Experimental Evidence of a Strong Image Force between Highly Charged Electrosprayed Molecular Ions and a Metal Screen

Youichi Omori1, Hyun-Jin Choi2, Yasuaki Mukai2, Toshiyuki Fujimoto3, Tomoya Tamadate2, Takafumi Seto2, Yoshio Otani2, Mikio Kumita2*

1 Sanzen Seishi Co. Ltd., Kanazawa, Ishikawa 920-0338, Japan
2 School of Natural System, College of Science and Engineering, Kanazawa University, Kanazawa, Ishikawa 920-1192, Japan
3 Department of Applied Sciences, Muroran Institute of Technology, Muroran, Hokkaido 050-8585, Japan

ABSTRACT

We investigated the capturing mechanisms of highly charged macromolecular ions of polyethylene glycol electrosprayed onto a metal screen. Our experiments assessed how the charge state, size of the macromolecular ions, and filtration velocity affected the penetration of the ions through the metal screen. The single fiber efficiencies were plotted as functions of the Peclet number and image force parameter. Highly charged molecular ions had much higher collection efficiencies than neutralized macromolecules, suggesting the presence of a strong image force between the ions and metal surface. The single fiber efficiency by image force was proportional to the square root of an image force parameter predicted by theory. When using the prefactor of 9.7 proposed by Alonso et al. (2007), we found fair agreement between the experimental data and theoretical predictions on the collection efficiency of highly charged molecular ions with mobility diameters from 2.6 to 4.8 nm and numbers of electrical charges from 2 to 7. The experimental evidence from our study reveals that image force contributes strongly to the collection of multicharged macromolecular ions by a metal wire screen.

Keywords: Image force; Metal screen; Electrospray; Molecular ion.

INTRODUCTION

When a charged particle approaches a neutral solid surface, a short-range force between the particle and induced dipole, a so-called “image force”, is created. Image force is a well-known mechanism of particle collection by air filters (Brown, 1993), especially when the particles possess a high number of charges (Yoshioka et al., 1968) or the particle size falls in the nanometer range (Alonso et al., 2007; Heim et al., 2010). Yoshioka et al. (1968) measured the collection efficiency of electrically charged oil droplets with a 1 µm diameter by a neutral glass fiber filter. The number of charges per droplet was controlled using a pin-to-plate type discharge electrode. The collection efficiency of 60-charged particles (1 µm) was about 40% higher than that of uncharged particles in their experiment. Lundgen and Whitby (1965) measured the collection efficiency of highly charged (~300 to +320 elemental charges) particles with 0.1 and 1 µm diameters using electrically neutral filters made of felt, urethane, and glass fiber. They reported that the collection efficiency increased from 16% (uncharged particles) to over 99% when the particles carried +320 electrical charges. To evaluate the effect of image force in a diffusion limited regime (image force parameter, $K_{IM} < 10^{-5}$), Alonso et al. (2007) experimentally measured the collection efficiency of nanoparticles ($\text{ZnCl}_2$ and NaCl) with diameters from 25 to 65 nm by a metal screen (aluminum and stainless steel). The image force had contributed significantly to the mechanism by which the charged nanoparticles, even the particles with small numbers of electrical charges, were collected in their experiment.

As reported in previous studies, image force has a significant influence on the mechanism by which highly charged nanoparticles are collected. Few reports, however, have investigated the effect of image force on the collection of very small particles (< 10 nm). New factor to consider emerge in a size regime of < 10 nm, such as the thermal rebound (Wang and Kasper, 1991) and the effects of Brownian diffusion and image force in combination (Alonso et al., 2007). Heim et al. (2010) investigated the collection efficiencies of tungsten oxides nanoparticles (1.2 to 8 nm, neutral and monovalent) and electrosprayed molecular ions by metal meshes (nickel and stainless steel). The efficiencies of nanoparticle collection in their experiments...
were in good agreement with the predicted collection efficiency of particles with diameters larger than 3 nm. They also found, however, that image force has only a minor effect on the collection efficiency of nanoparticles, because the number of charges of their test particles was unity.

