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Intensification of mass transfer and reaction in electrically disturbed liquid-liquid systems

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HIGHLIGHTS

- Visualization of electrically induced disturbances during mass transfer.
- Promotion of electrically induced interfacial turbulence is accurately predicted.
- Evidence of time dependent mass transfer is confirmed.
- Simulations successfully match the visual disturbance patterns and rates observed.
- Electrostatic intensification of interfacial enzymatic activity demonstrated.

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ABSTRACT

A new study of electrically induced disturbances and mass transfer at a liquid-liquid interface as a means of process intensification is presented. Visualization of electrically induced disturbances during mass transfer of ethanol from an aqueous phase into an extracting solvent, n-decanol is demonstrated. Mass transfer rates were measured for extraction of ethanol from an aqueous electrically charged pendant droplet into a continuous phase of n-decanol. In a second part, mass transfer rates of ethanol into n-decanol across a planar interface in the presence of a DC electrical field are presented. Thirdly, results are presented of electrostatic spraying of aqueous enzyme solutions into an immiscible triglyceride ester oil phase. The effect of electrical field on specific interfacial rate of reaction was determined. The first part of the study demonstrated the positive effect of electrical disturbance on mass transfer rate from the pendant droplet. Time dependent mass transfer was also shown, consistent with earlier mass transfer studies with uncharged pendant drops. The mass transfer study using the planar interface provided further confirmation of the positive effect of electrically induced interfacial turbulence on mass transfer. The experimental data are successfully compared with simulations based on rigorous numerical solutions of the controlling equations. The visual disturbance pattern at the interface and rates of mass transfer were accurately predicted. The reactor experiments clearly show a significant positive effect of electrical charge on the specific rate of hydrolysis. This latter finding opens up the possibility of intensification of enzymatic catalytic activity using electrical fields. The potential for electrically induced enhancement of other reaction systems involving liquid-liquid interfaces such as in the case of phase-transfer catalysis is highlighted.

1. Introduction

It is well known that liquid-liquid extraction processes can be intensified by externally applied electric fields. Fields [17,36,37,3,39]. Intensification is an important part of the development of green engineering which aims to make processes more compact with lower inventory, taking up less space, and improving process efficiency. Understanding some of the fundamental phenomena which underpin intensification is necessary for optimal equipment and process design. Electrostatic enhancement of mass transfer in liquid-liquid processes is a good example of an intensification technique. Based on the above referenced work and other work, electrostatic enhancement of mass transfer in solvent extraction processes may be explained by increases in interfacial area due to improved dispersion and drop break-up. The acceleration of drops through the continuous phase may also lead to higher rates of mass transfer due to improved rates of interfacial shear. A

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third possibility is that interfacial turbulences are promoted by the electrical field which may also contribute to improvements in mass transfer fluxes. Promotion of interfacial turbulence is especially interesting because a number of novel liquid-liquid systems such as those involving homogeneous catalysts, or involving enzymes which are inter-facially active, potentially could be intensified by the application of electrical fields. Interfacial turbulence or Marangoni effects are manifestations of spontaneous interfacial flow driven by interfacial tension gradients. The effective interfacial tension at an electrically charged liquid-liquid interface can be reduced due to the electrostatic force at the drop surface by the electric field as noted by Stewart and Thornton [36,37]. Onset of interfacial turbulence observed at a liquid-liquid interface in the presence of an externally applied electric field has been reported in the literature [1,8]. Clear evidence of increases in interfacial turbulence due to the presence of an externally applied electrical field was reported. Significant influence of the direction of the applied field was noted as were differences between DC and AC applied fields [6]. These Marangoni phenomena have been successfully visualized using Schlieren light interrogation both at the surface of pendant droplets and at planar liquid-liquid interfaces.

The time-dependent nature of interfacial turbulence in uncharged liquid-liquid systems has also been reported [10]. Schlieren light studies of interfacial turbulence in drops suspended from a nozzle showed that turbulence produced during mass transfer decayed rapidly with time. Later work [30,9] showed that the time dependence was also reflected in observed mass transfer from a hemispherical, quasi-steady state aqueous pendant drop for the extraction of uranium into tri-n-butyl phosphate. Review of the literature suggest that time dependent mass transfer in a liquid-liquid system in the presence of an electric field has not been studied either experimentally or through quantitative simulations.

A range of optical experimental techniques has been reported which include the Schlieren technique [18,24,25,6], a laser photochromic dye tracer technique [38], holographic interferometry [26,7] those based on microscopic observations of reflected or transmitted light [31] and microinterferometric and Mach-Zender interferometric methods [23]. The principle exploits the refractive index gradient occurring in the vicinity of the liquid-liquid interface. In the current paper, the Schlieren light technique for visualization of time dependent mass transfer is described. The ethanol-water–1-decanol system was used as a simple model extraction system in which the n-decanol exhibits a reasonable extraction affinity for ethanol relative to water.

