



Full length article

Effect of Alkanes on interfacial tension of Fish Oil-AgNO₃ and on flow patterns in PFA mini-channel

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ABSTRACT

The multiphase flow with reaction and mixing of the extraction process at mini/micro scale continues to be an area of active research. In mini/micro-fluidic systems, the surface forces increase until gravitational forces no longer have a significant impact on the hydrodynamics of the system. Interfacial tension (IFT) forces begin to play a more predominant role in determining flow patterns due to the reduction of channel diameter. The flow pattern strongly depends on the physical properties of fluids and dimension of the channel. Recently, the flow of Fish oil-AgNO₃ in PFA mini-fluidic channel is stratified and attempted to bring slug flow pattern by addition of alkanes. In order to tune flow pattern, the various proportions of alkanes were added into this binary system and then evaluated IFT for Fish Oil EE–Water, Fish Oil EE–Silver nitrate Solution and Hexane-Fish Oil EE-Silver nitrate at 25°C using Spinning drop tensiometry. The Eotvos number and flow transition map between capillary number and Froude number for these experimental fluids are evaluated and commented the dominating forces for flow transition from stratification to slug flow. The addition of alkanes into the fish oil phase does elevate the interfacial tension significantly and then the slug flow pattern was anticipated in mini-channel. But the flow visualization investigations confirmed that the stratification of flow was observed even addition of alkanes into the fish oil phase. The reason for stratification would be the reduction of interfacial tension at the interface and reversible chemical reaction between fish oil ethyl ester and silver nitrate solution.

Keywords: Liquid-Liquid extraction process; Interfacial tension; Spinning drop tensiometry; Flow patterns

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1. Introduction

The interfacial tension of a binary mixture is fundamental properties in process design of Liquid –Liquid Extraction process since it plays an important role in interphase heat and mass transfer. The molecules at the surface of both of these liquids experience unbalanced forces of attraction. These unbalanced forces at the surface of separation between the two immiscible liquids (i.e., at the interface) give rise to interfacial tension. Silver based solvent extraction is a novel extraction process for concentration/separation of Omega 3 PUFA from fish oil. This extraction process is carried out in ~1.59 mm ID mini-fluidic channels. In the case of mini-fluidic extraction process, the chemical reaction occurs at the interface between aqueous and organic phase. The properties of the interface can dramatically influence the performance of the extractor (mini channel) yet not significantly influence the equilibrium properties. In addition to that, Interfacial properties of the binary system not only control the flow dynamics and patterns in the mini-channel but also the rate of extraction. In this case, the flow of a mixed phase of fish oil and silver nitrate solution at “Y” junction forms stratified flow. To alter flow patterns, alkanes are added to elevate the interfacial tension between fish oil ethyl esters and silver nitrate solution. The interfacial tension of various experimental fluids is evaluated by spinning drop tensiometry.

This work thus explored the interfacial surface force variations with practical fish oil/solvent/silver nitrate mixtures using spinning drop tensiometer to explore the observed variation in flow pattern.

2. Materials and methods

In order to evaluate the impact of alkane addition on interfacial tension, Properties of fish oil and silver nitrate solutions, non-polar organic solvents such as hexane were added to the fish oil ethyl esters in the following ratios:

1. 100 wt.% 18/12EE Fish Oil –EE
2. 10 wt.% Hexane and 90 wt.% 18/12EE Fish Oil-EE
3. 50 wt.% Hexane and 50 wt.% 18/12EE Fish Oil-EE

2.1. Evaluation of IFT using spinning drop tensiometry

The interfacial tension was evaluated for 18/12EE–water, 18/12EE–silver nitrate solution, hexane-18/12EE–silver nitrate solution and hexene–18/12EE–silver nitrate solution at 25 °C. The experiments were carried out in a spinning drop tensiometer (SITE 100) with Drop Shape Analysis Software (DSA2).The interfacial tensions are calculated from the Vonnegut equation.

$$\gamma = \frac{(\rho_{heavyPhase} - \rho_{lightphase})\omega^2 R^3}{4} \quad (1)$$

2.2. Experimental system for flow patterns studies

In the experimental set up, each phase was pumped through a 1.5 meter length of tubing submerged in a temperature controlled reservoir at 10°C to pre-cool the solution, after which time the phases were contacted in a Y-junction. Then Y-junction acts mixing section between two immiscible phases and the outlet of Y-junction is connected to a mini-channel which comprises of a length of 1 m and inside diameter 1/16th inch. The flow patterns for different combinations of flow velocities (rates) are observed visually and photographed by a high speed camera (PCO Dimax). The high speed video camera was set to capture images of process fluids flow at a frame rate of up to 650 frames per second.

