Supplementary Materials: Protein assembly and network formation at fluid interfaces: Effect of the oil

Jotam Bergfreund,^{*,†} Michael Diener,[†] Thomas Geue,[‡] Natalie Nussbaum,[†] Nico Kummer,^{¶,†} Pascal Bertsch,[†] Gustav Nyström,^{¶,†} and Peter Fischer^{*,†}

†Institute of Food, Nutrition and Health, ETH Zürich, 8092 Zürich, Switzerland

Laboratory of Neutron Scattering and Imaging, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland

¶Laboratory for Cellulose & Wood Materials, Swiss Federal Laboratories for Materials Science and Technology (Empa), Dübendorf, 8600 Switzerland

> E-mail: jotam.bergfreund@hest.ethz.ch; peter.fischer@hest.ethz.ch Phone: +41 (0) 44 632 53 49



Figure S1: Circular dichroism (CD) measurements of a) BLG, BSA, and LSZ. The solid lines indicate the measurements of the pristine protein solution and the dotted lines show the CD curve after 24 h of exposure to 2 mM DTT solution. b) CD spectra of the buffer and the 2 mM DTT solution. CD spectra were obtain on a CD spectrometer (JASCO, Easton MD, US) equipped with a CD-426S/426L Peltier cell using a Hellma quartz glass high-performance cuvette with a 1 cm path length. Protein samples were measured at a protein concentration of $0.25 \text{ g}\cdot\text{L}^{-1}$. CD spectra were obtained in the range from 190 – 260 nm at a scanning rate of 50 nm·min⁻¹ with a data pitch of 0.2 nm, standard sensitivity, a D.I.T. of 4 s, a bandwidth of 1 nm and averaging 10 accumulations.



Figure S2: Amplitude sweeps of BLG (purple), BSA (blue), and LSZ (green). At *n*-octane, 1-chlorooctane and 1-octanol interfaces.

Table S1: Measured data and literature data of the dilatational rheology, including the initial interfacial tension γ_{ow} of the clean oil-water interfaces, the interfacial tension after 12h of adsorption γ , the interfacial pressure after 12h of adsorption Π , the normalized interfacial pressure after 12h of adsorption π^* , the dilatational storage modulus E', the dilatational loss modulus E'', protein concentration c, the ionic strength I, and the pH of the aqueous phase. The reference numbering refers to the bibliography in the manuscript.

