Thermo-rheology of a proline-based surface active ionic liquid: mixtures with water and *n*-octane

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Abstract

Surfactant flooding is one of the most promising techniques to recover oil from unprofitable reservoirs. Surface active ionic liquids can overcome the limitations of current surfactants. Rheology of injecting solutions and formed slugs is critical in the evaluation of an enhanced oil recovery process. Thermo-rheological behaviour of a biodegradable surface active ionic liquid, [ProC₄]DS, and the corresponding binary and ternary mixtures with water and *n*-octane were studied. All flow curves exhibited shear-thinning and thixotropic behaviour. Viscoelastic behaviour of ternary samples depended strongly on [ProC₄]DS content. Three different regions were identified: typical liquid-like behaviour, weak gel and true gel. Thermal profiles indicated that tested systems were fully thermoreversible.

Keywords: Keywords: *n*-Octane; Proline butyl ester dodecyl sulphate; Surface active ionic liquid; Thermal reversibility; Viscoelasticity; Water.

1. Introduction

Surfactant flooding has been studied as a promising Enhanced Oil Recovery (EOR) technique. Adding surfactants reduces the capillary forces that trap the oil in the rock pores. As surfactants contact rock surfaces, wettability may be changed. Frequently, a slug of water containing polymer follows the surfactant solution in order to get homogeneous displacement inside the well, by reducing the difference between water and oil viscosities, avoiding the formation of digitations [1].

Recently, surface active ionic liquids (SAILs) have been proposed as an alternative to traditional surfactants to improve surfactant EOR methods, by overcoming some limitations of common surfactants [2]. The main SAILs advantage is that they can be functionalised according to the requirements of a specific reservoir, especially for high temperatures and salinities where the choice of conventional surfactants is limited [3]. The use of co-surfactants may be avoided and the high viscosity of many SAILs may help to get a homogeneous flow without adding polymers [4].

Rheological knowledge of injecting fluids at reservoir conditions is fundamental to design and evaluate an EOR process [5]. Even with the importance that SAILs are gaining in EOR, to the best of our knowledge, no studies are found about the rheology of SAILs solutions focusing on this application. However, the non-Newtonian character of the injecting fluid and slugs formed in the reservoir affect oil recovery efficiency. Moreover, the existence of liquid crystals in the injection fluid is undesirable: they can cause plugging and surfactant retention. Hence, measuring apparent viscosities is essential before proposing any optimal formulation for EOR. Furthermore, ionic liquids (ILs) are able to form gels [6], and the use of gels as permeability reducing agents to improve oil recovery has been proposed [7].

Besides the mentioned EOR application, emulsions obtained with ILs and

without the addition of stabilizers are of great interest in materials synthesis [8], and gels have applications as catalysts for chemical transformations or as electrolytes in energy applications [6]. Trivedi *et al.* [8] highlight the interest in the synthesis of new surfactants for high-end applications and propose the use of SAILs based on amino acids with a superior surface activity and solvent miscibility: amino acid ester dodecyl sulphate ionic liquids.

In this work, with the aim of analysing the viability of using highly biodegradable amino acid-based SAILs in EOR applications, proline butyl ester dodecyl sulphate ([ProC₄]DS) is selected as surfactant. *n*-Octane is selected as model oil due to its ability to mimic crude oil behaviour. The goal is to carry out a preliminary study required in oil recovery projects: the rheological behaviour of the formulation proposed to extract oil. Thus, in this work, the thermo-rheological and thermo-reversible characterisation (from 25 to 55°C) of the IL [ProC₄]DS and its mixtures with water and *n*-octane are presented. Steady-shear flow curves and frequency sweeps are determined. The structural evolution of the mixtures is monitored throughout temperature profiles. Selected samples are also analysed by microscopy.

