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Electrochemistry of single droplets of inverse (water-in-oil) emulsions⁺

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We demonstrate the feasibility of electrochemically detecting individual water droplets dispersed in an oil phase (inverse emulsions) *via* the use of a redox probe confined in the droplet phase. The water droplets were tagged with potassium ferrocyanide, and were injected into an electrolyte cyclohexene/dichloromethane oil solution. *Via* simple cyclic voltammetry scans it is shown that single water droplets from a water-in-oil emulsion can be detected provided that rapid anion transfer from the oil to the water phase maintains electroneutrality in the droplet.

The physiochemical properties of emulsions (liquid colloids), have received much scientific attention in recent years.¹⁻³ In general, emulsions can be classified into two categories: (type I) oil-in-water emulsion (O/W) and (type II) water-in-oil emulsion (W/O). Such biphasic interfaces underpin the chemistry of applications as diverse as those of shampoos, liquid phase separations, phase transfer catalysis, corrosion, demineralization, leaching, drug delivery and the operation of living cells.⁴⁻¹⁰ Many of these involve redox and charge transfer processes across the interface, and in particular ion transport.¹¹ Consequently, electrochemistry may be a powerful tool to probe the relevant mechanistic and rate details. Traditionally, such studies have been conducted using a four electrode system comprising two reference and two counter electrodes with a macroscopic biphasic interface.¹² Subsequently, and building on the pioneering work of Scholz et al. on the voltammetry of immobilized particles,^{13,14} Marken et al.15 studied oil droplets immobilized on the surface of an electrode. This latter work developed rapidly and Hellberg¹⁶ was the first to detect stochastic capacitative signals arising from an adhesion process of a single liposome impacting a polarized electrode from bulk solution.

Later, it was shown that faradaic signals can be observed upon collision of individual O/W droplets containing a redox active species,^{17–19} so providing analytical insight on the molecular content of an individual emulsion. Together with this analytical insight, information on the kinetics and thermodynamics of ion transfer could be gained.²⁰ Hitherto, the electrochemistry of O/W emulsions (type I) has been addressed exclusively; in the present work we report on the electrochemical detection of individual W/O emulsions (type II) hence generalising the feasibility of electrochemically monitoring of single emulsion droplets formed by any two immiscible phases. This combines the ease of the electrode-droplet impact electrochemistry with the single event approach recently developed by Laborda et al.21 and allows the facile monitoring of ion transfer at the water/oil interface. Moreover, it is shown that cyclic voltammetry coupled to low noise electronics allows the electrolysis of the content of water-in-oil droplets and the clear inference of the chemical identity of the ion transferred in or out of the droplet as a result of the need to maintain net electro-neutrality.

First, water-in-oil emulsions were prepared by controllably injecting water droplets with and without 0.50 M potassium ferrocyanide into a solution composed of cyclohexene/dichloromethane (1:1). 1% Span 80 was used as an emulsifier (see ESI†). During the water droplet injection the solutions were stirred vigorously to allow the formation of emulsions. The resultant solutions contained high concentrations of water droplets with sizes ranging from 80–500 nm in radius, as demonstrated by Dynamic Light Scattering (DLS) measurements (see Fig. S1, ESI†), using known viscosity of the mixed solution (η = 0.53 mPa s²²) and refractive index of 1.43.^{23,24}

Next, the emulsions were investigated voltammetrically. For all measurements, a carbon fibre disk microelectrode ($r = 3.5 \mu$ M) was used as a working electrode, Ag wire was used as a 'pseudo' reference electrode and a Pt wire served as the counter electrode, with all electrodes placed in the oil phase. The 3 – electrode setup together with an in-house built low noise potentiostat²⁵ enabled the investigation of the electrochemical properties of the W/O emulsions and potentially the electrolysis of redox species

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Fig. 1 Cyclic voltammetry of W/O emulsions in DCM/cyclohexane mixture. (a) Without 'redox probe' (black line) and with 0.5 M potassium ferrocyanide confined 'redox probe' (red line) without electrolyte in the oil phase (b) W/O emulsions with 0.5 M potassium ferrocyanide and 0.1 M of TBA⁺ClO₄⁻ in the oil phase. A scan rate of 10 mV s⁻¹ was used in all experiments.

