Routine, ensemble characterisation of electrophoretic mobility in high and saturated ionic dispersions

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Abstract

Understanding how particles behave when suspended in a liquid medium is important to many applications as it is critical to determining their stability. A key indicator of this is a particles zeta potential.[1] The zeta potential of a particle can be measured by passing an electric current through the liquid and using light scattering to detect how quickly the particle moves and which electrode it moves towards (the electrophoretic mobility), this technique is called electrophoretic light scattering (ELS).

ELS is commonly used to measure the zeta potential of particles however a limitation of the technique is that passing an electric current through samples with a high or saturated ionic strength such as in biological conditions or seawater causes degradation of the samples due effects such as agglomeration of particles at the electrodes, precipitation of the salt, denaturation of fragile materials.

Using a sample loading method called diffusion barrier and the Zetasizer Advance range of instruments, we have demonstrated how ELS can be used to measure high and saturated ionic strength dispersions, such as up to 4M KCl, and the effect of these dispersions on the stability of the particles including the Hoffmeister series.

Theory

When a particle is suspended in a liquid, a layer of ions forms around the particle known as the Stern layer then further out from the particle is a diffuse layer of ions in the liquid, collectively these two layers are known as the double layer.[1] In between these two layers is the slipping plane at which there is an electric potential. This potential is the particles zeta potential and determines whether particles will be attracted to each other within solution (unstable) or repulse each other (stable). If the zeta potential is highly negative or positive then the repulsive zeta potential force is able to overcome the attractive forces of the particles such as Van der Waals forces meaning the particles repulse each other. The zeta potential of a particle is calculated from its electrophoretic mobility. This calculation uses the Henry equation, however this equation makes assumptions which do not hold up for high ionic dispersions therefore we have presented our results as electrophoretic mobility to ensure they do not show errors that occur due to these assumptions.[1]

The expected effect of increasing the ionic strength of a dispersion on the particles electrophoretic mobility is that the double layer collapses and greatly reduces in distance from the particle, this in turn reduces the electrophoretic mobility of the particles.[2] This of electrophoretic mobility indicates that the repulsive forces of the particles have decreased and this means that they are more likely to aggregate.

Figure 1. Diagram showing the electrical double layer that forms around particles in liquid dispersions

