

Sequential adsorption of polyglycerol polyricinoleate and protein at the oil-water interface: An interfacial rheology study

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Several authors have reported that the presence of water-soluble surface-active compounds (e.g., proteins) strongly influences the absorption behaviour of polyglycerol polyricinoleate (PGPR) at oil-water interfaces, where the simultaneous adsorption of PGPR and proteins has been studied by dynamic surface tension and interfacial dilatational rheology [1, 2]. In order to further understand the interaction between proteins and PGPR in the emulsion stabilization mechanism, this study investigated the sequential adsorption of PGPR and proteins (i.e., whey protein isolate (WPI), sodium caseinate (NaCas) and bovine serum albumin (BSA)) at the oil-water interface by using a modified drop tensiometer allowing external phase exchange.

Experimental setup: modified drop tensiometer allowing external phase exchange (Teclis, Tracker, France) (Figure 1) [3]

Adsorption of 0.2 % PGPR 4175 (Palsgaard) to glyceryl triheptanoate-water interface
↓
Analysis of interfacial rheology of 0.2% PGPR 4175
↓
Phase exchange (peristaltic pump, Ismatec, Germany)
↓
Adsorption of 0.5% Protein to 0.2% PGPR 4175 interface
↓
Analysis of interfacial rheology of mixture (PGPR 4175-protein)

