Supplementary Informations

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August 30, 2020

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1 Polyvalent ions

The description of diffusiophoresis in the literature [1, 2, 3, 4] for electrophoresis based diffusiophoresis usually describe a salt whose two ions have the same valence, or charge number ($Z_\pm$). This is not always the case, especially if, to optimise the β parameter, one uses a large highly charged molecule with many counter-ions. Here, the derivation for the general case of ions polyvalence is shown. An electric field is assumed to appear to prevent the charge density from being non-zero. The diffusion of small ions is slowed down while the diffusion of larger ions is accelerated by this field. As the density of charge is assumed to be zero, $\vec{\nabla} \cdot \vec{E} = 0$ from Maxwell equations. Each ionic species has a concentration c_i, a diffusion coefficient D_i, and a mobility μ_i. The motion is controlled by the convection-diffusion equation:

$$\frac{\partial c_i}{\partial t} = D_i \nabla^2 c_i - \mu_i \vec{E} \cdot \vec{\nabla} c_i$$

The mobility μ_i depends on the charge and on the diffusion coefficient:

$$\mu_i = \frac{D_i q_i}{k_B T} \tag{1}$$

The condition of charge neutrality can be written as $\sum c_i q_i = 0$. Taking the derivative with respect to time and integrating over space leads to a formula for the electric field needed to avoid charge separation:

$$\vec{E} = k_B T \frac{\sum q_i D_i \vec{\nabla} c_i}{\sum q_i^2 D_i c_i} \tag{2}$$

This is further simplified in the case of a single anion and cation with charge $q_\pm = \pm Z_\pm e$, where e is the elementary charge. In this case, the concentration of the ions are proportional to the salt concentration c:

$$\vec{E} = \frac{D_+ - D_-}{D_+ Z_+ + D_- Z_-} \frac{k_B T}{e} \vec{\nabla} \ln c \tag{3}$$

This leads to the definition of a new unit-less parameter β_Z that describes uniquely the salt contribution to the diffusiophoresis.

$$\beta_z = \frac{D_+ - D_-}{D_+ Z_+ + D_- Z_-} \tag{4}$$

If the ions have the same valence ($Z_+ = Z_-$), the usual result is recovered, and $\beta_Z = \beta / Z$. The diffusiophoretic coefficient therefore depends only on the protein mobility μ_p and on the salt β_Z coefficient:

$$\Gamma_p = \frac{k_B T}{e} \mu_p \beta_Z \tag{5}$$

A similar derivation can be used to derive the salt diffusion coefficient D_s:

$$D_s = D_+ D_- \frac{Z_+ + Z_-}{D_+ Z_+ + D_- Z_-} \tag{6}$$

From the main text, the unitless coefficient that controls diffusiophoresis is Γ_p / D_s:

$$\frac{\Gamma_p}{D_s} \propto \frac{1}{Z_+ + Z_-} \left(\frac{1}{D_-} - \frac{1}{D_+} \right) \tag{7}$$

The inverse of the diffusion coefficient is proportional to the hydrodynamic radius. Therefore, maximising the diffusiophoretic effect correspond to maximising the difference between the ionic hydrodynamic radii.

2 COMSOL Simulations

The theoretical solution for the semi-infinite channel predict a concentration that is much higher than what is seen in the experiments. To understand this discrepancy, COMSOL simulations are done in one, two, and three dimensions. In one dimension, the salt and protein concentration are fixed at the dead-end inlet. In two and three dimensions, the main channel and the flow are

simulated. An example of the proteins distribution is shown in Figure (1), where a half circle can be seen in two and three dimensions where the main channel flow penetrates in the dead-end. While the intensity of the one dimensional simulation is very close to the intensity predicted by the theoretical solution, as shown in Figure (2), the intensities of the higher dimensional simulations have much lower intensities. When the profiles are normalised however, the solution seems to fit perfectly. A small offset can be seen in two and three dimensions that will lead to a small underestimation of the diffusiophoresis coefficient, as discussed below.

