CHEMICAL DEMULSIFICATION OF MODEL WATER-IN-OIL EMULSIONS WITH LOW WATER CONTENT BY MEANS OF IONIC LIQUIDS

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Abstract - The demulsification of model water-in-oil (w/o) emulsions containing 1% wt. water by [Omim][PF$_6$] and Aliquat® 336 ionic liquids (IL) as demulsifiers was investigated in batch mode at different temperatures (30, 45 and 60 °C) and demulsifier concentrations (2.5×10^{-3}, 1.2×10^{-2} and 2.9×10^{-2} mol L^{-1}). The model oil is a mixture n-heptane/toluene (70/30% wt.) with 1% wt. of Span® 83 as a surfactant. Experimental results showed that the main differences in demulsification dynamics between systems containing IL and blank (i.e., in the absence of demulsifier) are detected at 30 °C and for short demulsification times ($t\leq4$ h). In particular, the demulsification efficiency is 8, 21 and 74% for the blank sample, [Omim][PF$_6$] and Aliquat® 336 tested under the more concentrated IL condition, respectively. The superior demulsification performances of Aliquat® 336 with respect to [Omim][PF$_6$] were related to the greater molecular weight and more hydrophobic character of its cation, likely able to induce a faster desorption of the surfactant at the w/o interface and consequently promoting water droplet coalescence. Moreover, the kinetic demulsification data were successfully interpreted by an empirical pseudo-first order model. In general, the obtained outcomes encourage future research efforts in the use of ionic liquids for the removal of low water fractions from w/o emulsions.
Keywords: Model water-in-oil emulsions; Ionic liquids; Demulsifiers; Demulsification kinetic.

INTRODUCTION

The formation of water-in- oil (w/o) emulsions is a critical issue in industrial applications such as the petroleum sector. In fact, emulsified water can corrode refinery equipment and the water-dissolved salts can poison catalysts in downstream processing facilities (Issaka *et al.*, 2015; Sullivan *et al.*, 2007). Additionally, w/o emulsions usually exhibit viscosities significantly higher than crude oil, thus increasing the pumping costs for the transport of oil in pipelines (Peña *et al.*, 2005). The formation of emulsions is promoted by the mixing in the equipment used in both the stages of petroleum extraction and refining and they are stabilized by the presence of natural surfactants (Karcher *et al.*, 2015). Surface active agents commonly occurring in crude oils, such as asphaltenes, resins, waxes and solid particles, form rigid films at the water-oil interface, which prevent the coalescence of water droplets (de Oliveira *et al.*, 2010; Fortuny *et al.*, 2007; Issaka *et al.*, 2015; Schramm, 1992; Silva *et al.*, 2013; Sjöblom *et al.*, 2003; Yang *et al.*, 2009). Numerous techniques are currently available for breaking w/o emulsions, including mechanical methods (e.g., gravity settlers or centrifugal separators), application of electric

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fields (electrocoalescers), conventional heating and microwave demulsification, pH adjustment, membrane separation and chemical demulsification (Abdurahman *et al*., 2007; Djuve *et al*., 2001; Ekott and Akpabio, 2010; Guzmán-Lucero *et al*., 2010; Hajivand and Vaziri, 2015; Issaka *et al*., 2015; Yang *et al*., 2009). The mechanical separators and electrostatic grids commonly adopted for the destabilization of crude oil emulsions have high equipment volume and high cost for the installation on offshore platforms as main drawbacks (Ekott and Akpabio, 2010).

The application of chemical demulsifiers is one of the most common strategies applied for resolving w/o emulsions, and it involves the use of amphiphilic molecules which, thanks to their interfacial activity, accelerate the interfacial film rupture, thus promoting the flocculation and coalescence of the water droplets (Abdurahman *et al*., 2007; Cendejas *et al*., 2013; Djuve *et al*., 2001; Ekott and Akpabio, 2010; Guzmán-Lucero *et al*., 2010; Kang *et al*., 2006; Issaka *et al*., 2015; Silva *et al*., 2013). The main advantage of chemical demulsification relies on the possibility of its easy integration into already existing w/o separation units without the need of equipment shutdown and with relatively small capital costs (Ekott and Akpabio, 2010). Different classes of demulsifiers are commercially available including co-polymers of polyoxyethylene and polyoxypropylene or alkylphenol-formaldehyde resins, alkoxylated amines, or mixtures of them (Cendejas *et al*., 2013; Guzmán-Lucero *et al*., 2010; Issaka *et al*., 2015). Current research efforts are focused on the development of cost-effective and environmentally friendly chemical demulsifiers characterized by high water separation efficiency and demulsification rate, so as to meet the oil company specifications (the maximum allowable water cut in crude oil is generally 0.1–0.5%) (Abdul-Wahab *et al*., 2006; Cendejas *et al*., 2013; Guzmán-Lucero *et al*., 2010; Issaka *et al*., 2015). In addition, the combination of chemical demulsifiers with microwave or ultrasound, which accelerate the water separation process, is considered to be an attractive route to minimize the dosage of chemicals and consequently their utilization cost (Issaka *et al*., 2015). In this framework, the use of ionic liquids (IL) for the destabilization of w/o emulsions is a very promising option (Guzmán-Lucero *et al*., 2010; Lemos *et al*., 2010; Silva *et al*., 2013). In fact, IL can exhibit high affinity for w/o interface thanks to their amphiphilic nature, and they can interact with the polar fractions of crude oil due to their high dielectric properties (Guzmán-Lucero *et al*., 2010; Lemos *et al*., 2010).