Method

In this study we measured the electrophoretic mobility of 200nm polystyrene latex dispersed in a range of salts and concentrations up to 4M to develop methodology for working with such high ionic strengths and pH adjusted to pH 7. As mentioned in the introduction, measurements at these sort of strengths will typically have issues with sample degradation. Including agglomeration at electrodes, precipitation of salt and outgassing of bubbles. These particles and bubbles can then travel into the measurement window and cause further agglomeration in this key area. These agglomerates and other particulates will then cause the measurement data to be noisy and the result quality poor. However, in this study we used the sample loading method, diffusion barrier, to negate this issue. This method is described in Fig 2.
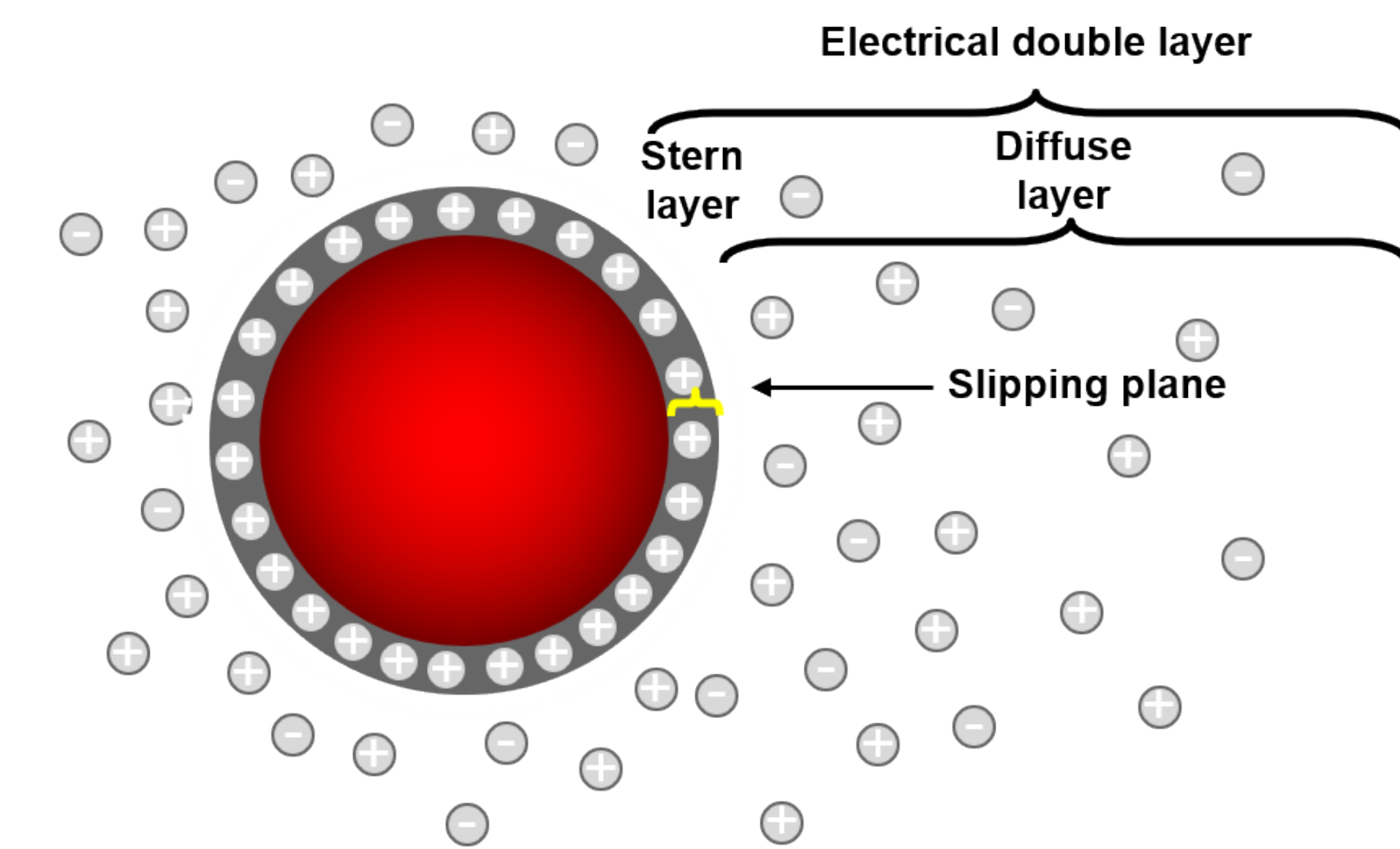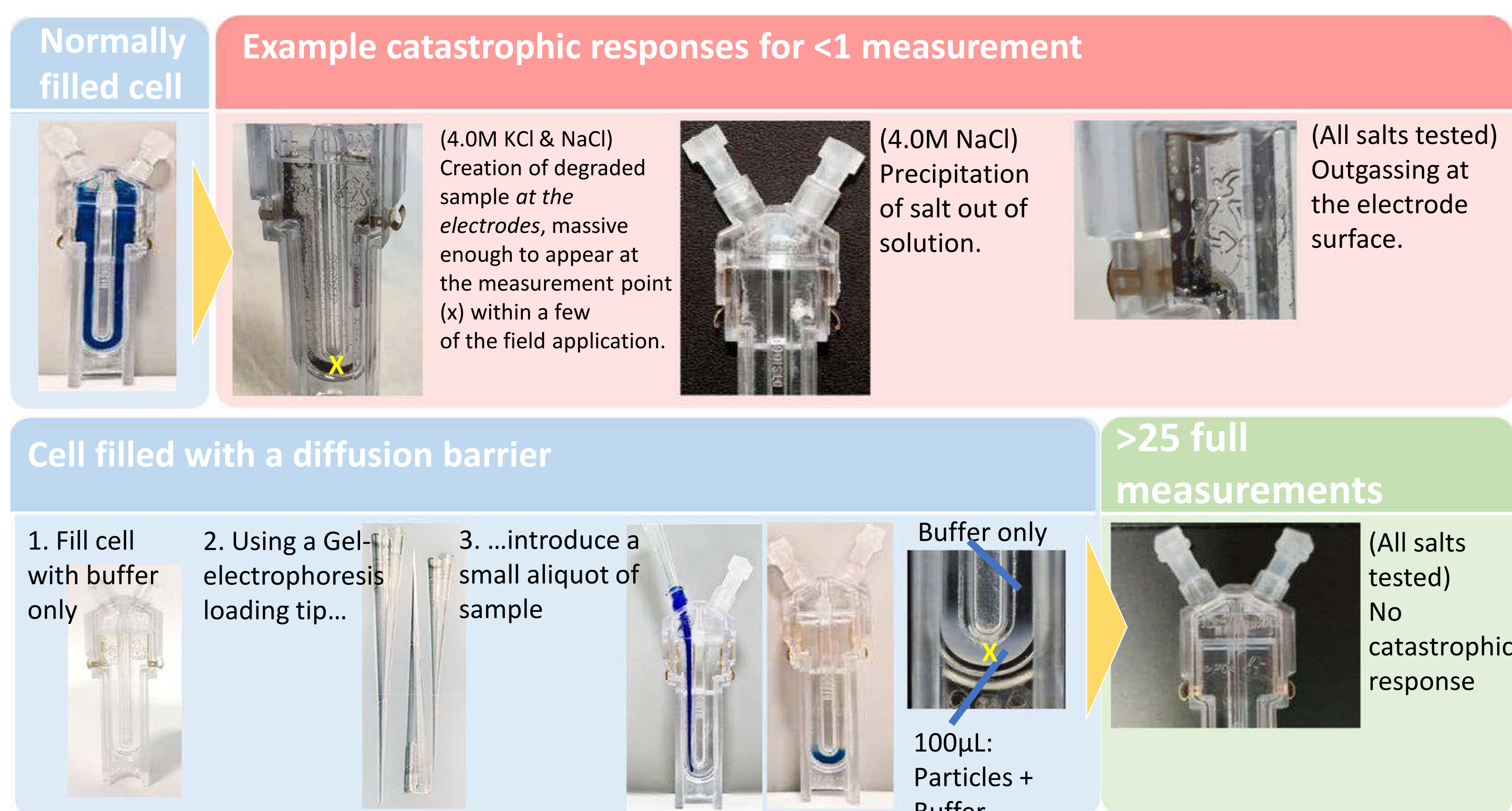