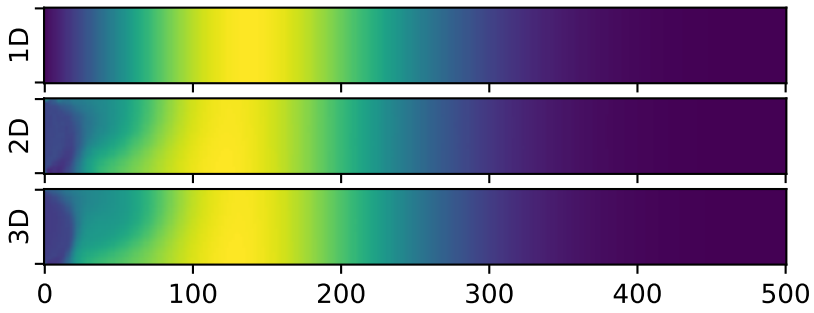

Figure 1: Spatial distribution of the concentration in the channel for the COMSOL Figures after two minutes. The colormap are normalised for each plot, so the intensities can't be compared here.

3 Experiments

The experiments have been replicated with more proteins. The results are shown in Figure (3). All new proteins have a negative charge at pH 7 and therefore match the bovine serum albumin results: A peak appears for $LiCl$, no diffusiophoretic effect is apparent for KCl, and the diffusion id hindered for KIO_3.

The salt concentration ratio is an important parameter as it limits the concentration of buffer that can be used with the proteins. Even using proteins without buffer can significantly decrease the diffusiophoretic strength. BSA is itself an ionic molecule, and is accompanied by many counter-ions. The molecular weight of BSA is typically three orders of magnitude higher than a salt such as LiCl. Assuming the concentration of counter-ions is a thousand times higher than the protein concentration, we see that Figure (4) is consistent with the simulation results discussed in the main text: decreasing the concentration from $1000\mu M$ to $100\mu M$ result in a peak ten times higher, while the next decrease of an order of magnitude only increases the peak height by 30%. The concentration of any salt or counter-ions should therefore be at least two orders of magnitude lower than the dead-end salt concentration. The next test is to verify if the diffusiophoresis coefficient dependence is really as strong as Figure (4C) from the main text seems to indicate. To that end, we compare $NaOH$ with $LiCl$, as the β coefficient of the first is twice as large. To avoid a large effect from the massive change in pH, we select thyroglobulin, whose electro-phoretical mobility is roughly constant for pH of 7 and above [5]. As shown in Figure (5), the peak is 16 times higher with a simple doubling of the diffusiophoretic coefficient.

4 Fits

The simulations show a good agreement with the theoretical solutions after normalisation. Fitting the profiles therefore appears to be a promising way of extracting informations about the proteins. To validate this approach, the simulated profiles are fitted with the theoretical solution. As the theoretical solution assumes a semi-infinite channel, the profiles with significant intensity in the last fifth of the channel are excluded. Similarly, the part of the profiles between the main channel and the peak are not fitted as the intensity difference changes this part of the profiles. From Figure (2), we expect a slight offset in the fitted diffusiophoresis coefficient and a good agreement with the diffusion coefficient. This is indeed what is shown in Figure (6). The error on the diffusion coefficient is consistently smaller than 10% and the error on the diffusiophoresis appears to have a constant offset of -25%. A closer look at a few simulations leads to a better understanding of these