Moreover, IL are characterized by high thermochemical stability and tunable chemico-physical properties, which allow selecting the cation-anion pair more suitable to treat a specific w/o emulsion and make them potentially applicable for high temperature demulsification (Olivier-Bourbigou *et al*., 2010). Literature studies concerning the application of IL for separation of w/o emulsions demonstrated that both the cation and anion of the IL greatly affect its interfacial activity (Guzmán-Lucero *et al*., 2010; Lemos *et al*., 2010; Silva *et al*., 2013). For example, Lemos *et al*. (2010) investigated the use of [Omim][BF$_4$] and [Omim][PF$_6$] for the separation of w/o emulsions. The authors observed that [Omim][PF$_6$] determined a faster decrease of the interfacial tension and a greater demulsification efficiency with respect to [Omim][BF$_4$] IL. This behavior was ascribed to both the greater anion size and the lower solubility in the aqueous phase of [Omim][PF$_6$] which hinder the aggregation of this IL in the medium, thus favoring its activity as demulsifier. Moreover, Silva *et al*. (2013) studied the effect of different imidazolium and pyridinium IL on the demulsification of a heavy crude oil whose water content was set at 40% wt. The authors highlighted that a longer cation alkyl chain determines a higher hydrophobic character of the IL, thus inducing a greater water separation from the w/o emulsion. This was related to a greater affinity of these IL for the water/oil interface, which favors the displacement of the natural surfactants.

The literature analysis suggests that the properties of ILs make them potential good candidates for separating w/o emulsions, even if this research topic is at an early stage of investigation. It is also underlined that the high current cost of ILs represents the main issue limiting their application as demulsifiers on large-scale dehydration processes. Consequently, much research effort is still needed to optimize their use (i.e. determining the best operating conditions that minimize the IL dosage required to obtain a desired dehydration efficiency) and make them economically competitive with commercially adopted demulsifiers. Additionally, IL demulsification performances have been tested for systems containing high water fractions (generally varying in the range 20–50% wt.), whereas their potential applicability for resolving low water-content emulsions has not yet been investigated. For w/o emulsions containing low water fractions, the greater distance between water droplets in the sample is expected to determine a lower probability of droplet collisions, and definitely lower demulsification performances with respect to the high water-content systems (Fortuny *et al*., 2007).

Moreover, it should be remarked that the water content emulsified in crude oil can vary in a wide range as a function of the crude oil properties and of the water amount used in both stages of petroleum extraction and desalting (Fortuny *et al*., 2007; Guzmán-Lucero *et al*., 2010; Sullivan *et al*., 2007). Consequently, the analysis of IL separation efficiency for very dilute w/o emulsions is considered to be of practical interest. In this context, this paper aims at providing a contribution in the assessment of the applicability of ionic liquids for separating w/o emulsions with low water content, by adopting a model emulsified system as a first stage of investigation.

In this work, [Omim][PF$_6$] and Aliquat® 336 IL were investigated as demulsifiers for the separation of model w/o emulsions containing 1% wt. of water. Batch separation tests were performed at different temperatures (30, 45 and 60 °C) and IL concentrations (2.5×10^{-3}, 1.2×10^{-2} and 2.9×10^{-2} mol L^{-1}), in order to evaluate the effect of the operating parameters on the performances and on the kinetics of the process. The separation efficiency *vs* time patterns were also analyzed in the light of an empirical pseudo-first order model to estimate the characteristic demulsification kinetic constants. The application and validation of this simple kinetic model can be considered as a useful tool for the design of w/o demulsification units which, to the best of our knowledge, has not been proposed yet in the pertinent literature concerning the demulsification processes.

