analytical chemistry

Article

pubs.acs.org/ac

Anomalous Mobility of Highly Charged Particles in Pores

Yinghua Qiu,[†,‡] Crystal Yang,[§] Preston Hinkle,[†] Ivan V. Vlassiouk,[∥] and Zuzanna S. Siwy*[,†,§,⊥]

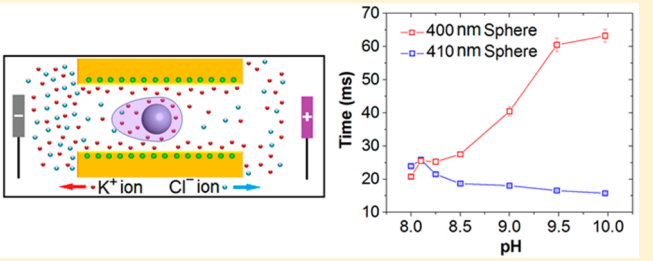
[†]Department of Physics and Astronomy, [§]Department of Chemistry, and [⊥]Department of Biomedical Engineering, University of California, Irvine, California 92697, United States

[‡]School of Mechanical Engineering and Jiangsu Key Laboratory for Design and Manufacture of Micro-Nano Biomedical Instruments, Southeast University, Nanjing 211189, China

[∥]Oak Ridge National Laboratory, Bethel Valley Road, Oak Ridge, Tennessee 37831, United States

Supporting Information

ABSTRACT: Single micropores in resistive-pulse technique were used to understand a complex dependence of particle mobility on its surface charge density. We show that the mobility of highly charged carboxylated particles decreases with the increase of the solution pH due to an interplay of three effects: (i) ion condensation, (ii) formation of an asymmetric electrical double layer around the particle, and (iii) electroosmotic flow induced by the charges on the pore walls and the particle surfaces. The results are important for applying resistive-pulse technique to determine surface charge density and zeta potential of the particles. The experiments also indicate the presence of condensed ions, which contribute to the measured current if a sufficiently high electric field is applied across the pore.



Mobility of charged colloidal particles in electrolyte solutions has been a subject of discussion for a few decades. The discussions are stimulated by unexpected findings showing a nonmonotonic dependence of the particle mobility on its surface charge density.[1−8] After an initial increase, when the charge density reaches a certain threshold, the mobility either saturates or starts decreasing. The effect was first described for charged polymers[9−14] and further extended to spheres and planes.[15]

One explanation that was put forward is based on the deformation of the electrical double layer of counterions around a particle caused by the applied electric field.[3,16−18] This double-layer polarization induces an additional drag force acting on the particle and consequently leads to lower particle mobility. Another explanation for the existence of maximum of the particle mobility in its dependence on the surface charge is provided by the ion condensation model.[9,10,15,19] When the surface charge density of a polymer or particle reaches a threshold, often such that the ratio of the Bjerrum length and distance between charges exceeds 1, nearby counterions collapse on the surface reducing its zeta potential and consequently particle mobility. It is important to mention that the ion condensation model does not take into account possible influence of electric field on the structure and composition of the electrical double layer.

Here we show how passage of particles through single pores in resistive-pulse technique can elucidate the interplay between these two models and explain surface charge-dependent mobility of particles. Single pores have been used for the detection and characterization of single particles for half a century.[20−27] Particles are observed as they pass through single pores as a transient decrease of the current called the resistive pulse. Volume of the particles can be determined from the pulse amplitude. Electrokinetic velocity of individual particles is found from their translocation times knowing the applied voltage and pore length. Zeta potential of particles is often measured as a slope of the passage time with voltage,[28,29] assuming faster translocations indicate higher surface charges/zeta potentials. The experiments presented here point to the necessity of performing additional measurements in order to elucidate the relationship between translocation time and surface charge density of transported objects.

Reported here resistive-pulse experiments were performed with single micrometer-sized pores and 400 nm in diameter polystyrene particles. Two types of particles contained carboxyl groups at estimated densities which differed by a factor of 6. Surface charge density of the carboxylated particles was regulated by the level of the carboxyl groups' dissociation via solution pH.[1] We found that the relative electrokinetic mobility of the two types of particles was strongly pH dependent. At pH 8, the particles with higher surface charge translocated faster than the more weakly charged particles. Increasing the pH inverted the charge−translocation time relationship, so that at pH 10 the more highly charged beads had a mobility three times lower than the mobility of the less charged beads. Inspired by earlier theoretical and numerical work on particles passage through pores,[30−33] the results are explained by

Received: June 1, 2015
Accepted: July 16, 2015

DOI: 10.1021/acs.analchem.5b02060
Anal. Chem. XXXX, XXX, XXX−XXX

interplay of (i) ion condensation and (ii) double-layer polarization, as well as (iii) electroosmosis induced by charges on the pore walls and particle surface. Electroosmotic flow caused by the charges of the translocating object was predicted before for polyelectrolytes and charged particles.[31−35] This work shows that the electroosmotic component is also important for submicron rigid, highly charged spheres in conditions where the particle radius is ∼200 times larger than the screening length.