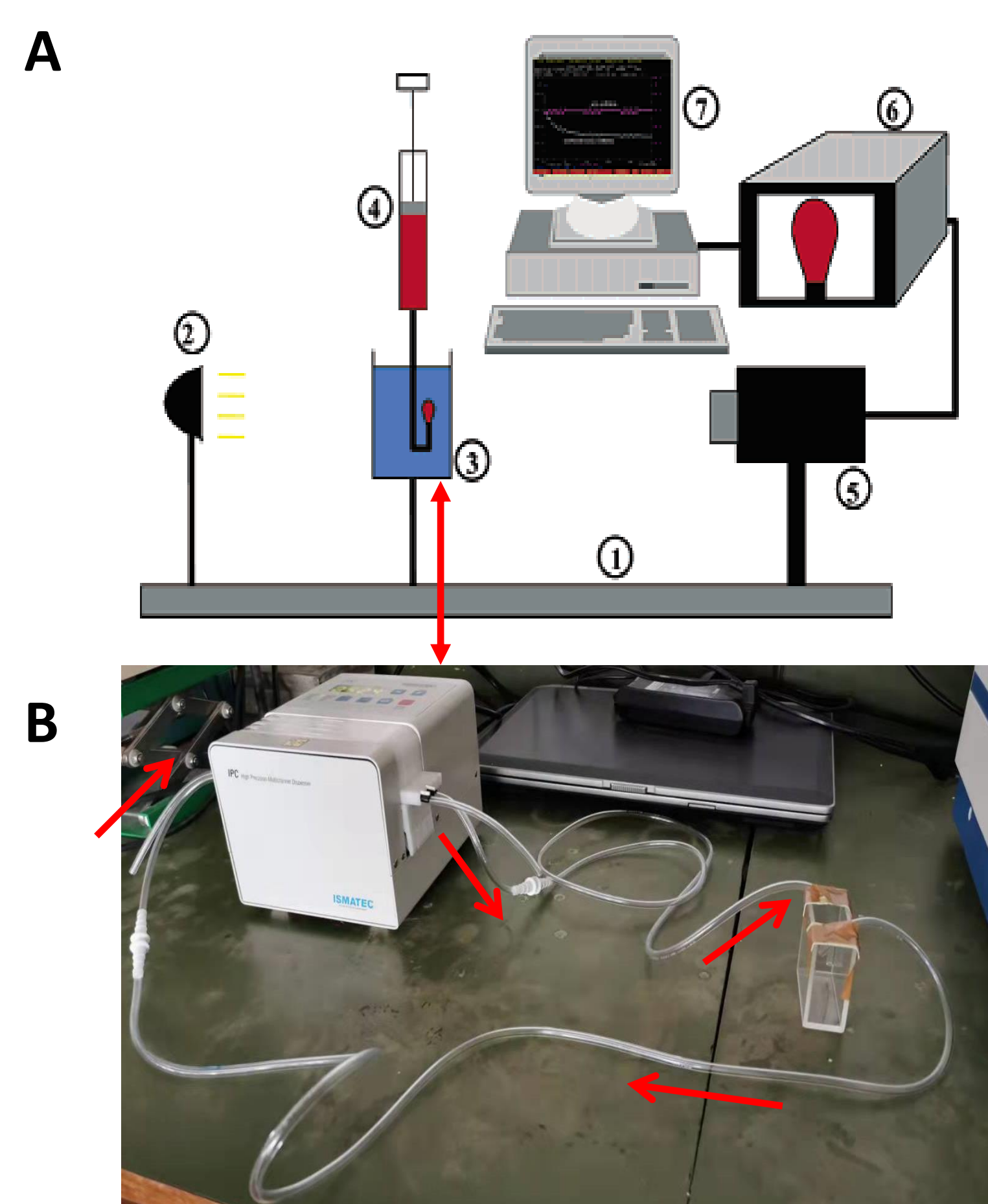


Figure 1. Schematic illustration of drop tensiometer (A) [4] and phase exchange using peristaltic pump (B).

RESULTS

Table 1. Dynamic interfacial tension (γ), dilatational elastic modulus (ϵ_d) and viscous modulus (η_d) of 0.2 % PGPR 4175 as a function of adsorption time. Amplitude and frequency are 15 % and 0.1 Hz, respectively.

Time (s)	5000	10000	15000	20000	30000
γ (mN/m)	6.34±0.10 ^a	6.05±0.14 ^b	6.01±0.22 ^b	6.00±0.19 ^b	5.98±0.21 ^b
ϵ_d (mN/m)	12.29±0.19 ^b	13.70±0.74 ^a	13.72±0.59 ^a	13.75±0.29 ^a	13.89±0.67 ^a
η_d (mN/m)	3.46±0.06 ^b	3.71±0.10 ^a	3.73±0.13 ^a	3.82±0.13 ^a	3.82±0.08 ^a

^a and ^b: different superscript letters in a row indicate significantly different results (p -value <0.05).