EXPERIMENTAL SECTION

Preparation of Model Water-in-Oil Emulsions

The study of chemical demulsification of w/o emulsions required a preliminary analysis, devoted to the formulation of a model emulsion simulating the typical compositions of those occurring in the petroleum industry. It is worth observing that the crude oil composition strongly depends on its geographical origin, thus not allowing the generation of a single representative mixture. However, crude oil is generally composed of saturated and aromatic hydrocarbons and natural surfactants (asphaltenes, resins) (Martínez-Palou *et al*., 2013). In the model oil adopted in this work, the saturated/aromatic hydrocarbons composition was simulated by a mixture of n-heptane and toluene 70/30% wt., commonly adopted in the literature and named "heptol" (Krawczyk *et al*., 1991). The emulsifier chosen to mimic the presence of natural surfactants in crude oil was sorbitan sesquioleate (Span® 83), which was selected due to

its low value of the Hydrophilic Lipophilic Balance (HLB) index equal to 3.7 (Constantinides and Scalart, 1997). In fact, this value of the HLB index for Span® 83 falls in the range 3-6, commonly indicated in the literature as the one for which surfactants are able to stabilize w/o emulsions (Hait and Moulik, 2001). Moreover, Abdulbari *et al*. (2011) also verified the stability of water-in crude oil emulsions in the presence of Span® 83 as a surfactant.

All reagents were reagent grade and purchased from Sigma-Aldrich.

The preparation of the model w/o emulsions was carried out as follows. For each sample, 1% wt. of Span® 83 was added to 36.9 g of heptol (50 mL) in a beaker, and the obtained mixture underwent 15 min of sonication in an Elmasonic P60 H ultrasonic bath (operated at 80 kHz and 180 W) to improve the mixing of the surfactant in the hydrocarbon phase. Then, 1% wt. of double-distilled water was added to the heptol/Span® 83 mixture to mimic the water content of the w/o emulsions (emulsification step). The obtained mixture was further sonicated for 2 h in cyclic mode with substitution of water in the ultrasonic bath each 15 min in order to maintain the bath temperature around 25 °C. The cyclic sonication treatment was required to prevent a strong increase in the water bath temperature, which is detrimental to an effective emulsification process.

Demulsification Tests

After the formulation of the model w/o emulsion, the demulsification tests were carried out by adding the IL as demulsifier and monitoring the time-evolution of the water content in the emulsion. The IL selected for the experimental campaign are trioctylmethylammonium chloride (Aliquat® 336, MW=404 g mol^{-1}) and 1-methyl-3-octylimidazolium hexafluorophosphate ([Omim][PF$_6$], MW=340 g mol^{-1}), both purchased from Sigma-Aldrich. The molecular structures of the adopted ionic liquids are reported in Figure 1. Three concentration levels (C_{IL}) were investigated for both the ILs: C_{IL}=2.5×10^{-3}, 1.2×10^{-2} and 2.9×10^{-2} mol L^{-1}. The IL operating concentrations were chosen to reproduce the typical dosages of the demulsifiers adopted for treating real w/o emulsions (Borges *et al*., 2009; Cendejas *et al*., 2013; Guzmán-Lucero *et al*., 2010; Lemos *et al*., 2010; Silva *et al*., 2013). The dispersion of the IL in the emulsion was favored by means of a 15 min sonication treatment (which allowed obtaining a uniform liquid system, as verified from visual inspection of the prepared samples). The demulsification tests were performed in a thermostatic bath at three different
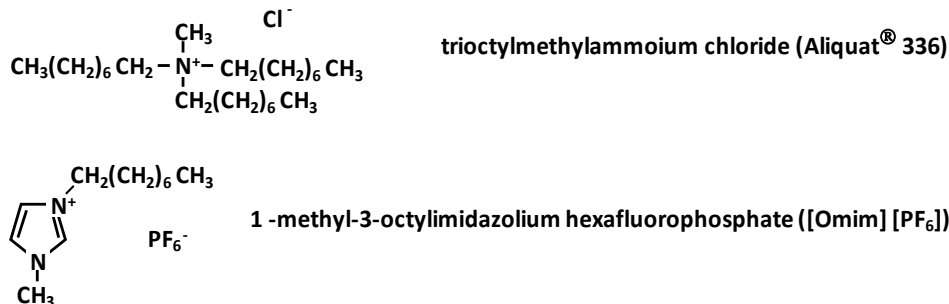
$$CH_3(CH_2)_6\,CH_2 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_2(CH_2)_6\,CH_3}{|}}{N^+}} - CH_2(CH_2)_6\,CH_3 \quad\quad Cl^-$$

trioctylmethylammoium chloride (Aliquat® 336)

1 -methyl-3-octylimidazolium hexafluorophosphate ([Omim] [PF$_6$])

Figure 1: Aliquat® 336 and [Omim][PF$_6$] molecular structures.

