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Simulations employing finite element methods at liquid|liquid interfaces

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Abstract

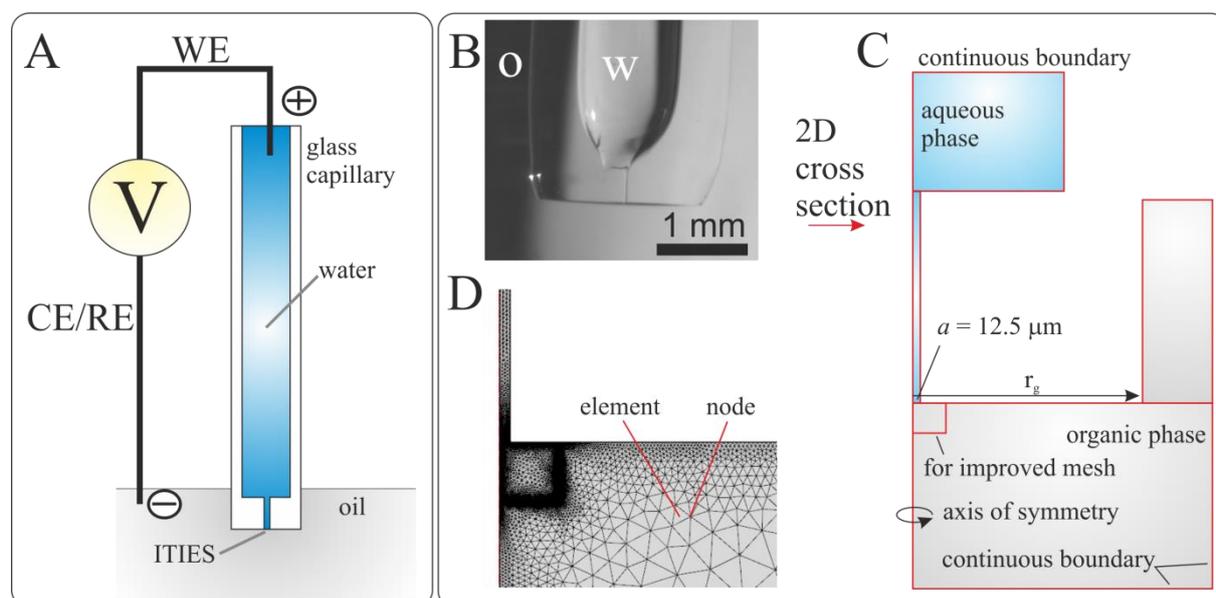
Simulated curves compared to recorded data have provided a breadth of insight into mechanisms and kinetic aspects of charge transfer at the liquid|liquid interface (LLI). This is often performed with software employing finite element methods (FEMs). The advent and application of this asset to soft interfacial chemistry has allowed a more facile exploration of geometric considerations, the role of interfacial size (from macro to nano), while simultaneously expanding to include homo/heterogeneous reactions such as electrocatalytic, photochemical, nanoparticle interactions, etc. This article hopes to provide insight into the status of the field of LLI FEM studies as well as provide a perspective as to what role simulations and numerical analysis will play in the future.

1. Introduction

Finite element simulation software is ultimately a synthesis of established analytical equations with geometric components. These can then contain complex material properties or be combined with multiple equation sets, *e.g.* heat transfer with electrical conduction. The degree of complexity of these systems necessitates their numerical simulation. To facilitate this, the geometry is subdivided by a mesh consisting of elements, *e.g.* free triangular or quadrilateral. In this *discretisation*, the problem is then solved for each element and subsequently compared

to the whole. FEM has been an invaluable utility for electrochemists in battery, materials, mass transport problems, *etc.* and has been comprehensively reviewed by Britz and Strutwolf [1]. More complex simulations of electrochemical systems, for example by molecular dynamics or by density functional theory, are outside the scope of this article.