2. Materials and Methods

2.1. Materials

n-octane (Sigma-Aldrich, > 99 wt%) and deionized water were used. The SAIL proline butyl ester dodecyl sulphate ([ProC₄]DS) was synthesised according the procedure published by Trivedi *et al.* [8]. The structure (Fig. 1) and purity was verified by ¹H NMR and ¹³C NMR spectroscopy.

2.2. Methods

2.2.1 Phase behaviour

Mapping of water/[ProC₄]DS and [ProC₄]DS/*n*-octane systems was performed preparing mixtures by weight ($\pm 10^{-7}$ kg) with content varying in 10 wt%. Mapping of the water/[ProC₄]DS/*n*-octane ternary system was made preparing binary mixtures water/*n*-octane (two phases) with content varying in 20 wt% and adding the SAIL sequentially until covering the full ternary region. To define different regions in the ternary diagram at 25°C, samples were observed under visible and polarised light after homogenization using vortex mixing.

2.2.2 Preparation of samples

Binary (B1-B6) and ternary (T1-T6) mixtures (Table S1) of the different regions identified in the phase diagram (Fig. 1), were prepared by weight for the rheological study.

2.2.3. Rheological measurements

Rheological measurements were conducted in triplicate on a stress-controlled rheometer (MCR 301, Anton Paar, Austria) using sand-blasted parallel plate geometry (50 mm diameter, 0.25 mm gap) to prevent wall slip. Preliminary tests were performed using a Couette cell to corroborate the absence of errors due to wall slip, and to guarantee a homogenous flow field. Samples were placed on the rheometer-measuring system and covered with paraffin oil to prevent solvent evaporation. Samples were measured within 24 hours of their preparation and kept at rest (5 min) before measuring to allow thermomechanical equilibration.

Steady-shear flow curves (apparent viscosity, η (Pa s), vs. shear rate, $\dot{\gamma}$ (s⁻¹)) were obtained by, firstly, decreasing and, afterwards, increasing shear rates (0.001 to 100 s⁻¹) following a logarithmic ramp. Measurements were performed from 25 to 55°C, in steps

of 10°C ($\pm 0.01^\circ\text{C}$) for [ProC₄]DS and at 25°C for binary and ternary systems.

Frequency sweeps (storage (G') and loss (G'') moduli (Pa) vs. angular frequency, ω (rad s⁻¹)) of above samples were obtained at 25°C using small amplitude oscillatory shear testing at linear viscoelasticity conditions ($< 20\%$ strain). Then frequency sweeps (1 to 100 rad s⁻¹) were programmed at 10% strain.

Temperature sweeps for the IL [ProC₄]DS and its mixtures with water and *n*-octane were carried out from 25 to 55°C at 1°C min⁻¹. To evaluate the thermal reversibility of ternary systems, a modified protocol was employed [9]. After frequency sweep determinations, samples were heated to 55°C (1°C min⁻¹). Then a time sweep test (1 Hz, 10% strain) was made at 55°C (30 min). After that, samples were cooled to 25°C (1°C min⁻¹). After cooling, a time sweep test was performed at 25°C (30 min) and a final frequency sweep test was performed.

Statistical analyses were performed using ANOVA with PASW Statistics (IBM SPSS Statistics 22.0.0). Whenever the variance analyses indicated differences among means, a Scheffé test was used to differentiate means with 95% confidence ($p \leq 0.05$).

2.2.4. Differential scanning calorimetry

Differential scanning calorimetry (DSC) experiments were carried out on the [ProC₄]DS in a TA Instruments Q2000 differential scanning calorimeter with a precision of $\pm 1^\circ\text{C}$. Samples were encapsulated in aluminium hermetic pans with lids of the same material. Cooling and heating rates of 5°C/min between -90 and 100°C and 0.5°C min⁻¹ between 25 and 55°C were used, and three cooling–heating cycles were carried out. It was ensured that the curves for the second and third cycle were essentially coincident, and the results from the third cycle were displayed.

2.2.5. Polarized optical microscopy

Samples possessing birefringence were analysed at room temperature by spectral confocal microscopy (Leica TCS SP2) with polarized light.