operating temperatures (30, 45 and 60 °C), for each IL type and concentration. The determination of the time-variation of the water content in the emulsion was performed by analyzing at fixed times 1.5 mL samples of each emulsion, sampled from the upper zone of the beaker, by means of a volumetric Karl-Fischer titrator (KFV20 Mettler Toledo). The analysis of the water content in the emulsion was performed until it reached a constant value indicating no further separation. A sample without IL addition (blank sample) was also prepared in order to analyze the water separation in the absence of the demulsifier in the system and for the sake of comparison with the IL containing samples. The determination of the water content in the emulsion at different times allowed the determination of the dynamic demulsification pattern for each investigated system *via* evaluation of the dehydration efficiency $\phi(t)$, defined as:

$$\phi(t) = \frac{\omega_0 - \omega(t)}{\omega_0} \tag{1}$$

where ω_0 and $\omega(t)$ [–] represent the water concentration (% wt.) in the w/o emulsion at $t=0$ and t, respectively.

Mathematical Modelling of Kinetic Demulsification Patterns

The ϕ *vs* t experimental profiles were interpreted in the light of a simple pseudo-first order kinetic model. For a pseudo-first order model (here termed as PFO), the time variation of the demulsification efficiency can be expressed as a function of a linear driving force:

$$\frac{d\phi(t)}{dt} = k\left[\phi_{\max} - \phi(t)\right] \tag{2}$$

where ϕ_{max} is the maximum separation efficiency experimentally determined and k [min^{-1}] is a first-order kinetic constant. By imposing the initial condition $\phi(t=0)=0$, Eq. (2) can be solved by the separation of variables method, obtaining the following integral form of the PFO model:

$$\phi(t) = \phi_{\max}\left[1 - \exp(-kt)\right] \tag{3}$$

The PFO model was applied to interpret all the demulsification kinetic profiles obtained at different temperatures and IL concentrations and the corresponding k values were determined as best-fitting parameter *via* the least square method.

RESULTS AND DISCUSSION

[Omim][PF$_6$] and Aliquat® 336 Demulsification Tests

Figure 2 (a)–(i) reports the time evolution of the demulsification efficiency $\phi(t)$ of [Omim][PF$_6$] and Aliquat® 336 IL demulsifiers at three different concentration levels ($C_{IL}=2.5\times10^{-3}$, 1.2×10^{-2} and 2.9×10^{-2} mol L^{-1}), tested at T=30, 45 and 60 °C. The dynamic dehydration patterns for the model w/o emulsions without IL addition (blank sample) are also reported for the sake of comparison.