Figure 2. Top: Example of the issues seen with a normally filled cell. Bottom: Description of how a cell is filled with a diffusion barrier
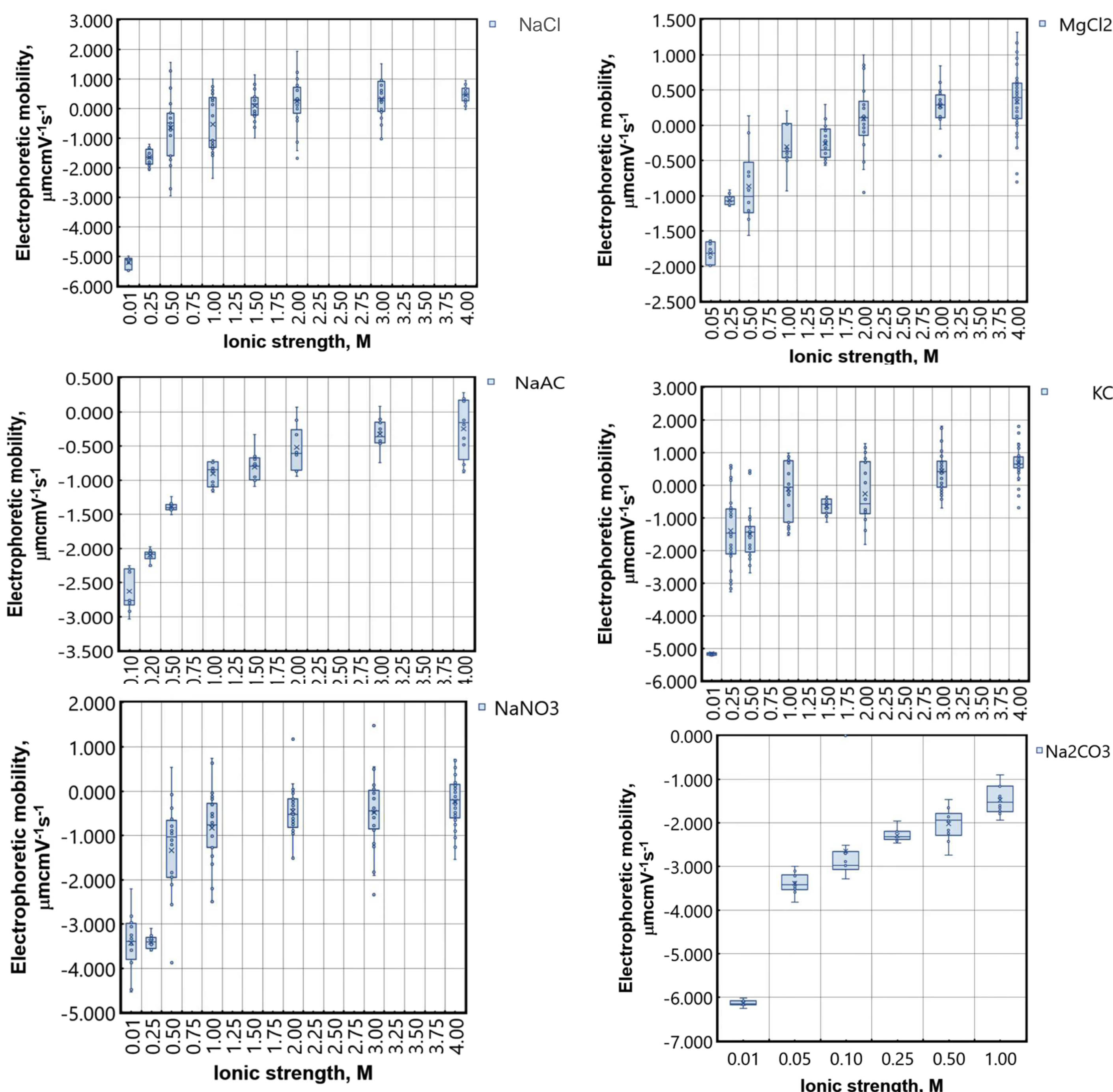