Electrochemistry at interfaces between two immiscible electrolyte solutions (ITIES) is a distinct and versatile area of contemporary electrochemistry, as summarised by recent reviews [2-7]. This review will focus on digital simulations of electrochemical processes at ITIES, highlighting the applications as well as the perspectives. Scheme 1 illustrates the development of a simulation from the experiment, in this case an interface held at the tip of a pipette – a micro-ITIES, as well as mesh refinement. Refining the mesh can be a particularly challenging aspect of the FEM; too fine and run-times become prohibitively long, too coarse and the result is not accurate or precise. Great care should be given to this step, with comparison using simple mechanics to known analytical solutions before moving forward with more exotic systems.



Scheme 1: **A** schematic of a micropipette ITIES experimental setup; **B** photograph of the pipette tip immersed in an organic phase (o) with an aqueous (w) solution held inside and the interface at the tip; **C** the pipette tip converted to 2D axial symmetric geometry, taking advantage of the infinite rotational symmetry C_∞ element of the cylindrical capillary and further reducing it in half greatly reduces the computational effort and simulation run time; **D** The mesh surrounding the simulated ITIES. A box has been added to better refine the mesh in the area of hemispherical diffusion in the vicinity of the ITIES on the o side.

2. Charge transfer simulations at an ITIES

While conventional electrochemistry operates at a solid|liquid interface, *e.g.* metal (Pt, Au, *etc.*) or carbon, fundamentally analogous charge transfer reactions can take place at LLIs such as water|oil (w|o), or even w|ionic liquid (w|IL). This means that the same electrochemical techniques (*e.g.*, cyclic voltammetry (CV)) and theory of charge transfer can be transposed to so-called soft interfaces. This is advantageous as LLI electrochemistry is not limited to redox electrochemistry, but also includes simple and facilitated ion transfer (FIT) reactions, where ions are pushed or pulled across an interface. Simple ion transfer (IT) is given through the following:

$$i_w^z \leftrightarrow i_o^z \quad (1)$$

Ions are manipulated by biasing the potential across the ITIES using electrodes immersed in either phase. The potential drop is localised across the w|o interface (~ 1 nm) and called the Galvani potential difference ($\phi_w - \phi_o = \Delta_o^w \phi$). $\Delta_o^w \phi$ is controlled *via* electrodes positioned in either phase. In this way, $\Delta_o^w \phi$ is similar to E or the potential drop across a solid|liquid boundary and the kinetics of IT are often handled using Butler-Volmer equations [2]. These equations often form the basis for most simulations, which can then be expanded upon for further complexity. Indeed, the driver for digital simulations is often the absence of a simplified analytical solution.

3. Fundamental Studies

Droplet or thick-film modified electrodes are one macro-ITIES system often simulated, with electron transfer (ET) across the electrode-droplet interface coupled to IT across the LLI. Dassie *et al.* [8] recently explored a solid electrode completely covered by a thick organic film, which was then immersed in an aqueous phase, using a 1D simulation. They showed [8] that the coupled effect of ET at the solid|o interface with IT at w|o had an appreciable influence on the shape, peak-to-peak potential difference, as well as the mid-peak potential in the i - V curve. The numerical simulations could satisfactorily explain deviation from the 59 mV expected for a reversible ET or IT reaction. This approach is actually similar to typical ionophore based ion-selective electrodes (ISE), where a solid conducting polymer is used for ET that is coupled with transfer of an analyte ion across the water-membrane interface. Simulations of these kinds have been considered by Lewenstam utilising Nernst-Planck-

Poisson equations [9], and by Amemiya [10,11] and Bakker [12,13] for the fully electrolyte supported case; *i.e.* Fick's laws of diffusion.

These simulations were extended to 2D to study coupled ET-IT reactions upon collision of organic droplets with an electrode [14], considering both diffusion and migration. In this case, the secondary or tertiary current distribution was also solved to show that the iR drop in the toluene solution is negligible. Furthermore, both the entire electrode|o and w|o surface are electrochemically active, despite higher current densities at the three-phase boundary. From comparison with the experimental data, it was apparent that the colliding droplets had quite high contact angles with the electrode after collision.