confined within single droplets. The microelectrode was introduced into the emulsified solution and voltammograms were measured by scanning from -0.20 V vs. Ag to 0.80 V vs. Ag and back to -0.20 V vs. Ag, which provided a suitable electrochemical window to observe ferrocyanide oxidation. As shown in Fig. 1a, in the presence of the ferrocyanide containing emulsion a broad redox peak is observed at E_p = 300 mV vs. Ag reference electrode. The magnitude of this voltammetric feature increases as a function of the submersion time of the electrode (Fig. S2, ESI⁺). Hence, it is concluded that this feature likely arises from the electro-oxidation of ferrocyanide adhered to the electrode surface probably in the form of droplets so that electrochemically the system behaves similarly to that of threephase junction required for the electrolysis of immobilized oil droplets.^{4,14,15} Upon addition of suitable supporting electrolyte (0.1 M tetrabutylammonium perchlorate) to the oil phase, a clear cathodic shift is seen for the surface bound wave, with redox peak at E_p = 105 mV vs. Ag reference electrode, likely indicating a more thermodynamically favourable process,²⁶ but subject to the use of a 'pseudo' reference electrode. In addition to the observed surface bound wave, clear stochastic oxidative events were observed at higher overpotentials during the course of the voltammetric scan (Fig. 1b). These stochastic events are similar to previously reported results of nanoparticles oxidation where discrete events expressed as current spikes are seen during voltammetric²⁷ and chronoamperometric scans and reflect the electrochemistry of an individual colloid. Thus the spikes likely signal the arrival of new droplet at the interface via diffusion from bulk solution.

The above results demonstrate that without electrolyte in the oil phase no current spikes were observed. The altered behaviour of the system in the presence and absence of electrolyte in the oil phase signals the role of the electrolyte in the charge transfer process. Specifically, the effect of anions at the oil phase likely arises from their potential role in neutralizing the charge upon ferrocyanide oxidation:¹⁴

$$\operatorname{Fe}(\operatorname{CN})_{6}^{4-}(\operatorname{aq}) + \operatorname{X}^{-}(\operatorname{oil}) \rightleftharpoons \operatorname{Fe}(\operatorname{CN})_{6}^{3-}(\operatorname{aq}) + \operatorname{X}^{-}(\operatorname{aq}) + \operatorname{e}^{-}$$

It is worth noting the existence of surface bound wave in the two voltammograms including when no electrolyte is used, indicating that on the voltammetric time scale (seconds) the charge transfer process is not significantly impeded. The oxidation and reduction of the immobilized droplets as seen in Fig. 1a probably reflects slow injection of anion impurities from the oil phase or alternatively depletion of potassium cations from the water phase to the oil phase. However, rapid individual oxidation of droplets arriving from the bulk (time scale of ms) cannot be seen unless a suitable anion such as 0.10 M ClO₄⁻ was used as part of the supporting electrolyte in the oil phase (Fig. 1b). Consequently, the nature of the electrolyte added to the oil phase was examined. It can be seen from Fig. S3 (ESI[†]) that the cyclic voltammograms measured differ with the choice of the anion X⁻ used in the oil phase. Thus, the most hydrophilic anions, ClO_4^- or $BF_4^{-,28,29}$ allow the electrochemical detection of single W/O droplet collisions during the voltammetric scan, while larger hydrophobic anions such as FAP⁻ and $[NTf_2]^{-30,31}$ (or without any electrolyte) do not exhibit this stochastic process. The voltammograms of the emulsified solutions with CF₃SO₃⁻ and PF₆⁻ anions in the oil phase produced only rare events of stochastic collision, with as much decreased impact frequency compared to more hydrophilic anions³² (for example see single spike observed in Fig. S3b when $CF_3SO_3^-$ was used in contrast with the 31 spikes shown in Fig. S3d when BF₄⁻ was used, ESI[†]). These results are consistent with the reported values of the Gibbs energy of the anion transfer from organic solvents to water for various of the ions here considered:33-37

$$\Delta G_{\mathrm{PF}_{6}^{-}}^{0,\mathrm{O}\to\mathrm{W}}\left(-4.2 \text{ kJ mol}^{-1}\right) \gg \Delta G_{\mathrm{ClO}_{4}^{-}}^{0,\mathrm{O}\to\mathrm{W}}\left(-14.9 \text{ kJ mol}^{-1}\right)$$
$$> \Delta G_{\mathrm{BF}_{4}^{-}}^{0,\mathrm{O}\to\mathrm{W}}\left(-17 \text{ kJ mol}^{-1}\right)$$

Hence, it can be understood that thermodynamic consideration should be taken into account for selecting the appropriate electrolyte, together with kinetic requirement of sufficiently rapid insertion of anions from the oil phase to the water droplet if single droplet processes are to be seen.