We studied the effect of image force on the particle collection in the course of investigation of thermal rebound of sub-10 nm particles. Since we have neither definite generation method nor the measurement methods for sub-10 nm particles, we employed macromolecular ions as a monodisperse test particles generated by an electrospray, which is a powerful tool for producing molecular ions (Yamashita et al., 1984). However, we found that the electrospray generates highly charged macromolecular ions so that the collection efficiency of these ions was significantly affected by the image force. Consequently, we must account for the image force in the interpretation of collection efficiency data for elucidating the thermal rebound of sub-10 nm particles.

In the present study, we generated highly charged polyethylene glycol (PEG) molecular ions (from +2 to +7) with diameters below 5 nm by an electrospraying PEG with various molecular weights. We measured the collection efficiency of highly charged molecular ions through wire screens as a function of mobility diameters and numbers of charges and compared the experimental data with the empirical equation reported by Alonso et al. (2007) in order to examine whether the empirical equation obtained for particles larger than 10 nm holds for sub-10 nm particles.

**COLLECTION OF CHARGED NANOPARTICLES BY IMAGE FORCE**

The influences of image force were evaluated by a dimensionless image force parameter, $K_{IM}$, given by

$$K_{IM} = \left( \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} \right) \frac{C q^2 e^2}{12\pi^2 \mu e d_p d_f^2}$$

where, $\varepsilon_1$ and $\varepsilon_0$ are dielectric constants of the fiber and vacuum, $C$ is the Cunningham slip correction factor, $q$ is the number of charges on the particle, $e$ is the elementary charge, $\mu$ is the air viscosity, $u$ is the air flow velocity, $d_p$ is the particle diameter, $d_f$ is the fiber diameter. Single fiber efficiency by image force is known to be proportional to the square root of $K_{IM}$ such that,

$$\eta_{IM} = \alpha \sqrt{K_{IM}}$$

where, $\alpha$ is a constant of proportionality, which takes different value in different reports. When Yoshioka et al. (1968) measured the collection efficiency of dioctyl phthalate by a glass filter mat, they reported an $\alpha$ value of 2.3 from experiments using 1 mm particles ($10^{-6} < K_{IM} < 10^{-3}$). A few years earlier, Lundgen and Whitby (1965) reported an $\alpha$ value of 1.5 from experiments on solid spherical aerosol particles with diameter ranging from 0.1 $\mu$m to 1 $\mu$m ($2 \times 10^{-6} < K_{IM} < 3 \times 10^{-5}$). In the diffusion regime, the total single fiber efficiency, $\eta_t$, is expressed as the sum of the single fiber efficiencies of diffusion, image force, and the combined effect of diffusion and image force as,

$$\eta_t = \eta_D + \eta_{IM} + \eta_{DIM}$$

The single fiber collection efficiency of diffusion, $\eta_D$, is expressed by the following equation (Cheng and Yeh, 1980):

$$\eta_D = 2.7 Pe^{-2.3}$$

where, $Pe$ is the Peclet number given by

$$Pe = \frac{ud_f}{D}$$

where $D$ is the diffusion coefficient. The third term of Eq. (3), $\eta_{DIM}$, is the single fiber efficiency by a combination of two capturing mechanisms, diffusion and image force.

Alonso et al. (2007) found that the pure image force effect was negligible in the diffusion regime ($200 < Pe < 3600, 10^{-7} < K_{IM} < 10^{-5}$) and obtained the following equation for $\eta_{DIM}$ (combined effect):

$$\eta_{DIM} = 2.97 K_{IM}^{0.59}$$

They also fitted the experimental data by assuming that $\eta_{DIM}$ was proportional to the square root of $K_{IM}$, and it also shows reasonable agreement between the experimental data when $\alpha = 9.7$ as follows:

$$\eta_{DIM} = 9.7 \sqrt{K_{IM}}$$

Fig. 1 shows the size dependency of single fiber efficiency by image force, $\eta_{IM}$, calculated by Eq. (7) with changing numbers of charges, $q$ ($u = 0.25$ m s$^{-1}$). The solid line and dashed lines respectively represent the single fiber efficiency by pure diffusion and by diffusion and image force combined. As the figure shows, the single fiber efficiency increases with $q$ and decreases with the particle diameter. The image force effect is clearly significant when the particles carry more than several electrical charges. Highly charged nanoparticles of this type can be generated by electrospray atomization.