3. Results and Discussion

3.1 Phase behaviour

The water/[ProC₄]DS and [ProC₄]DS/*n*-octane binary systems were found to be miscible, forming homogeneous samples in all the range of concentration.

The ternary system water/[ProC₄]DS/*n*-octane showed a bi-phasic region (2 ϕ) at low SAIL content and a monophasic domain where increasing [ProC₄]DS content caused a transition from typical liquid-like behaviour (L) to gel-like character (G), through different samples with birefringence (LC) (Fig. 1).

3.2. [ProC₄]DS

Fig. 2 shows the flow curve of the pure ionic liquid, [ProC₄]DS, at 25°C and 55°C. [ProC₄]DS exhibited shear-thinning behaviour. The apparent viscosity values agree with those evaluated for other non-Newtonian SAILs like 1-butyl-3-methylimidazolium [C₄mim]DS [10], and shear-thinning ILs [11, 12]. The return flow curve did not match with the outgoing curve. This thixotropic behaviour was also found in other non-Newtonian SAILs, favoured by long alkyl chains (typically 12 as in this SAIL) [13]. The existence of aggregates or clusters in ILs [14] could be suggested as the cause of this behaviour favoured under shear for the breaking and recovery of those aggregates. Taking account of hysteresis is essential to the accurate manipulation of fluids in real world applications.

Armelin et al. [15] proposed the Carreau model for the modelling of other thixotropic materials:

$$\eta = \eta_{\infty} + \frac{B^* - \eta_{\infty}}{[1 + (k\dot{\gamma})^2]^{\frac{(1-n)}{2}}} \quad (1)$$

being η_{∞} (Pa s) the infinite-shear rate viscosity, k (s) the characteristic time, $\dot{\gamma}$ (s^{-1}) the shear rate and n (-) the flow index. The original term, η_0 , was renamed to B^* , as a fitting parameter, due to the lack of Newtonian plateau at low shear rates in [ProC4]DS systems. The fittings were successful ($R^2 > 0.991$) in the tested shear rate range (Table S2).

As expected, the [ProC4]DS apparent viscosity decreased, following ($R^2 > 0.997$) an Arrhenius relationship ($\eta(T) = A \exp(-E_a/(RT))$), with increasing temperature at each shear rate, Fig. S1. Arrhenius behaviour was also found in protic ILs [16], whereas Vogel–Fulcher–Tammann behaviour was reported in other cases [17]. The Arrhenius temperature-dependence found for [ProC4]DS suggests that this SAIL can be classified as a “strong” liquid [18]. The latter authors explained that this phenomenon is a general property of all glass-forming liquids and, with the suitable solvent, crystal liquids can be formed. $-E_a/R$ (K^{-1}) varied between 6604 and 5513 with shear rate increasing from 0.001 to 100 s^{-1} , indicating that the thermal effect on viscosity is more pronounced at low shear rates.

Regarding the hysteresis loop, the area became smaller with increasing temperature (halving from 25 to 55°C). Thixotropic dependence with temperature was previously reported [15]. This fact could be related to the structural order-disorder of the IL interactions. Since the viscosity is reduced with increasing temperature, the interactions broken on the way out are easier to regenerate on the return where mobility is promoted and therefore the cycle (linked to the energy of the structure changes) diminishes.

