

## Interfacial Phenomena in Solvent Extraction and Its Influence on Process Performance

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**Abstract:** Solvent extraction is now finding applications in a broader range of fields than the past. Many of these applications require process equipment with shorter contact times, and in some cases to the point where the traditional equilibrium stage approach is not a good model for predicting performance. In addition, feed streams are becoming lower in concentration of the solute. This means greater feed to solvent flow ratios are being used and so loss of organics as entrainment in the feed is more of a concern both economically and environmentally. These trends mean that a greater emphasis is being placed on the kinetics of extraction and stripping in models to predict performance and on formation and coalescence of drops to control entrainment. This paper reviews recent advances in the tools for investigating kinetics and coalescence in solvent extraction processes and some of the insights that are being uncovered in these fundamental processes in solvent extraction technology.

**Key words:** solvent extraction; drop coalescence; liquid interface; kinetics

### Introduction

Solvent extraction is a selective and powerful separation technology that is finding applications in a broader range of fields than the past. In particular, applications in the pharmaceutical and environmental clean up area require the treatment of very dilute feeds with high phase ratios, sometimes in excess of 10:1. Also, in the more traditional areas such as in mining operations, there is a need to reduce organic inventory and organic losses as well as treat lower concentrations of solute in the feed. All of these drivers are causing operators to examine other types of contactors with lower organic holdup, shorter residence time, and lower organic carry over. Today, this has led to the installation of columns in the mining industry and interest in inline mixers,

and membrane contactors as alternatives to the traditional mixer settler technology. Each of these new contacting devices goes some way to achieving the required goals. However, the traditional models of equilibrium stages that are usually used are not easily applied to these types of equipment as in many cases the residence time of the organic in the contactors is of the same order as the half life of the reaction required for the extraction of the solute, thus requiring a detailed knowledge of the kinetics as well as the equilibrium data for modelling. As the extraction reaction in many cases occurs at the interface, the properties of the interface can dramatically influence the performance of the extractor yet not significantly influence the equilibrium properties. Interfacial properties also control the hydrodynamics of extraction. Small increases in surfactant level dramatically reduce interfacial tension, and the lower interfacial tension results in smaller drop sizes and increased carryover. Thus, interfacial proper-

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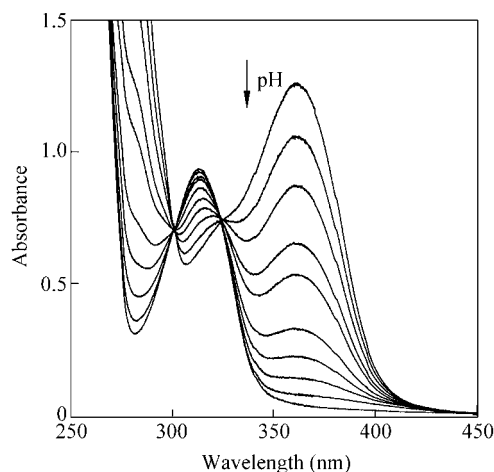
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ties control not only the hydrodynamics in a liquid dispersion but also the rate of extraction. However, we do not have a good model of the interface that enables us to predict how quickly drops coalesce or how changes in interfacial properties influence the kinetics of extraction. This has been the motivation for our research over this last 15 years and a review of this will be presented in the next sections.

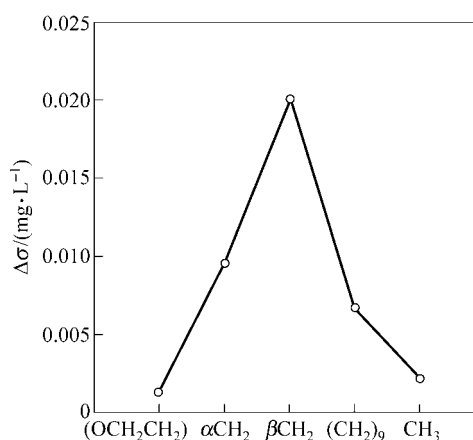
## 1 Influence of Interfacial Phenomena on the Kinetics of Metal Ion Extraction