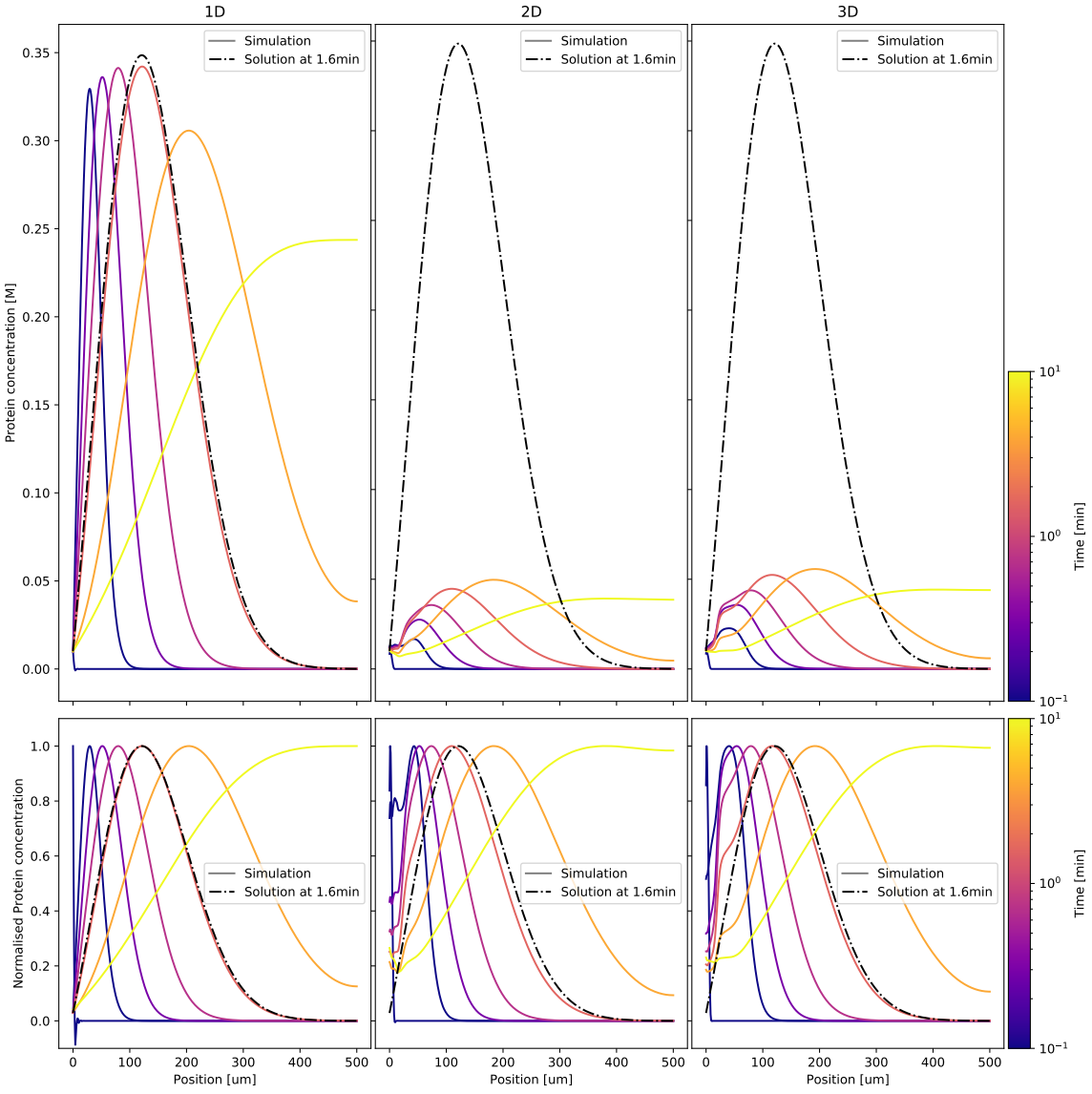

Figure 2: Comparison of one, two, and three dimensional simulations. The intensity of the partial differential equation and the one dimensional simulation are similar and much larger that two and three dimensional simulations. When normalised, the three simulations are almost indistinguishable.

