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Effect of fluid properties on ultrasound assisted liquid-liquid extraction in a microchannel

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ABSTRACT

When immiscible liquids are subjected to an ultrasonic field, they form emulsions. This principle has been used to improve the mass transfer characteristics of a liquid-liquid extraction process in microreactor systems. The formation of emulsion and its characteristics are prominently dependent on the properties of the liquids used and this also holds true for emulsion brought about by ultrasound. This paper focuses on the properties of fluids that are reported to have an influence on the cavitation behaviour, namely viscosity, interfacial tension and vapour pressure. These properties were examined by changing the solvent of the organic phase in the hydrolysis of p-nitrophenyl acetate. The study is performed by comparing pairs of solvents that are different in one property but similar in the other two. The pairs selected are toluene – chlorobenzene for viscosity, toluene – methyl Isobutyl ketone for interfacial tension and methyl isobutyl ketone – 2-Methyl tetrahydrofuran for vapour pressure effects. A qualitative study was performed with a high-speed camera in flow to understand the emulsification initiation mechanisms and behaviours. These findings were further explored by performing the sonicated emulsion in a batch-sonicated reactor. The quantitative analysis of the fluid properties was evaluated and compared based on the relative percentage increase in yield upon sonication with respect to their individual silent conditions. The quantitative results were further supported by the quantification of the emulsion performed with an FBRM probe. The results indicate a two times improvement in yield with solvent of lower viscosity as 2 times more droplets were formed in the emulsion. Both the solvent systems with higher interfacial tension and vapour pressure had an improved yield of 1.4 times owing to larger number of droplets formed.

1. Introduction

Ultrasound is researched as a useful tool to improve different aspects of various chemical processes [1–4]. This improvement by sonication (i.e., application of ultrasound) can be attributed to cavitation induced in a liquid medium and the various chemical and physical effects associated with it [5–13]. One of the applications of ultrasound is the creation of emulsion in a heterogeneous system by virtue of the physical effects [14–17]. This particular behaviour has been used to improve liquid-liquid extraction processes, as emulsification can increase interfacial area for mass transfer. Ultrasound is exceptionally useful when used in combination with microreactors as it provides a non-contact method of mixing [8], where application of other active methods of mixing would prove challenging or sometimes outright impossible owing to the very small characteristic size of the microchannel.

The advantages of the use of ultrasound as an active method of improving mixing and hence the mass transfer characteristics in combination with microreactor setups was already established in many publications [15,16,18]. A direct method for this particular combination was proved to be especially fruitful when considering the heterogeneous hydrolysis of *p*-nitrophenyl acetate reaction [19–21]. The influence of the design, ultrasound signal parameters and process parameters were studied. These studies were performed for one particular biphasic system of toluene and water, but emulsification is a process which is very much dependent on the fluid properties. Therefore, an interesting perspective would be to understand the influence that the choice of biphasic system has on the emulsification by ultrasound. The initiation mechanism of emulsification by ultrasound was explained in a previous publication [19], wherein the bubbles created as a result of cavitation either tend to form clusters of small bubbles or large individual bubbles which vibrate along the interface of the two liquids, disturbing it and causing one phase to move into the other creating the emulsion. Even if the emulsification of the two phases is brought about by the vibration of the bubble at the interface of the two phases, the readiness of the liquid to form cavitation bubbles plays an

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important role. This readiness to form cavitation bubbles greatly depends on certain fluid properties.

The cavitation by ultrasound in a liquid is a result of a large negative pressure being applied on the liquid during the rarefaction cycle of the wave which causes the molecules to be pulled apart, exceeding the critical molecular distance required to hold the liquid intact [3,13,22,23]. The effects of fluid properties on cavitation are well investigated [22–28]. It has been reported that cavitation is readily formed in liquids of low viscosity, lower surface tension and higher vapour pressure. The higher the viscosity, the more difficult to form cavitation bubbles as a greater negative pressure will be required to overcome the intermolecular force [22]. With respect to surface tension, it has been shown by adding non-polar hydrophobic solids to water that the cavitation threshold increases with decrease in surface tension [27]. A higher vapour pressure might lead to an easier formation of cavitation bubbles, but the cavitation effects are less intense due to the introduction of vapour into the bubble (i.e. cushioning effect) [22]. As these three fluid properties were reported to have a direct influence on the sonication behaviour, they were selected for further consideration in this study. It is worth mentioning that any effects associated with the collapse of cavitation bubbles are not considered, due to the length of time that the cavitation bubble persists in the liquid [19], it is concluded that most of the physical effects are brought about by the vibrating stable cavitation bubbles or degassing bubbles and not by the collapse of transient bubbles.