Fig. 3 displays the frequency sweep of [ProC4]DS at 25°C obtained after the steady-shear measurements (similar to pre-shear step). The elastic, G' , and viscous, G'' , moduli increased linearly ($R^2 > 0.997$) with increasing angular frequency, with $G'' > G'$

for the entire frequency range, indicating a typical liquid-like behaviour [19]. Note here that this viscoelastic behaviour ($G'' > G'$) is related to the fact that mechanical spectrum was obtained after a pre-shear step, where hypothetically the possible existing clusters were broken. The slope of $G' (\approx 1.50) > G'' (\approx 0.97)$ suggested a trend towards solid-like behaviour at larger frequencies ($> 100 \text{ s}^{-1}$). This behaviour can be followed from $\tan \delta$ (G''/G'), which dropped from 10.8 (at 1 rad s^{-1}) to 1.2 (at 100 rad s^{-1}), tending to $\tan \delta=1$ (solid-like behaviour) at larger frequencies. The above slope values agree with those reported for different ILs [20] and other materials such as liquid crystal polymers [21], with quadratic ($G' \propto \omega^2$) and linear ($G'' \propto \omega^1$) dependencies at low frequencies, $< 1 \text{ rad s}^{-1}$. Deviations from theoretical values can be explained owing to the absence of experimental data at lower frequencies.

Fig. 4 shows the temperature effect on the viscoelastic behaviour of [ProC₄]DS. Note here that this spectrum, with $G' > G''$ at the lowest temperatures, was obtained without a previous pre-shear of the sample. The heating profile exhibited a progressive decrease of G' and G'' moduli (about ten times) with rising temperature (from 25 to 55°C). The drop rate of viscous and elastic moduli was slow below $38.0 \pm 1.5^\circ\text{C}$ and dramatically rose at this temperature. Both moduli showed both plateaus at temperatures above 40°C. Even, a crossover point was clearly observed around aforementioned temperature. Again, this thermal transition could be related with the clusters hypothesis indicated above for steady-shear measurements. Namely, the drop of the complex viscosity and the both viscoelastic moduli suggests to be related to the disappearance of the clusters, promoting the IL molecules. This thermal transition was not observed by DSC experiments (Figs. S2). This seems to be in agreement with evidence presented by other authors [22] who showed that large conformational changes in ILs occur at very little energy cost. Even though, further studies should be necessary in order to give

further insight around this thermal transition.

3.3. Binary systems

Figs. 5 and S3 show representative flow curves of tested binary systems at 25°C. Apparent viscosity values were lower than those of the SAIL, as observed for other binary mixtures from protic and aprotic ILs with water [20]. All binary mixtures exhibited shear-thinning behaviour and decreases in apparent viscosity with increasing solvent content. This drop at a fixed shear rate was higher for water/[ProC₄]DS systems when compared with [ProC₄]DS/*n*-octane systems at similar SAIL content. This suggests that interactions are promoted in the presence of water by hydrogen bonding. Brown et al. [10] identified hydrogen bonding with the sulphate group for alkyl-sulphate based ILs. At higher [ProC₄]DS content, high shear-thinning behaviour was observed at high shear rates in both cases. Time-dependant features of [ProC₄]DS were reduced in magnitude in the presence of tested solvents when compared with the SAIL. Other authors [21] found this behaviour in liquid crystal polymers, accounting for the differences in the return flow curve by possible structural changes in the liquid crystals or even droplet deformations.

Table S3 summarises the Carreau model parameters obtained for experimental flow curves ($R^2 > 0.981$). Fitting parameters for the outgoing and return curves displayed the same trends. Namely, B^* , infinite shear-rate viscosity (η_∞) and the consistency index (k) rose significantly with increasing [ProC₄]DS content, as expected from experimental flow curves in both binary systems. This behaviour agreed with those data reported for numerical simulations in emulsions [23], where a surfactant was also present. The latter work indicated that the k increase involves a higher rate of breakdown of the agglomerated structure. Lower k values in the return flow curve suggest that the broken

interactions can be more easily rearranged on the return since mobility is favoured at lower apparent viscosities. The flow index, n , also increased (from 0.23 to 0.38) with increasing [ProC₄]DS content (from 10 to 90%) for water mixtures. These values were significantly lower than those calculated for the SAIL. Similar results were found with other anionic surfactant ILs with water or different hydrocarbons [10]. The above tendencies also match with those reported for other traditional surfactants [24].

