SIZE MEASUREMENTS OF GASBORNE FULLERENE C\textsubscript{60} AND POLY(AMIDOAMINE) (PAMAM) DENDRIMERS USING A DIFFERENTIAL MOBILITY ANALYZER (DMA)

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**ABSTRACT** The electrical mobility of a C\textsubscript{60} negative ion was measured as an inherently monodisperse spherical nanoparticle of 1 nm diameter in He, Ne, and Ar gas using the differential mobility analyzer (DMA). The measured inverse mobilities were larger than those calculated from a hard-sphere collision model. We suggested that this behavior could be ascribed to the potential force of interactions between the C\textsubscript{60} negative ion and the gas molecule. Additionally, poly(amidoamine) (PAMAM) dendrimers of generations 2 through 6 were aerosolized by an electrospray aerosol generator and their electrical mobility spectra observed using a DMA. We succeeded in measuring the electrical mobilities of the monomer and dimer ions of these dendrimers. The experimental results suggested that PAMAM dendrimers are useful as standard particles in the range of a few nanometers.

**Keywords:** differential mobility analyzer (DMA), fullerene, size standard, electrospray, PAMAM dendrimer

**1. INTRODUCTION**

A differential mobility analyzer (DMA) has been used to perform in-situ size measurements of gasborne nanoparticles [1]. The DMA can measure the electrical mobility of charged nanoparticles, which is a function of the nanoparticle diameter. Thus, it is important to establish a relational formula to convert the electrical mobility into the nanoparticle diameter. Although Stokes-Cunningham relation [2] is widely used for diameter determination of the DMA, it has not been verified for nanoparticles in the several-nm-diameter range because of a lack of standard particles with well-defined diameter in this range so far. In this study we measured electrical mobilities of a C\textsubscript{60} negative ion [3,4] and poly(amidoamine) (PAMAM) dendrimers [5] as an inherently monodisperse nanoparticle of 1 nm diameter and 3-15 nm diameter using the DMA.

**2. ELECTRICAL MOBILITY MEASUREMENTS OF FULLERENE C\textsubscript{60}**

**2.1 Experimental**

The experimental setup is similar to the one used in the previous measurement [2,3]. Figure 1 shows the schematic view of the experimental setup consisting of (a) a C\textsubscript{60} vapor source, (b) an \textsuperscript{241}Am neutralizer, (c) a DMA, and (d) a Faraday cup electrometer (FCE). The C\textsubscript{60} monomer was prepared by evaporating its powder in an alumina boat heated to 673 K. The C\textsubscript{60} monomer dispersed in a noble gas (He, Ne, and Ar) was introduced to the \textsuperscript{241}Am neutralizer, and then ionized. A flow rate $Q_{a}$ of the noble gas (4.0, 2.0, and 1.0 SLM (standard liter per minute) in He, Ne, and Ar gas, respectively) was regulated by MFC-2 (mass flow controller-2). The negative ions of C\textsubscript{60} were transported into the DMA with an outer radius $R_{2}$ of 33 mm, an inner radius $R_{1}$ of 25 mm, and a classification length $L$ of 18.0 mm. The mobility analysis of these ions was performed with a sheath noble gas flow $Q_{sh}$ (flow rate of 27.5 SLM) regulated by MFC-1. The mobility at the voltage $V$, which was applied to the inner rod, is given as

$$Z_{p} = \frac{Q_{a} \ln(R_{2}/R_{1})}{2\pi \nu V}.$$  \hspace{1cm} (1)

The current of the classified ions was measured by the FCE. The mobility spectra were obtained by measuring the current as a function of inverse mobility $Z_{p}^{-1}$. We measured these spectra under the low pressure $P=14.7$ kPa to avoid formations of C\textsubscript{60} oligomers at higher pressures.

**2.2 Results and Discussions**

Figure 2 shows the measured mobility spectra. The ion current divided by the current at the peak (normalized current) is plotted against the inverse mobilities. The inverse mobilities of the C\textsubscript{60} monomer negative ion at the peak obtained in He, Ne, and Ar were found to be 2404, 6033 and 12594 Vsm\textsuperscript{-2}, respectively. Note that the value of the measured inverse mobility in He sheath gas (2404 Vsm\textsuperscript{-2}) was close to the value obtained by Mesleh and co-workers (2321 Vsm\textsuperscript{-2}) [6].

Table 1 compares the measured inverse mobilities $Z_{\text{exp}}^{-1}$ with the inverse mobilities calculated from hard-sphere collision model.
\[ Z_{\text{hs}}^{-1} = \frac{2}{3g} \sqrt{2 \pi \hbar N (d_p + d_g)^3}, \]

where \( T \) is the temperature, \( \mu \) is the reduced mass of the particle and sheath gas molecule, \( k \) is the Boltzmann constant, \( N \) is the number density, \( d_p \) and \( d_g \) are the diameter of the particle and gas molecule, respectively, and \( q \) is the electrical charge of the particle. As shown in Table 1, all the measured inverse mobilities were larger than the inverse mobilities calculated from the hard-sphere collision model. In particular, the enhancement, which was defined as 100\((Z_{\text{exp}}^{-1}-Z_{\text{hs}}^{-1})/Z_{\text{hs}}^{-1}\) in %, increased gradually with an increase of polarizability volume or Lenard-Jones parameters of the noble sheath gas. The enhancement in Ar was about 50\%, while that in He was slight.

As suggested by Li and Wang [7], in the size region of C\(_{60}\) it is necessary to consider the influence of the potential force of interactions between the particle and the sheath gas molecules on the electrical mobility. Their theory indicates that the stronger the interaction forces are, the more the real inverse mobility of the particles will deviate from the inverse mobility calculated from hard-sphere collision model. Therefore, it is likely that the observed anomalous behavior in the mobility analysis of the C\(_{60}\) negative ions originates from the potential force of interactions as predicted by them.

