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Morphology and Shear Viscosity of Aqueous Two-Phase Biopolymer-Surfactant Mixtures

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ABSTRACT

The relation between composition, rheology and morphology in phase separated pullulan-sodium dodecyl sulphate systems containing sodium chloride has been investigated using rheo-optical methods. The rheological measurements showed that the apparent viscosity of these aqueous two-phase systems depends on the chemical composition of each phase, their volumetric composition and the viscosity ratio of the separated phases. Optical observations revealed a droplet like morphology over a wide range of shear rates at low to moderate volume fraction of pullulan-rich phase. In some mixtures, string phases were observed at higher volume fractions of pullulan-rich phase and shear rates. Simultaneous analysis of the rheological data and observed structures at different shear rates/compositions indicates a close link between rheology and morphology of aqueous two-phase systems and provides a simple tool for predicting morphology on the basis of rheological data.

Key words: *aqueous two-phase systems, pullulan, SDS, rheology, co-continuity*

1. INTRODUCTION

Phase separated mixtures of biopolymers and surfactants containing salt are frequently used in food and HPC (Home and Personal Care) industries to create a desired product texture [Goddard and Ananthapadmanabhan (1998); Lundin *et al.* 2000)]. In such aqueous two-phase systems (ATPS) one phase is enriched in the polymer with a small amount of the surfactant present and the second phase is enriched in surfactant with a small amount of polymer present [Piculell and Lindman (1992)] with both phases containing salt. As the rheology and the structure of many products frequently determine their quality, a good understanding of the relation between composition (chemical and volumetric) and rheology of the separated phases as well as the rheology and the structure of their incompatible mixtures is very important.

The relation between composition and structure in quiescent (unaffected by shear) systems has been extensively investigated, and phase diagrams for biopolymer/biopolymer, biopolymer/salt and biopolymer/surfactant systems allowing identification of single-phase and two-phase regions in those mixtures are common in the literature [Zaslavsky (1995); Piculell and Lindman (1992)].

The effect of composition and shear rate on the morphology of phase separated sodium alginate/sodium caseinate mixtures has been recently discussed by Pacek et al 2001. They reported that, as the volume fraction of one phase increases the morphology evolves from a simple dispersion, through complex multiple dispersions to string phases observed at certain combinations of shear rate and volumetric composition, which were frequently in the phase inversion region. The rheological behaviour of phase-separated aqueous biopolymer mixtures and their individual phases has been subject of a number of studies [Stokes *et al.* (2001); Wolf *et al.* (2001); Wolf and Frith (2003); Ding *et al.* (2005)]. It has been reported that biopolymer mixtures with an emulsion-like microstructure follow the same relations as classical emulsions and polymer blends (of emulsion structure) albeit the interfacial tension in such systems is of the order of 10^{-6} Nm^{-1} rather than 10^{-3} Nm^{-1}. The development of string phases under the influence of shear has been investigated in more detail for gelatin/dextran mixtures [Wolf and Frith (2003)]. String phases were directly observed in the blends with roughly equal phase viscosities as well as for

blends with disparate phase viscosities. For the latter, compositions showing string phase formation are symmetric to the phase inversion composition. Also, the minimum dispersed phase volume fraction for which string phases were observed was higher for blends with viscosity ratio around unity [Wolf and Frith (2003)]. Application of rheological models reported in the literature to identify occurrence of string phases in ternary polymer solution was partially successful [Wolf and Frith (2003)]. The rheological model by Kume and Hashimoto (1995) predicting string phase morphology was successfully applied for viscosity ratios close to unity but application of the model by Jeon and Hobbie (2001a) gave ambiguous results with regard to the prediction of string phase formation [Wolf and Frith (2003)].

Despite the growing interest in polymer-surfactant ATPS, their rheological behaviour and their morphology under shear has so far received little to no attention. Instead, the rheological behaviour of single-phase (homogeneous) polymer-surfactant mixtures has been extensively investigated [Merta and Stenius (1997); Bataille *et al.* (1997)] and the apparent viscosity of such systems has been used to monitor the onset of interactions between the polymer and the surfactant [Merta and Stenius (1997)]. The rheological behaviour of single-phase polymer-surfactant mixtures, where the polymeric components have been hydrophobically modified, has also been investigated, mostly due to the fact that hydrophobically modified polymers are frequently used as viscosity enhancers [Bataille *et al.* (1997)].

Recently Spyropoulos (2006) investigated the effect of salt on the morphology of SDS-pullulan-NaCl blends and found that the morphology under quiescent (no influence of shear) conditions strongly depends on the concentration of salt. In the present paper, we report on the effect of salt and volumetric composition on rheology-morphology relationships of SDS-pullulan-NaCl blends in well controlled shear flow, as well as on the effect of salt on the rheological behaviour of the separated phases. The selected mixture is representative for surfactant-biopolymer systems. SDS is a commonly used surfactant and pullulan was chosen as a model biopolymer (linear molecule, non-gelling) that has been used in previous studies [Ding *et al.* (2005)]. A microscope-video-computer system [Pacek *et al.* (1994)] has been used to monitor and analyse the morphology of the mixtures at different volumetric and chemical compositions in a wide range of shear rates realised in a glass Couette device. A

standard rotational rheometer also fitted with concentric cylinders was used to measure flow curves in the same range of shear rate. Rheological data were analysed using models developed for oil-aqueous two-phase systems with droplet morphology [Choi and Schowalter (1975)]. Models developed for immiscible blends of synthetic polymers showing string phase formation under shear [Jeon and Hobbie (2001a)] and their applicability on string formation in surfactant-biopolymers ATPS are also discussed.