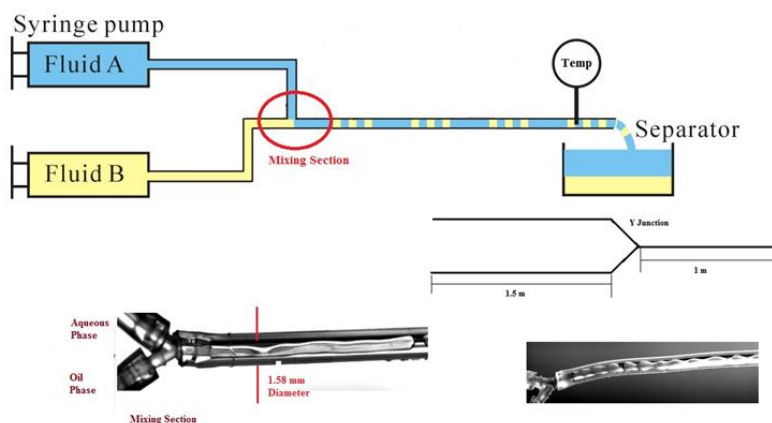


Fig. 1. Experimental set up and mixing section. The flow patterns at “Y” the mixing section have been captured by high speed camera.

3. Results and discussion

Interfacial tension between organic and aqueous phases plays a major role in LLE experiments. The larger the interfacial tension, the more difficult it is to form emulsions but the easier it is to separate immiscible phases by coalescence. Low interfacial tension aids dispersion and thus improves contacting mass-transfer efficiency, but can make subsequent separation difficult. At high interfacial surface tensions, slug flow is the predominant flow pattern observed in mini-fluidics. As most of the previous analogous fish oil systems where slug flow profiles were observed used pure alkanes as a solvent with quantities of pure components of Omega 3 PUFA dissolved, it is expected that the interfacial tension in these systems is higher than that present when commercial fish oils are employed.

In previous literature, the flow patterns observed using idealized fish oil analogues was slug-flow, with significant discussions presented as to why this flow pattern is beneficial. Within this work, a stratified flow pattern was observed, which has significant implications on relative residence times of the oil and aqueous phases and overall system performance.