Fig. S4 shows the binary systems viscoelastic behaviour in terms of $\tan \delta$ (G''/G'). The values of this parameter decreased with increasing frequencies for both water/[ProC₄]DS and [ProC₄]DS/*n*-octane mixtures. G' and G'' values increased with increasing frequencies and decreased with increasing solvents content, which is in good agreement with steady-shear measurements. Although all binary mixtures exhibited predominantly viscous behaviour ($G'' > G'$) at the studied frequency ranges, the dependence of G' modulus with the frequency was larger (approximately 10 times) than that shown by the corresponding G'' modulus. This means that tested binary mixtures displayed a typical liquid-like behaviour [25]. The magnitudes of both moduli are consistent with those found for other surfactant ILs [11].

Despite their interesting rheological properties, it must be noted that it was found that with time and high temperature the SAIL [ProC₄]DS can undergo hydrolysis. In fact, this is also a problem associated with the traditional surfactant sodium dodecyl sulphate [26]. Depending on the application, this SAIL may have to be discounted.

3.4. Ternary system

Samples of the monophasic ternary regions (Table S1) selected by visual scanning were prepared for further characterisation. Samples T1 and T2 (L region), samples T3 and T4 (LC region) and T5 and T6 (G region) were tested.

Fig. 6 presents flow curves of T1, T3 and T6 at 25°C. Ternary systems featured a

strong shear-thinning character, with a drop in apparent viscosity between thirty (T1) and forty (T6) times over the tested shear rate range. At the highest shear rates, the apparent viscosity achieved a plateau. A slight decrease in the plateau interval with the [ProC₄]DS content towards higher shear rates was observed. This plateau shift suggests that the [ProC₄]DS molecules are probably more able to become rearranged due to the viscosity drop with decreasing [ProC₄]DS content. Previous works [17] attributed above behaviour to changes in the liquid structure. The presence of lamellar lyotropic liquid crystal phases (arranged in parallel layers) favoured at the highest shear rates, could explain the aforementioned behaviour [27]. The apparent viscosity of ternary systems at a constant shear rate increased (about twenty times) with increasing [ProC₄]DS content (from 20 to 84 wt%, T1-T6) (Table S4). This could be explained by the formation of emulsions or liquid crystals in the presence of water and the hydrocarbon, which involves molecules with different sizes leading to greater friction and therefore an increase of the ternary systems' apparent viscosity [28]. High shear-thinning behaviour, the lack of a Newtonian plateau at low shear rates, a plateau at high shear rates, and considerable increase of apparent viscosity with [ProC₄]DS content, are all related to interactions between the [ProC₄]DS and water/*n*-octane promoted at low shear rates that increase the number of junction zones [17]. In contrast, at high shear rates, the weaker junction zones allow the structure to be stabilized more readily. Ternary systems also exhibited thixotropic behaviour. Differences in hysteresis loop magnitudes were observed among tested ternary samples depending on [ProC₄]DS content, being more noticeable at the largest [ProC₄]DS concentrations below 1 s⁻¹, since the return flow curve is more impeded at low shear rates for the samples with the largest apparent viscosities. These results support the above hypothesis about the ease of network formation at low shear rates and stabilization of the ternary systems at high shear rates.

Table S3 shows the Carreau model parameters for ternary systems ($R^2 > 0.979$). As expected, the same trends were found for the parameters from outgoing and return flow curves, with lower values for those corresponding to return flow curves. B^* and k parameters increased with increasing [ProC4]DS content, with a greater dependence on the B^* parameter. The increase in [ProC4]DS content caused a decrease (from 0.14 to 0.05) in the flow index, indicating that shear-thinning behaviour showed a dependence on [ProC4]DS, water and hydrocarbon content at the tested temperatures. No significant differences were observed in this parameter between T1 and T2 and from T3 to T6. Infinite shear-rate viscosity rose (from 0.03 to 0.61 Pa s) with increasing [ProC4]DS content (from 20 to 84, wt%). These trends are in good accordance with those reported for protic IL ternary mixtures [16] and other thixotropic materials [15].