As a general overview, the results clearly testify that both the tested IL are effective in inducing a higher water separation with respect to the blank sample, mainly at 30 °C and under more concentrated demulsifier conditions (i.e., $C_{IL}=2.9\times10^{-2}$ mol L^{-1}). Moreover, Aliquat® 336 displays better demulsification performances when compared to [Omim][PF$_6$], particularly at low temperature, while the differences reduce as the temperature increases. The analysis of the kinetic demulsification data is detailed in the following for the different experimental conditions investigated.
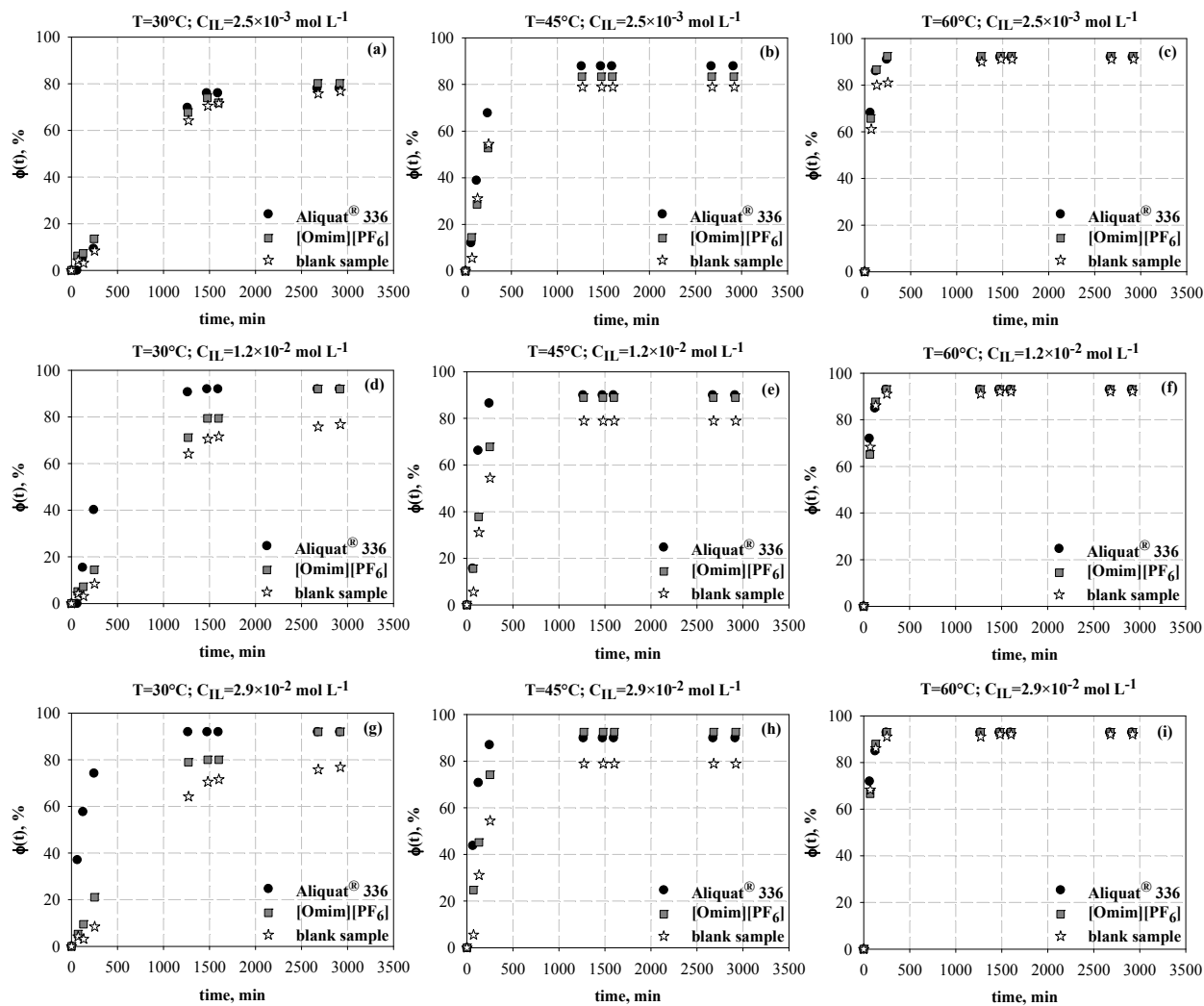
Figure 2: Demulsification performances for model water-in-oil emulsions of [Omim][PF$_6$] and Aliquat® 336 IL tested at 30, 45 and 60 °C and at different ionic liquid concentrations (C_{IL}): (a)–(c) C_{IL}=2.5×10^{-3} mol L^{-1}, (d)–(f) C_{IL}=1.2×10^{-2} mol L^{-1}, (g)–(i) C_{IL}=2.9×10^{-2} mol L^{-1}.

Figure 2 (a), (b) and (c) compares the demulsification patterns of the tested IL, obtained at C_{IL}=2.5×10^{-3} mol L^{-1} at 30, 45 and 60 °C, respectively. At T=30 °C there is no significant difference in the demulsification patterns of both the IL with respect to the blank sample (Figure 2 (a)). All the samples reach a ϕ_{max} value of about 80% in two days and the water separation trends are similar in all the cases. In particular, for low concentration of both the IL no appreciable chemical demulsification occurs at T=30 °C, and the water separation could be mainly due to the thermal collisions between droplets, inducing their coalescence. The experimental results at 45 °C (Figure 2 (b)) witness an increase in water separation rate for all the samples; in particular, after 4 h a dehydration efficiency of about 70% was

reached with Aliquat® 336. The plateau values are attained for all the samples after 21 h with ϕ_{max}=90 and 84% for Aliquat® 336 and [Omim][PF$_6$], respectively (78% is the maximum demulsification efficiency observed for the blank). Finally, at 60 °C (Figure 1 (c)) the dynamic demulsification profiles obtained for both IL tested at C_{IL}=2.5×10^{-3} mol L^{-1} and the blank practically overlap.

The effect of the operating temperature on demulsification efficiency obtained for both the ILs tested at C_{IL}=1.2×10^{-2} mol L^{-1} is sketched in Figure 2 (d)–(f). At T=30 °C (Figure 2 (d)), the sample containing Aliquat® 336 shows a higher dehydration rate with respect to both [Omim][PF$_6$] (at the same concentration) and the blank; ϕ_{max} is nearly 93% for Aliquat® 336 after approximately 1500 min, whereas

a similar value is obtained for [Omim][PF$_6$] after 2 days (ϕ_{max}=80% for the blank sample after 2 days). For an operating temperature of 45 °C (Figure 2 (e)), an increase in water separation rate is observed for all the samples. The sample containing Aliquat® 336 reaches its water separation efficiency plateau (90%) after 4 h, while for [Omim][PF$_6$] the same value is obtained after 21 h; the blank sample experiences a ϕ_{max}=80% after 21 h. Finally, at 60 °C (Figure 2 (f)) the dehydration trends for all the sample are practically equivalent.