**METHODS**

**Preparation of Multicharged PEG Molecular Ions**

Fig. 2 shows the experimental setup used in this study. Highly charged electrosprayed molecular ions were used as test particles in the filtration experiments. Polyethylene glycol (PEG) with the monodisperse molecular weight from 2,000 to 21,300 were purchased from Sigma Aldrich ($M_w = 10000$), Wako ($M_w = 2000$, 4600) and Agilent Technologies ($M_w = 21300$). PEG (0.005 to 0.043 wt%) and 0.1 wt% ammonium acetate were dissolved in a water/methanol (50:50) solution for the electrospray atomization. The mixture of water/methanol solution, and the addition of ammonium acetate
have been widely employed in order to increase the electrical conductivity of precursor solution in electrospray process (Lenggoro et al., 2002). In addition, the correlations between PEG concentration and charging state were reported in our previous research (Maekawa et al., 2014).

The PEG solution was introduced to the capillary (Hamilton, Model 7747-02, inner diameter of 110 µm, outer diameter of 240 µm) via a syringe pump at a constant flow rate of 100 to 200 µL h\(^{-1}\). High voltage (2.5–3 kV) was applied to the capillary to obtain a stable cone jet under observation by a CCD camera (Sony, Model XC-75). as shown in Fig. 3. The gap distance between syringe tip to electrical ground was set to 0.3 cm. The generated droplets were carried by dry clean air at flow rate of 3 to 5 L min\(^{-1}\). Part of the gas flow was introduced into a differential mobility analyzer (DMA) (Laboratory-made, Vienna type, Winklmayr et al. 1991) to obtain mono-mobility particles. The number concentrations of the DMA classified particles were monitored using a condensation particle counter (CPC) (TSI, Model 3776, Fig. 2(a)).

The charging state of the test particles was investigated by introducing the DMA-classified PEG molecular ions to a neutralizer (\(^{241}\)Am) and measuring the mobility distribution of the neutralized PEG molecules measured by a Nano-
SMPS (TSI, Model 3085 nano-DMA and the CPC, Fig. 2(b)). At the test particles were very small (< 5 nm), the molecular ions classified by the Nano-SMPS were assumed to be monovalent. The number of electrical charges of the PEG ions could therefore be estimated as a function of the diameter by changing the 1st DMA voltage (for mobility scanning) and measuring the size distributions of the ions with the Nano-SMPS.

**Evaluation of Collection Efficiency**

Mobility-classified molecular ions of known sizes and numbers of charges were introduced to the filtration experiment system. Fig. 4 shows the experimental setup for measuring the filtration efficiency. The effect of the image force in the diffusion regime was assessed by comparing the penetration data of highly charged PEG ions (Fig. 4(a)) with the penetration data of neutralized PEG molecules (Fig. 4(b)). The diffusional loss of the ions during transport was cancelled by measuring the penetration using two identical filter holders (Alonso et al., 2007; Heim et al., 2010) arranged shown in Fig. 4. Most of the tubes and connections were made of metal (electrically grounded) and set at the shortest possible lengths to minimize the diffusional loss of ions during transport.

A stainless steel (SUS) screen (fiber diameter, $d_f = 30$ µm, packing density, $\alpha = 0.177$) was installed in one of the filter holders for use as the model filter. The diameter of the effective filtration area was 24 mm. The filtration velocity was adjusted from 0.25 to 0.40 m s$^{-1}$ by adding clean makeup air before the ions entered the filter holders. The flow was switched between the filter and the blank holder by three-way valves. The number concentration with and without filtration was measured by the CPC.

**RESULTS AND DISCUSSION**

**Characterization of the Charged Molecular Ions**

Fig. 5 shows contour plots of the electrical mobility (multicharged particles measured by the 1st DMA) against the particle diameter (singly charged particles measured by the 2nd DMA) for (a) PEG2000, (b) PEG4600, (c) PEG10000, and (d) PEG21300. The number concentration is represented as a difference of color (red is the highest concentration). Each of upper panels shows the CPC count plotted against particle diameters measured by directly introducing electrosprayed ions into the Nano-SMPS with a neutralizer. Two kinds of products were identified in the size distributions. The first peak observed at the smaller particle sizes could be attributed to single molecular ions, since the diameter of these first peaks increased with the increasing molecular weight of the PEG. The second peak was thought to be composed of residual nanoparticles generated by the drying of the electrosprayed droplets containing multiple PEG molecules. The diameter of this peak increased with increasing concentrations of the PEG solutions.