2. EXPERIMENTAL

2.1 Materials

The anionic surfactant sodium dodecyl sulfate (SDS, 95% purity) was purchased as a powder from Sigma. Pullulan powder (Pullulan 20, molecular weight 200,000) was acquired from Hayashibara Company Ltd, Japan. Sodium chloride (NaCl, 99.5% purity) was purchased from Sigma. All materials were used with no further purification. Sodium azide (NaN$_3$) added to the mixtures in a very small concentration (0.03% w/w) was purchased from Fisons Scientific Equipment and also used as supplied.

2.2 Methods

As phase separation occurs when incompatible biopolymers or biopolymer and surfactant are mixed together, in principle, it is possible to obtain the dispersion by simultaneously dissolving SDS powder and pullulan powder in an aqueous solution of NaCl. After dissolution, phase separation occurs but the volumetric ratio of the separated phases is not known *a priori* (unless an accurate phase diagram is available). Also, the physical properties of the separated phases are not known. Therefore, a different procedure similar to preparation of well defined biopolymer blends [Pacek *et al.* (2001); Wolf and Frith (2003)] was adopted. First SDS powder and pullulan powder were dissolved in water containing the required amount of NaCl and sodium azide in a jacketed stirred vessel fitted with a Rushton turbine impeller. In total, mixtures from five pullulan-SDS-NaCl systems of different chemical compositions shown in Table 1 were prepared.

Table 1 →

At each composition the resulting dispersions were stirred for 24 hours to allow the separated phases to chemically equilibrate followed by leaving the mixtures un-stirred for a further 24 hours to allow complete separation into the SDS-rich top phase and the pullulan-rich bottom phase; after the 24 hours no change in the volumetric composition of all systems was observed suggesting that they reached an equilibrium state. The volume and the density of each separated phase were measured and the chemical composition analysed as reported earlier [Spyropoulos (2006)] following a procedure used elsewhere [Pudney *et al.* (2004)] for the determination of the chemical composition of aqueous two-phase mixtures of biopolymers. The results are summarised in Table 2.

Table 2 →

For each system, exact volumes of separated phases were mixed in a stirred vessel to prepare a wide range of mixtures with both composition (volume fraction ranging between 0 and 1) and physical properties of each phase well defined. Mixtures were transferred to the glass Couette device where they were sheared for approximately one hour, after which the mixtures' flow curves were measured using a Carri-med CSL 100 rheometer with concentric cylinder geometry at 25°C. The morphology of all mixtures was analysed in the glass Couette device using a video-microscope-computer system [Pacek *et al.* (1994)]. Images were recorded in an overlapping (with the rheological analysis) range of shear rates at 25°C and over a wide range of volumetric compositions. During preparation of the mixtures and during further measurements no bulk phase separation was observed.

3. RESULTS AND DISCUSSION

3.1 *Effect of salt on rheological behaviour of separated phases.*

The flow curves of the pullulan-rich and the SDS-rich phases resulting from phase separation in 12% pullulan-12% SDS mixtures with different NaCl concentrations were obtained. The average measured viscosities $\bar{\eta}$ (for the whole

shear rate range, 1-100s^{-1}) for both coexisting phases resulting from all five investigated systems are given in Table 3 together with the calculated error intervals.

Table 3 →

A selection of the measured flow curves is shown in Figs. 1(a) and 1(b) respectively. The viscosity data from these flow curves were fitted to the power-law model:

$$\eta = K \cdot \dot{\gamma}^{n-1},$$

[1]

where η is the mixture viscosity, $\dot{\gamma}$ the applied shear rate, K the consistency constant and n the power-law index. The viscosity of the selected mixtures (η_{sel}, average for the whole shear rate range, 1-100s^{-1}) is also given in Table 3 together with the calculated K and n values.

Figure 1 →

The separated phases obtained from the mixtures of different NaCl concentrations were practically Newtonian at all salt concentrations. The on-set of shear thinning at higher shear rates observed for the SDS-rich phases obtained for mixtures from system (*iv*) with the highest salt concentration (0.5m), can be attributed to the shape of the SDS micelles under high salinity conditions. Hayashi and Ikeda (1980) reported that SDS monomers, in aqueous solutions of 0.45M NaCl and higher, self-aggregate to form cylindrical micelles. It has been reported [Tepe *et al*. (1995)] that such cylindrical species subjected to high shear tend to align in the direction of the flow reducing the apparent viscosity of the solution.

