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Photoluminiscence response of Ru(II) complex immobilized in SiO_2-based matrix to dissolved oxygen in beer

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Abstract

The possibility to use the photoluminescence of Ru(II) tris(4,7-diphenyl-1,10-phenathroline) dichloride, immobilized in sol–gel produced SiO_2-based matrix for the determination of dissolved oxygen concentration in beer is studied. Organically-modified silane (octyltriethoxysilane) and mixtures from tetraethoxysilane and octyltriethoxysilane are used as precursors for matrix production. Spin- and dip-coating techniques are applied for films deposition. The predeposition ultrasound treatment of the sol ensures a good sensitivity and a linear sensor quenching response to oxygen in $1 \div 6$ ppm O_2-concentration interval. The CO_2 present practically has no effect on the films performance. Their photoluminescence show rather good stability on prolonged storage in beer.

Keywords: Oxygen sensors; Ru(II) complex; Sol–gel technology; Photoluminescence; Dip-coating; Spin-coating

1. Introduction

Oxygen has an impact throughout the malting and brewing process. It would not be possible to malt barley or ferment wort without the contribution from oxygen. Oxygen reacts with many compounds present in mash, wort and beer, which have an impact on the quality of the final product. Oxidation post fermentation is damaging to the taste and colloidal stability of the beer [1,2]. The excess of oxygen may cause (through a chain of reactions) very rapid collapse of the foam [3]. In order to guarantee highest taste and quality standards, residual dissolved oxygen concentration in bottled beer is keeping under control. Standard procedures for the determination of oxygen in beer bottles are based on electrochemical methods by means of the Clark electrode [4]. Due to their advantages luminescence probes for determination of dissolved oxygen are rather promising for control of the dissolved oxygen levels throughout the brewing process [3,5,6]. The measurement principle is based on the dynamic luminescence quenching of a sensor dye by oxygen. Recently developed sensors explore the changes in the luminescence decay time resulted in the influence of O_2 [2]. Elastomers are applied as dye immobilization matrix [5].

Sol–gel produced SiO_2-based films are often used to provide a micro porous immobilization matrix in which analyte-sensitive fluorophore is entrapped. In the optical oxygen measurements Ru(II) tris(4,7-diphenyl-1,10-phenathroline) is commonly applied as such a fluorophore. The intensity of its photoluminescence emission at 610 nm (caused by blue light illumination) depends on the O_2 content in the analyzed medium. In the literature available no data on the use of such an approach to the dissolved oxygen monitoring in beer were found [3].

Recently we studied in some details the conditions for the preparation of alkoxysilanes based gels and of films deposition in order to obtain films with a good sensitivity and reproducibility of the gaseous and dissolved oxygen measurements with a satisfactory long life time. In the present paper we report results from an attempt to apply the films produced for dissolved oxygen measurements in beer.

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2. Materials and methods

2.1. Materials for films production

Tetraethoxysilane (TEOS, >98%), octyltriethoxysilane (OtEOS, >98%), produced by Merck, Ru(II) tris(4,7-diphenyl-1,10-phenathroline) (100%, delivered by Alfa Aesar) and ethanol (EtOH, p.a., 96%) were used as initial materials. Glass microscope slides, cleaned sequentially using deionized water, methanol and acetone followed by a final deionized water rinse were used as substrates.

2.2. Analyzed samples

Seven types of Bulgarian made and five types of imported bottled beer, randomly chosen, were analyzed at room temperature, as received. The O_2-free (<0.1 ppm) samples from beers and from distilled water were prepared by bubbling of high-purity N_2 for 3 h through the liquid put in closed vessel with a hydraulic gate. CO_2-free deoxygenated water was obtained by the same way but using water preliminary boiled for 2 h at reflux. The water samples with different O_2 concentration were prepared by bubbling of N_2 or O_2 for different periods of time through distilled or CO_2-free distilled water. CO_2-saturated water samples were prepared by bubbling of CO_2 for 2 h through distilled water. The O_2 concentration in the so prepared samples was measured in N_2-filled glove box by an oxymeter Hanna Instruments 9145 with a precision of ±1.5% of the full scale. The oxymeter is working on the electrochemical principle and is not influenced by the presence of CO_2.