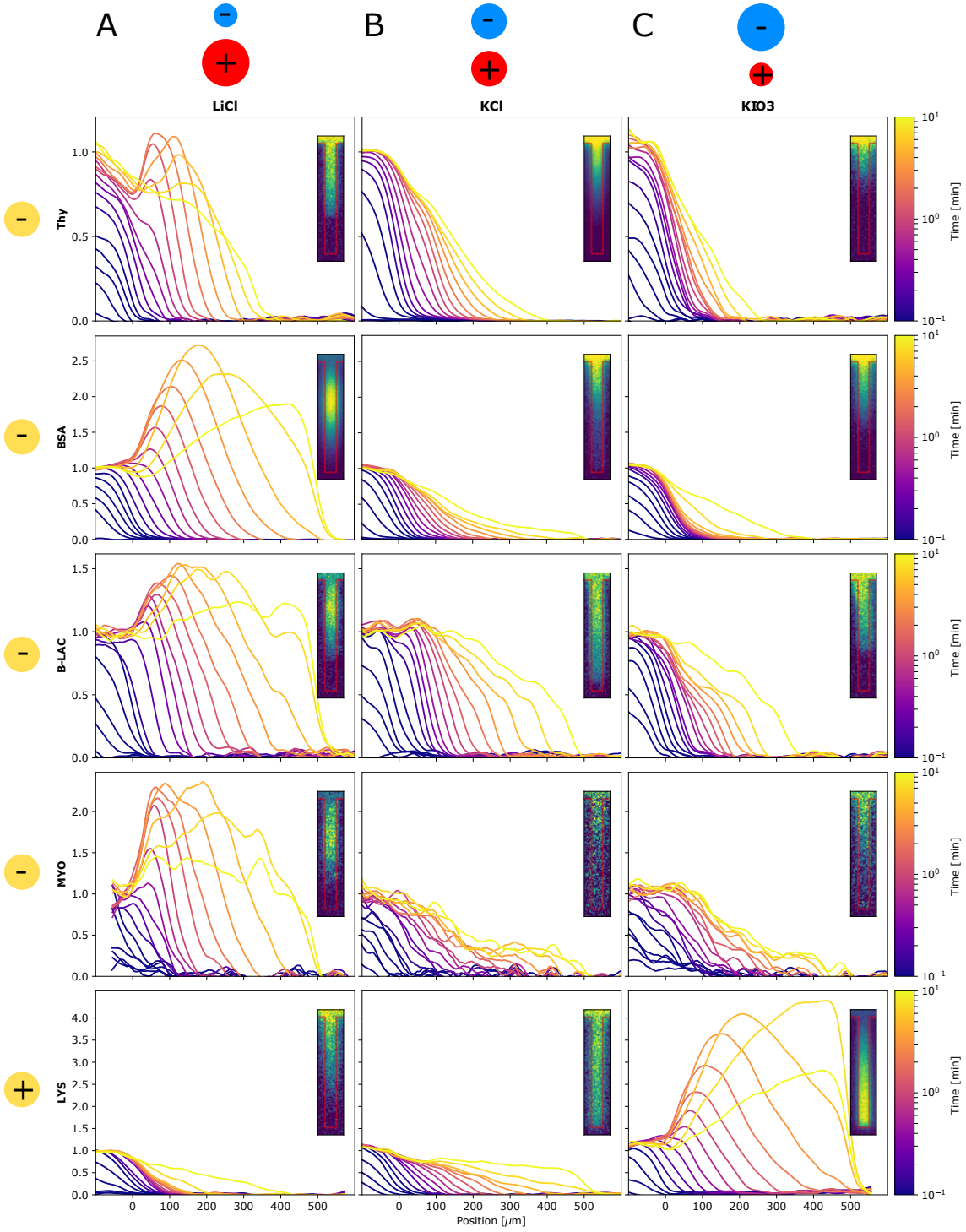

Figure 3: Diffusiophoresis of proteins in salt gradient. The proteins are Thyroglobulin (Thy), Bovine Serum Albumin (BSA), Beta-Lactoglobulin (B-LAC), Myoglobin (MYO), and Lysozyme (LYS). The salts are Lithium chloride (LiCl), Potassium chloride (KCl), and Potassium iodate (KIO3). If the smaller salt ion has the same charge as the protein, a concentration peak appears in the channel. If the larger salt ion has the same charge as the protein, the diffusion in the channel is reduced. If the two ions have similar charge, no effect is visible.