A comparison of the demulsification kinetics at C_{IL}=2.9×10^{-2} mol L^{-1} is reported in Figure 2 (g)–(i). At T=30 °C, the dehydration efficiency is significantly higher for Aliquat® 336 with respect to [Omim][PF$_6$] and to the blank sample, mainly for shorter demulsification times. Indeed, the efficiency is 40% after 60 min and 74% after 4 h (*vide infra*). At T=45 °C and 60 °C (Figure 2 (h) and (i)), the dynamic patterns are similar to those discussed for C_{IL}=1.2×10^{-2} mol L^{-1} (cf. Figure 2 (e) and (f)).

In general, the attainment of a dehydration efficiency plateau, not corresponding to a complete water separation, could be explained considering that, in the first stage of the process, there is a greater number of droplets in the emulsion with an associated higher frequency of droplet collision promoting their fast coalescence and separation (Azizi and Nikazar, 2015). On the contrary, for longer test times the concentration of droplets in the upper zone of the beaker is likely to be low to allow a sufficient collision frequency for residual water separation, at least under the experimentally adopted time-scale of observation.

From the experimental data, it is possible to conclude that the main differences in the demulsification dynamic patterns between the systems containing IL and the blank sample are observed at 30 °C and for short demulsification times (t≤4 h). These observations are important in the light of a practical applicability of IL as chemical demulsifiers, because short operational times and lower temperatures improve the economics of the water separation process. For a comparative analysis, Figure 3 reports the demulsification efficiency obtained for both the investigated ILs at T=30 °C and after 4 h. The results clearly show that, in the case of [Omim][PF$_6$], only a minor improvement in demulsification performances is obtained with respect to the blank sample after 4 h, and that the trend is weakly monotonic with the IL concentration. Moreover, the demulsification efficiency is 21 and 8% under more concentrated IL condition and for the blank sample, respectively. When Aliquat® 336 IL is taken into account, a remarkably higher water separation efficiency is observed. Moreover,

when the demulsifier concentration increases, the efficiency is significantly higher: $\phi(t)$=40 and 74% for C_{IL}=1.2×10^{-2} and 2.9×10^{-2} mol L^{-1}, respectively.
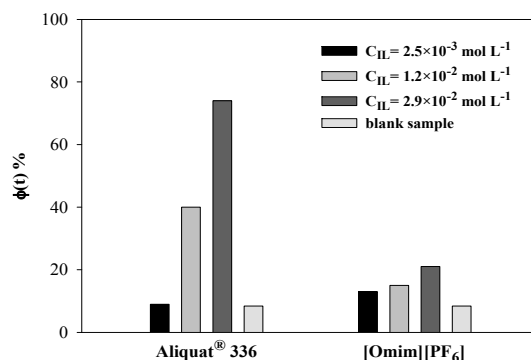

Figure 3: Demulsification efficiency for model water-in-oil emulsions derived for [Omim][PF$_6$] and Aliquat® 336 IL at 30 °C and after 4 h test (the blank sample is reported for comparison).

The experimental evidences hitherto discussed emphasize the important effect of the IL concentration/chemico-physical nature and of temperature on the water separation efficiency. In particular, the favorable effect of the IL concentration was mainly observed at lower operating temperatures (i.e., 30 and 45 °C). Contextually, in accordance with the experimental results retrieved in this study, Bhardwaj and Hartland (1994) reported better demulsification performances by increasing the demulsifier concentration, observing a faster adsorption rate at the water/oil interface for a greater demulsifier amount, which in turn should speed up the displacement of natural surfactants and hence the droplet coalescence. On the other hand, an increase in the temperature also promotes faster adsorption kinetics of the demulsifier at the w/o interface (Bhardwaj and Hartland, 1994). Moreover, the reduced differences of the demulsification efficiency between samples in the presence of IL and the blank at 45 and 60 °C could be related to the increase of coalescence and sedimentation rate, independent of the presence of IL. In fact, as the temperature increases the collision efficiency of the water droplets increases, favoring their coalescence (Azizi and Nikazar, 2015; Kim, 1999). In addition, at higher temperature, the continuous phase viscosity decreases, determining a higher sedimentation rate and therefore faster demulsification kinetics (according to Stokes' law) (Souza *et al.*, 2015). In conclusion, at higher temperature, the effect of IL is completely hidden, all the samples show the same kinetic patterns and the use of the IL as demulsifier does not provide any significant

improvement in the demulsification performances.