Meanwhile, the exact mechanism of electron transfer across LLIs has been a subject of controversy [2]. This topic was recently revisited by combination of experiments and FEM simulations of ET between ferrocene (Fc) and hexacyanoferrate (FeCN_6^{4-}) [15]. Comparison with experimental and simulated CVs indicate that the likely mechanism is one of potential independent Fc partitioning to w with subsequent Fc oxidation/ FeCN_6^{4-} reduction in the bulk aqueous phase, followed by potential dependent Fc^+ transfer back from w \rightarrow o. These data agree well with the earlier experimental and simulated results of Osakai [16]. If a gold nanofilm was added to the interface, it behaves as a bipolar electrode and electrons are shuttled through the gold film in a heterogeneous interfacial redox electrocatalysis [15,17].

1D simulations have provided insight into differential capacitance at the back-to-back double layers formed when a LLI is established. These showed that the width and symmetry of the two interfacial regions are crucial parameters and experimental capacitance data could be used to estimate the width of the interfacial region, which the authors suggest is ~ 3.3 nm [18]. FEM was also used to calculate the current distribution in a large rectangular cell with smaller electrodes, ruling out the current distribution as an explanation for the driving force for a Marangoni shutter where gold nanoparticles, adsorbed at the ITIES, move to the center of the cell and to the edges as a function of the applied polarisation [19].

Additionally, FEM has been utilised for detailed characterisation of a flexible thin layer electrochemical flow cell for ultrasensitive amperometric detection at an ITIES, reaching nanomolar detection limits [20]. If ITIES based devices become more common, this kind of simulation will be extremely useful for device optimisation. The recent use of macro scale (mm \rightarrow cm) models suggests that there is a thriving field of study for bulk material properties, their interaction with the LLI, and the fundamental interrogation of the LLI's physical properties.

With the rapid development of modern micro [21,22], and nano fabrication techniques, there was a push towards miniaturisation owing to a number of benefits. These included reduced capacitance/solution resistance due to the lower operational current range and thus, no longer required iR -compensation. This meant that the interfacial surface (*e.g.* radius of a disc interface) was smaller than the diffusion layer thickness ($\delta \approx (Dt)^{1/2}$) at most scan rates and hence steady state current profiles were generated. This improved mass transport increases the experimental sensitivity permitting the exploration of faster charge transfer reactions and had a concomitant increased interest towards their characterisation through simulation. A recent perspective by Arrigan and Herzog [6] in this journal examined simple IT and so the concept is only briefly introduced here. Additionally, electrochemistry at macro, micro, and nano interfaces has been reviewed recently [5,7]. One of the first simulations by Girault *et al.* [23] focused on the position of the LLI at a micropore; on either side or within a microchannel. This was extended to interfaces housed at the tip of pulled borosilicate or quartz glass capillaries [24,25]. Kakiuchi *et al.* [24] examined the geometric effect combined with a viscous secondary phase, specifically w|IL *vs.* w|o interfaces, where the diffusion coefficient is 3 to 4 orders of magnitude lower for the former *vs.* the latter. This causes the i -V profile to resemble a macro-ITIES signal with linear diffusion dominating in both IT directions owing to the increased viscosity in the IL phase, whereas w diffusion is confined by the pipette walls. In 2009 Amemiya *et al.* [25] examined the effect had by taper angle on pulled quartz pipettes, the diffusion of species, and the resultant i -V signal. They demonstrated that forward and reverse waves could characterise the geometric and transport properties of the pulled pipette [25] with a high degree of sensitivity. Simultaneously, micro LLI arrays have been developed and explored by groups like Alvarez de Eulate *et al.* [26] with the goal of understanding interface location and its impact on i -V curves.