Only the molecular ions from the first peaks were used as test particles for the filtration experiment, as the particles in the second peak may have been mixtures of multicharged residual particles of various sizes and numbers of charges. Each of the solid lines in Fig. 5 represents the relationship between the electrical mobility of the particles, $Z_p$, and the particle diameter, $d_p$, as a function of the number of charges, $q$, given by the following Eqs. (8) and (9):

$$Z_p = \frac{g e C(d_p)}{3 \pi u d_p}$$  \hspace{1cm} (8)

$$C = 1 + \frac{2\lambda}{d_p} \left[ 1.246 + 0.420 \exp \left( -0.87 \frac{d_p}{2\lambda} \right) \right]$$  \hspace{1cm} (9)

where $C$ is the slip correction factor, and $\lambda$ is the mean free path.

By comparing the lines with contour plots we find, that the PEG ions have 2 to 7 charges, depending on the molecular weight. Table 1 summarizes the relationship of the molecular weight with the mobility diameter and number of electrical
Fig. 4. Experimental setup to measure the collection efficiency.

charged. Disappointingly, the resolution of the 1st DMA used for mobility classification was too low to accurately classify molecular ions with the different numbers of charges (Saucy et al., 2004). Its resolution was sufficient, however, to eliminate residual nanoparticles, as shown in Fig. 5. We therefore compared our experimental data with the theoretical values by assuming that all of the test particles had the same number of charges (see Table 1).

Collection of Highly Charged Molecular Ions

Fig. 6 shows penetration data of the four PEG species through an SUS wire screen with and without electrical neutralization at filtration velocities of 0.25 m s⁻¹. The solid line and dashed line represent the theoretical penetration curves for uncharged and singly charged macromolecules, respectively. As the figure shows, experimentally obtained penetration of neutralized macromolecules (solid circles) decreases with decreasing diameter, which suggests that the main capturing mechanism is diffusion. It also shows fair agreement with the predicted penetration data for uncharged macromolecules (only diffusion) or singly charged ions.

When the charged particles are neutralized to the equilibrium charging state, the fractions of the charged particles are estimated to be about 1% for 2 nm and 3% for 5 nm particles by Fuchs’ charging theory (Fuchs, 1963). From these estimates, conclude that the experimentally obtained penetration values should closely agree with the predicted curve for uncharged macromolecules. We find, however, the predicted curve diverges from the experimentally obtained values, possibly due to the residual electrical charge on the particles. On the other hand, we clearly see that the multicharged ions (open circles) have a much lower penetration than the neutralized species. We attribute this result to the significant contribution of the image force between the multicharged particles and SUS wire screen.

To analyze the effect of image force, we converted the penetration, \(P\), to the single fiber efficiency, \(\eta\), given by Eq. (10):

\[
P = \exp\left(-\frac{4}{\pi} \frac{\alpha L}{d_i} \frac{n_{\text{screen}}}{\eta}\right)
\]

where \(\alpha\) is the packing density of the wire screen, \(L\) is thickness of wire screen, and \(n_{\text{screen}}\) is number of wire screen. Fig. 7 shows the experimental single fiber efficiencies of neutralized macromolecules and multiply charged ions obtained from Eq. (10), plotted as functions of the Peclet number, \(Pe\) (Eq. (5)). Each symbol in Fig. 7 represents the series of data for the specific molecular weights of PEG (shown in Table 1) with changing filtration velocity. The experimental single fiber efficiency of the multicharged species (open symbols) showed various tendencies at different molecular weights (diameters) and charge states. In contrast, the single fiber efficiencies of the neutralized macromolecules determined experimentally (closed symbols) could almost be summarized into a straight line as a function of \(Pe\) and agreed fairly well with the predicted efficiencies for both neutralized (solid line) and singly charged ions (broken line), as previously mentioned. The broken, dashed, and dotted lines in Fig. 7 represent the theoretical single fiber efficiencies for multicharged ions (1 to 11 charges) obtained from the sum of Eqs. (4) and (7). As previously mentioned (Fig. 5), the numbers of charges obtained experimentally were 4.4 for PEG₄₆₀₀, 6.4 for PEG₁₀₀₀, and 7.2 for PEG₂₁₃₀₀.