EXPERIMENTAL METHODS

Single Pore Preparation. Single pore membranes in two polymer materials poly(ethylene terephthalate) (PET) and polycarbonate (PC) were prepared by the track-etching technique.[36] Foils of 12 μm thick PET and 30 μm thick PC were first irradiated with single energetic heavy ions at the Institute for Heavy Ions Research in Darmstadt, Germany.[37] After the irradiation, the foils were subjected to wet chemical etching, which leads to preparation of single pores whose opening diameter increases linearly with the etching time. Etchings of PET and PC pores were performed in 0.5 M NaOH, 70 °C and 5 M NaOH, 50 °C, respectively. Average diameter of etched pores was measured by recording current−voltage curves in 1 M KCl and relating the pore resistance with its geometry.[27,38]

Particles. The particles used in the resistive-pulse experiments were purchased from Bangs Laboratories, Fisher, IN. Carboxylated polystyrene particles 410 and 400 nm in diameter as well as unmodified thus uncharged 400 nm polystyrene (PS) particles were used in all shown measurements. The diameter and surface charge densities quoted in the Article were reported by the manufacturer. Zetasizer Nano ZS, Malvern Instruments Ltd. was used to confirm that the diameter of the particles does not significantly change with pH. It is important to mention that the surface charge densities given by the manufacturer should be used only in a comparative manner: surface charge density of the 400 nm carboxylated particles was six times higher than the surface charge density of carboxylated 410 nm particles. The zeta sizer was also used to measure zeta potential of the particles as a function of pH in 100 mM KCl.

Ion Current Recordings and Particle Detection. Resistive-pulse experiments were performed from suspensions prepared in 100 mM KCl, with pH values ranging from 8 to 10, containing 0.1% of Tween 80. The concentration of all particles was $\sim 10^9$ particles/mL. Ion current measurements were performed with Axopatch 200B and 1322A Digidata (Molecular Devices, Inc.) using sampling frequency of 20 kHz. The data were subjected to low-pass Bessel filter of 1 kHz.

Comsol Modeling. Coupled Poisson−Nernst−Planck and Navier−Stokes equations were solved using the Comsol Multiphysics 4.3 package.[39] Cylindrical pores (5 μm long) were connected with 20 μm long cylindrical reservoirs; the diameter of the modeled pore was 800 nm. The surface charge density of the pore walls was set to −0.25 e/nm^2. A very fine triangular mesh of 0.1 nm was used close to the charged walls. In the remaining parts of the modeled structures, the mesh was reduced to the point when no change in the observed concentration profiles and currents was observed upon further mesh decrease. Passage of particles with surface charge density of −0.25 or −0.75 e/nm^2 was considered. The dielectric constant of the solution ε = 80, particle ε = 4, and diffusion coefficients 2 × 10^{-9} m^2/s were used for both potassium and chloride ions. In all calculations, a potential difference of 0.1 V was applied to the right reservoir while the left reservoir was grounded.

RESULTS AND DISCUSSION

Figure 1 presents resistive pulses created by three types of particles with diameter of ∼400 nm passing through a single poly(ethylene terephthalate) (PET) pore with an average opening diameter of 770 nm. Particles (410 nm) were carboxylated at the reported density of 1.6 groups per 100 Å^2; example pulses of the particles are shown in blue in Figure 1a. Passage of 400 nm carboxylated particles with six times higher surface charge density is shown in red in Figure 1b. We also present data of 400 nm unmodified polystyrene particles, which passed through the pore by electroosmosis (green traces in Figure 1c). In order to record passage of all particles for the same voltage magnitude and voltage polarity, mixtures of the particles were placed on both sides of the membrane. According to the scheme in Figure 1d, the charged particles

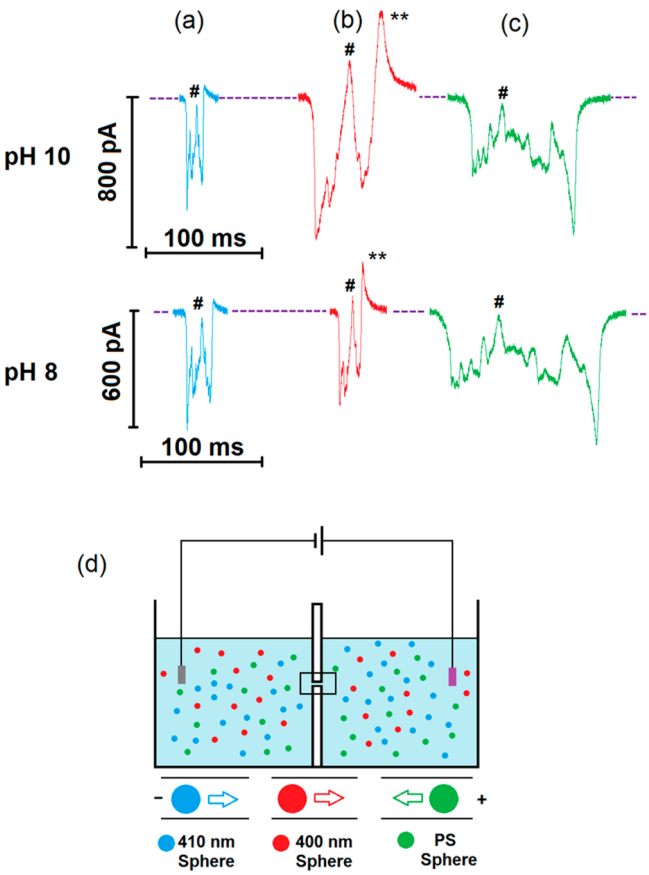


Figure 1. Passage of single particles through a pore with an average opening diameter of 770 nm recorded at 800 mV. (a)−(c) Traces of three types of particles: (a) 410 nm and (b) 400 nm in diameter carboxylated polystyrene particles (marked in blue and red, respectively) and (c) 400 nm unmodified/uncharged polystyrene particles (green traces). The 400 nm charged particles had ∼6 times higher surface charge density than the charged 410 nm particles. (d) Scheme of the conductivity cell used for the experiments. Mixture of all particles was present on both sides of the membrane. The two types of charged particles passed through in the direction of electrophoresis (from left to right in the scheme); the uncharged particles translocated in the opposite direction. The symbol # indicates the widest location of the pore as traced by all particles; the dashed line marks the baseline current level.