Fig. 7 shows frequency sweeps of T1, T3 and T6 at 25°C. With a constant water/*n*-octane ratio, the viscoelastic behaviour of the ternary samples depended strongly on the [ProC4]DS content. G' and G'' values increased with increasing SAIL concentration, at a fixed frequency. Nevertheless, three different frequency sweeps were identified. The first one (T1 and T2, representative of L region) exhibited a typical liquid-like behaviour. This behaviour was found for other SAIL mixtures at low concentrations in the presence of water and similar hydrocarbons [29]. Concerning the second one (T3 and T4, representative of LC region), G' showed a plateau in the lowest frequency range with $G' > G''$ and both moduli slightly frequency dependent, indicating weak gel behaviour. In this case, G' dominates and holds a fixed value over a large frequency spectrum, G'' increases smoothly until crossing over with G' . The crossover point is shifted to higher frequencies with increasing [ProC4]DS content. The above viscoelastic behaviour agrees with that reported for mixtures of chitin with 1-allyl-3-methylimidazolium bromide [30]. Earlier work [17] found similar behaviours for

lyotropic liquid crystals formed by self-assembled neutral lipids and water, indicating that this behaviour corresponds to the leathery transition. Similar frequency sweeps were used to identify liquid crystalline phases in dodecyl polyoxypropylene ether/water systems [19]. The transitions from liquid to liquid crystalline phases were also related to a competition between the increase of the free energy associated with loss of orientational entropy, and a drop in the free energy related to additional interactions [10]. The third one (T5 and T6, representative of G region) exhibited true gel behaviour, with $G' > G''$ over the tested frequency range with both moduli almost invariant with changing angular frequency. These results agree with those tendencies reported for gels based on 1-allyl-3-methylimidazolium bromide IL [30]. Overall, the above results highlight that rheology can be used to detect and characterise these kinds of transitions, describing the viscoelastic behaviour of complex ternary systems like water/[ProC₄]DS/*n*-octane, where the increase in [ProC₄]DS content causes the formation of a stronger network with a clear transition from liquid-like to gel-like behaviour.

Microscopic studies were also conducted to corroborate rheological findings. Black micrographs (not shown) confirmed the liquid-like character of T1 and T2. In contrast, T3 and T4 exhibited lamellar liquid crystals, the amount of liquid crystals increasing with [ProC₄]DS content (Fig. 1). The existence of lyotropic lamellar phases for ternary systems was also found [31] for triethylammoniododecyloxycyanobiphenyl bromide, water and hexane mixtures. Interestingly, T5 and T6 corresponding to gelled systems showed maltese crosses. A micrograph for sample T6 was taken just after the sample preparation (Fig. 1) and after some minutes the birefringence started to diminish. The visual texture of T5 and T6 was very similar to gels from a cationic surfactant mixture in aqueous solution [32].

Fig. 8 shows thermo-rheological profiles of T4, as representative of gelled systems (T3-T6). Heating (Fig. 8a) and cooling (Fig. 8b) profiles exhibited similar patterns. In both processes, a progressive drop (about ten times) of viscous and elastic moduli with increasing temperature (from 25 to 55°C) was observed, corroborating that flow was favoured at the highest temperatures [12]. The rate of decrease of both moduli was slower at the lowest temperatures ($37.5 \pm 2.5^\circ\text{C}$) and increased notably above that temperature. A crossover point around $48 \pm 3^\circ\text{C}$ for heating profiles corresponding to samples from T3 to T6 was observed. This behaviour nicely matches with the pure SAIL thermal profile. The crossover point disappeared during cooling profiles, suggesting that the above transition is related to a possible gel break [9]. No significant differences were observed in the frequency sweeps obtained after heating/cooling cycles when compared with those detailed above. This fact, together with the thermal profiles, indicates that tested ternary systems are strongly thermoreversible. The knowledge of SAIL stability conditions is critically relevant in order to establish the optimum applications.