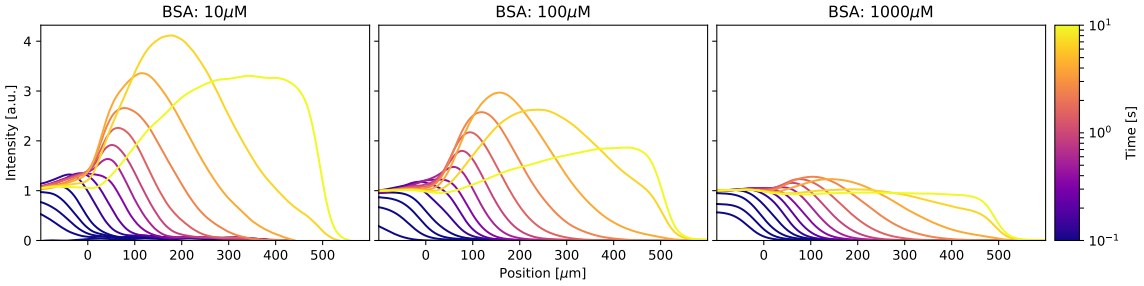

Figure 4: Effect of protein concentration on diffusiophoresis for BSA. The salt is 2M LiCl.

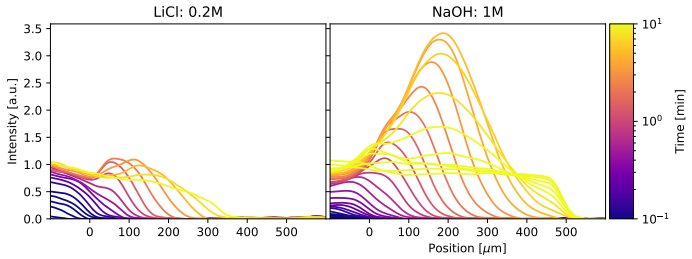

Figure 5: Effect of diffusiophoretic coefficient on 1uM Thyroglobulin. The salts are 0.2M LiCl and 1M NaOH.

graphs. The diffusiophoresis coefficient seems to increase slightly with the salt ratio as shown in Figure (6A). For ratios close to one, the concentration is much lower, as shown in Figure (7A). The fitted coefficient increases when the diffusiophoretic effect disappear. The following simulations are done with the lowest channel salt concentration. In Figure (6B), the fitted diffusion becomes much higher when the diffusion coefficient is low. This is unsurprising as the slope becomes really steep and doesn't change much, as shown in Figure (7B). Effects such as numerical diffusion could easily explain this change in fitted diffusion coefficient. The diffusiophoresis coefficient on the other hand appears to be roughly constant. In Figure (6C), the diffusion coefficient is quite stable when varying the diffusiophoresis coefficient. The fitted diffusiophoresis coefficient itself however shows a relative increase for lower values of the simulated diffusiophoresis coefficient. As shown in Figure (7C), this could be explained by the simulation taking more time to converge to the theoretical solution. This problem is even more apparent in Figure (6D), where the fitted diffusiophoresis appears much too large for low salt diffusion. Looking at Figure (7D), the problem appears: only the first times don't have a significant fluorescence at the end of the channel. Unfortunately, these times are before the simulation converged to the theoretical solution.