Though not influencing the character of the flow curve, NaCl concentration affects the level of viscosity, this is particularly pronounced for the SDS-rich phases and less so for the pullulan-rich phases. The viscosity of the pullulan-rich phase decreases by approximately 50% as NaCl concentration increases from 0.25m to 0.5m as shown in Fig. 1(a) and Table 3. This might be explained by the small reduction of the concentration of SDS in the pullulan-rich phase. This has been attributed to a possible increase in incompatibility between the two macro-components (pullulan and SDS) driven by the addition of salt [Spyropoulos (2006)]. It is also possible that the

observed viscosity reduction results from contraction of the biopolymer chain due to screening of electrostatic interactions caused by the addition of the electrolyte [Bataille *et al.* (1997)].

The effect of NaCl concentration on the apparent viscosity of the SDS-rich phase is dramatic; see Fig 1(b) and Table 3. An increase of NaCl concentration from 0.25m to 0.31m leads to an approximately two-three fold increase of the apparent viscosity. A further increase in NaCl concentration to 0.4m leads to a more than ten-fold increase of viscosity whilst a higher increase from 0.4m to 0.5m affects another 15-fold viscosity increase [see Figure 1(b)]. An increase of concentration above 0.5m had practically no effect on the apparent viscosity (data not shown).

The initial increase of the SDS-rich phase viscosity corresponding to the increase of NaCl concentration from 0.25m to 0.4m can be explained either by the increase of SDS concentration in the SDS-rich phase with increasing salt concentration [Spyropoulos (2006)] or by micellar growth [Hayashi and Ikeda (1980); Quina *et al.* (1995)]. Quina *et al.* (1995) reported that, in aqueous solutions, SDS micelles are growing whilst maintaining their spherical shape for NaCl concentrations of up to ~0.4m. The steep increase observed for a further salt concentration increase to 0.5m can be explained by a change of the shape of the SDS micelles from spherical to cylindrical/rod-like. Hayashi and Ikeda (1980) reported a transition from spherical to rod-like SDS micelles for a NaCl concentration of ~0.45M. Here, the drastic viscosity increase was observed between 0.31m and 0.5m what might indicate that the change in micellar shape occurs gradually. Once all the micelles assumed a cylindrical/rod-like shape, further addition of NaCl has a minimum affect on viscosity. The cylindrical shape of the SDS micelles at the highest NaCl concentration also explains the observed slight shear-thinning behaviour as discussed above.

3.2   *Rheological behaviour of two-phase systems -Effect of volumetric composition*

The rheological behaviour of the investigated mixtures is discussed in terms of flow curves measured at different volumetric compositions and in terms of apparent viscosities. Literature correlations for the apparent viscosity of different liquid-liquid

two-phase systems were applied to experimental data to assess their suitability for predicting apparent viscosities for sheared surfactant-biopolymer mixtures.

For emulsions of spherical or slightly deformed droplet morphology the experimental apparent viscosities were compared with the values calculated from semi-empirical correlation developed by Choi and Schowalter (1975) for synthetic polymer mixtures:

$$\eta \cong \eta_c \left[1 + \phi \frac{(5\lambda + 2)}{2(\lambda + 1)} + \phi^2 \frac{(5\lambda + 2)^2}{2(\lambda + 1)^2} \right] \qquad [2]$$

and from correlations developed for concentrated emulsions [Pal (2001)] by Phan-Thien and Pham (Eq. [3]) and Yaron and Gal-Or (Eq. [4]):

$$\left(\frac{\eta}{\eta_c} \right)^{2/5} \left[\frac{2 \left(\eta/\eta_c \right) + 5\lambda}{2 + 5\lambda} \right]^{3/5} = (1 - \phi)^{-1} \qquad [3]$$

$$\eta = \eta_c \left(1 + \frac{5.5 \left[4\phi^{7/3} + 10 - \left(84/11 \right)\phi^{2/3} + \left(4/\lambda \right)\left(1 - \phi^{7/3} \right) \right]}{10 \left(1 - \phi^{10/3} \right) - 25\phi \left(1 - \phi^{4/3} \right) + \left(10/\lambda \right)\left(1 - \phi \right)\left(1 - \phi^{7/3} \right)} \right) \qquad [4]$$

where η_c is the viscosity of the continuous phase, $\lambda = \eta_d / \eta_c$ (η_d is the viscosity of the dispersed phase) is the viscosity ratio, and ϕ is the droplet (dispersed) phase volume fraction. Eqs [2] - [4] were tested by correlation with the experimentally obtained viscosity data for those mixtures exhibiting droplet morphologies. It was found that Eqs [3] and [4] tend to overestimate the measured mixture viscosity and that Eq [2] gave the best correlation (Fig. 2). It was therefore decided for Eqs [3] and [4] not to be used in the discussion of the rheological behaviour studied here for mixtures of droplet morphology. The discussion that follows is only facilitated by the use of Eq [2] developed by Choi and Schowalter (1975).

Figure 2 →

The apparent viscosity of mixtures showing string phases was calculated from a correlation developed by Jeon and Hobbie (2001) for phase separated polybutadiene (PB)-polyisoprene (PI):

$$\eta \cong \eta_c \left[1 + \phi \left(\frac{1}{\lambda} - 1 \right) \right]^{-1} \qquad [5]$$

It has also been suggested [Wolf and Frith (2003); Jeon and Hobbie (2001)] that the viscosity at high shear rate in ATPS, where string phase formation takes place, follows the log-additivity rule [Glasstone *et al.* (1941)] developed for miscible liquids (single phase systems):

$$\log(\eta) = \phi_1 \log \eta_1 + \phi_2 \log \eta_2 \qquad [6]$$

where ϕ_i the volume fraction of liquid *i* of viscosity η_i.