DOI: 10.1021/acs.analchem.5b02060
Anal. Chem. XXXX, XXX, XXX−XXX

passed through the pore from left to right; the uncharged spheres from right to left. All particles were examined in 100 mM KCl with pH values between pH 8 and pH 10. pH value of the bulk electrolyte modulated the degree of deprotonation of carboxyl groups, as shown before experimentally by titration of suspensions of carboxylated polystyrene particles[1] and by molecular dynamics simulations.[40] Increasing pH from 8 to 10 was shown to increase the particles' surface charge density by a factor of ~2.[1]

There are a few features of the recordings which we would like to discuss. First, the pulses of all particles are characterized by large undulations of the current. As reported by us before, the peaks and valleys of the pulses correspond to longitudinal irregularities of the pore diameter; i.e., local diameter is dependent on the axial position.[27,41,42] This is supported by our recordings: events of the 410 nm charged particles and 400 nm uncharged polystyrene particles are a mirror image of each other due to their opposite direction of transport (Figure 1d, Figure S1). Moreover, the character of pulses of these two types of particles is independent of the solution pH, further confirming the pulses indeed reflect the pore topography; note the difference in the translocation times, which will be discussed below.

The pulses created by the heavily charged 400 nm particles change however with the increase of pH (Figures 1, S2). When discussing their pulses let us first point to the existence of the large current increase at the end of the particles' passage (marked as ** in Figure 1). As explained by us in our previous report, a charged particle modulates ionic concentrations at both pore entrances due to particle-induced concentration polarization.[43] A negatively charged particle present at the pore end in contact with a positively biased electrode increases concentration of counterions, which are sourced from this pore opening to pass through the pore; this transient increase of ionic concentrations is observed as a current increase above the baseline value, seen in our case at the end of the pulses (Figure 2). Presence of the particle however also depletes local concentrations of co-ions; thus, when the particle is on the membrane side in contact with a negatively biased electrode, i.e., the side from which co-ions are sourced, an additional current decrease superimposed on the decrease caused by the excluded volume of the particle is recorded. Indeed passage of 400 nm heavily charged particles starts with a current decrease whose magnitude at pH 10 exceeds the current decrease recorded at pH 8 and for other types of studied particles.

As suggested by the existence of a very shallow current decrease in pulses of the uncharged polystyrene particles (marked as # in Figure 1), this particular pore had a large cavity in the middle. The surprising feature of the 400 nm charged beads is that in this location at all studied pH values, the particles caused a current increase above the baseline current, especially pronounced at pH 10. One can understand this observation by treating the pore as two pores in series connected by a larger reservoir (Figure 2). The applied voltage will drop mostly over the narrower zones (regions 1 and 3 in Figure 2) so that the electric field in the wide reservoir (region 2) will be the weakest. When a particle exits the first narrow zone (position 2 in Figure 2), it causes an increase of the local cation concentration, and a higher current is observed. When the particle enters the second narrow part of the pore (position 3, Figure 2), anionic concentration in this position becomes depleted, and a decrease of the current is observed. Exit of the particle from the pore (position 4, Figure 2) is again

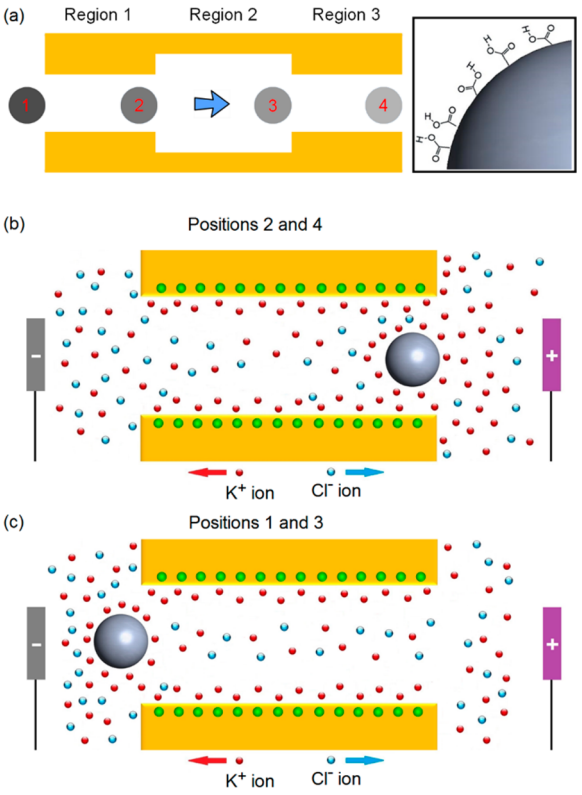


Figure 2. (a) Scheme of a pore with a large cavity in the middle and of a carboxylated particle. Presence of a negatively charged particle at pore entrances modulates local concentration of ions: it increases concentration of cations and lowers local anions concentration. (b) In positions 2 and 4, local enhancement of cation concentration causes current enhancement (# in Figure 1b corresponding to position 2, and ** to position 4), because cations are sourced from these entrances.[43] (c) In positions 1 and 3, depletion of anion concentration caused by the particle leads to a current decrease.

accompanied by a large current increase. The experiments show that highly charged particles passing through pores with undulating diameter can modify ionic concentrations in the pore to a large extent so that resolution of the pore topography by the particles is diminished.