There are many ways of measuring kinetics in solvent extraction systems, and excellent reviews available in Refs. [1,2]. Development of techniques that measure the kinetics and not a mixture of kinetic and hydrodynamic effects was our aim. We chose ultraviolet and visible (UV-Vis) spectroscopy with stopped flow initially. In this equipment, the extractant ligand is solubilised into a micelle solution, and a separate solution containing the metal ion is made up. These two solutions are mixed and the rate of extraction can be followed by following the development of the spectra of the complex (Fig. 1). This was very successful and eliminated any effect of hydrodynamics. The question of where the ligand was relative to the interfaces still needed to be addressed. This was



**Fig. 1** UV-Vis spectra of HNAPO [LIX84] with pH showing appearance of absorption band due to deprotonated species generation. Micelle phase of 0.074 mol/L  $G_{12}A_8$  with  $3 \times 10^{-4}$  mol/L HNAPO. Solid lines correspond to pH values of 12.9, 12.5, 12.0, 11.5, 11.3, 10.9, 10.5, 10.3, 9.8, and 8.4 in descending order for  $\lambda_{max} = 387$  nm.

examined using nuclear magnetic resonance (NMR). As most of these ligands contain aromatic rings the ring current from the aromatic ring perturbs the proton NMR spectra of the non ionic surfactant molecules. By watching which proton is perturbed, it is possible to determine where the ligand molecule is relative to the interface (Fig. 2)<sup>[3,4]</sup>. The picture emerging is that it is different for each extractant. It depends on the relative interfacial activity of both the extractant, the complexing agent, and also the nature of the organic phase.



**Fig. 2** Difference in NMR chemical shifts of different groups of protons in a micellar solution of 0.060 mol/L  $C_{12}E_8$  in the absence and presence of 0.0044 mol/L Kelex 100 at pH 6.0.

A recent study on the influence of surfactants on the kinetics of extraction of Ni by LIX84 indicates that the addition of small amounts of sodium dodecyl sulfate (SDS), a cationic surfactant, increases the rate of extraction as the negatively charged surfactant attracts the nickel ions, and therefore, the local concentration of Ni at the interface increases resulting in faster kinetics. As the concentration of SDS increases further, the rate is seen to decrease due to a competition at the interface between the SDS and the ligand (LIX84), reducing the concentration of ligand at the surface. This can now be explained in terms of the surface excess and the charge at the interface and is presented in detail in the paper.

Thus, the traditional approach of including the rate constant as an extra resistance in a resistance in series model of the form shown in Eq. (1) and assuming this is constant is not always accurate.

$$\frac{1}{K_{ox}} = \frac{1}{k_x} + \frac{1}{k_R} + \frac{m}{k_y} \quad (1)$$

where  $K_{ox}$  is the overall mass transfer coefficient;  $k_x$  is the  $x$ -phase mass transfer coefficient;  $k_R$  is the reaction rate constant;  $k_y$  is the  $y$ -phase mass transfer coefficient;  $m$  is the slope of the equilibrium line.

In the past, the larger residence times have lead to the major resistance being diffusive in nature and so the reaction rate term could be ignored.

With the overall mass transfer coefficient constant, engineers could do a pilot scale experiment, estimate the efficiency which is related to the mass transfer coefficient and then apply that to any scale. If the reactive term is controlling,  $K_{ox}$  may no longer be constant. It is influenced by small concentrations of surfactants and changes in concentration can change the kinetics resulting in different dependencies on, for example, pH. Thus, small changes in a number of interfacial properties can influence the efficiency of contactors dramatically and make predictions inaccurate. This is particularly important for operators who might be considering the use of a different flocculating agent or mining a part of the ore body with higher organic material.

## 2 Drop Coalescence

One of the key determining factors in controlling the performance of extraction equipment is drop size. The aim of designers of equipment is to produce a uniform drop size of the dispersed phase in a continuous phase. This determines the interfacial area, the mass transfer coefficient, and so the mass transfer performance. It also determines how long the drops take to coalesce and so the maximum throughput. Smaller drops mean smaller throughputs. Yet there are no accurate models for predicting drop breakage and coalescence. We have been focusing on the processes controlling droplet coalescence.