The flow curves as well as the apparent Newtonian viscosity-volume fraction relationship for mixtures from systems (*i*), (*ii*) and (*iii*), all of which have phases of disparate viscosities, are shown in Fig 3. For reasons becoming apparent below, the corresponding graph for mixtures resulting from system (*iv*) also of disparate phase viscosities are plotted separately in Fig 4. Finally, Fig 5 shows the results for the mixtures of separated phases with similar viscosities [system (*v*)]. For each mixture, flow curves are shown in the left column of the figures, together with the viscosity of the individual phases (selected flow curves also shown in Fig 1) for comparison, while the viscosity-volume fraction relationships are shown in the right column.

Figure 3 →

Mixtures from systems (*i*) – (*iii*) were practically Newtonian and at all volume compositions power-law index *n* was greater than 0.93 (Fig 3). Small fluctuations in the experimental data observed at low volume fractions of the pullulan-rich phase are artefacts due to limitations in the measurement sensitivity of the rheometer employed. The increase of volume fraction of pullulan-rich phase up to ~85% for mixtures from systems (*i*) and (*ii*) and ~75% for mixtures from system (*iii*) causes a monotonic viscosity increase. As the volume fraction of the pullulan-rich phase is increased further, the apparent viscosity suddenly rises up to the level of pure pullulan-rich

phase or just above as for system (*iii*). At higher volume fractions of pullulan-rich phase, viscosities are lower (flow curves not shown, see plots of apparent viscosity versus volume fraction of pullulan-rich phase), hence, there appears to be a composition at which the mixture shows maximum viscosity. In all three systems the phase volume composition at which the maximum viscosities are observed corresponds to the phase inversion compositions, e.g. the composition at which pullulan-rich phase become the continuous phase [Spyropoulos (2006)]. After phase inversion, further increase of the volume fraction of pullulan-rich phase leads to mixtures with lower volume fraction of dispersed phase (now SDS-rich phase), therefore the apparent viscosity decreases. Overall, the observed interplay between the volumetric composition and the apparent viscosity in the aqueous pullulan-SDS-NaCl mixtures from systems (*i*) – (*iii*) is similar to that observed in oil/aqueous mixtures. Similar behaviour has also been reported for phase separated mixtures of synthetic polymers [Jeon and Hobbie (2001)].

Eq [2] was used to describe the effect of volumetric composition on the apparent viscosity of the mixtures from systems (*i*), (*ii*) and (*iii*). Very good agreement between the prediction and experiment has been obtained for mixtures with viscosity ratios the furthest away from unity [mixtures from system (*i*), $\lambda \sim 80$ or $\lambda \sim 0.01^*$] but as this viscosity ratio moves closer to unity, the accuracy of the prediction decreases [mixtures from system (*ii*), $\lambda \sim 53$ or $\lambda \sim 0.02$ and mixtures from system (*iii*), $\lambda \sim 28$ or $\lambda \sim 0.05$].

The results for mixtures from system (*iv*) at different volume fractions of pullulan-rich phase, shown in Figure 4, indicate that the behaviour of these mixtures is, in a sense, more complex since they are much more affected by shear.

Figure 4 →

For mixtures of up to approximately 10% pullulan-rich phase volume fractions ($\lambda \sim 0.04$) and at low shear rates (below 5 s^{-1}), a weakly non-Newtonian behaviour can be observed and the apparent mixture viscosity increases with increasing volume fraction of pullulan-rich phase (dispersed), which implies a typical droplet-type

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* The first viscosity ratio corresponds to those mixtures where SDS-rich phase is continuous while the second one to those where pullulan-rich phase is continuous.

morphology. At approximately 10% of pullulan-rich phase the apparent viscosity reaches a maximum. As the volume fraction further increases, the viscosity is monotonically decreasing and reaches the viscosity of the pure pullulan-rich phase at approximately 90% of pullulan-rich phase. The initial increase of viscosity is again typical for dispersed systems, but further monotonical reduction can be explained by phase inversion occurring at 10-15% of pullulan-rich phase [Spyropoulos (2006)]. At higher shear rates ($\sim 20s^{-1}$) an increase in volume fraction of the pullulan-rich phase leads to a monotonical reduction of the viscosity from 7 Pa.s (SDS-rich phase) to 0.12 (pullulan-rich phase), which, in the region where the SDS-rich phase is continuous ($\lambda \sim 0.04$), can only be explained by formation of string phases. The above results are in good agreement with the literature description of the mechanism of string phase formation. It has been postulated that string phases result from a shear-enhanced coalescence rate [Wolf and Frith (2003)]. At higher shear rates string phases might result from an increase of the coalescence rate caused by an increase in the number of shear-induced collisions between drops. It has been further suggested [Hashimoto *et al.* (1995)] that these string phases can be stable only when undulations of the surfaces of the strings are strongly inhibited by the high shear rate. The latter is supported by findings showing break-up of the strings in the systems studied here upon cessation of the flow [Spyropoulos (2006)]. Whilst for dilute mixtures (low volume fractions of either phase) and at low shear rates Eq [2] qualitatively gives reasonable agreement with experimental results, in concentrated mixtures (higher volume fraction of either phase) and at low shear rates it fails to predict the apparent viscosity. On the other hand, Eq [6], strictly valid for single-phase mixtures correlates very well with the experimental data obtained at high shear rates both for dilute and concentrated mixtures. This again indicates string structures (bi-continuous structure) at high shear rates in concentrated and dilute mixtures and also at low shear rate in concentrated mixtures.