The complexity of these models was increased to examine FIT processes with typically 3-4 processes being considered [3]. This has led to studies at the w|IL interface [27] where ILs have been shown to be excellent solvents for metal ion extraction, but also the utility of somewhat exotic organic solvents, like CHCl_3 [28]. In the latter [28], a phospholipid, 1,2-dimyristoyl-sn-glycero-3-phosphocholine (DMPC), highly soluble in CHCl_3 ($\epsilon=4.81$), was investigated at a blunt pulled micro-ITIES ($\text{Ø} = 25 \mu\text{m}$). This confirmed that the analytical solution of FIT, formulated for a macro-ITIES, was transposable to the micro-ITIES platform employed.

4. Electrocatalytic reactions

Owing to its biomimetic nature, there are a number of valuable electrocatalytic reactions such as the O_2 reduction reaction (ORR) that are of considerable interest. This is exemplified through the recent work of Girault *et al.* [29-31], examined through a macro ITIES 1D simulation. Therein, Girault and co-workers examined the ORR (see Figure 1) using decamethylferrocene (DMFc), and other metallocenes as catalyst/electron donor in the oil phase and H_2SO_4 as the proton source in the aqueous phase. Protons are pushed across the interface at high positive potentials and coordinate with DMFc in the bulk oil phase in the vicinity of the ITIES. While the DMFc hydride formation, and subsequent oxidation, were treated as bulk processes, the speed of the reaction indicated that the reaction layer was very small, $\sim 50 \mu m$, compared to the diffusion layer thickness without O_2 reduction, $\sim 200 \mu m$ [29]. Simulated and experimental CVs were compared through two curve features: (i) the absence of a proton return peak in the edge-of-scan profile and (ii) the $DMFc^+$ transfer peak intensity. Through a similar process, this group examined the surprising O_2 reduction at LLIs in the presence of alkali metals or rather their hydration sphere, whose protons are made acidic as they transfer across the ITIES [30,32].

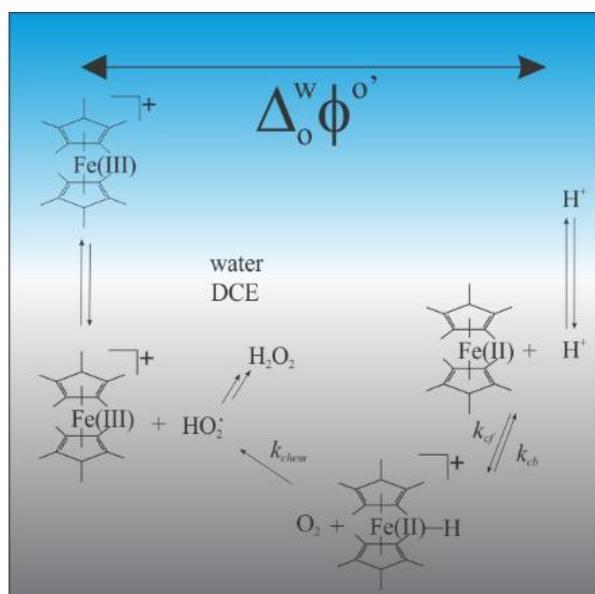


Figure 1: Mechanism of O_2 reduction using decamethylferrocene (DMFc) as both electron donor and catalyst and the liquid|liquid interface, between water|1,2-dichloroethane (w|DCE) acts as the junction for charge separation. Adapted with permission from [29].

Optimising or predicting the reaction layer thickness of a system is a valuable utility when trying to incorporate additional *in situ* detection methods to complement the electrochemical ones, such as electrogenerated chemiluminescence, SECM, *etc.*

5. SECM simulations

SECM digital simulations have been utilised extensively for LLIs. For example, H₂O₂ generated from O₂ reduction by DMFc at a trifluorotoluene|water (TFT|w) interface was probed by a SECM tip sensitive to H₂O₂, and the experimental results were compared with FEM simulated curves. If the H₂O₂ generation was modelled as a constant flux from the ITIES, simulations show negative feedback close to the interface, while the experiments show continuous increase also close to the interface. Hence, a model considering H₂O₂ generation within the 50 μm thick uniform reaction zone was considered to obtain better agreement with the experimental data [33].