Another feature of the recordings in Figure 1 is the dependence of the translocation time on the solution pH, studied in more detail in Figure 3. Behavior of 410 nm charged particles follows an expected trend: increase of pH leads to an increase of the particle surface charge density; thus, the particles translocate the fastest at pH 10 (Figure 3a, b).

Properties of the translocation velocity of the 400 nm carboxylated particles are however very different. At pH 8 they translocate faster than the 410 nm particles in agreement with their higher surface charge. At solutions of higher pH, however, the passage time of the charged 400 nm particles increases drastically, and at pH 10 their translocation velocity is more than three times lower than that of the less charged particles and comparable to the velocity of uncharged particles (Figure 3 d).

Slowing down of the highly charged particles is especially striking when studying a mixture of the particles with a pore whose opening is sufficiently large to allow for the particles to overtake each other. Figure 4 shows recordings through a 1.1 μm in diameter pore in a polycarbonate (PC) film. Pulses created by the 400 and 410 nm particles can be easily

DOI: 10.1021/acs.analchem.5b02060
Anal. Chem. XXXX, XXX, XXX−XXX

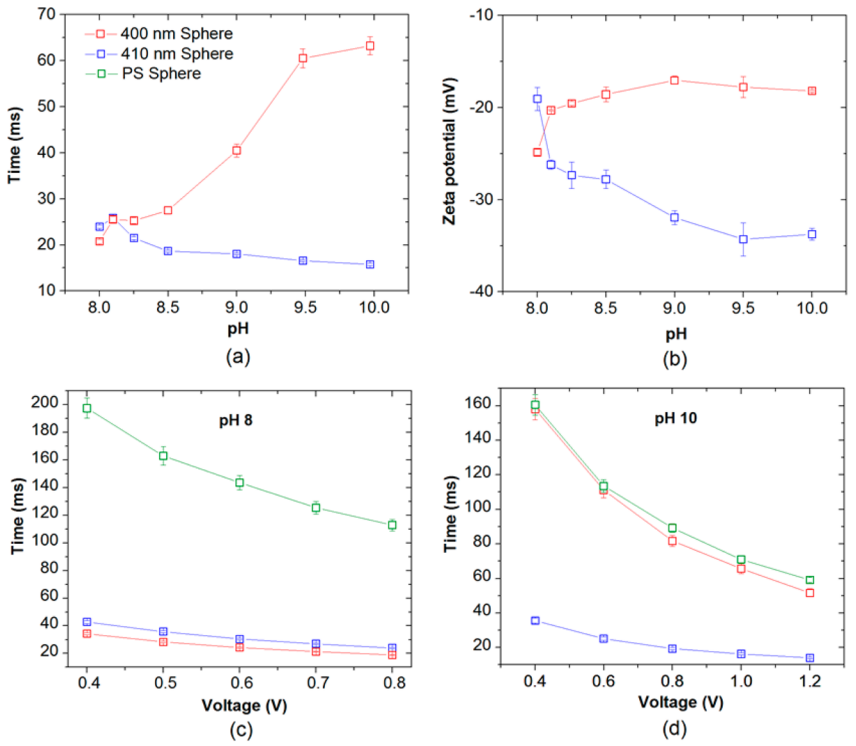


Figure 3. (a) Translocation time as a function of pH of 410 and 400 nm in diameter carboxylated particles at 800 mV. (b) Zeta potential of 410 and 400 nm particles in 100 mM KCl as a function of pH. (c), (d) Translocation times for three types of particles as a function of voltage at pH 8 (c) and pH 10 (d). The recordings were performed with a single 770 nm in diameter pore in 100 mM KCl.

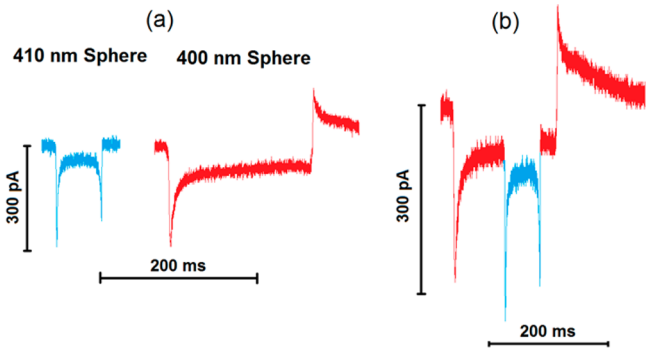


Figure 4. (a) Example ion current pulses of individual 410 and 400 nm particles passing through a single 1.1 μm in diameter pore in a 29 μm thick PC membrane under 1 V. (b) The fast 410 nm particle (blue trace) overtakes the slow 400 nm particle (red trace) in the pore.

distinguished from each other, because the more charged 400 nm particles produce a current increase when they exit (Figure 4a). Figure 4b presents a pulse in which passage of a single 400 nm charged particle (red trace) is interrupted by an entrance and a quick exit of a 410 nm bead (blue trace). The second entering particle is indeed the less charged one, because its exit does not have the characteristic current increase.