This work aims at combining the various effects brought about by the properties of liquid individually and their effects on emulsification, to understand their influence on sonicated liquid-liquid extraction in a microchannel. This work focuses on the influences of the fluid properties for the best design [20] and process conditions initially observed in the previous publications [19,20]. Also, this helps to understand whether the rate of extraction, which is affected by the properties of the liquid, can be overridden by the effect of sonication.

2. Materials and methods

2.1. Reactor and experimental setup

The sonication experiments are performed in flow; the reactor and experimental setup are explained in detail in a previous publication [20]. Some of the basic arrangement details of the setup are briefly discussed here. The reactor used is the five-interval contact reactor, which implies that there are five points of contact per channel of the plate. The reactor consists of an aluminium plate with four square channels cut through it, with the sides equalling the diameter of the tubing to be placed in it (inner diameter 0.8 mm, outer diameter 1.6 mm). The tubes passing through the channels are held in place with a Plexiglas plate bolted at the four corners of the plate. The whole assembly is screwed onto a multi frequency transducer (20,40,60 kHz), and is connected to an amplifier and a waveform generator to define the parameters of the input sound wave. The two phases to be mixed are pumped through a T-junction using a syringe pump. The mixed phases leaving the reactor are collected and separated in a separating flask. The two-phase system exiting the reactor is studied with a high-speed camera for the flow rates range of 0.1–1 ml/min.

2.2. Selection of solvents

To understand the influence of solvent properties on sonication for liquid-liquid extraction, the two-phase system was studied with different organic solvents. For most cases the heterogeneity in liquid systems is caused using an aqueous and organic liquid. For this study the aqueous phase is kept constant. For the organic phase common industrial solvents were selected (Table 1), based on their properties in relation to their influence on sonication behaviour.

The physical properties that are reported to influence the ultrasound transmittance and cavity formation in the liquid are the viscosity, surface tension and vapour pressure [22]. Since this study deals with a system of two immiscible liquid phases, the interfacial tension of the solvents in water is considered instead of the surface tension even though the cavitation formation is affected by surface tension. This choice is rationalized by the fact that the emulsification behaviour that promotes the improved mass transfer between the phases is directly affected by the interfacial tension between the two phases. Additionally, the relevance of this statement is further discussed in Section 3.2.2. Density is shown in Table 1 for the understanding the top and bottom layers obtained on separation. For this study, two solvents are compared based on the difference in the property to be assessed but as much as possible similar in the other properties that influence the ultrasound. To study the influence of viscosities the solvents studied are toluene and chlorobenzene, for the influence of interfacial tension toluene is compared to methyl isobutyl ketone (MIBK) and for the influence of vapour pressure MIBK is compared to 2-Methyl tetrahydrofuran (2-Methyl THF). The selected compounds do not provide a perfect set of variations with pairs differing in only one property, but they are the closest match available from commonly used solvents in chemical industry, to understand the effect of different solvents on sonication. In addition, dichloromethane was used to further understand the effect of very large vapour pressure on sonicated segmented flow. The Laplace length scales (λl) indicative of the influence of the inertial forces and the interfacial forces were also calculated for each of the solvents with respect to pure water to understand its usability with the size of the tubing (0.8 mm) used.

Table 1
Properties of solvents at 20 °C.

Chemical Name	Viscosity	Interfacial Tension	Vapour pressure	Density	λ_l
	cP	mN/m	mm Hg	g/ml	mm
Water	0.89	–	19	1	1
Toluene	0.59	37.75	23.2	0.86	5.3
Methyl Isobutyl Ketone	0.61	10.57	16.5	0.801	2.3
2-Methyl tetrahydrofuran	0.47	3.29	155	0.86	1.5
Chlorobenzene	0.8	40.94	9.5	1.106	6.3
Dichloromethane	0.44	28.4	376	1.33	3.0

These properties expect interfacial tension is taken from Handbook of Organic Solvent Properties by Ian Small wood (2012) [29]. The interfacial tensions are obtained by the pendent drop method. The λ_l is estimated based on the properties.

2.3. Reaction

To quantify the influence of ultrasound on these various parameter a proper extractive process needs to be identified that can be used with the different solvents. The hydrolysis of *p*-nitrophenyl acetate was considered to serve the required purpose. This reaction has been used to study sonication of heterogeneous systems for different design and process conditions [15,16,18,19]. The original reaction is as shown in Fig. 1.

The original reaction uses toluene as the solvent. To understand the usability of the different solvents for the reaction, the solubility of *p*-nitrophenyl acetate in these solvents was first studied. The compound was dissolved at identical concentration (0.05 M) as for toluene and checked visually for un-dissolved particles. This was further tested along with the possibility of by-product formation in a proton NMR (300 MHz Bruker Avance 300 Spectrometer). The solvent content in the organic phase was evaporated in a rotavapour and residue obtained was dissolved in deuterated chloroform and analysed with a proton NMR. The spectra showed consistency in the compound dissolved and no by-