As already highlighted in the Introduction, both the nature of the cation, (in terms of molecular weight and length of side chains), and of the anion (in terms of size and water solubility) of ILs can greatly affect the interfacial activity of the demulsifier (Guzmán-Lucero *et al*., 2010; Lemos *et al*., 2010; Silva *et al*., 2013). In this context, the greater molecular weight of Aliquat® 336 (MW=404 g mol^{-1}) with respect to [Omim][PF$_6$] (MW=340 g mol^{-1}) is likely to be a key factor to explain its better demulsification performances, favoring its ability to act as flocculant for gathering up water molecules (Abdurahman *et al*., 2007). Moreover, the higher hydrophobic nature of the cation of Aliquat® 336 could further explain its better demulsification performances, in accordance with recent literature observations (Silva *et al*., 2013). In fact, Aliquat® 336 has three C8 alkyl chains in its cation, whereas a single C8 chain is present in [Omim][PF$_6$] cation (see Figure 1).

Mathematical Modelling of Demulsification Tests

Table 1 reports the values of the kinetic constant *k* obtained by applying the pseudo-first order model (PFO) (cf. Eq. (3)) to the demulsification data obtained for [Omim][PF$_6$] and Aliquat® 336 IL, tested at different operating temperatures (30, 45 and 60 °C) and concentrations (C_{IL}=2.5×10^{-3}, 1.2×10^{-2} and 2.9×10^{-2} mol L^{-1}). The kinetic model outputs for the blank sample are also reported for the sake of comparison. As an example, Figure 4 depicts the trends of the PFO model for both [Omim][PF$_6$] and Aliquat® 336 at fixed IL concentration (2.9×10^{-2} mol L^{-1}) and tested at *T*=30 °C (representing the most interesting demulsification conditions observed in this study).

Table 1: Kinetic constants derived from PFO model for model water-in-oil emulsions by using [Omim][PF$_6$] and Aliquat® 336 ionic liquids (blank sample is reported for comparison).

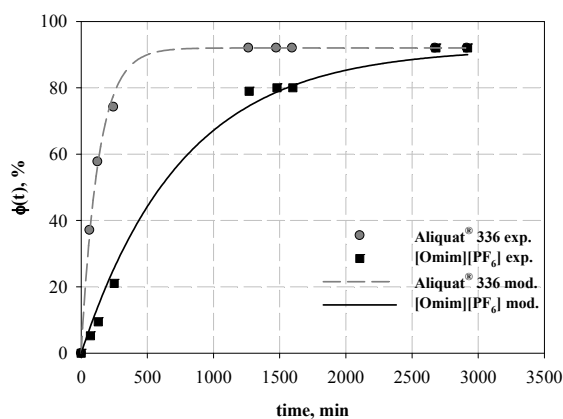|		C_{IL}=2.5×10^{-3} mol L^{-1}			C_{IL}=1.2×10^{-2} mol L^{-1}			C_{IL}=2.9×10^{-2} mol L^{-1}		
[Omim][PF$_6$]	T [°C]	30	45	60	30	45	60	30	45	60
	R^2 [–]	0.985	0.983	0.999	0.989	0.988	0.998	0.993	0.995	0.998
	k [min^{-1}]	1.4×10^{-3}	5.2×10^{-3}	2.0×10^{-2}	1.2×10^{-3}	4.6×10^{-3}	1.9×10^{-2}	1.3×10^{-3}	5.5×10^{-3}	1.9×10^{-2}
Aliquat® 336	T [°C]	30	45	60	30	45	60	30	45	60
	R^2 [–]	0.967	0.997	0.999	0.985	0.943	0.999	0.998	0.997	0.999
	k [min^{-1}]	1.4×10^{-3}	3.5×10^{-3}	1.9×10^{-2}	2.2×10^{-3}	8.1×10^{-3}	2.3×10^{-2}	7.6×10^{-3}	1.2×10^{-2}	2.2×10^{-2}
blank sample	T [°C]	30	45	60						
	R^2 [–]	0.970	0.976	0.989						
	k [min^{-1}]	1.3×10^{-3}	3.7×10^{-3}	1.8×10^{-2}						

Figure 4: Comparison between experimental (symbols) and theoretical PFO (lines) kinetic demulsification profiles derived for [Omim][PF$_6$] and Aliquat® 336 IL at 30 °C and for C_{IL}=2.9×10^{-2} mol L^{-1}.

The statistical analysis, in terms of the coefficient of determination (R^2) values reported in Table 1, and the modelling kinetic profiles (Figure 4) clearly testify that the PFO model provides a very good interpretation of all the set of experimental data in the whole t-range, for both [Omim][PF$_6$] and Aliquat® 336 IL and under all the tested experimental conditions. From a deeper inspection of the modelling data the following considerations can be drawn:

▪ For each tested IL concentration, k monotonically increases with temperature, in accordance with the experimental observations; as already discussed, this trend could be justified by an increase in droplet coalescence (higher collision frequency) and sedimentation rate at higher temperature (Azizi and Nikazar, 2015; Kim, 1999). For example, in the case of [Omim][PF$_6$] tested under more concentrated IL conditions (C_{IL}=2.9×10^{-2} mol L^{-1}), at T=60 °C k is equal to 1.9×10^{-2} min^{-1}, which is about 3.5 and 15 times greater than the values retrieved at 45 and 30 °C, respectively. Similarly, for Aliquat® 336 investigated at the same concentration level, a rise in the operating temperature from 30 to 60 °C triples the kinetic demulsification constant.