These experiments also prompted us to ask a question whether the confined volume of the micropore is sufficient to reveal existence of intraparticles interactions, especially in the case when the particles overtake each other. Previous theoretical studies indeed revealed importance of particles' charges not only in electrokinetic but also coagulation processes, and stability of suspensions.[44,45] It was shown that electrostatic and/or van der Waals interactions between particles could not be neglected if the distance between them was sufficiently small. If the particles interact with each other when in the pore (Figure 4b), their passage time and relative current change should be different from the values measured when the particles translocate individually (Figure 4a). Our preliminary analysis (data not shown) revealed that the 410 nm particles overtaking the slower 400 nm ones do not influence passage time or current blockage of either of the particles, suggesting lack of interactions. In future studies, we will perform similar experiments with narrower pores with expectation to observe modulation of passage time and possibly even in situ particle coagulation occurring in a pore.

Pores in PC films are known to be smooth due to amorphous character of the material.[46] Thus, the recordings in Figure 4 indicate that the translocation of the 400 nm charged particles is slowed down at pH 10 independently of the pore 3D topography.

In order to explain the dependence of the passage time on pH, we first measured zeta potential, $\zeta_{particle}$, of the particles in 100 mM at pH between 8 and 10, as shown in Figure 3b. Translocation velocity of a particle can be related with $\zeta_{particle}$ via the Smoluchowski equation, taking into account zeta potential of the pore, ζ_{pore}, which induces electroosmotic transport of the solution opposing the electrophoretic motion[47]

$$V_{translocation} = (\zeta_{particle} - \zeta_{pore})E/\eta$$

where E is the applied electric field and η solution viscosity.

Zeta potential of the 410 nm less charged particles increases with pH, and consequently, the magnitude of $V_{translocation}$ increases as well (Figure 3a). In contrast, $\zeta_{particle}$ of the more charged 400 nm particles becomes lower at higher pH values and reaches a plateau at ~pH 8.5. This saturation of $\zeta_{particle}$ with surface charge can be understood via the ion condensation model. It was predicted and shown experimentally that for

DOI: 10.1021/acs.analchem.5b02060
Anal. Chem. XXXX, XXX, XXX−XXX

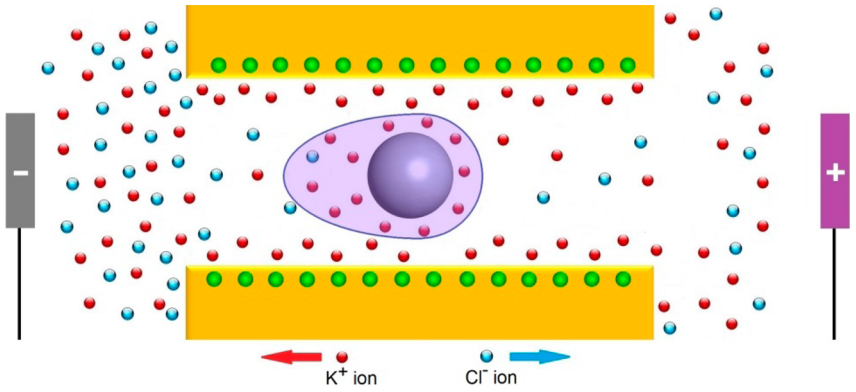


Figure 5. Scheme showing electric field induced distortion of the counterions' cloud around a moving particle.[3,16,17,31,32]

sufficiently high surface charge densities, nearby counterions can collapse on the particle lowering the overall magnitude of $\zeta_{particle}$ as well as the number of counterions available for ionic transport.[9,10,15] Using formulas derived by Manning,[15] we confirmed that the surface charge density of the used particles estimated by the manufacturer was indeed higher than the critical value needed for ion condensation (~0.013 C/m^2). The measured decrease of $\zeta_{particle}$ for the 400 nm particles (Figure 3b) was however insufficient to quantitatively explain the drastic slowing down of the particles seen in Figure 3a: $\zeta_{particle}$ decreased only by a factor of 0.2 when pH was increased from pH 8 to pH 10, while the velocity decreased by a factor of 3 over the same pH interval.

Further explanation of our experimental data can be provided by the double-layer polarization, i.e., a distortion of the electrical double layer of the particles under the influence of electric field.[3,16,17] A zone with higher ionic concentrations is created in the rear part of the particle; the front part of the particle is in contact with a zone with depleted ionic concentrations (Figure 5).[17,31,32] The counterions' distribution was shown to exert an additional drag force, which opposes the electrophoretic transport. The model by O'Brien and White[3] was derived for low external electric fields and considered zeta potential, $\zeta_{particle}$, as the control parameter; higher surface charge density was assumed to lead to higher zeta potential values.[3] The nonmonotonic dependence of the particle mobility on $\zeta_{particle}$ was explained by the quadratic dependence of the drag force on $\zeta_{particle}$. Since the magnitude of $\zeta_{particle}$ is less than 1 V and the electrophoretic force increases with zeta potential linearly, only for sufficiently high values of $\zeta_{particle}$ does the additional drag becomes crucial for the translocation. For a particle that is 200 nm in radius moving in a solution of 100 mM KCl, the decrease of the particle mobility from its maximum value due to double-layer polarization was predicted below ~40%.[3]

The counterions' cloud will become more asymmetric for particles with a higher surface charge density.[3,31] The increase of surface charge of the highly charged 400 nm particles with pH is evidenced in our experiments by the increase of the relative amplitude of the ion current positive spike present at the end of resistive pulses (marked as ** in Figure 1). A particle with more surface charges brings a larger number of counterions which temporarily increase ionic concentrations at one of the pore entrances and increase measured ion current (Figure 6). Interestingly, the relationship of the peak magnitude with pH agrees semiquantitatively with the previously reported pH dependence of surface charge density of suspensions of

