Evanescent-wave cavity ring-down spectroscopy applied to electrochemical ion transfer at liquid–liquid interfaces

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ABSTRACT

Cavity Ring-Down Spectroscopy has been successfully applied to investigate liquid–liquid interfaces in an electrochemical environment. It has been demonstrated that this technique is very sensitive to detect changes in the concentration of species at the interface which absorb at the incident wavelength. Thus, we have shown that this technique can be employed to follow diverse processes at liquid–liquid interfaces involving concentration changes produced by the applied potential. In our contribution, we show for the first time a spectroscopic response of Evanescent Wave Ring-Down Spectroscopy directly originated by charging/discharging processes and ion transfer at the electrochemical double layer of a liquid–liquid interface.

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1. Introduction

Cavity ring-down spectroscopy (CRDS) is a powerful technique with ultrahigh-sensitivity due to the extremely long effective path lengths, in some cases of the order of many kilometres. The principles of the method are well described in several reviews [1–3]. An advantage is that the ring-down time τ does not depend on the amplitude of the light intensity inside the cavity.

Besides the simple configuration for gas phase samples, CRDS has been also employed to analyse condensed media, although some complications must be overcome, since the sample has to be supported by a suitable medium [4–6]. As we have recently demonstrated, a flowing liquid film [7] and a soap film are also suitable for this purpose [8].

An interesting extension of this technique is its application to investigate dynamic processes occurring at interfaces, which makes use of the evanescent wave (EW). In this EW-CRDS approach, the incorporation of an interface into the cavity where total internal reflection (TIR) takes place, ensures that the exponential decay of the light intensity will be sensitive to absorptive losses within the evanescent field beyond the interface. The characteristic penetration depth is given by:

$$d_{\mathrm{p}} = \frac{\lambda}{2\pi\sqrt{n_1^2\sin^2\theta - n_2^2}} \tag{1}$$

where λ is the wavelength of light, n_1 and n_2 are the refractive indices of the two media composing the interface, and θ is the angle of incidence, which should be larger than the critical angle in order to produce TIR. In the case of our experimental configuration for the interface DCM/water, d_{p} is about 200 nm. This approach has been mainly used with optical devices (e.g. prisms, see [3] and references therein). These designs are suited to study adsorption processes. In a recent work of our group, we have coated the surface of a standard quartz prism with active amino-group sites to immobilize target molecules, and it was possible to detect femtomole quantities of labelled biomolecules [9].

Further attractive applications of EW-CRDS are the combinations with other analytical techniques. Particularly, the complementation with electrochemical methods can provide valuable information on interfacial processes under potential control. First attempts have been made by Mazurenka et al. [10] monitoring electrogenerated species within a thin-layer electrochemical cell. In these experiments, the mass transport-limited oxidation of ferrocyanide to ferricyanide in aqueous solution takes place at an electrode located just above the quartz surface of a prism (at 25–250 μm) which forms part of the

cavity. The response accompanying both cyclic voltammetric and step potential chronoamperometry experiments at a variety of electrode-surface distances was presented, and the results were shown to be well reproduced in modeling by finite element methods. Although this was a promising approach, which has also been used to study adsorption/dissolution processes of metallic nano-particles on silica [11], the spectroscopic response was governed by chemical species and processes immediately above the quartz surface, which in turn were driven by the diffusion field extending from the electrode operating under amperometric control, but not from the electrochemical interface itself. The probe-to-quartz surface distance was much greater than the distance the evanescent wave penetrates into the solution.

Recently [3], preliminary EW-CRDS experiments at a liquid/air interface have been reported. Combined EW-CRDS / surface pressure response during a series of repeated film compressions and expansions of a mixed Langmuir film of a labelled phospholipid, has been shown. The periodic and reproducible change in interfacial absorbance with time has been explained by changes in the number of adsorbed molecules within the EW region during film compression and expansion.

In our contribution, we show for the first time a spectroscopic response of EW-CRDS originated by charging / discharging processes and ion transfer at the electrochemical double layer of a liquid–liquid interface.