When two drops approach each other, they form a thin film of the continuous phase between them. Drainage of the film occurs, resulting in the thinning of the film. The system is stable or metastable when a film of uniform thickness is maintained over long time periods. Generally, the presence of additives such as a surfactant is required to achieve this type of stability. These additives adsorb at the droplet interface and

form a barrier limiting film drainage due to electrostatic and/or steric effects. The rate of film drainage is an important factor in the determination of film stability. The profile of a drop, i.e., the shape it adopts, as film drainage occurs, contains information regarding the influence of hydrodynamics and interfacial properties on the film drainage process. During the early stages of film thinning, hydrodynamics and the density difference between the two liquid phases dominate the drainage rate. It is not until the film is relatively thin that interfacial forces become significant enough to affect the rate of drainage. The continued thinning of the liquid film and ultimate stability of the system are controlled by these surface forces.

Due to the importance of film drainage, many theoretical studies<sup>[5,6]</sup> have attempted to model this phenomenon. However, accurate modeling has not been successfully achieved, partly due to the complexity of film drainage/coalescence. The inability of available experimental techniques to supply the necessary data has also made it difficult to compare the proposed theory with the experimental results.

Over the past few decades, experimental innovations<sup>[7-9]</sup> have made the measurement of film thickness and the profiling of deformable droplets approaching an interface possible. One such method is the technique of interferometry<sup>[10]</sup>, which is based on the theory of light interference. This technique has allowed successful determination of droplet profiles and enabled measurement of the thickness of a draining film. However, interferometry cannot accurately determine the critical thickness of a film at the point of rupture. Interferometry is also restricted since it cannot profile droplets in real time.

We have been using imaging ellipsometry/reflectometry to study the droplet deformation during film drainage since it overcomes the limitations associated with interferometry. Imaging ellipsometry/reflectometry is capable of measuring the film thickness profile across a droplet approaching an interface in real time until the point of film rupture with greater accuracy than interferometry. Additionally, since imaging ellipsometry/reflectometry is an imaging technique, the entire droplet is sampled simultaneously, thus eliminating the problems associated with sampling time differences that are inherent to

interferometry.

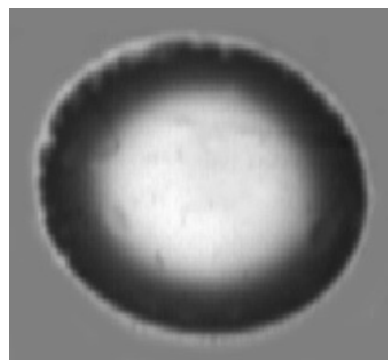
Imaging ellipsometry/reflectometry has previously been used to profile the shape of the deformable droplet approaching and interface<sup>[10]</sup> and also utilized in the investigation of siloxane oil droplets spreading on solid surface<sup>[7]</sup>, as well as the study of film drainage and of an organic droplet (squalene) approaching a hydrophilic, negatively charged silica surface, in an aqueous continuous phase containing the non-ionic surfactant  $C_{12}E_8$ .

The details of this last experiment are given elsewhere<sup>[11]</sup>. The experiment consists of observing a drop approaching a silica plate from above and capturing the image. A typical image is shown in Fig. 3.

From this image, thickness can be obtained and plotted as a function of time. Refer to Figs. 4 and 5.

Figures 4 and 5 show the effects of non-ionic surfactant on the drainage process. As can be seen on initial approach, the droplet was observed to deform into a dimple shape. This type of behavior is not uncommon<sup>[6,11,12]</sup>.