Mirkin *et al.* proposed ET/IT as a new mode of SECM operation, using a nanometer sized pipette filled with an organic phase containing a neutral redox mediator [34]. This redox mediator can partition into the aqueous phase and undergo redox reactions at the substrate. The ions produced in this ET reaction can be transferred into the organic filling solution of the nanopipette in an IT reaction, giving rise to a measurable IT tip current. Transfer of other ions at the tip can be used for distance control in negative feedback mode. Digital simulations were employed to study the ET/IT feedback considering (i) the partitioning of neutral redox species from the pipette to the external solution, (ii) diffusion of these species to and their oxidation (or reduction) at the conductive substrate, (iii) diffusion of the reaction product to the pipette orifice, and (iv) IT at the tip ITIES. This approach was later used to detect short-lived intermediates of electrocatalytic O₂ reduction, by using O₂ as a redox mediator for the ET reaction, and measuring the IT current of the O₂⁻ intermediate [35]. Additionally, simulations can be used to generate analytical approximations, as done recently by Mirkin and Amatore *et al.* [36] for the ET/IT SECM configuration where the surface-generated ionic species is either chemically stable or participates in a first- or second-order homogeneous reaction.

Furthermore, digital simulations of SECM have been used to study the kinetics of O₂ reduction by DMFc in acidified DCE in an EC' mechanism, where DMFc generated at the SECM tip reacted homogeneously with O₂ and protons to regenerate the initial DMFc⁺.

Through comparison of simulated and experimental curves an apparent rate constant for the homogeneous reaction was obtained [37].

Nanopores fabricated in a nanocrystalline silicon membrane have been probed by SECM with a high degree of resolution achieved through the use of a nanopipette [38]. FEM simulation was employed to investigate the spatial resolution of the approach [38]. This report has interesting implications towards biological cellular imaging particularly when combined with the following: (i) the recent work by Mauzeroll *et al.* [39] that used high speed SECM imaging with a Pt disc micro electrode in conjunction with a forced convection numerical model to study the redox properties of live cells; (ii) as well as the work of Ding *et al.* [40] in the development 3D topographical simulation for their live cell investigations. The combination of these three works suggests one direction SECM and numerical analysis could take. That is, rapid bio-imaging of cells using liquid|liquid junction scanning probes with a high degree of spatial resolution. With this, a more comprehensive picture of bio-cellular processes could be gained in conjunction with the simultaneous response of live cells to external stimuli. The LLI offers the possibility to investigate using non-redox active charged species. This is demonstrative of one potential avenue for FEM simulation development and application.

6. Multiphysics approach

Dassie *et al.* have studied the effect of forced hydrodynamic convection on both IT and FIT, both theoretically and experimentally [41]. This is an example of a typical approach where the fluid velocity was assumed independent of the distance from the stirrer [41], as demonstrated by Levich. These kinds of models are relatively easy to solve, but the model accuracy can be rather limited. However, recent development in both computer hardware and software has made more complex models accessible even on tabletop computers. For example, recently Dassie *et al.* proposed a novel electrochemical methodology to determine the partition coefficient of neutral weak bases [42]. In this case, forced convection by a rotating rod in the top phase was used to enhance the mass transfer to and from the top phase, and the relationships between charges transferred during the forward sweep of the CV at different rotation rates and at different pHs allow determination of the partition coefficients of weak bases. Models of varying complexity were developed to validate the methodology, whereas magnetic resonance imaging (MRI) was utilised to experimentally validate the computational fluid dynamic (CFD) simulations, both in 2D and 3D. This article is an example of the

complex combination of both CFD simulations with those of mass transfer in two phases, acid-base reactions, partitioning of neutral species, and potential controlled IT. The discrepancy between the simulated and experimental velocity values show that further development is still required especially for 3D modelling, but the trends are reproduced remarkably well, as shown in Figure 2.