| Protein | Oil | γ_{ow} | γ | П | π^* | \mathbf{E}' | E" | с | Ι | $_{\rm pH}$ | ref |
|---------|----------------|---------------|----------|--------|---------|---------------|--------|---------|------|-------------|------|
| | | [mN/m] | [mN/m] | [mN/m] | [] | [mN/m] | [mN/m] | wt $\%$ | [mM] | | |
| LSZ | n-Octane | 52 | 21.4 | 30.60 | 0.59 | 59 | 3 | 0.01 | 10 | 7 | |
| LSZ | 1-Chlorooctane | 35 | 17 | 18.00 | 0.51 | 41 | 5 | 0.01 | 10 | 7 | |
| LSZ | MCT | 26 | 15 | 11.00 | 0.42 | 37 | 4 | 0.01 | 10 | 7 | |
| LSZ | 1-Octanol | 8.7 | 5.3 | 3.40 | 0.39 | 10 | 0.5 | 0.01 | 10 | 7 | |
| BSA | n-Octane | 52 | 24 | 28.00 | 0.54 | 50 | 6 | 0.01 | 10 | 7 | |
| BSA | 1-Chlorooctane | 35 | 19.5 | 15.50 | 0.44 | 42 | 5 | 0.01 | 10 | 7 | |
| BSA | MCT | 26 | 15.2 | 10.80 | 0.42 | 13.3 | 1 | 0.01 | 10 | 7 | |
| BSA | 1-Octanol | 8.5 | 6 | 2.50 | 0.29 | 2.4 | 0.5 | 0.01 | 10 | 7 | |
| BLG | n-Octane | 52 | 20 | 32.00 | 0.62 | 60 | 5 | 0.01 | 10 | 7 | |
| BLG | 1-Chlorooctane | 35 | 15.6 | 19.40 | 0.55 | 37 | 5 | 0.01 | 10 | 7 | |
| BLG | MCT | 26 | 14.9 | 11.10 | 0.43 | 38 | 5 | 0.01 | 10 | 7 | |
| BLG | 1-Octanol | 8.5 | 5.9 | 2.60 | 0.31 | 7.2 | 0.6 | 0.01 | 10 | 7 | |
| | | | | | | | | | | | |
| | | | | | | | | | | | |
| BLG | Decane | 50 | 17.1 | 32.90 | 0.66 | 52.68 | 0.44 | 0.01 | 10 | 7 | [29] |
| BLG | Dodecane | 51.00 | 22.30 | 28.70 | 0.56 | 60.62 | 5.28 | 0.01 | 10 | 7 | [29] |
| BLG | Tetradecane | 51.5 | 22.9 | 28.60 | 0.56 | 62.90 | | 0.01 | 10 | 7 | [29] |
| BLG | Hexadecane | 51.50 | 27.00 | 24.50 | 0.48 | 64.32 | 6.08 | 0.01 | 10 | 7 | [29] |
| BLG | Cyclohexane | 50.00 | 20.50 | 29.50 | 0.59 | 62.39 | 4.69 | 0.01 | 10 | 7 | [29] |
| BLG | Decaline | 50.00 | 20.00 | 30.00 | 0.60 | 60.38 | 4.58 | 0.01 | 10 | 7 | [29] |
| BLG | Toluene | 36.30 | 17.05 | 19.25 | 0.53 | 47.32 | 3.04 | 0.01 | 10 | 7 | [29] |
| BLG | Limonene | 37.00 | 16.80 | 20.20 | 0.55 | 45.00 | 4.60 | 0.01 | 10 | 7.4 | [29] |
| LSZ | Hexadecane | 53.3 | 27.3 | 26.00 | 0.49 | 70 | 4 | 0.005 | 100 | 6.7 | [53] |
| BSA | MCT | 27 | 16 | 11.00 | 0.41 | 25 | | 0.010 | 30 | 6.7 | [54] |
| BLG | MCT | 27 | 15 | 12.00 | 0.44 | 23 | | 0.010 | 30 | 6.7 | [54] |
| BLG | tetradecane | 51.3 | 21.3 | 30.00 | 0.58 | 55 | | 0.010 | 30 | 6.7 | [55] |
| BLG | Sunflower oil | 31.2 | 11.2 | 15.00 | 0.48 | 20 | | 0.010 | 30 | 6.7 | [55] |
| BSA | tetradecane | 51.3 | 20.7 | 30.60 | 0.60 | 51 | | 0.010 | 30 | 6.7 | [55] |
| BSA | Sunflower oil | 31.2 | 16.2 | 15.00 | 0.48 | 22.3 | | 0.010 | 30 | 6.7 | [55] |
| BLG | Paraffin oil | 48 | | | | 45 | | 0.010 | 75 | 7 | [56] |
| BLG | tert-butanol | 1.96 | 1.5 | 0.46 | 0.23 | 2.3 | | 0.100 | | | [57] |
| BSA | tert-butanol | 1.96 | 1.65 | 0.31 | 0.16 | 0.38 | | 0.100 | | | [57] |
| LSZ | tert-butanol | 1.96 | | | | 0.06 | | 0.100 | | | [57] |
| BLG | tetradecane | 50 | 20 | 30.00 | 0.60 | 45 | | 0.013 | 10 | 7 | [58] |
| BLG | Sunfloweroil | 29 | 18 | 11.00 | 0.38 | 30 | | 0.018 | 10 | 6.8 | [58] |
| BLG | Tetradecane | 53 | 25 | 28.00 | 0.53 | 65 | | 1.840 | 150 | 7 | [27] |
| BLG | olive oil | 29.5 | 17 | 12.50 | 0.42 | 30 | | 1.840 | 150 | 7 | [27] |
| BLG | tetradecane | 52.5 | 23.5 | 29.00 | 0.55 | 60 | | 0.094 | 10 | 7 | [59] |



Figure S3: Amplitude sweeps of BLG (purple) and LSZ (green) after the injection of DTT. At *n*-octane, 1-chlorooctane and 1-octanol interfaces.



Figure S4: Adsorption behavior of DTT to *n*-octane, 1-chlorooctane, and 1-octanol, depicted as interfacial pressure over time. The experiment was performed with a droplet profile tensiometer.