Table 1 Experimental conditions used for the investigation of single water droplet electrochemistry. The variable was the nature of the anion at the oil phase and the corresponding occurrence of current spikes, or no spikes, is indicated

Water phase	Oil phase	Spikes
0.50 M K ₄ Fe(CN) ₆	None	No
0.50 M K ₄ Fe(CN) ₆	$0.10 \text{ M TBA}^{+}\text{ClO}_{4}^{-}$	Yes
0.50 M K ₄ Fe(CN) ₆	$\mathbf{F}_{\mathbf{F}} = \mathbf{F}_{\mathbf{F}} = \mathbf{F}_{\mathbf{F}}$ 0.10 M TBA ⁺ BF ₄ ⁻	Yes
0.50 M K ₄ Fe(CN) ₆	F = 0 F =	Rare
0.50 M K ₄ Fe(CN) ₆	F = F = F = F $F = F = F$ $F = F$	Rare
0.50 M K ₄ Fe(CN) ₆	$\begin{array}{c} & \Theta \\ F_3CF_2C & F \\ F_7 & CF_2CF_3 \\ F_3CF_2C & F \\ 0.10 \text{ M TBA}^{\dagger}[FAP]^{-} \end{array}$	No
0.50 M K ₄ Fe(CN) ₆	$[C_{10}M]^{+}[NTf_2]^{-}$	No

The results of all anions used are summarised in Table 1 where it can be concluded that small hydrophilic anions such as ClO_4^- or BF_4^- allow the observation of single W/O droplet collision during the voltammetric scan.

Further investigation of the electrochemical process was conducted via chronoamperometry. Measuring the current as a function of time at a specific applied potential allows the designation and resolution of the integrated charge of each individual current spike. Fig. 2a shows the chronoamperometry of water emulsions in DMC/cyclohexane solution with 0.1 M of $TBA^+ClO_4^-$ in the oil phase, with and without 0.50 M potassium ferrocyanide. The current was measured over a 50 s time scale with the electrode held at an oxidative potential of 0.80 V vs. Ag wire. As can be seen, a 'featureless' current-time plot was observed in the case where the W/O emulsions did not contain a redox probe (black chronoamperogram). However, when the emulsions contained 0.50 M potassium ferrocyanide together with 0.10 M $TBA^+ClO_4^-$ as an oil phase electrolyte, clear stochastic current spikes were observed (red chronoamperogram). The duration of the oxidative current spikes was around 10 ms (Fig. 2a inset), consistent with the shape of the oxidative events being limited by the electrical response of the measurement system (lowpass filter 100 Hz).³⁸ From integration of the individual spike features the charge passed per event can be measured. Fig. 2b depicts the distribution of the injected charge per single collision of a water droplet, where the mean charge is found to be $\mu_Q = 11.7 (*/2.33) \text{ fC.}^{39,40}$

From the calculated charge and assuming a spherical droplet and 100% oxidation of the droplet content, the effective mean radius of the water droplets were determined to be $\mu_r = 39$ (*/1.32) nm (calculation in ESI†). Assuming the diffusion coefficient of the water droplet is inversely proportional to the radius of the droplet (under assumption of a spherical shape) as predicted by the Stokes–Einstein equation, then the expected electrode collision frequency has a size dependency.⁴¹ Consequently, the 'nano-impacts' technique is biased towards the observation of smaller sized particles. Conversely, the unweighted size measured *via* the DLS is biased towards the larger particles with higher intensity of light scattering by larger particles. Hence,



Fig. 2 Chronoamperometry of water emulsions in DMC/cyclohexane solution at 0.80 V vs. Ag wire. (a) Without 'redox probe' (black line) and with confined 0.50 M potassium ferrocyanide (red line). (b) Histogram of the injected charge distribution from a single W/O emulsions with 0.50 M potassium ferrocyanide and 0.10 M of $TBA^+CIO_4^-$ in the oil phase.