As the interaction forces between the C\(_{60}\) negative ions and the sheath gas molecules (He, Ne, and Ar), both the ion-induced dipole interactions and the van der Waals interactions can be considered. Such interaction forces in the case of Ar gas molecules work stronger than those in the case of Ne or He, because of the relatively higher polarizability and Lenard-Jones parameter \( \epsilon \) (the depth of potential) of Ar gas molecules (see Table 1). Consequently, it is likely that the stronger interaction forces between the C\(_{60}\) negative ion and Ar molecule enhanced the inverse mobility of the C\(_{60}\) negative ion in Ar. On the other hand, in the case of He sheath gas, very minute interaction forces are at work between the C\(_{60}\) negative ion and He gas molecule, since both the polarizability volume and \( \epsilon \) of He gas molecules are less than 10\% of those of Ar gas molecules. This explanation is consistent with the slight enhancement of the inverse mobility in He.

### 3. ELECTRICAL MOBILITY MEASUREMENTS OF PAMAM DENDRIMERS.

#### 3.1 Experimental

Figure 3 shows the schematic diagram of the experimental setup, consisting of (a) an electrospray aerosol generator (TSI Model 3480), (b) a DMA (same type in Sec. 2), (c) a \(^{24}\)Am neutralizer, and (d) a condensation particle counter (CPC; TSI Model 3025A).

The sample solutions were prepared by diluting a methanol solution of PAMAM dendrimers of generations 2 through 6 with an aqueous ammonium acetate buffer. The buffer was 20 mM ammonium acetate solution created by dissolving ammonium acetate in ultrapure water. The sample liquid flow rate through the capillary was set to be 0.43 mL/min. The high voltage \( V_{\text{ES}} \) was applied between 1.8 and 2.4 kV at the capillary tip so that the electrospray was operated in the "cone-jet" mode. Filtered air \( Q_{\text{air}} \) (1.6 SLM) was supplied to the spray chamber. In addition, filtered CO\(_2\) gas of a flow rate of \( Q_{\text{CO}_2} \) (0.1 SLM) was mixed to stabilize the electrospray against corona discharge. The air/CO\(_2\) gas mixture carried the aerosolised PAMAM dendrimers.

#### Table 1. Comparison of the inverse mobilities calculated for C\(_{60}\) using the hard-sphere model with the measured inverse mobilities, and polarizability volume and Lenard-Jones parameter of each gas molecule.

<table>
<thead>
<tr>
<th>sheath gas</th>
<th>inverse mobility [Vsm(^{-2})]</th>
<th>enhancement [%]</th>
<th>polarizability volume [Å(^3)]</th>
<th>Lenard-Jones parameter</th>
<th>σ [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>measured ( Z_{\text{exp}}^{-1} )</td>
<td>hard-sphere ( Z_{\text{hs}}^{-1} )</td>
<td>4.8</td>
<td>0.21</td>
<td>10.2</td>
</tr>
<tr>
<td>Ne</td>
<td>2293</td>
<td>5317</td>
<td>13</td>
<td>0.39</td>
<td>35.6</td>
</tr>
<tr>
<td>Ar</td>
<td>8171</td>
<td>12594</td>
<td>54</td>
<td>1.63</td>
<td>120</td>
</tr>
</tbody>
</table>
Table 2 shows the values for the mobility diameter correction factor, and the dynamic gas viscosity of the gas. Table 2. Measured mobility diameters of the PAMAM dendrimer monomer ions, and literature values of the PAMAM dendrimer diameters as measured by (GPC) [8] and (SAXS) [9].

<table>
<thead>
<tr>
<th>Generation</th>
<th>$D_p$ (mobility diameter) [nm]</th>
<th>$D$ (GPC) [nm]</th>
<th>$D$ (SAXS) [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>2.44</td>
<td>2.45</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3.08</td>
<td>3.08</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>3.73</td>
<td>3.80</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>4.94</td>
<td>5.07</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>5.70</td>
<td>5.80</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>8.10</td>
<td>8.24</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>9.70</td>
<td>10.40</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>11.40</td>
<td>13.70</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>14.82</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.2 Results and Discussions

Figure 4 shows the measured electrical mobility spectra of the negative and positive ions of the PAMAM dendrimers of generations 2 through 6. The number concentration divided by the maximum concentration (normalized concentration) is plotted against the inverse mobility. All the electrical mobility spectra have two peaks: a higher left-hand peak and a lower right-hand peak. The left-hand peak was assigned to the monomer ions of the PAMAM dendrimers, since it was observed as a particle with the lowest inverse of electrical mobility. However, it is reasonable to assume that the right-hand peak was due to dimmer ions of the PAMAM dendrimers, since it was observed as a particle with the second lowest inverse of electrical mobility.

In the framework of Stokes’ law of resistance, the mobility diameters $D_p$ were obtained by solving the following equation [2]:

$$Z_p^{-1} = \frac{3\pi \eta D_p}{qC_v}$$

where $Z_p^{-1}$, $C_v$, and $\eta$ are the inverse of the electrical mobility of monomer ions at the peak, the Cunningham correction factor, and the dynamic gas viscosity of the gas.

Table 2 shows the values for the mobility diameter $D_p$ of the relevant PAMAM dendrimer monomer ions. In Table 2, the values for the diameter in the literature on PAMAM dendrimers as measured by gel permeation chromatography (GPC) [8] and small angle X-ray scattering (SAXS) [9] are shown. All the mobility diameters obtained in the present experiments were found to be smaller than the diameters obtained by other measurement techniques.

REFERENCES