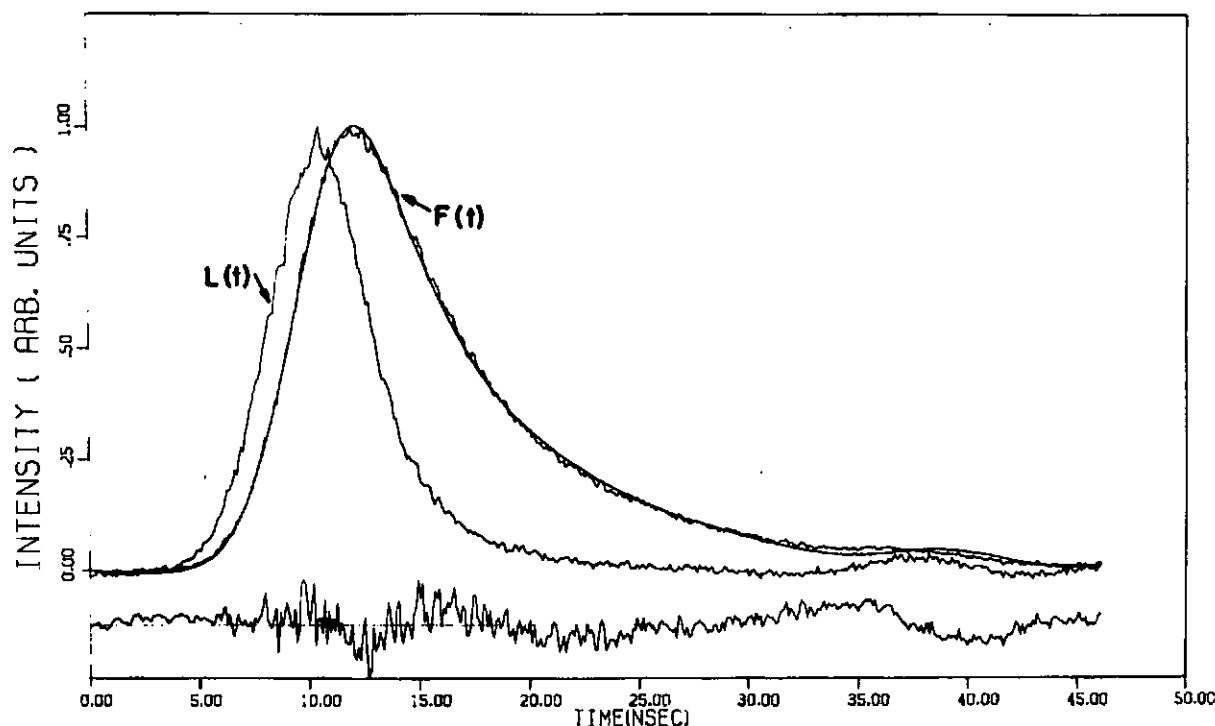


Fig. 4. Analysis of the fluorescence decay of melanoidin. $L(t)$ is the profile of the excitation lamp and $F(t)$ is the experimental profile of the fluorescence. Superimposed on $F(t)$ is the least-squares fit to the experimental points assuming a bi-exponential decay. The lower trace shows the deviations between the calculated curve and the experimental data.

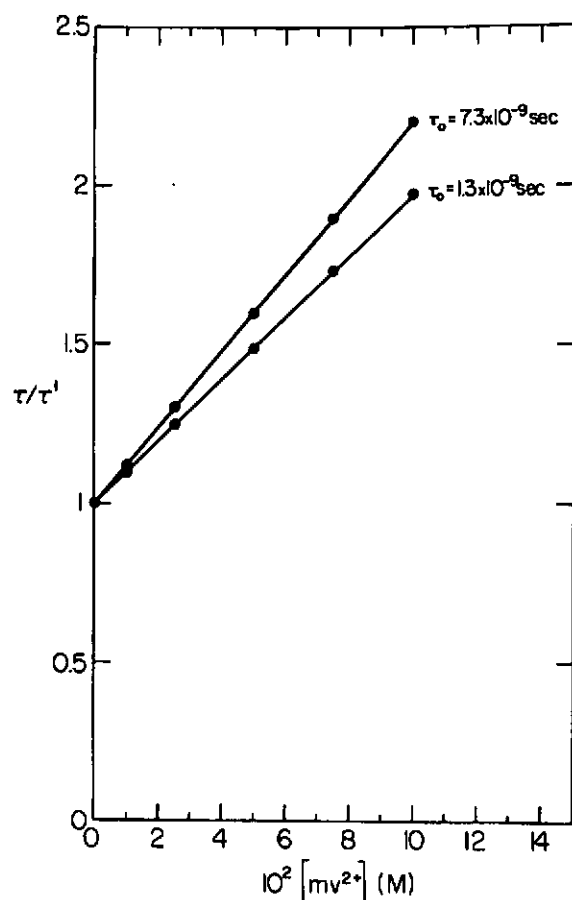


Fig. 5. Stern-Volmer plots of melanoidin fluorescence as quenched by MV^{2+} . The graphs are plotted assuming a fluorescence decay described by a sum of two exponents with corresponding lifetimes of 7.3 and 1.3 ns.

Acknowledgements

We wish to thank Prof. I. Dostrovsky, Dr V. Bromfeld and Prof. R. Tenne (Weizmann Institute) for critical reading of the manuscript.

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