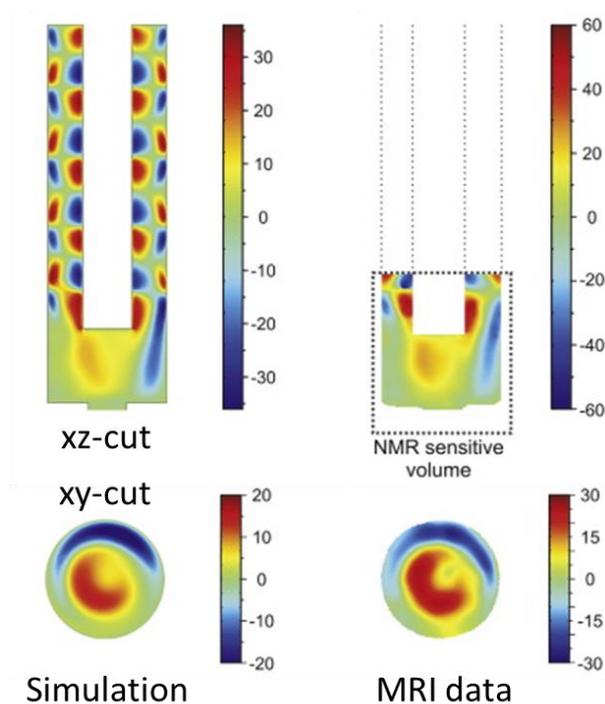


Figure 2: A Comparison of the z -velocity maps obtained for the aqueous phase in a cylindrical cell, with a rotating rod ($r = 3$ mm) at $\omega = 62.8$ Hz from 3D FEM simulation of laminar flow (left) and from MRI, both in y , z -planes. ITIES is located at the bottom of the figure, and there is negligible convection in the DCE phase. The asymmetry results from a slight misalignment between the rotating rod and the cell. Adapted with permission from ref. [42].

Moving boundary model was utilised by Unwin *et al.* [43], who used a 1D FEM model to study amine (jeffamine D230) transfer from an expanding droplet into an aqueous solution. Microelectrochemical measurements at expanding droplets were used to probe the potentiometric response of a pH sensitive microelectrode, and this response could be converted to give the concentration profile of the amine as a function of the electrode-droplet separation when the measurement was coupled with time-lapse microscopy. The theoretical concentration profile obtained with a moving plane model in COMSOL to describe the expanding droplet matched well the experimental data [43]. Moving boundaries are important

for applications where shape and size of the droplet changes over time, for deposition of solids at LLI *etc.* and further development is expected to see these models utilised for understanding these effects better. For example, the shape of a droplet on an electrode depends on the applied potential, so digital simulations corroborated by experiments would be beneficial for understanding the electrochemical response upon droplet collision with an electrode.

7. Photochemical charge transfer reactions

Another example of utilising multiphysics digital simulations was demonstrated by Girault *et al.* for investigating photochemical reactions at LLIs under hydrodynamic convection in a system for conversion and storage of solar energy: *photo-ionic cells*. The solar energy is converted to chemical energy in a homogenous photochemical reaction between a sensitiser and a quencher, and stored by extraction of the photoproduct into the organic adjacent phase (as shown in Figure 3A), followed by physical separation of the phases. The energy can be recovered electrochemically with a biphasic fuel cell to produce electricity on demand [44]. Photochemical reactions have a large number of parameters affecting the quantum yield and efficiency of the system, so digital simulations are useful to pinpoint the most critical ones for further optimisation. This requires coupling of simulations for both the light absorption and the mass transport of reactants, as well as computational fluid dynamics to account for the fluid flow, and some results are illustrated in Figures 3B-D. The FEM simulations were used to evaluate the conditions required to reach large quantum yields of over 50 %: long excited state lifetime (in the order of 10-100 μ s), large partition coefficient for the hydrophobic photoproduct, reasonable dye concentrations and large redox potential difference between the sensitiser and the quencher [44]. Simulations also show that the photoreaction should take place very close to the LLI to minimise the diffusion lengths and time to avoid recombination reactions. Further simulations were performed to evaluate the effect of the droplet size on the attainable quantum yield [45]. These papers give an example of utilising digital simulations for “debottlenecking”, where the effect of the different parameters are evaluated to give guidelines about what is required to achieve high utilisation of light.