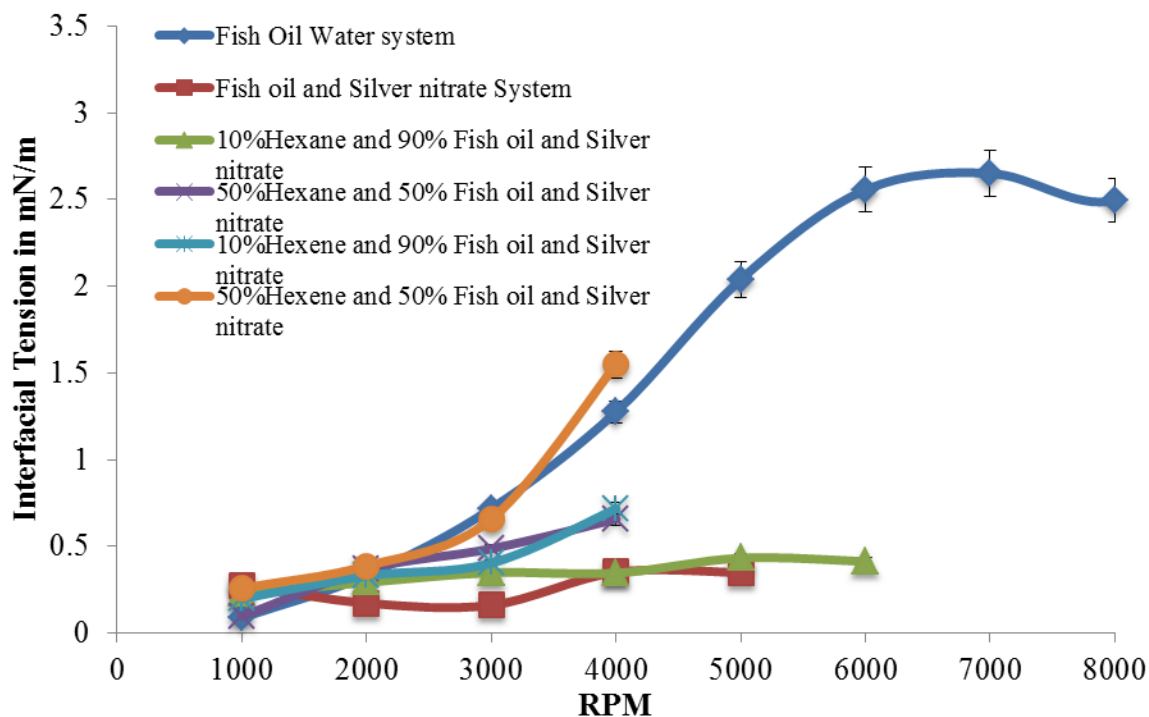


Fig. 2. Interfacial tension of experimental fluids using spinning drop tensiometry.

3.1. Flow patterns in mini-fluidic channel

Q _{Oil} (ml/min)	Q _{Aque} (ml/min)	Fish Oil Water System	Fish Oil Silver nitrate System	10% Hexane 90% Fish Oil Silver Nitrate System	50%Hexane 50%Fish Oil Silver Nitrate System	Hexane- Silver Nitrate system
3.33	10					
3.33	10					
3.33	10					
1.47	5					
1.47	5					
1.47	5					
1.47	5					
0.666	2					
0.666	2					
0.666	2					
0.666	2					

Fig. 3. Flow patterns observed in 1/16th ID of PFA mini-channel. Oil Phase enters from bottom at various flow rate and Silver nitrate enters from top in “Y” junction at various flow rates. In Fish Oil water system, Stratified, Wavy annular and plug, slug flow patten were observed. The stratified flow patten only observed in Fish Oil Silver nitrate system, 10 Hexane 90 Fish Oil –Silver nitrate System, 50Hex50 Fish Oil Silver Nitrate system. But In Hexane Silver nitrate system, Slug flow pattern was observed at 5 ml/min flow rate of silver nitrate and 1.47 ml/ min of Hexane.

The IFT data would suggest a significant variation in interfacial tension depending on whether or not silver nitrate is present in the solution, and if hexane are added to the fish oil, the fish oil and distilled water had interfacial tension which was in the upper limit of the instrument’s ability to measure, as illustrated by the steady rise in calculated surface tension with RPM (where RPM’s above 7000 to 9000 can create some difficulties in the equipment used). In

contrast (Fig. 2), fish oil in silver nitrate solution was at the lower end of the instrument's capabilities, where the interface would breakup up rapidly at rotation rates before stable interfacial tension measurements could be obtained. The 10 % wt. of hexane addition resulted in an apparent increase in interfacial tension. 50% of hexane had a significant increase in the interfacial tension, rapidly moving past the instrument's ability to measure accurately. However, the addition of hexane either 10 % or 50 % to fish oil with silver nitrate system does not change the flow pattern in the mini-channel and cause only stratified flow pattern with silver nitrate solution (Fig. 3).

3.2. Influence of various dominating force to control flow patterns

In multiphase flow at mini/micro scale, the dimensionless number Eotvos number is defined as the ratio between gravity forces to interfacial tension force of the fluids. It is found to be important in channel size classification.