As the figure illustrates, the experimental single fiber efficiencies of multicharged ions increased with increasing number of charges and agreed fairly well with the predicted lines with corresponding numbers of charges. This result provides quantitative evidence of a strong image force between the multicharged molecular ions and the SUS wire screen even in the diffusion regime.

To reiterate, Alonso et al. (2007) reported that a prefactor \(\alpha\) of 9.7 validly applied to estimation of the image force for multicharged (maximum 3) nanoparticles in the diffusion regime (mobility diameters from 25 to 60 nm). In the present study, we extend the validation of the prefactor down to molecular ions as small as 2.6 nm (Fig. 6). In contrast, Heim et al. (2010) performed filtration experiments for singly charged nanoparticles in the diameter range from 1.2 to 8 nm using a metal screen. The dominance of Brownian diffusion as the mechanism of particle capture in their experiment reduced the contribution of pure image force to a negligible level. They tentatively explained this dominant effect of Brownian diffusion by the weak image force it for...
Fig. 5. CPC count and tandem result of PEG ions.

Table 1. Mobility diameters and charging characteristics of PEG ions.

<table>
<thead>
<tr>
<th>Molecular weight of PEG [g mol⁻¹]</th>
<th>Concentration of PEG [wt%]</th>
<th>Mobility diameter [nm]</th>
<th>Number of charges [-]</th>
<th>Average number of charges [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,000</td>
<td>0.005</td>
<td>2.6</td>
<td>1–2</td>
<td>2.25</td>
</tr>
<tr>
<td>4,600</td>
<td>0.023</td>
<td>3.1</td>
<td>2–7</td>
<td>4.38</td>
</tr>
<tr>
<td>10,000</td>
<td>0.02</td>
<td>4.1</td>
<td>3–9</td>
<td>6.37</td>
</tr>
<tr>
<td>21,300</td>
<td>0.043</td>
<td>4.8</td>
<td>5–12</td>
<td>7.27</td>
</tr>
</tbody>
</table>
small numbers of charges (single), a phenomenon identified in Fig. 7 (the small difference between neutral and singly charged particles).

In summary, Fig. 8 plots the single fiber efficiency for the charged particles (the sum of pure image force plus image force and diffusion in combination), $\eta_{IM} (= \eta_T - \eta_D)$, as a function of the image force parameter $K_{IM}$. Our experimental data and Alonso’s results are plotted as open symbols, and closed symbols, respectively. The solid line represents the single fiber efficiency predicted by Eq. (7). As the figure shows, our experimental results agree fairly well with the line predicted by Alonso’s prefactor of 9.7. Our study confirms that Alonso’s prefactor of 9.7 can be applied in our experimental ranges ($d_p = 2.6$–$4.8$ nm, $q = 2$–$7$), which correspond to $10^{-3} < K_{IM} < 10^{-2}$.

**CONCLUSIONS**

We prepared multicharged ions carrying 2 to 7 elementary charges by an electrospray method, and investigate the mechanism by which they were collected by a SUS wire screen. The multicharged molecular ions had lower penetration than the neutralized molecules due to the image force acting between the multicharged molecular ions and SUS wire screen. The single fiber efficiency by image force also turned out to be proportional to the square root of an image force parameter predicted by theory, and the experimental and theoretical values showed fair agreement.
when we using the prefactor of 9.7 proposed by Alonso et al. (2007) even in the $K_{IM}$ ranges from $10^{-3}$ to $10^{-2}$. This study demonstrates the strong contribution of image force in the collection of multicharged molecular ions by an SUS wire screen.

REFERENCES


Received for review, April 14, 2016
Revised, June 14, 2016
Accepted, June 14, 2016