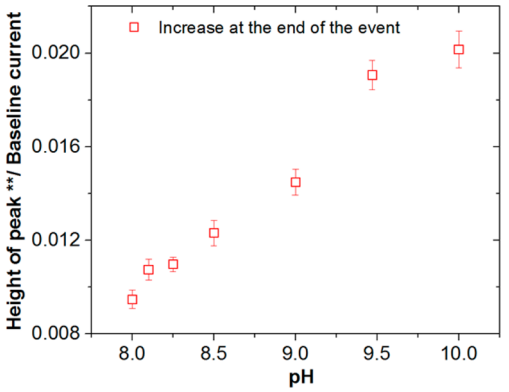


Figure 6. Relative magnitude of the current increase at the end of resistive pulses of 400 nm in diameter charged particles (marked as ** in Figure 1b) as a function of pH, at 800 mV.

carboxylated particles.[1] The relative maximum current observed experimentally (Figure 6) and the measured surface charge density (Figure 1 in ref 1) changed by a factor of 2 in the pH range between 8 and 10.

Surface charge density of the 410 nm particles is lower so that even at pH 10 the additional drag force due to counterions' cloud distortion does not lead to significant slowing down of the particles.

A combined effect of ionic condensation and polarization of electrical double layer was considered theoretically before at low applied electric fields for polyelectrolytes and particles.[30−35] The earlier work revealed that additional effects have to be taken into account when a particle is moving through a charged pore. The particle motion will be influenced by the electro-osmotic flow generated by the charged pore walls as well as charges on the moving object. For negatively charged particles and pores, electroosmosis opposes the electrophoretic translocation. Figure 7 shows numerical modeling of radial velocity profiles of a solution in the pore when a 400 nm in diameter particle is located at the pore axis. The modeling was performed by numerically solving coupled Poisson−Nernst−Planck and Navier−Stokes equations.[43] Computational resources restricted us to studying particles that differ in surface charge by a factor of 3, instead of the factor of 6 that our two charged, experimentally studied particles have. Two types of particles characterized by surface charge density of −0.25 and −0.75 e/nm^2 were therefore considered. The obtained results suggest that the electroosmotic flow of solution is induced by both surface charge of the pore and surface charge of the particle,

DOI: 10.1021/acs.analchem.5b02060
Anal. Chem. XXXX, XXX, XXX−XXX

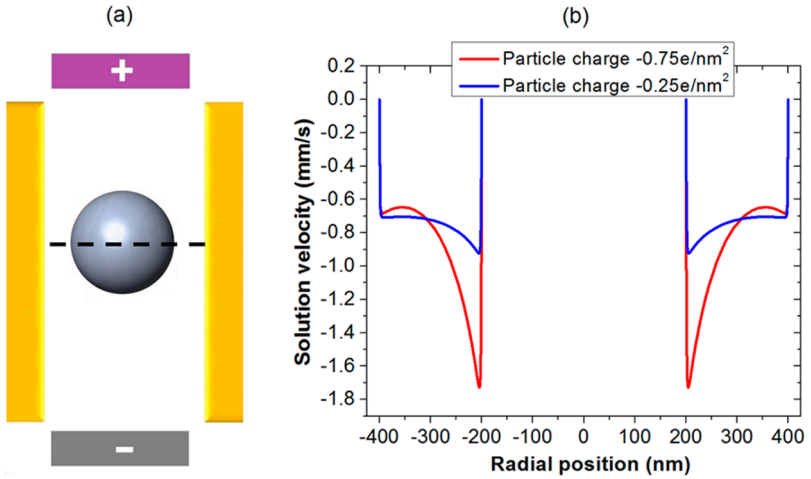


Figure 7. Numerical modeling of solution velocity in a single 5 μm long pore with diameter of 800 nm and two types of particles with surface charge density of −0.75 and −0.25 e/nm^2, respectively. The presented solution represents radial velocity distribution along the dashed line as shown in the scheme on the left. A value of 0.1 V was applied across the pore. The surface charge density of the pore walls was set to −0.25 e/nm^2.

and the more charged particles translocate slower. The predicted here effect of electroosmosis on the particle transport is more significant than reported in previous numerical studies.[31,35] We believe the augmented electroosmotic flow shown in Figure 7 is caused by the high electric fields used in our modeling and experiments.

We conclude that the dramatic slowing down of the highly charged particles at pH 10 in pores is caused by a collective effect of three factors: (i) ion condensation, (ii) polarization of the particle double layer, and (iii) electroosmotic flow induced by pore walls and surface charge of the particles.

An interesting question however remains whether our data can reveal existence of condensed ions. The theory of ion condensation is electrostatic in nature, and we hypothesize that the externally applied voltage might be able to release some of the condensed ions, which would influence the shape of recorded resistive pulses. These electric field induced effects would not be seen in the classical experiments of zeta potential measurements since the electric fields to which the particles are subjected are low. With 1 V applied across an 11 μm long PET pore, the resulting electric field is about 100 times higher than that in a zeta sizer.

The effect of electric field on the number of mobile counterions can be studied by analyzing again the magnitude of the ion current increase at the end of pulses of the 400 nm in diameter particles (marked as ** in Figure 1) but this time with respect to voltage. If the number of counterions brought by the particle and available for ion transport was independent of voltage, the relative current change should also be voltage independent. Analysis of the pulses in the 770 nm pore (Figure 8), and two other independently prepared pores, revealed a strong increase of the relative current increase with voltage. The data therefore suggest that the number of condensed ions might indeed be dependent on the magnitude of the external electric field.