Figure 5 →

Figure 6 →

The flow curves of equi-viscous mixtures from system (*v*) for increasing volume fraction of pullulan-rich phase are shown in Fig. 5. In dilute mixtures (up to approximately 25% of pullulan-rich phase) the apparent viscosity is only very weakly

increased with the increase of volume fraction of pullulan-rich phase and reaches maximum at approximately 25%. A further increase of the volume fraction of the pullulan-rich phase up to approximately 80% leads to a gradual reduction in the apparent viscosity. This indicates, as discussed above, either phase inversion occurring at 25% or a change of morphology from dispersed droplets at low volume fractions to bi-continuous structures in more concentrated dispersions. An increase of volume fraction above approximately 80% has no further effect on the apparent viscosity, neither at low nor at high shear rates. The effect of volume fraction on apparent viscosity in concentrated mixtures (volume fraction of one phase above approx 20%) is relatively well correlated by Eq [6], developed for single-phase mixtures of two fluids, however it fails for dilute mixtures. It appears that in dilute mixtures the apparent viscosity is very weakly dependent on the volume fraction, especially with pullulan-rich phase continuous. Eq [2], developed for dispersed systems, was found to strongly over-predict the apparent mixture viscosity (right column graph in Fig. 5). The fact that in concentrated dispersions, the viscosity is well correlated by Eq [6] might indicate that in this region mixtures of system (*v*) behave like a single-phase system, which is caused by the observed co-continuity [Spyropoulos (2006)]. A similar rheological behaviour was reported by Utracki (1991) for immiscible synthetic polymer mixtures with the first indication of phase co-continuity in these systems observed near 16% volume fraction of one polymer. Wolf and Frith (2003) also show that the apparent viscosity of the gelatin-dextran phase separated system at high shear rate is well correlated by Eq [6].

CONCLUSIONS

The effect of chemical and volumetric composition on the morphology and rheology of phase separated SDS-pullulan-NaCl mixtures and the effect of NaCl on the rheology of the separated phases in these systems have been investigated. It has been found that in all cases the separated phases are practically Newtonian. The viscosity of the pullulan-rich phases slightly decreases with increasing NaCl concentration, which can be explained either by pullulan being "salted out", or by the changes in the structure of the biopolymer molecules in the presence of salt. At low NaCl concentration (up to 0.3m) the viscosity of the SDS-rich phase slowly increases

with increasing salt concentration. However, as the NaCl concentration reaches 0.4m the viscosity increases by a factor of 100, with further addition of salt having no effect on the viscosity. The initial increase of the SDS-rich phase viscosity with increasing NaCl concentration can be explained by an increase of the SDS concentration in the SDS-rich phase whereas the step increase that followed is probably caused by a transition from spherical to rod-like SDS micelles at NaCl concentrations close to 0.4m.

Rheological analysis of the pullulan-SDS-NaCl mixtures revealed that the shear mixture viscosity depends on the viscosity ratio, the viscosity of the continuous phase and the volumetric composition of the mixtures. At low shear rates the viscosity/composition relation for mixtures of disparate phase viscosities followed the pattern typical for oil/aqueous dispersions and an increase of the volume fraction of the dispersed phase leads to an increase in the apparent mixture viscosity. Optical observations have revealed practically spherical droplet morphology under these conditions [Spyropoulos (2006)]. At higher shear rates, in mixtures with the highest absolute viscosity of the SDS-rich phase (initially continuous), a reduction of viscosity with increasing volume fraction of pullulan-rich phase was observed indicating string-like mixture morphology.

The apparent viscosities of relatively diluted equiviscous mixtures (up to 25% of one phase) increase with increasing volume fraction in both the $\lambda<1$ and $\lambda>1$ regimes. In more concentrated mixtures (phase inversion region) the viscosity slowly decreases as the volume fraction of the initially dispersed phase increases, which again indicates presence of a co-continuous morphology.

The apparent viscosity of mixtures made of phases of very different viscosities at low shear can be predicted from correlations developed for oil/aqueous systems or polymer mixtures having a simple dispersed structure. However, these models overestimate the apparent viscosities of the equiviscous mixtures. A model developed for string morphology [Jeon and Hobbie (2001a)] underestimates the high shear viscosities of mixtures showing string phases. In such mixtures the logarithmic-mixing rule was found to best correlate the viscosity/composition dependence, even though homogenisation was not observed in investigated mixtures.