Salt	NaOH	LiCl	NaCl	KCl	CsCl	KIO_3	HCl
β	-0.597	-0.326	0.207	-0.019	0.005	0.298	0.642

Table 1: Values of different β coefficients at 25^{o}C. Values taken from [6, 7] for LiCl, CsCl and $KI0_3$. ; and from [8] for NaCl and KCl

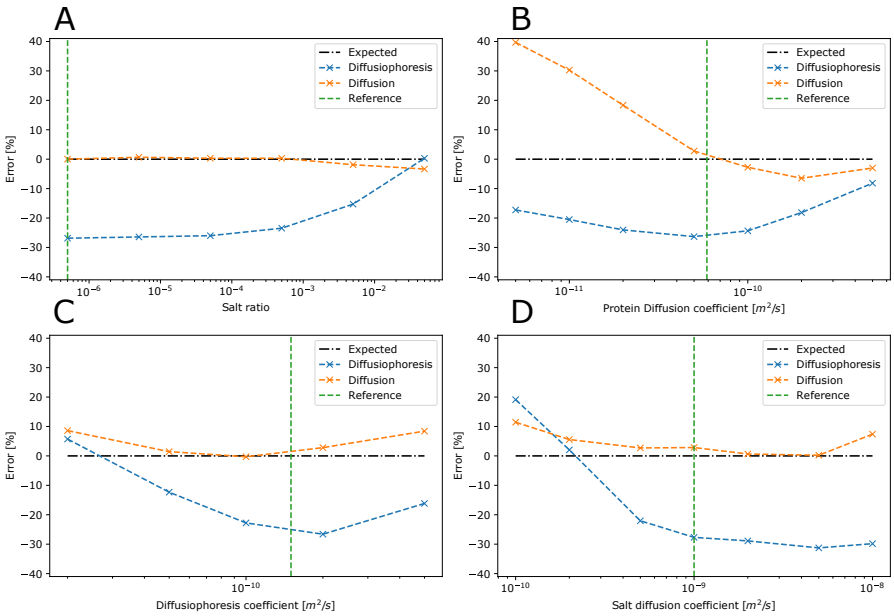

Figure 6: Error in the fit of the simulations. The blue lines represent the error on the diffusiophoresis coefficient, and the orange lines the error on the diffusion coefficient. The reference value is the same between the four graphs.

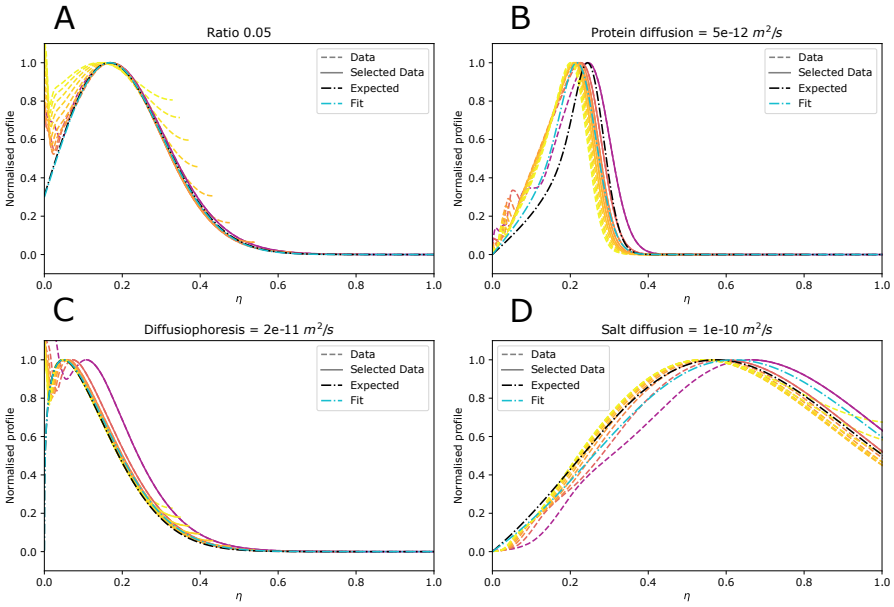

Figure 7: Selected simulations profiles and fits

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