Figure 3. Boxplots of the electrophoretic mobility measured for each salt with increasing concentration.

Results

Presented in Fig. 3 are the results of the electrophoretic mobility measurements for each salt at a range of concentrations. All salts were measured up to 4M except for sodium carbonate which we were unable to source a strong enough corresponding acid to reach pH 7 without significantly diluting the salt. All salts were successfully measured over 20-30 data points per molarity, avoiding catastrophic effects such as outgassing or precipitating out.

A surprising outcome of the measurements is an apparent charge inversion of the particles which is shown by a reversal in the sign of the electrophoretic mobility. This is clearly demonstrated with the chlorine salts but not the acetate, nitrate or carbonate salts. The results also suggest that the point at which the electrophoretic asymptotes follows the Hofmeister series, with the value of the asymptote dependent on the identity of the ionic species present.[2,3] Additionally, anions have been found to have a larger effect than cationic species.[4] Anions specific to this study are ordered as $C_2H_3O_2^{-2}$ (acetate) > Cl^- > NO_3^-, where the order is based on increasing ion hydration.

Similarly, the cationic species studied should follow the rule, $K^+ > Na^+ > Mg^{2+}$.

Conclusion

Using a standard laboratory ensemble light scattering instrument we find that the diffusion barrier method, which isolates the dispersed phase from the electrodes, prevents the catastrophic sample degradation, outgassing and precipitation observed when the particles are in contact with the electrode surface. This tool enables the routine, ensemble characterisation of high ionic strength dispersions in small sample volumes and short measurement times.

We have reproduced a number of electro-kinetic effects predicted by theory to exist at and approaching saturated ionic conditions in aqueous dispersions, including asymptotic and non-zero electrophoretic mobility, an ion-specific value of the asymptote and charge inversion. tools should help accelerate the ongoing development of a complete electrokinetic theory of elevated ionic strength systems and their application to important contemporary problems in the environmental sciences, pharmacology and industrial and pharmaceutical manufacturing.

Future Work

This study has enabled applications that previously ELS could not be used with and we plan to explore two of these in the future:

- Characterisation of microplastics in sea water
- Characterisation of samples in physiological media

If you have an interest in this work and would like to take part in a collaborative study or paper then please contact one of the authors.

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