4. Conclusions

The rheological and optical characterisation of [ProC4]DS and the mixtures with water and *n*-octane showed a palette of systems with a wide range of viscoelastic and structural features, which could be useful for different industrial applications. [ProC4]DS can be classified like shear-thinning and thixotropic fluid. This IL showed a thermoreversible transition at $38.0 \pm 1.5^\circ\text{C}$ evaluated by means of rheological measures. [ProC4]DS/*n*-octane and water/[ProC4]DS mixtures showed shear-thinning, thixotropic and liquid-like behaviour. The ternary system exhibited two transitions in the monophasic region: from liquid-like to weak gel with liquid crystals and true gel

behaviour with increasing [ProC4]DS content. The absence of liquid crystals in aqueous solutions at low SAIL content is a good starting point for EOR applications, thus encouraging future studies in the presence of salts. True gel behaviour appears at too high SAIL content (> 80 wt%) to be applied as a permeability reducing agent in the proposed application. Nevertheless, there is a wide range of applications for IL gels. From the industrial point of view, a relevant advantage is the strongly thermoreversible characteristics of the studied ternary system.

Acknowledgements

Dr Ana Soto acknowledges the Ministry of Economy and Competitiveness (Spain) for support throughout project CTQ2015-68496-P (including European Regional Development Fund) and Dr Emilia Tojo (University of Vigo) for the synthesis of the SAIL.

Declarations of interest: none

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Figure caption

Fig. 1. [ProC₄]DS structure, studied binary and ternary mixtures and polarized optical micrographs of ternary (T3, T4, T6) systems.

Fig. 2. Flow curves for [ProC₄]DS at 25°C (closed symbols) and 55°C (open symbols).

Fig. 3. Frequency sweep for [ProC₄]DS at 25°C: closed – storage modulus (G'), open – loss modulus (G''), line – $\tan \delta$.

Fig. 4. Temperature sweep for [ProC₄]DS: closed – storage modulus (G'), open – loss modulus (G'').

Fig. 5. Flow curves for water/[ProC₄]DS at 25°C: B1 (triangles), B2 (diamonds), B3 (squares), B4 (crosses).

Fig. 6. Flow curves for water/[ProC₄]DS/*n*-octane systems at 25°C: T1 (square), T3 (triangles), T6 (diamonds).

Fig. 7. Frequency sweeps for water/[ProC₄]DS/*n*-octane at 25°C: T1 (square), T3 (triangles), T6 (diamonds); closed – G' , open – G'' .

Fig. 8. Thermo-rheology for T4: (a) heating from 25 to 55°C, (b) cooling from 55 to 25°C and (c) frequency sweep at 25°C: closed – G' , open – G'' .

446 **Symbols used**

447

448	A	[Pa s]	fitting parameter
449	B^*	[Pa s]	fitting parameter
450	E_a	[J/mol]	energy of activation
451	G'	[Pa]	elastic modulus
452	G''	[Pa]	viscous modulus
453	k	[s]	characteristic time
454	n	[-]	flow index
455	R	[J/(K mol)]	ideal-gas constant
456	R^2	[-]	coefficient of determination
457	T	[K]	absolute temperature
458	$\tan \delta$	[-]	damping factor (G''/G')

459

460 *Greek symbols*

461	$\dot{\gamma}$	[s ⁻¹]	shear rate
462	η	[Pa s]	apparent viscosity
463	η_∞	[Pa s]	infinite-shear rate viscosity
464	2ϕ	[-]	bi-phasic region
465	ω	[rad s ⁻¹]	angular frequency

466

467 *Abbreviations*

468	DSC	differential scanning calorimetry
469	EOR	enhanced oil recovery
470	G	gel
471	IL	ionic liquid
472	L	liquid
473	LC	liquid crystal
474	SAIL	surface active ionic liquid

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