Scheme 1 Two possible outcomes taking place upon a collision of a water droplet with a polarized electrode.

the discrepancy between the size measurement made by the nanoimpacts methodology (39 nm) and that obtained from DLS 80–500 nm, may in part reflect the differing diffusion coefficients of the poly-dispersed particles, alternatively just partial oxidation of the droplet content occur at the time scale of the impact.^{42,43}

From these results, we postulate the following mechanism for ferrocyanide oxidation confined in W/O droplets, shown in Scheme 1. At the first, redox probe tagged water droplets in oil move freely in solution (Scheme 1). Upon random collision of a single droplet at the electrode surface, the rate of ferrocyanide oxidation will depend on the ion transfer from the oil phase to the water phase. When a large hydrophobic anion is used, ion transfer from the oil phase to the water phase is less favourable, $\Delta G_{X^-}^{0,O \to W} > 0$ (Scheme 1(2b)). Consequently, stochastic events of individual collision are not seen. On the other hand when the ion transfer is energetically favourable $\Delta G_{X^-}^{0,O \to W} \ll 0$, for example when small hydrophilic anions are used, fast anion transfer from the oil phase to the water phase takes place allowing the necessary charge neutrality process to occur rapidly. This is reflected by the observed current transients of single emulsions colliding with the microelectrode (Scheme 1(2a)). In addition to any stochastic events, a surface bound wave is seen in all cases, which implies that a slow oxidation process is feasible as discussed above, including when no electrolyte is used. However, the kinetics of the ion transfer injection between the two immiscible phases will be the dominant factor for observing fast heterogeneous oxidation events of the water tagged droplets.

In conclusion, we have evidenced the electrochemical measurement of single droplets content from an emulsified solution (water-in-oil), one at a time. The strength of the technique relies on the simplicity of the experimental setup, which is based on cyclic voltammetry at slow scan rates and a redox probe confined in the droplet. From the voltammograms, the biphasic chemistry underlying the charge injection is shown to be dependent on the ionic composition of the electrolyte in the oil phase. Regardless of the anion used and also in the case of no electrolyte in the oil phase, a surface bound wave is seen during the slow scan voltammetry, indicative of reaching net charge neutrality over long time scales (seconds). However, rapid (ms time scale) stochastic events arising from single droplet electrochemistry can be observed only when small, hydrophilic anions are used since they allow fast charge net electro-neutrality to occur via ion transfer from the oil phase to the water phase. The latter observation can be explicitly seen using cyclic voltammetry measurements coupled to a low noise electronic apparatus. The strength of probing single collision event during slow voltammetric scan is manifested by the ability to gain insight of ionic transfer in a single experiment, similar to previous reports on nanoparticle/ionic liquid solution.²⁷ It is therefore concluded that very rapid ion transfer from the oil phase to the water phase is necessary for the charge transfer to occur at colliding droplets and may be a rate determining step of the process.

The present study shows that it is possible to electrochemically probe emulsions existing in any desired two immiscible phases by making use of redox tags inside the droplet.⁴ Also, the large Ohmic resistance of the non-aqueous phase and the large capacitive currents at the liquid/liquid interface commonly seen in the classic four-electrode arrangements,¹² can be largely overcome with the presented approach.

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- 42 Theoretically, the expected frequency of emulsions impacting a micro-electrode can be calculated by integrating the Shoup-Szabo equation.⁴³ The collision frequency will increase with increased electrode size and particles concentration and decreased particles size (higher diffusion coefficient). The experimental spike frequency (~ 12 Hz, see Fig. S4, ESI[†]) was close to the theoretically predicted frequency for 39 nm droplets (~ 5.8 Hz). Since the experimentally observed is not significantly higher than the theoretically expected frequency it cannot be fully concluded if a full oxidation of the droplet content occurs during a single stochastic impact event as opposed to an alternative interpretation of nonexhaustive oxidation of the ferrocyanide load of larger droplets.
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