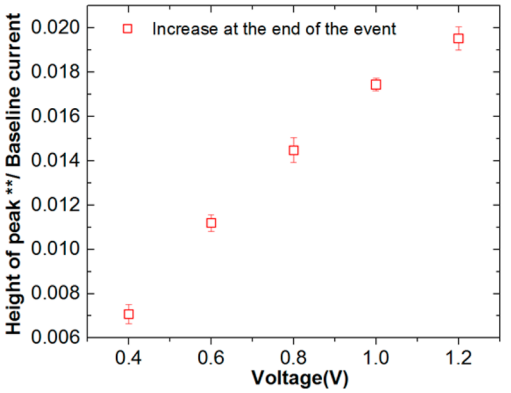


Figure 8. Relative magnitude of the current increase at the end of resistive pulses of 400 nm in diameter charged particles (marked as ** in Figure 1b) as a function of voltage, at pH 9.

CONCLUSIONS

Resistive-pulse experiments with highly charged particles revealed a nontrivial dependence of the particles' mobility on their surface charge density. Increase of the particles' surface charge with pH can lead to significant decrease of their translocation velocity. This anomalous behavior was observed with 400 nm in diameter particles whose surface contained high density of carboxyl groups. The presented experiments suggest that in order to relate mobility of particles with their zeta potential, it might be insufficient to perform experiments in only one pH solution. When studying highly charged particles, it will be necessary to compare their resistive pulses with measurements of known particles to identify potential anomalous mobility. High surface charge density of translocating particles can also be identified via the presence of a current increase above the baseline current, creating a bimodal character of a resistive pulse.[43,48]

The experimental observation of low mobility of highly charged particles is in accordance with the double-layer polarization model, which pointed to the asymmetric character of the counterions' cloud surrounding a charged, moving particle in a solution.[3,16,17] The results are also in agreement with previously reported numerical modeling on the importance of the double-layer polarization and ion condensation in translocation of polyelectrolytes and charged particles.[30−32,35] The earlier models were however developed for low external electric fields, and the reported here data revealed existence of new effects at higher voltages. For example, analysis of resistive pulses provided evidence for the existence of condensed ions around the highly charged

DOI: 10.1021/acs.analchem.5b02060
Anal. Chem. XXXX, XXX, XXX−XXX

particles; these ions could be released and could contribute to the measured ion current in high electric fields applied across the pore. It is also possible that the effect of polarization of the electrical double layer on particle transport is more dominant for higher external voltages. In addition, the data and modeling revealed an importance of electroosmotic flow induced by the charges on the pore walls as well as charges on the particles, which additionally slowed down the motion of charged particles. Our future experimental studies will focus on applying these effects in developing new ways of separating particles by their surface charge properties.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.analchem.5b02060.

Experiments of particle passage at pH values between 8 and 10 (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: zsiwy@uci.edu. Tel. 949-824-8290. Fax 949-824-2174.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Irradiation with swift heavy ions was performed at the GSI Helmholtzzentrum für Schwerionenforschung GmbH, Darmstadt, Germany. We very much appreciate helpful discussions with Prof. Salvador Mafé from the University of Valencia in Spain. This research was supported by the National Science Foundation (CHE 1306058). Y.Q. acknowledges financial support from the China Scholarship Council (CSC 201406090034).

