Supporting Information

Surface Properties of Spider Silk Particles in Solution: Combining Direct Force Measurements and Electrophoretic Mobility

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1. Surface structure of dried eADF4(C16) particles

The surface structure of dried spider silk protein particles has been examined by scanning electron microscopy. Figure S-1 shows the surface structure of an exemplary particle at higher magnification in addition to the overview image in Figure 1 a.
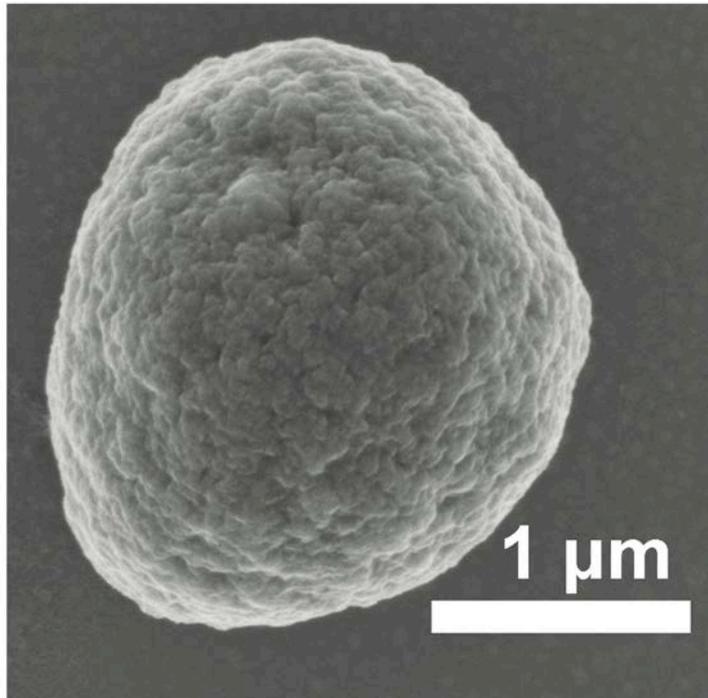
Fig. S-1 Scanning electron microscopy image of an eADF4(C16) particle in the dehydrated state.

2. Calculation of ζ -potentials and electrophoretic mobilities

2.1 Electrophoretic Mobility in the Framework of the O'Brien and White Theory

The surface charge density of the spider silk particles is described by a simple model for their surface chemistry. This model is based on the number density of ionizable groups and their corresponding pK_a-values.[1],[2] The resulting surface charge density is then used to calculate the diffuse layer potential.[3] The electrophoretic mobility is finally obtained from the diffuse layer potential in the framework of the theory of O´Brien and White.[4] It can be determined by interpolation of tabulated values as given for example in the book of Hunter.[5] Additional parameters necessary for the interpolation are particle radius and limiting conductance of the electrolyte solutions. Analogous calculations are available in the literature where surface chemistry and electrophoretic mobility have been related. [6]-[11] More general algorithms than used here are available in the literature.

2.2 Electrophoretic mobilities of spider silk particles at high ionic strength as reported by Hofer et al.

Hofer et al. reported the electrophoretic mobility of spider silk protein particles comparable to ones used here, albeit at significantly higher ionic strength.[13] At high ionic strength, the deviations between the equation of Smoluchowsky and the theory of O'Brien and White are becoming significantly smaller. According to the Smoluchowsky equation the ζ–potential and the electrophoretic mobility are related by:[5]

$$\mu = \frac{\varepsilon_r \varepsilon_0}{\eta} \zeta \qquad\qquad\qquad \text{(S-1)}$$

Where η is the viscosity, while ε_r and ε_0 are the relative permittivity of the electrolyte and of vacuum, respectively. It should be pointed out that in the framework of the Smoluchowski equation no local minima are expected in the electrophoretic mobility, contrary to the ones observed in Figure 2b).

Figure S-2 compares the experimental data reported by Hofer et al. with our model. Again, the theoretical mobilities have been calculated with the parameters given in

Table 1. A conversion by equation (S-1) of the ζ-potentials reported in ref.[13] gains the same results, although particle radii of 260.5 nm have been used for the calculations, as reported in Ref. 13.
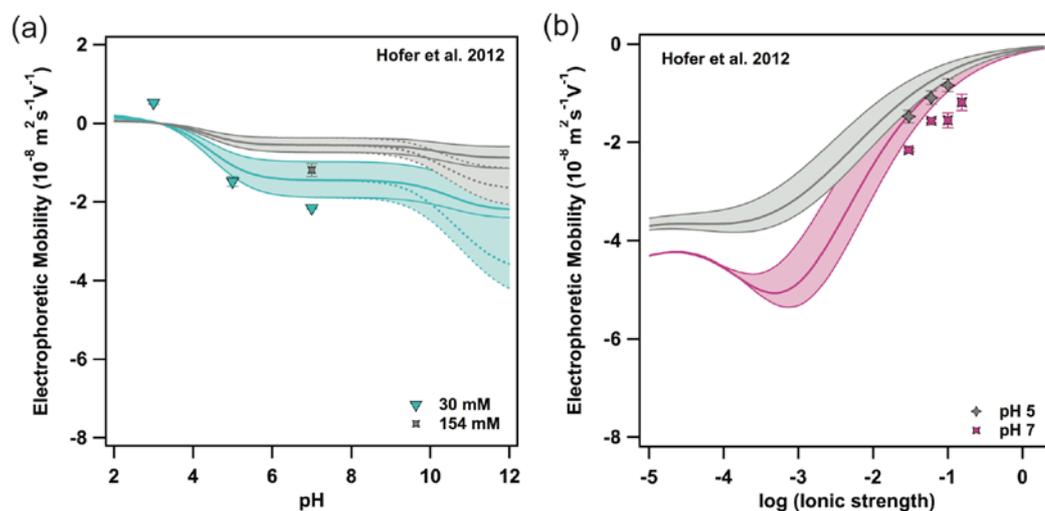
Fig. S-2 Electrophoretic mobility as a function of a) pH and b) ionic strength. The data points are from Hofer et al.[8] , while the lines represent calculations based on the theory of O'Brien and White with the parameters summarized in Table 1 except a different average particle radius of 260.5 nm.

Figure S-2 demonstrates that the model and parameters summarized in Table 1 also provide an accurate description of the electrophoretic mobilities of spider silk particles at high ionic strength, in particular for electrolyte solutions that resemble physiological conditions.

3. References for supporting information

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