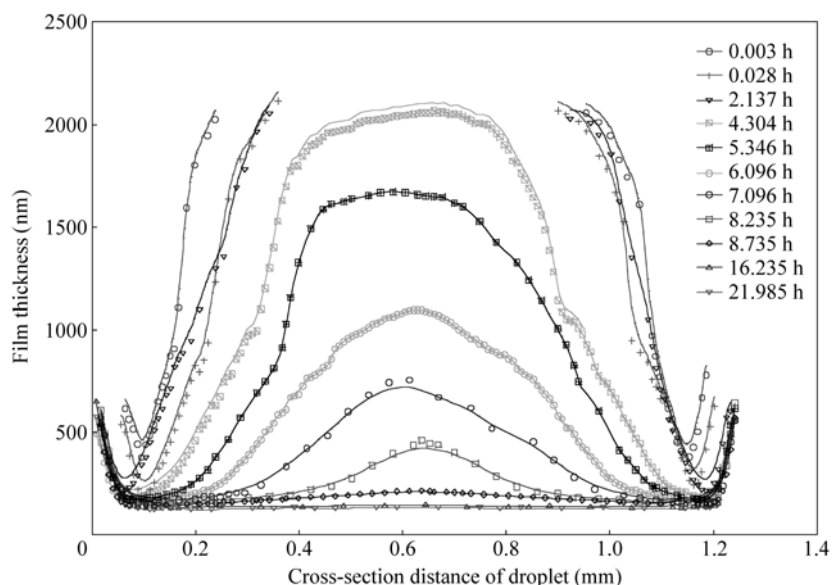
At the periphery of the drop, the film is relatively thick compared to that at the centre of the drop, since the drop's centre corresponds to the point of closest approach to the surface. The film at the drop's centre therefore experiences hindered flow compared to flow at the film's periphery. This difference in the rate of film drainage across the drop leads to a buildup of



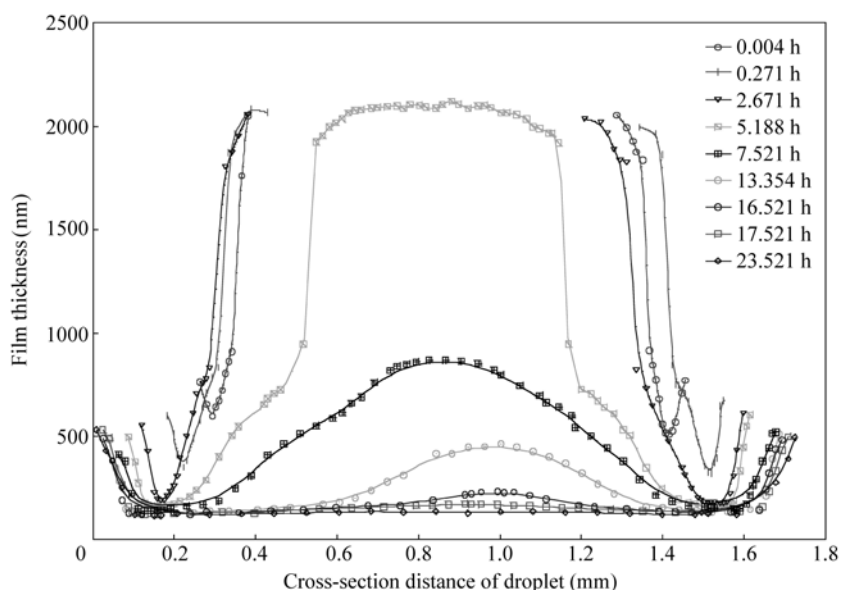
**Fig. 3** Typical grey-scale image of a droplet approaching a solid surface in an aqueous continuous phase. The darker regions signify thin film areas. The lighter the areas correspond to region where the film is thick. Thus, in this case, the film is thinner at the barrier ring of the droplet and thicker at the centre, which corresponds to dimpling of the droplet.

the fluid at the film's centre and hence the drop dimples.

After dimpling, film drainage continues at the periphery of the film, i.e., the barrier ring, at a steady rate, whereas drainage at the centre of the droplet is retarded. Once the thickness of the film at the barrier ring approaches the equilibrium film thickness, the drainage rate at the barrier ring decreases and the centre of the droplet starts to thin at faster rate than before. Thus, the film profile evolves such that the degree of dimpling continuously decreases until, eventually, a thin film of uniform thickness is formed. This is the equilibrium position on the system.



**Fig. 4** Film drainage profile across a squalene droplet approaching hydrophilic silica surface in the continuous phase containing  $3.5 \times 10^{-6}$  mol/L  $C_{12}E_8$ .