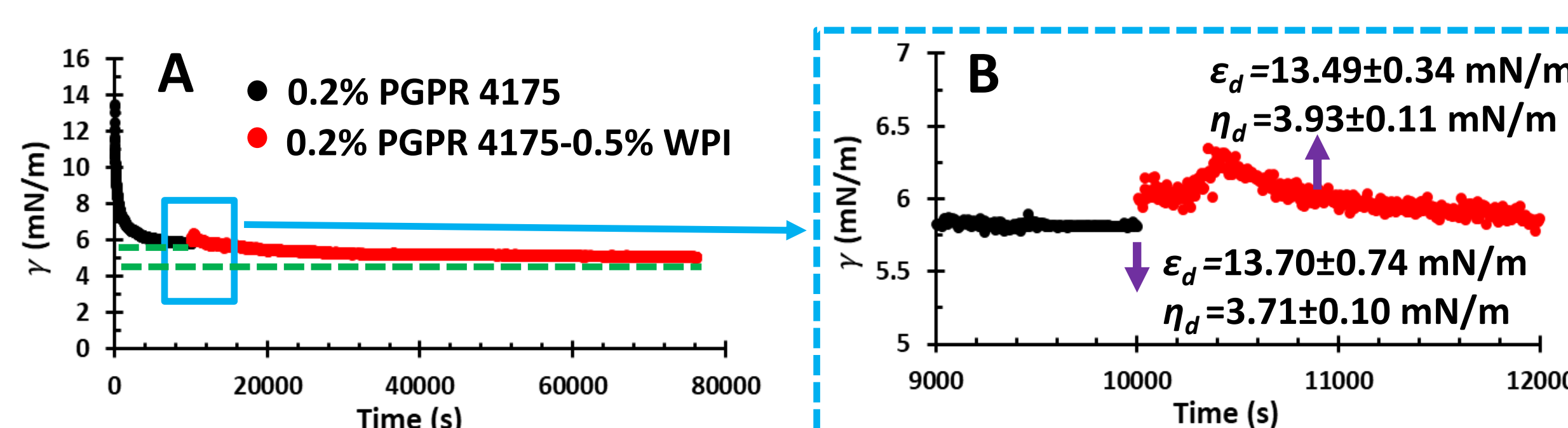


Figure 2. Interfacial tension of 0.2 % PGPR 4175 at oil/water interface after addition of 0.5 % of WPI solution to the water phase. B is an enlarged version of the part marked by the blue box in A.

Table 2. Dynamic interfacial tension (γ), dilatational elastic modulus (ϵ_d) and viscous modulus (η_d) of different types of 0.5 % protein. Amplitude and frequency are 15 % and 0.1 Hz, respectively.

Sample	γ (mN/m)	ϵ_d (mN/m)	η_d (mN/m)
0.5% WPI	11.72 ± 0.17 ^b	25.54 ± 0.16 ^a	4.48 ± 0.55 ^b
0.5% NaCas	11.09 ± 0.17 ^c	4.84 ± 0.14 ^c	1.06 ± 0.02 ^c
0.5% BSA	12.09 ± 0.12 ^a	19.21 ± 0.76 ^b	6.36 ± 0.72 ^a

^a, ^b and ^c: different superscript letters in a column indicate significantly different results (p -value <0.05).

Table 3. Effect of adding 0.5% of protein in the aqueous phase on the dynamic interfacial tension (γ), dilatational elastic modulus (ϵ_d) and viscous modulus (η_d) of 0.2% PGPR 4175 at an amplitude and frequency of 15 % and 0.1 Hz, respectively.

Sample	γ (mN/m)	ϵ_d (mN/m)	η_d (mN/m)
0.2% PGPR 4175	6.05 ± 0.14 ^a	13.70 ± 0.74 ^a	3.71 ± 0.10
0.2% PGPR 4175-0.5% WPI	4.60 ± 0.09 ^c	18.42 ± 0.29 ^d	3.91 ± 0.10
0.2% PGPR 4175-0.5% NaCas	5.33 ± 0.33 ^b	14.64 ± 0.29 ^b	3.94 ± 0.21
0.2% PGPR 4175-0.5% BSA	6.14 ± 0.20 ^a	15.59 ± 0.22 ^c	3.79 ± 0.18

^a, ^b, ^c and ^d: different superscript letters in a column indicate significantly different results (p -value <0.05).

DISCUSSION/ CONCLUSION

- Adsorption of 0.2% of PGPR 4175 was equilibrated at the glyceryl triheptanoate-water interface after 3 h (Table 1), then the change of continuous phase was performed.
- No change in the modulus of the 0.2% PGPR 4175 films was detected at the initial stage of protein addition (Figure 2).
- Interfacial tension of the pre-adsorbed 0.2% PGPR 4175 films was stabilized at around 6 mN/m and decreased with the addition of WPI and NaCas, whereas the addition of BSA had no effect on it (Table 2).
- Addition of the three types of protein increased the dilatational elastic modulus of the 0.2% PGPR 4175 films and the difference was similar to the interface of the three pure proteins (Table 2 and Table 3). However, no effect on its dilatational viscous modulus was observed (Table 3).
- ❖ Proteins may interact with previously adsorbed PGPR at the oil-water interface through hydrophobic interactions rather than replacing PGPR at the interface. However, further research is needed to determine the change in PGPR surface load at the oil-water interface in W/O emulsions with and without protein in the continuous water phase to further support this conclusion.

REFERENCES

- [1] Gülseren & Corredig (2012), Food Hydrocolloids, 29, 193-198; [2] Zhu et al. (2017), Food Hydrocolloids, 73, 194-202; [3] Li et al. (2022), Food Hydrocolloids, 128, 107570; [4] Miller & Liggieri (2009). Interfacial rheology (Vol. 1).