Analysis of the rheological data together with the observed structures/morphology of the mixtures at different shear/composition suggests a close link between rheology and morphology of these surfactant-polymer aqueous two-phase systems and provides a simple tool for predicting morphology on the basis of rheological analysis.

ACKNOWLEDGEMENTS

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Tables and table captions

Component code	Pullulan (% w/w)	SDS (% w/w)	NaCl (M)
System (*i*)	12.0	12.0	0.25
System (*ii*)	14.0	14.0	0.25
System (*iii*)	12.0	12.0	0.31
System (*iv*)	12.0	12.0	0.5
System (*v*)	12.0	12.0	0.4

Table 1. Chemical compositions of the systems used to produce the investigated mixtures.

System	Phase	Pullulan (% w/w)	SDS (% w/w)	Density (g.cm^{-3})
(i)	Pullulan-rich	19.59 ± 0.12	2.05 ± 0.06	1.083
	SDS-rich	2.62 ± 0.06	27.05 ± 0.11	1.048
(ii)	Pullulan-rich	18.57 ± 0.17	3.65 ± 0.02	1.095
	SDS-rich	7.07 ± 0.11	29.71 ± 0.22	1.050
(iii)	Pullulan-rich	17.92 ± 0.28	1.29 ± 0.07	1.082
	SDS-rich	2.00 ± 0.02	30.11 ± 0.12	1.052
(iv)	Pullulan-rich	16.48 ± 0.17	0.23 ± 0.07	1.079
	SDS-rich	1.22 ± 0.12	40.35 ± 0.62	1.066
(v)	Pullulan-rich	17.34 ± 0.39	0.71 ± 0.05	1.072
	SDS-rich	1.56 ± 0.12	34.06 ± 0.41	1.057

Table 2. Pullulan and SDS concentrations in separated phases (errors are single standard deviation). Densities of coexisting phases are also given.

System	Phase	$\overline{\eta}$ (Pa.s)	η_{sel} (Pa.s)	K	n	Λ
(*i*)	Pullulan-rich	0.650 ± 0.091	0.615	0.629	~1	78.78
	SDS-rich	0.008 ± 0.001	0.008	0.009	0.946	0.01
(*ii*)	Pullulan-rich	1.003 ± 0.118	1.071	1.161	0.964	53.26
	SDS-rich	0.023 ± 0.004	0.020	0.023	0.930	0.02
(*iii*)	Pullulan-rich	0.511 ± 0.069	0.558	0.576	0.986	21.20
	SDS-rich	0.031 ± 0.004	0.026	0.031	0.974	0.05
(*iv*)	Pullulan-rich	0.341 ± 0.070	0.299	0.304	0.988	0.04
	SDS-rich	8.286 ± 0.419	8.317	9.711	0.927	27.86
(*v*)	Pullulan-rich	0.346 ± 0.051	0.383	0.395	0.987	0.91
	SDS-rich	0.455 ± 0.063	0.421	0.433	0.988	1.10

Table 3. Average viscosities ($\overline{\eta}$) and viscosities of selected systems η_{sel} (calculated for the whole shear rate range) and consistency constants K and power-law indexes n calculated from the selected flow curves.
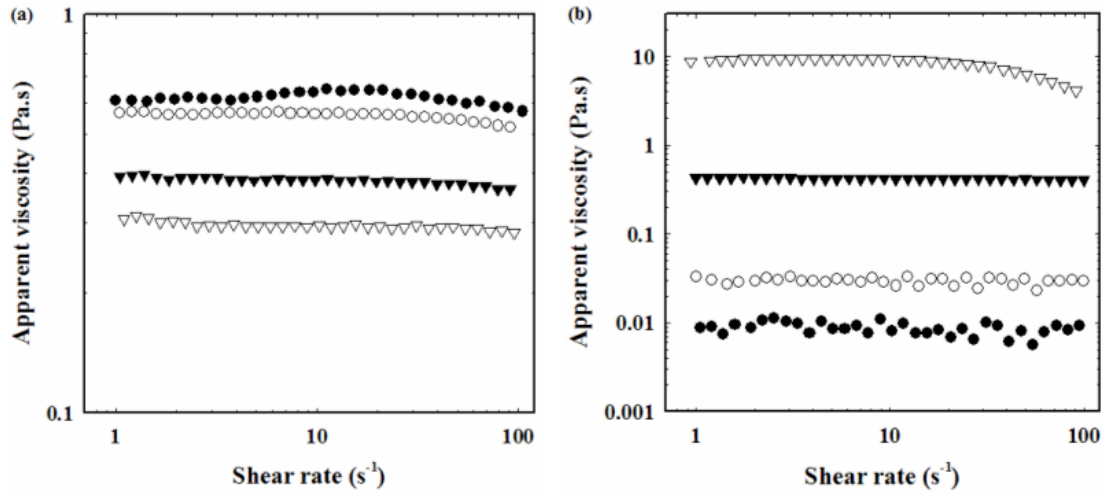
Figures and figure captions