2. Experimental

The experimental set up is shown in Fig. 1. Since this experiment is performed with an effective "liquid mirror," electrowetting on the cell walls and electrocapillary forces for the LL interface curvature may play a non-negligible role in the optical cavity stability and beam mode properties. Thus special attention has been paid in the design of the cell. Several geometries, sizes and materials have been tested to optimize the set up. The electrochemical cell of PTFE, mounted on an optical table, contains two mobile highly reflective mirrors provided by Layertec GmbH ($R > 99.99\%$ at 532 nm, curvature: 100 mm) at each lateral wall forming a cavity of about 70 mm of optical length. The laser beam enters the cavity through the back surface of one of these mirrors and strikes the liquid–liquid interface at an angle of 75°. This cell was filled with the organic (at the bottom) and the aqueous (on top) solutions and three electrodes were located inside the cell as usual. Two platinum wires were used as working and counter electrodes, and the reference electrode was Ag/AgCl immersed in an aqueous solution of 1.0×10^{-2} M tetraphenyl arsenium chloride (TPhAsCl) (Sigma). The base electrolyte solutions were 1.0×10^{-2} M LiCl (Merck p.a.) in ultrapure water (MilliQ RiOs 16, Millipore) and 5.0×10^{-4} M tetraphenyl arsenium tetrakis(4-chlorophenyl)borate (TPhAsTPhBCl) in dichloromethane (DCM). In some experiments different volumes of a solution of $Fe(phenantroline)_3^{2+}$ was added to the aqueous phase. Cyclic voltammetry was performed using an Autolab electrochemical system (with PGSTAT 302N potentiostat). The potentials values reported are the applied potentials which include $\Delta_o^w \varphi_{TPA+}^0 = -0.364$ V for the transfer of the reference cation, TPhAs +. The alignment of the system is finely adjusted to obtain the maximal signal. The light source was the second harmonic of a pulsed (9 ns–20 Hz) YAG-laser at 532 nm. The beam leaving the cavity was passed through a monochromator and detected using a photomultiplier (Hamamatsu R 928) and 500 MS/s digital storage oscilloscope (Tektronix TDS 320) with an 8 bit vertical resolution. The ring-down time τ was determined by a nonlinear fitting program (an example is shown in Fig. 1).

3. Results and discussion

The stability of the cavity for the interfaces investigated has been carefully verified. The ring-down time remains constant for long times in all the cases. However, a large difference in the absolute values has been obtained for the different systems. In the case of the interfaces built between DCM and air or DCM and water, an average value of about $\tau \approx 140 \pm 4$ ns has been observed, which indicates about 300 passes of the beam through the media. When lipophilic ions are dissolved in the organic phase, necessary for the electrochemical experiments, a drastic reduction of the decay time is observed ($\tau \approx 35 \pm 1$ ns). In spite of its shortness, even in this case a ring-down time can be analyzed. Independent spectrometrical experiments in bulk solution have shown a very weak but non-vanishing absorption of the salt. The absorbance can be calculated from the ring-down times through [9]:

$$L = \frac{d}{2.3\,c} \left(\frac{1}{\tau_{col}} - \frac{1}{\tau_o} \right) = \varepsilon\,C\,d_{op} \tag{2}$$

where τ_o and τ_{col} are the ring-down times measured in the absence and in the presence of the absorbing species, respectively; c is the speed of light, d is the total cavity length (7 cm in our case), C is the concentration of the absorbing species, ε is the molar extinction coefficient, and d_{op} is the optical path length. In this particular case, the sample fills the cavity such that $d_{op} = d$. Introducing the experimental parameters, we obtain $\varepsilon \approx 0.7$ M^{-1} cm^{-1}. However, it is possible that the ions adsorbed at the interface show an enhancement of the absorption coefficient and produce the noticeable decrease of the ring-down time.
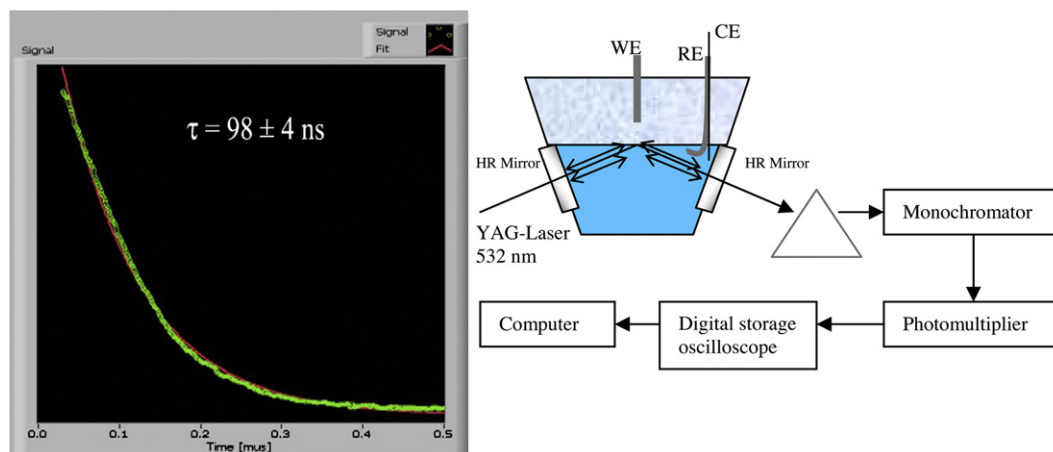