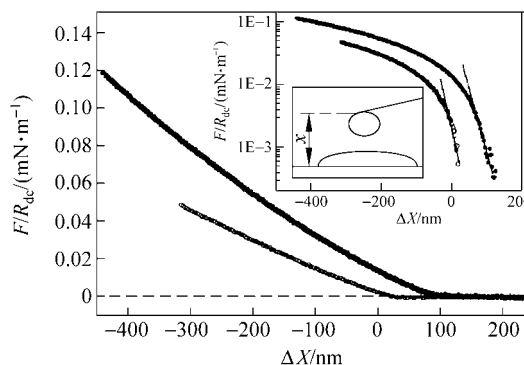
**Fig. 5** Film drainage profile across a squalene droplet approaching hydrophilic silica surface in the continuous phase containing  $1.0 \times 10^{-5}$  mol/L  $C_{12}E_8$ .

In this case, both surfaces are negatively charged and so a repulsive electrostatic force between them is balanced by the buoyancy force at a particular equilibrium separation distance. If the electrostatic force is weakened by the addition of ions to the system, the two surfaces will get closer together, slowing the drainage but also increasing the likelihood of coalescence. Thus, not only is the hydrodynamics of this drainage process important but also the interfacial forces between the drops as this controls the rate of drainage and the ultimate film thickness.

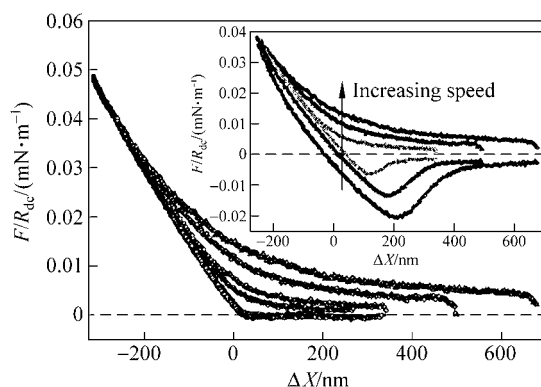
To develop a quantitative understanding of the forces between interfaces, the atomic force microscope (AFM) has been used. This involves suspending a drop on the end of an AFM cantilever<sup>[13]</sup> and a second drop on an AFM stage and pushing the two together (Fig. 6). Interpretation of the data is not straightforward as both surfaces deform and it is necessary to know the separation distance. This has to be calculated based on the force and deformability of the interface<sup>[13]</sup>. These experiments are extremely interesting as they show for slow approach speeds that the forces follow classical Deijaguin-Landau-Verwey-Ovenbeek (DLVO) theory of electrostatic and van der Waals forces. At higher approach speeds, hydrodynamics become important (Fig. 7). Other interesting results coming from this work are that the forces are different depending on the type of ion used. For example, a NaCl solution gives a different force curve than NaIO<sub>3</sub>. At this stage, we can

only speculate as to the reason.

These two new techniques for observing the influence of interfacial phenomena on coalescence have the potential to give important new insights into the underlying physics of droplet interaction and allow the development of quantitative models for coalescence in liquid-liquid systems.



**Fig. 6** The interaction force between two decane drops measured using AFM at 1 (open circles, bottom) and 10 mmol/L (filled circles, top) SDS and 1 mmol/L NaNO<sub>3</sub> background electrolyte in both cases. The force is scaled by the undistorted radius of the drop on the cantilever. The inset shows the geometry of the measurements where  $X$  is the distance from the bases of both drops. The lines on the logarithm plot show the limiting Debye lengths for the force measurements, which are 22 and 15 nm for the 1 and 10 mmol/L SDS concentrations, respectively.



**Fig. 7** The interaction of two decane drops in 10 mmol/L SDS measured with AFM as a function of approach velocities, where the two superimposed plots at 80 and 120 nm/s. The incremental increase in force corresponds to a sequential increase of approach velocities (0.54, 1.2, 3.5, and 6.6  $\mu\text{m/s}$ ). The inset shows the approaching and retracting forces for scan speeds of 1.2, 3.5, and 6.6  $\mu\text{m/s}$ , where the increase in speed corresponds to an increase in the magnitude of the forces.

### 3 Conclusions

This paper illustrates two new techniques for investigating fundamental forces and hydrodynamic phenomena at liquid interfaces and work on the influences of surfactants on the kinetics on extraction. Development of techniques such as above mentioned will help in developing an understanding of the underlying physics that will lead to better predictions of performance of solvent extraction equipment.

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