$$Eo = \frac{\Delta\rho g d^2_H}{8\sigma}$$

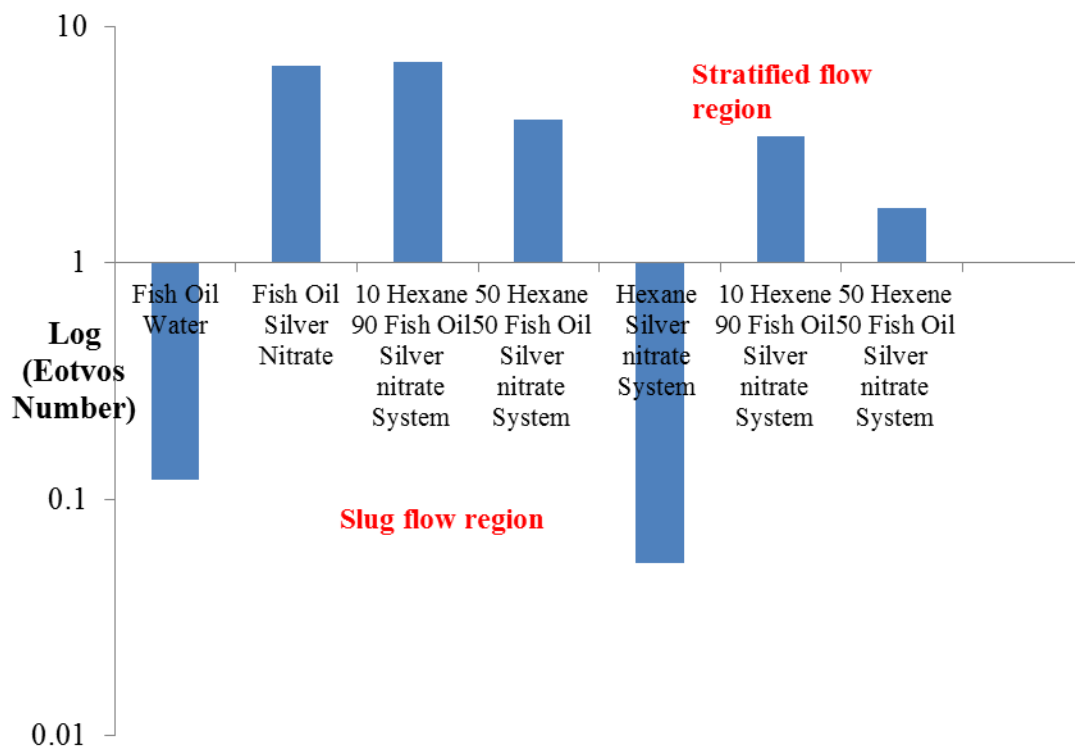


Fig. 4. Eotvos number (EO) is plotted versus the different experimental fluids.

In general, the interfacial forces play the most dominant forces especially in two immiscible phase flow in mini-channel. The threshold value set on the Eo depends on the physical phenomenon examined and varies in the range of 0.04-5. Furthermore, in micro/mini-channels, interfacial forces often dominate gravity forces $Eo < 0.05$. As can be seen in Fig. 4, Eotvos

numbers less than 0.02 is only for the fish oil & water and hexane and silver nitrate fluid pairs. The flow of these binary systems at mini scale causes slug flow formation. For all other systems, the interfacial tension is too low to give Eotvos number greater than 0.05 at 1/16" hydraulic diameter.