Fig. 1. Experimental set-up. WE: working electrode; RE: reference electrode; CE: counter electrode. A typical time decay τ (green line) and the corresponding fit (red line) are shown at left.
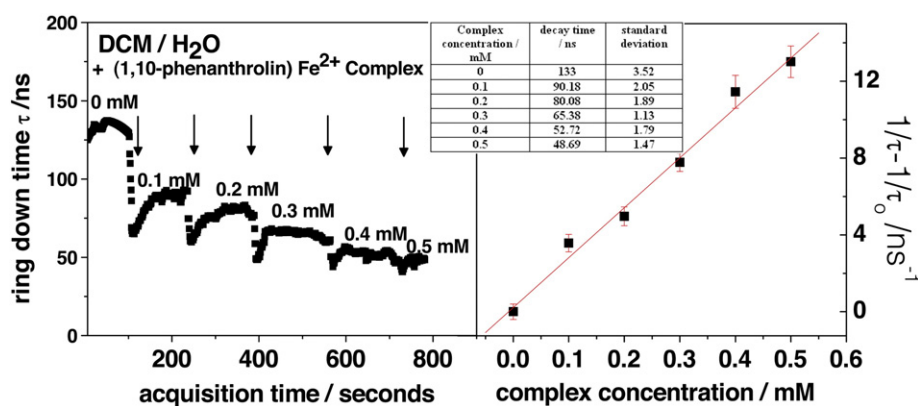
Fig. 2. (left) Effect on the ring-down time of successive additions of a colorant in the aqueous phase. (right) Losses calculated according to Eq. (2) for the different concentrations of colorant in the aqueous phase.

Fig. 2. shows the effect of successive additions of a colorant absorbing at 532 nm in the aqueous phase. Immediately after each additional droplet, a strong reduction in decay time is observed followed by a recovery. This is an effect of the interface perturbation (movement, concentration inhomogeneity). On the left, the decrease on the stabilized ring-down time as a function of colorant concentration is shown. On the right, a linear relationship of the losses is evident for the concentration range investigated.

We obtained a value of ε of about 38000 M^{-1} cm^{-1}, assuming as typical [3], an effective thickness of three times the calculated evanescent field penetration depth ($d_{op} \approx 600$ nm). This value seems to be much higher (about three times) than that obtained by conventional UV-visible spectroscopy measurement. One feasible explanation could be that an accumulation occurs near the interface. In surface adsorption experiments, the value ε could be different from that of the free species,

and resonant dispersion effects may make appreciable contributions to the observed losses as has been mentioned above in the case of the organic salt. Also the effective thickness could be larger. If we assume the bulk value of $\varepsilon = 8570$, the effective thickness results $d_{op} = 2.5$ μm. At the moment, we cannot distinguish between these both effects.

We can also estimate the lowest concentration that we can detect. As reported above, the addition of the first aliquot of colorant (0.1 mM) produces a decrease of 43 ns in decay time. If we consider the standard deviation of 3.5 ns as detection limit, we can distinguish a decrease of up to 8 μM in the concentration.