2.3. Films production methods and stability testing

To the water–ethanol solution of the precursors (mole ratio EtOH:water:precursor=4:1:0.25; pH of the added water 1, adjusted by HCl), the ruthenium compound (as ethanol solution) was added to the sol in such an amount that a concentration of 2.5 g/l in the so prepared precursor solution to be adjusted. TEOS or mixtures of TEOS+OtEOS (mole ratio 1) were used as precursors. The sol was stirred magnetically for 1 h and aged at 70 °C for 18 h to promote the hydrolysis and condensation prior to coating. In some more details the preparation mode is described in [7]. In parallel, a set of experiments was done applying ultrasound treatment of the sol before aging by means of ultrasound disintegrator Technopan UD 20 (Poland) for 45 min.

Films were deposited by dip-coating at 0.4 mm/s dipping rate at one immersion or by spin coating method (Spin coater Model KW-4A, USA) at 2000–4000 rpm spinning rate, 30 s time of spinning.

The thickness of the so produced films (1×1 cm), measured by a Talystep profilomer, depends on the deposition conditions and is typically around 300 nm for dip-coated films and 7–19 μm for the spin coated ones. Their morphology depends on the deposition mode and, mainly, on the precursor nature [8].

To study the effect of the prolonged action of the beer on the photoluminescence performance, some of the films were stored for 1 to 95 days at −5 °C in beer.

2.4. Photoluminescent measurements

The photoluminescent response (the intensity of the light emitted at 610 nm as a result of excitation by blue/410 nm/light) of the fabricated films was measured by Cary Eclipse device. The relative mean square deviation of the signal intensity is 0.5% (determined by measuring of 5 parallel water samples containing $7.28.10^{-4}$% O_2).

3. Results

3.1. Influence of the production mode on the films response to O_2

The precursors used, the peculiarities in the sol preparation and the films deposition mode applied (dip- or spin coating at different rotation speed) are shown in Table 1.

As it is well known the photoluminescence response of the films to the oxygen content in the analyzed sample is described by the Stern–Volmer equation $I/I_0=1+K_{sv}[O_2]$, where I_0 and I are the photoluminescence signals from O_2-free and O_2-containing samples, respectively, $[O_2]$ – oxygen concentration, K_{sv} – Stern–Volmer constant. The dependences I/I_0 vs $[O_2]$ obtained for the studied films applied for dissolved oxygen measurements in the studied sorts of beer are plotted on Fig. 1 and the calculated Stern–Volmer constants are summarized in Table 1 along with the correlation coefficients characterizing the fairness of the approximation of the experimental data with a straight line expected from the Stern–Volmer equation.

The results obtained show that the thinner films (dip-coated or spin-deposited at a higher spinning rate) show higher values of K_{sv}, i.e. higher oxygen response (films 1–3, Fig. 1a, Table 1). The film produced from OtEOS only shows a weaker quenching response and a little bit worse linearity of the Stern–Volmer plot (films 1, 4;

Table 1
Production mode and oxygen quenching response of the studied films

Film №	Matrix precursor (s)	Ultrasound treatment of the sol	Films deposition mode	Tested liquid	K_{sv}	Correlation coefficient
1	TEOS+OtEOS	No	dip	beer	0.278	0.998 [a]
2	TEOS+OtEOS	No	spin, 4000 rpm	beer	0.261	0.996 [a]
3	TEOS+OtEOS	No	spin, 2000 rpm	beer	0.212	0.992 [a]
4	OtEOS	No	dip	beer	0.196	0.991 [a]
5	TEOS+OtEOS	Yes	dip	beer	0.566	0.9985
6	TEOS+OtEOS	Yes	spin, 3000 rpm	beer	0.370	0.9954
5	TEOS+OtEOS	Yes	dip	water	1.559	0.9999
6	TEOS+OtEOS	Yes	spin, 3000 rpm	water	0.603	0.9999
5	TEOS+OtEOS	Yes	dip	CO_2-free water	1.558	0.9999
5	TEOS+OtEOS	Yes	dip	CO_2-saturated water	1.550	0.9999

[a] For the $[O_2]$ interval 3÷5.5 ppm.