3.3. Flow pattern maps based on Capillary number and Froude number

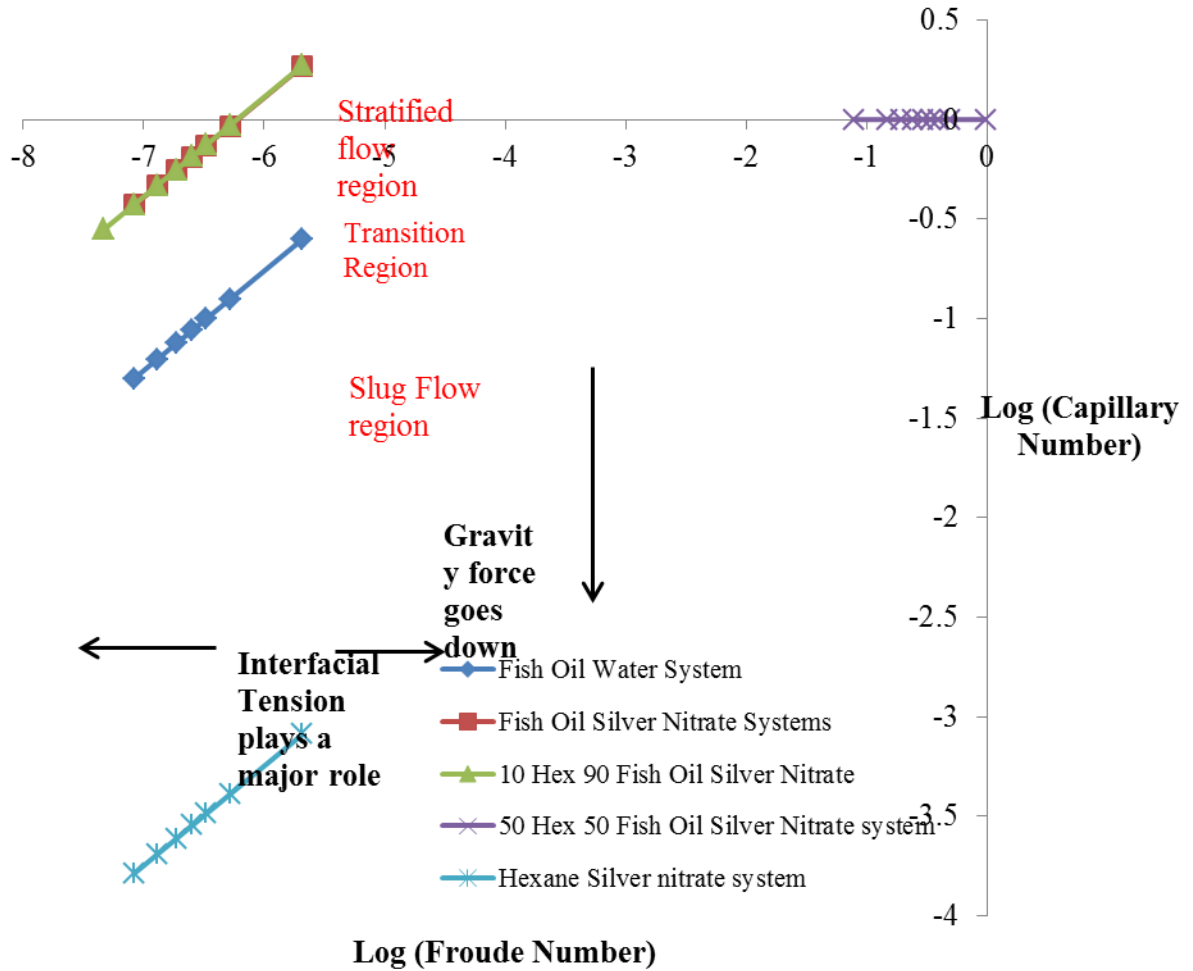


Fig. 5. The plot between Log (Ca) vs. Log (Fr) for fish oil water system, Fish Oil AgNO₃ system, 10 Hex 90 Fish Oil AgNO₃ systems, 50% Hex 50 % Fish Oil AgNO₃ system and Hexane AgNO₃ system flow in 1/16th inch ID of PFA mini-channel is shown below.

The ratio of inertia force to gravity force is expressed by Froude number (Fr) and the ratio between viscous force and interfacial force is expressed by Capillary number. Moreover, the analysis of flow pattern at mixing of aqueous phase and organic phase in Y-junction in mini-channel, The Froude number and capillary number are calculated for mixed phase (aqueous and organic) and the various forces action on the flow patterns are commented. In fish oil water system and hexane silver nitrate system, the flow transition from stratified flow to Slug flow ($Fr \llll 1$) is observed and at this point, inertial forces and

gravity forces are negligible ($Fr < 1$) and interfacial tension force dominates the inertial forces and cause onset of slug flow in the mini-channel whereas in the case of Fish Oil- $AgNO_3$ System, 10Hex 90 Fish Oil $AgNO_3$ System, 50% Hex 50 % fish Oil $AgNO_3$ system ($Ca > 0.1$), Inertial and gravity forces dominate interfacial tension forces due to the increase of density of silver nitrate solution and also weak interfacial tension between fish oil and silver nitrate and cause stratification in flow. Similarly, in the view of capillary number for hexane silver nitrate system, $Ca < 0.002$, Interfacial tension forces dominant the viscous forces which cause the slug flow in mini-channel even at flow rate of 5 ml/min. Generally, in the multiphase flow at mini/micro scale, Gravity force is negligible due to capillary force and interfacial tension force.

4. Conclusions

The observed flow patterns in the mini-fluidic contacting system were stratified due to reduction of interfacial tension between fish oil and aqueous concentrated silver nitrate solution even after addition of alkane into fish oil phase. However, the flow of fish oil water system and hexane silver nitrate system at mini scale forms slug flow pattern.

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