Figure 1. Flow curves of the **(a)** pullulan-rich and **(b)** SDS-rich phases from the 12% SDS-12% pullulan ATPS of: 0.25m (●), 0.31m (○), 0.4m (▼) and 0.5m (▽) salt. Sensitivity of the rheometer led to certain scatter of experimental results at the lowest viscosity.
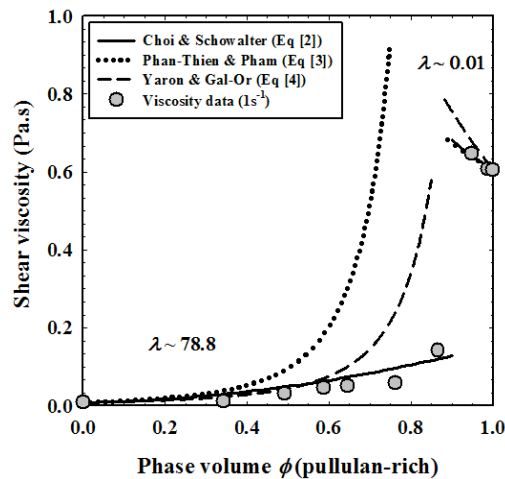

Figure 2. Comparison of Eqs [2]-[4] for the correlation of the rheological data for pullulan-SDS-NaCl aqueous mixture (*i*).
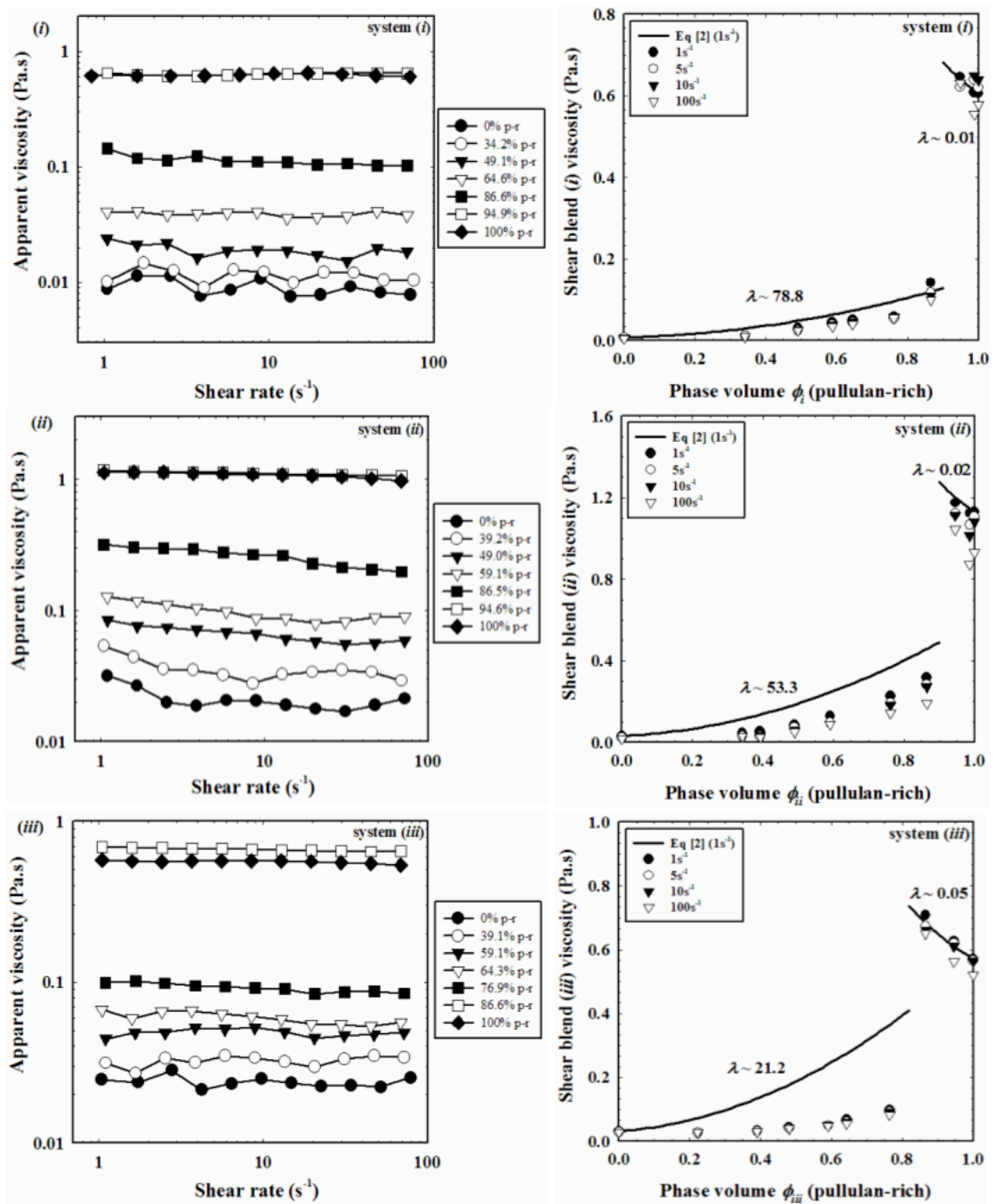
Figure 3. Rheological data for pullulan-SDS-NaCl aqueous mixtures: **(a)** mixture (*i*), **(b)** mixture (*ii*) and **(c)** mixture (*iii*) for increasing volume fraction of pullulan-rich phase (% p-r).