■ REFERENCES

(1) Quesada-Pérez, M.; Callejas- Fernández, J.; Hidalgo-Álvarez, R. *J. Colloid Interface Sci.* **2001**, *233*, 280−285.
(2) Fernandez-Nieves, A.; Fernandez-Barbero, A.; de las Nieves, F. J. *Langmuir* **2000**, *16*, 4090−4093.
(3) O'Brien, R. W.; White, L. R. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1607−1626.
(4) Schulz, S. F.; Gisler, T.; Borkovec, M.; Sticher, H. *J. Colloid Interface Sci.* **1994**, *164*, 88−98.
(5) Martin-Molina, A.; Quesada-Perez, M.; Galisteo-Gonzalez, F.; Hidalgo-Alvarez, R. *J. Phys. Chem. B* **2002**, *106*, 6881−6886.
(6) Huang, Q. R.; Dubin, P. L.; Moorefield, C. N.; Newkome, G. R. *J. Phys. Chem. B* **2000**, *104*, 898−904.
(7) Welch, C. F.; Hoagland, D. A. *Langmuir* **2003**, *19*, 1082−1088.
(8) Guo, X.; Kirton, G. F.; Dubin, P. L. *J. Phys. Chem. B* **2006**, *110*, 20815−20822.
(9) Manning, G. S. *Acc. Chem. Res.* **1979**, *12*, 443−449.
(10) Manning, G. S. *Ber. Bunsen-Ges.* **1996**, *100*, 909−922.
(11) Shaaban, A. H.; Ander, P. *Polym. Prep.* **1993**, *34*, 970−971.
(12) Hoagland, D. A.; Smisek, D. L.; Chen, D. Y. *Electrophoresis* **1996**, *17*, 1151−1160.
(13) Popov, A.; Hoagland, D. A. *J. Polym. Sci., Part B: Polym. Phys.* **2004**, *42*, 3616−3627.
(14) Gao, J. Y.; Dubin, P. L.; Sato, T.; Morishima, Y. *J. Chromatogr., A* **1997**, *766*, 233−236.
(15) Manning, G. S. *J. Phys. Chem. B* **2007**, *111*, 8554−8559.
(16) O'Brien, R. W. *J. Colloid Interface Sci.* **1983**, *92*, 204−216.
(17) Dukhin, S. S. *Adv. Colloid Interface Sci.* **1993**, *44*, 1−134.
(18) Saville, D. A. *J. Colloid Interface Sci.* **2000**, *222*, 137−145.
(19) Ohshima, H. *J. Colloid Interface Sci.* **2004**, *275*, 665−669.
(20) Coulter, W. H. U.S. Patent 2,656,508, 1953.
(21) DeBlois, R. W.; Bean, C. P.; Wesley, R. K. A. *J. Colloid Interface Sci.* **1977**, *61*, 323−335.
(22) Berge, L. I.; Feder, J.; Jøssang, T. *Rev. Sci. Instrum.* **1989**, *60*, 2756−2763.
(23) DeBlois, R. W.; Bean, C. P. *Rev. Sci. Instrum.* **1970**, *41*, 909−916.
(24) DeBlois, R. W.; Wesley, R. K. *J. Virol.* **1977**, *23*, 227−233.
(25) Harms, Z. D.; Mogensen, K. B.; Nunes, P. S.; Zhou, K.; Hildenbrand, B. W.; Mitra, I.; Tan, Z.; Zlotnick, A.; Kutter, J. P.; Jacobson, S. C. *Anal. Chem.* **2011**, *83*, 9573−9578.
(26) Gear, A. R. L.; Bednarek, J. M. *J. Cell Biol.* **1972**, *54*, 325−345.
(27) Pevarnik, M.; Healy, K.; Toimil-Molares, M. E.; Morrison, A.; Létant, S. E.; Siwy, Z. S. *ACS Nano* **2012**, *6*, 7295−7302.
(28) Ito, T.; Sun, L.; Crooks, R. M. *Anal. Chem.* **2003**, *75*, 2399−2406.
(29) Kozak, D.; Anderson, W.; Vogel, R.; Chen, S.; Antaw, F.; Trau, M. *ACS Nano* **2012**, *6*, 6990−6997.
(30) Hsu, J.-P.; Chen, Z.-S.; Tseng, S. *J. Phys. Chem. B* **2009**, *113*, 7701−7708.
(31) Yeh, L.-H.; Hsu, J.-P. *Soft Matter* **2011**, *7*, 396−411.
(32) Hsu, J.-P.; Tai, Y.-H.; Yeh, L.-H.; Tseng, S. *J. Phys. Chem. B* **2011**, *115*, 3972−3980.
(33) Zhang, M.; Ai, Y.; Kim, D.-S.; Jeong, J.-H.; Joo, S. W.; Qian, S. *Colloids Surf., B* **2011**, *88*, 165−174.
(34) Luan, B.; Aksimentiev, A. *Phys. Rev. E* **2008**, *78*, 021912.
(35) Zhang, X.; Hsu, J.-P.; Chen, Z.-S.; Yeh, L.-H.; Ku, M.-H.; Tseng, S. *J. Phys. Chem. B* **2010**, *114*, 1621−1631.
(36) Fleischer, R. L.; Price, P. B.; Walker, R. M. *Nuclear Tracks in Solids: Principles and Applications*; University of California Press: Berkeley. CA, 1975.
(37) Spohr, R. German Patent DE 2 951 376 C2, U.S. Patent 4 369 370, 1983.
(38) Apel, P.; Korchev, Y. E.; Siwy, Z.; Spohr, R.; Yoshida, M. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2001**, *184*, 337−346.
(39) Vlassiouk, I.; Smirnov, S.; Siwy, Z. S. *Nano Lett.* **2008**, *8*, 1978−1985.
(40) Schwierz, N.; Horinek, D.; Netz, R. R. *Langmuir* **2015**, *31*, 215−225.
(41) Pevarnik, M.; Schiel, M.; Yoshimatsu, K.; Vlassiouk, I. V.; Kwon, J. S.; Shea, K. J.; Siwy, Z. S. *ACS Nano* **2013**, *7*, 3720−3728.
(42) Innes, L.; Chen, C.-H.; Schiel, M.; Pevarnik, M.; Haurais, F.; Tomil-Molares, M. E.; Vlassiouk, I. V.; Theogarajan, L.; Siwy, Z. S. *Anal. Chem.* **2014**, *86*, 10445−10453.
(43) Menestrina, J.; Yang, C.; Schiel, M.; Vlassiouk, I.; Siwy, Z. S. *J. Phys. Chem. C* **2014**, *118*, 2391−2398.
(44) Hidalgo-Alvarez, R.; Martin, A.; Fernandez, A.; Bastos, D.; Martinez, F.; de las Nieves, F. J. *Adv. Colloid Interface Sci.* **1996**, *67*, 1−118.
(45) Felix, C.; Yaroshchuk, A.; Pasupathi, S.; Pollet, B. G.; Bondarenko, M. P.; Kovalchuk, V. I.; Zholkovskiy, E. K. *Adv. Colloid Interface Sci.* **2014**, *211*, 77−92.
(46) Müller, S.; Schötz, C.; Picht, O.; Sigle, W.; Kopold, P.; Rauber, M.; Alber, I.; Neumann, R.; Toimil-Molares, M. E. *Cryst. Growth Des.* **2012**, *12*, 615−621.
(47) Schoch, R. B.; Han, J.; Renaud, P. *Rev. Mod. Phys.* **2008**, *80*, 839−883.
(48) Lan, W.-J.; Kubeil, C.; Xiong, J.-W.; Bund, A.; White, H. S. *J. Phys. Chem. C* **2014**, *118*, 2726−2734.

DOI: 10.1021/acs.analchem.5b02060
Anal. Chem. XXXX, XXX, XXX−XXX