▪ At fixed temperature, an increase in the IL concentration does not produce a remarkable effect on the kinetic constant values in the case of [Omim][PF$_6$]. Conversely, for Aliquat® 336, an increase in the demulsifier concentration significantly accelerates the water separation process at each T level and mainly at 30 and 45 °C. For instance, for Aliquat® 336 tested at T=30 °C, the k value for C_{IL}=2.9×10^{-2} mol L^{-1} is 3.5 and 5.4 times those obtained at C_{IL}=1.2×10^{-2} and 2.5×10^{-3} mol L^{-1}, respectively. Anyway, at T=60 °C the differences between k values calculated for C_{IL}=1.2×10^{-2} and 2.9×10^{-2} mol L^{-1} become negligible, and k obtained for the lowest IL concentration (C_{IL}=2.5×10^{-3} mol L^{-1}) is only 1.2 times lower than the values obtained at higher C_{IL}. These results reflect exactly the experimental results.

▪ The comparison of the kinetic constants for both the tested IL highlights that, for the intermediate and more concentrated IL conditions, Aliquat® 336 displays k values generally greater than those obtained for [Omim][PF$_6$], in total accordance with the experimental demulsification patterns. For example, at C_{IL}=2.9×10^{-2} mol L^{-1} and 30 °C the kinetic constant computed for Aliquat® 336 is equal to 7.6×10^{-3} min^{-1}, a value 6-fold the one retrieved for [Omim][PF$_6$], under the same experimental conditions.

CONCLUSIONS

In this work, the dehydration of model water-in-oil (w/o) emulsions containing low water content (1% wt.) by either [Omim][PF$_6$] or Aliquat® 336 ionic liquid (IL) as demulsifiers was investigated. The w/o emulsion was simulated by a mixture of n-heptane and toluene (70/30% wt.) with 1% wt. of Span® 83 surfactant, acting as model hydrocarbon phase and surfactants naturally present in crude oil, respectively. After water emulsification by ultrasounds treatment, batch demulsifications tests were carried out at different temperatures (30, 45 and 60 °C) and IL concentrations (2.5×10^{-3}, 1.2×10^{-2} and 2.9×10^{-2} mol L^{-1}).

The experimental evidences highlighted that both the IL gave an improvement in water separation with respect to the blank sample (i.e., without any IL addition) and this effect is more marked at the lowest operating temperature (30 °C). Moreover, for all the investigated samples, a monotonic increase of the demulsification performances with temperature was observed. However, for T=60 °C, the demulsification patterns of both the samples with IL and of the blank overlap, making negligible the contribution of the IL. A comparison between the tested IL showed that Aliquat® 336 IL allows significantly faster demulsification kinetics with respect to [Omim][PF$_6$], at each investigated IL concentration and in particular at 30 °C. This behavior was mainly related to both a greater molecular weight and a more hydrophobic character of the cation of Aliquat® 336 IL. In fact, in accordance with the literature indications, both these factors favor the action of the demulsifier as flocculant and the displacement of natural surfactants at the w/o interface, hence promoting the water droplet coalescence.

The dynamic demulsification patterns were also analyzed in the light of a pseudo-first order kinetic model, which provided a satisfying interpretation of the experimental data under all the adopted operating conditions. The values of the kinetic constant (k) exactly reflected the observed experimental trends.

Concluding, the outcomes retrieved in this experimental study showed an interesting scenario for the use of ionic liquids in the field of dehydration of w/o emulsions containing low water content, for which non-chemical demulsification methods usually exhibit low separation efficiency. At relatively low IL concentration (2.9×10^{-2} mol L^{-1}) and low temperature (30 °C), a significant demulsification efficiency (i.e., 74%) can be reached after a short time (i.e., 4 h), with noticeable differences with respect to the blank

performances. However, further aspects should be analyzed in the future for a better interpretation of the demulsification mechanism in the presence of IL and to assess the potential practical applicability of ILs as demulsifiers, e.g., tests of IL performances for a real water-in-oil emulsions, analysis of the time-dependent droplet size distribution, application of microwave to improve the emulsion destabilization. A proper comparison of the dehydration performances of ILs with those of reference commercial demulsifiers can be also important for a more detailed techno-economic evaluation of the viability of the chemical demulsification process adopting ILs.

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