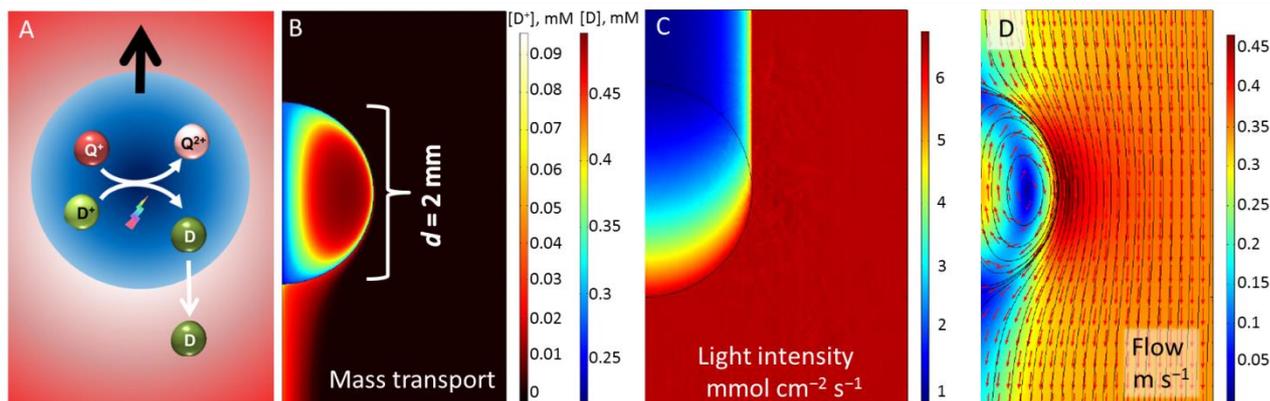


Figure 3: (A) Operating principle of the photo-ionic cell, where the dye is photoreduced in the aqueous phase and extracted into the organic phase. (B) Digital simulations of mass transport; (C) absorption of light; and (D) fluid flow are required to estimate the system performance and to determine the critical parameters. Here an example of a 2 mm diameter droplet of aqueous phase containing 0.5 mM of the dye, moving up at the terminal velocity of 0.34 m/s in organic phase, under ca. 1 sun illumination from below. Simulations were done in 2D axis symmetric mode [45].

8. Conclusions and Perspective

This perspective has shown that digital simulations have been utilised to analyse experimental results involving interfacial charge transfer reactions, moving interfaces, partition and complexation of species, photoreactions and forced hydrodynamic convection.

As computational power further increases and the requisite cost becomes more affordable, the use of simulation software towards geometric, materials, *etc.*, problems will become more ubiquitous and further exploit the ‘multi-physics’ aspect. That is to say, the inherent power of this method is not only to merge geometric and mass transport properties together, but is likely to expand to incorporate the interaction of other physical parameters, *e.g.*, capacitance models, surface tension (*e.g.* through moving boundary), as well as nanoparticle interactions, *etc.*, not to mention 3D aspects, pushing the frontier understanding and physical insight of complex processes of LLI systems. As stated in the review by Arrigan and Herzog [6] about miniaturised ITIES: “truly comprehensive models that incorporate mass transport, kinetics and capacitance, to enable a complete characterisation of a system under dynamic electrochemical conditions have yet to appear”. This review indicates that significant progress has been made in comprehensive modelling, and this trend will continue. However, it should be stressed that certain care has to be taken with simulations, and verification against experimental and analytical solutions should always be performed.

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Example of simulations of mass transfer, light adsorption and photoreactions, and hydrodynamics for evaluation of the system performance.