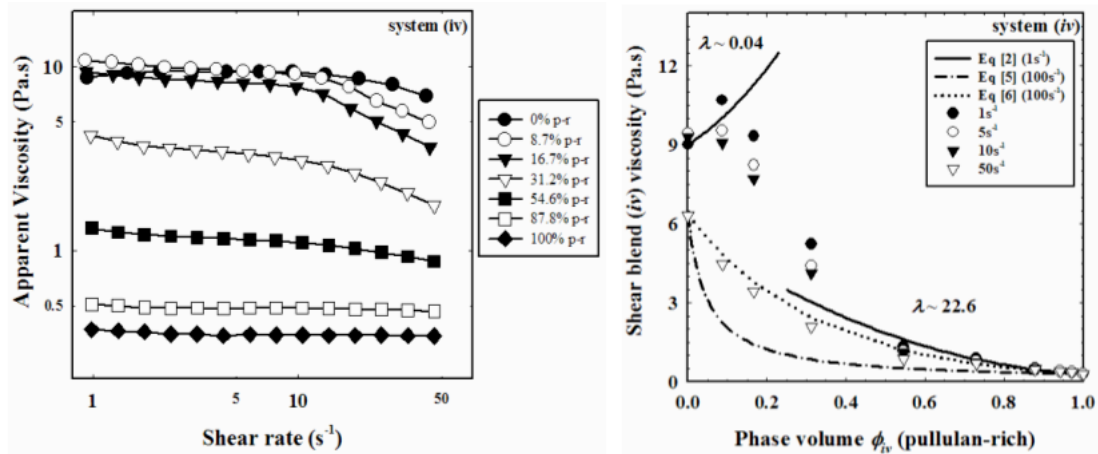**Figure 4.** Flow curves for pullulan-SDS-NaCl aqueous mixtures (*iv*) of increasing phase volume of pullulan-rich phase (% p-r).

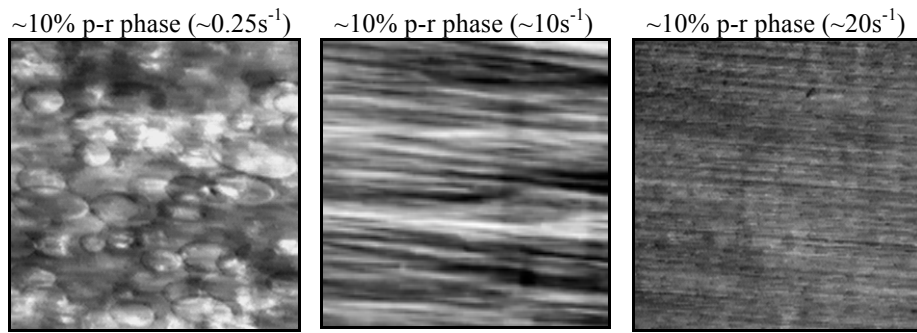~10% p-r phase (~0.25s^{-1})   ~10% p-r phase (~10s^{-1})   ~10% p-r phase (~20s^{-1})

Figure 5. Images of string phase development in a mixture from system (*iv*) with 13% phase volume of pullulan-rich phase and for increasing shear rates (given in brackets). The width of all images is approximately 600μm.
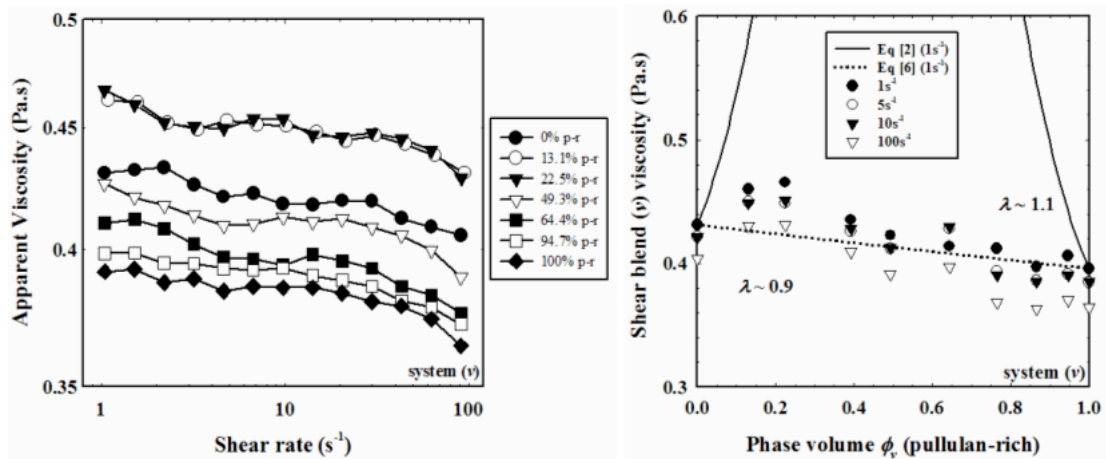

Figure 6. Flow curves for pullulan-SDS-NaCl aqueous mixture (*v*) of increasing phase volume of pullulan-rich phase (% p-r).