Finally, Fig. 3 shows the highlight experiment of this contribution, which demonstrates the sensitivity of EW-CRDS to investigate processes directly occurring at electrochemical interfaces. During a potential sweep at 7 mV/s applied at a polarizable liquid–liquid interface, the ring-down time has been recorded simultaneously with the current. In the double layer region, where an accumulation of ions takes place at both sides of the interface without occurrence of any transfer process, and no significant current is measured, the ring-down time is small ($\tau \approx 35 \pm 2$ ns). This value is almost that obtained at open circuit potential. This value of τ is also observed if the organic phase is in contact with pure water (without the LiCl salt). At the turning potential, where the ions transfer between both phases occurs and current is flowing, we observe an appreciable increase of the ring-down time ($\tau \approx 60 \pm 1$ ns). This change involves a decrease of a factor of about 2 in the interfacial concentration (estimated using Eq. (2) and considering the same εd). This factor seems rather larger if we take into account the current observed. This phenomenon is observed at both positive and negative turning points, when either the organic cation or the organic anion is transferred into the aqueous phase, producing a depletion of their concentration at the organic side of the interface. A tentative explanation is that the absorption coefficient of the organic salt, in both forms as cation and anion, is enhanced at the interface and produce the strong decrease on the ring-down time when they are adsorbed. Near the positive and negative turning points, the ions are transferred through the interface; therefore their concentration at the interface decreases, the absorption is diminished, and hence the ring-down time increases. More experiments with different salts and concentration are needed in order to quantify these effects.

Further addition of the colorant at the aqueous phase at open potential circuit, produces a decrease on the decay time to $\tau \approx 20 \pm 2$ ns. Electrochemical studies [12] indicate strong potential dependence of adsorption processes of the complex. However, the decrease on τ is too large and goes beyond the time scale to detect and measure accurately. Therefore, it is necessary to perform systematic investigations with various species having different absorption coefficients in order to elucidate this behaviour. These studies are already in progress.
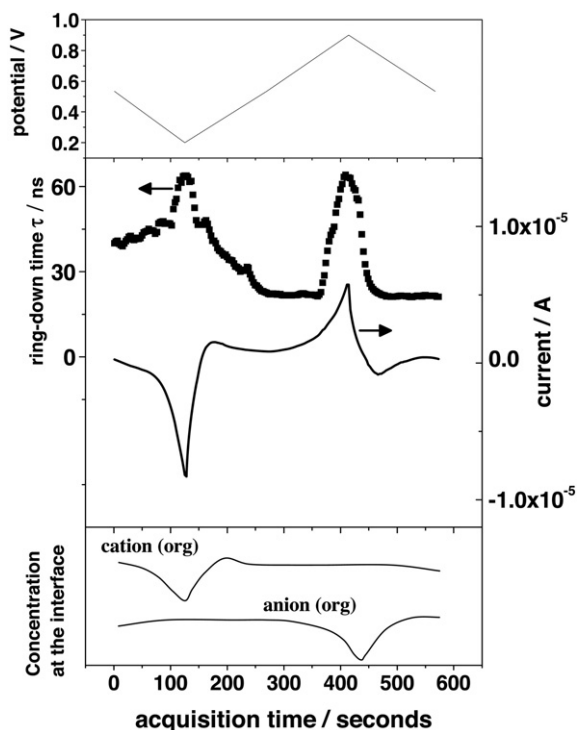

Fig. 3. (upper part) Potential–time program applied at the liquid–liquid interface. (middle part) Ring–down time and current response of the system. (bottom) Schematic representation of the concentration changes of cations and anions in the organic phase.

4. Conclusions

We have demonstrated that CRD-spectroscopy is a highly sensitive technique to detect small changes on the concentration of absorbing species at liquid–liquid interfaces. An advantage of this method in comparison with other spectroscopic techniques is that the ring-down time τ does not depend on the amplitude of the light intensity inside the cavity. A definite improvement of the ring-down method over other spectroscopic measurement is that it essentially measures absorption losses (and thus concentrations) directly in real-time and would appear to have great potential for the investigation of the kinetics of a wide range of electrochemical processes.

The important distinction with previous attempts is that in our case the response comes directly from the interface instead of being driven by the diffusion field extending from the electrode. This allows following kinetic charging–discharging processes without mass transport limitations. This report shows the first insights of the implementation of this method to electrochemical LL interfaces. Obviously, a systematic investigation is necessary to obtain quantitative results.

Acknowledgments

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