Another aspect of interest described here is electrically augmented mass transfer accompanied by accelerated rates of chemical reaction at a liquid-liquid interface. Earlier studies by the authors [27,28] showed substantial increases in reaction rates for the enzymatic hydrolysis of a tri-glyceride ester in the presence of an electrical field in a liquid-liquid system. The acceleration in reaction rate observed was initially attributed to reductions in drop size, increase in interfacial area, and increase in mixing. Recent analysis of these and other rate data, including measurement of drop size and hold-up indicate that rate enhancement in this system is not solely explained by decrease in drop size and increased mixing, but that the presence of electrical charge at the liquid-liquid interface may also play a role in the observed enhancement. Pribyl et al. [29] studied the effect of electrotransport processes upon enzymatic activity of penicillin acylase immobilised in a membrane reactor in the presence of an electrical field. This work showed that local stabilisation of pH due to electro-migration of H^+ ions in the presence of an externally applied electrical field significantly enhanced the observed enzyme activity. The degree of control however was limited by joule heating and consequential thermal enzyme deactivation. This built on earlier work of Snita and Marek [35] in which the Nernst Planck equations were used to study electrically induced ionic transport in an active enzymatic reacting system and to model distribution of concentration, electrical potential, and charge. Hydrogen ion concentration and pH profile in the region of the enzyme were calculable with significant inferences on enzyme activity. Other work by Sitnitsky [34], suggested a positive link between enzyme activity and the presence of a fluctuating electric field however this was based on theoretical analysis without conclusive experimental validation. The question of electrically enhanced enzymatic catalytic activity at a liquid-liquid interface remained unanswered.

The goals of the work are summarized as follows: firstly to confirm the electrically induced enhancement of mass transfer due to interfacial disturbance in a liquid-liquid system (a) using a pendant drop technique (b) using a planar liquid-liquid interface,(c) explore theoretical modeling of the electrically induced interfacial disturbances based on description of the interaction between dynamic interfacial tension and hydrodynamics close to the liquid interface. (d) show the influence of an electrical field on rate of an interfacially catalyzed enzymatic reaction

2. Theoretical

Modelling of interphase liquid-liquid mass transfer in the presence of an electric field starts with consideration of the controlling hydrodynamic equations together with the relationship which govern the influence of electrical forces upon interfacial geometry. In addition we consider the influence of interfacial tension gradients on localized disturbances close to the liquid-liquid interface.

Firstly there are the incompressible Navier-Stokes equations which govern the flow in the bulk two-phase domain as well as close to the liquid–liquid interface.

Equation of continuity is well known in the form of velocity divergence free regime:

$$\nabla \cdot \mathbf{u} = 0 \tag{1}$$

The momentum conservation equation for the velocity $\mathbf{u}$ and pressure p fields (simultaneously solved with Eq. (1)) is

$$\rho\left(\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u}\right) = \rho \mathbf{g} - \nabla p + \nabla \cdot \tau + \mathbf{s}_E \tag{2}$$

where the usual assumptions about stress tensor τ and the rate of deformation tensor $\mathbf{D}$ are defined in the following form

$$\tau = 2\mu \mathbf{D}, \text{ and } \mathbf{D} = 1/2[\nabla \mathbf{u} + (\nabla \mathbf{u})^T] \tag{3}$$

Combination of (2) and (3) results in the familiar form of the Navier Stokes equation However we assumed the extra momentum source resulting from the existence of electric field

$$\mathbf{s}_E = \sigma \mathbf{E} \tag{4}$$

accounting for the electroconvective effects associated with ion-drag phenomena. In this equation σ is the charge density of ion-like species and $\mathbf{E}$ the electric field strength. This is in agreement with existing theories [40].

Then, in order to describe the phenomena close to the liquid–liquid interface, we imposed the boundary condition expressing balance of forces at the interface [5,13].

$$-(p_2 - p_1)\mathbf{1} + (\tau_2 - \tau_1) \cdot \mathbf{n} = \gamma_{eff}\left(\frac{1}{R_1} + \frac{1}{R_2}\right)\mathbf{n} + \nabla \gamma_{eff} \tag{5}$$

This equation involves mechanical stresses resulting from the flow (on one left-hand side of Eq. (5)) and terms involving an effective surface tension γ_{eff} (on the right-hand side, see Eq. (7) below). The terms result in turn from the surface curvature (with the principal radii of curvature R_1 and R_2) as well as from its inhomogeneity due to concentration gradient of the active substance. Note that