Original Paper

Migration Behavior of Carbon Nanotube in Capillary Electrophoresis with Sodium Dodecyl Sulfate and Water-Soluble Nonionic Polymer

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Abstract
Single-walled carbon nanotube (SWCNT) was dispersed in an aqueous surfactant solution, and the dispersion of CNT was analyzed by capillary electrophoresis (CE). The dispersion was evaluated through a broad peak of the electropherograms, while the aggregation of the CNT was attributed to the shot signals in the electropherograms. Water-soluble nonionic polymer was also added in the separation buffer to examine the dispersion in the surfactant solution as well as to control the migration behavior. Polyethylene glycol, polyvinyl alcohol, and polyvinylpyrrolidone were examined. The electrophoretic mobility of the broad peak got smaller with increasing concentrations of the polymer examined. The theoretical number of plates of the broad peak was improved by the addition of the polymer. Moderately broad peak was preferable for the dispersion of the SWCNT in the surfactant solution.

Keywords: Carbon nanotube; Capillary electrophoresis; Surfactant solution; Water-soluble nonionic polymer; Theoretical number of plates

1. Introduction
Since the finding of carbon nanotube (CNT) by Iijima [1], one dimensional structure of CNT has attracted much attentions with their mechanical and electronic properties. Physical characterization of CNT has been made by microscopy and spectroscopy including SEM, TEM, SPM, Raman, IR, etc. [2]. Carbon nanotubes easily aggregate to form bundle structure through van der Waals force, and dispersion/unbundling is necessary to utilize the unique property of CNT. The aggregation is much serious in an aqueous solution because of the hydrophobic interaction. There are two major methods to disperse CNT in an aqueous solution. The first method is the oxidization of CNT with strong acids. The CNT is shortened by the oxidation, and carboxylic acid moieties are introduced to the CNT terminal. The second method is the adsorption of anionic substances to CNT. Anionic substances such as sodium dodecyl sulfate (SDS), polyaromatic compounds, or water-soluble polymer are used to disperse the nanotubes in an aqueous solution [3,4]. The solubilization of CNT with anionic surfactant is further utilized for the separation of metallic/semiconducting CNTs. Agarose gel electrophoresis with SDS was found to be helpful to separate metallic and semiconducting single-walled carbon nanotubes (SWCNTs) [5]. While semiconducting SWCNT is strongly retained on the gel, metallic SWCNT migrate in the gel by the solubilization with SDS. It is also found that gel chromatography with SDS eluent is useful to separate metallic/semiconducting SWCNT, as well as to fractionate the semiconducting SWCNTs [6]. It is also reported that CNTs dissolved in isopropyl alcohol migrate toward cathode by electrophoresis and they are aligned due to the anisotropy of their electrophoresis velocity [7].

Concerned with the purification/separation of CNT in an aqueous medium, capillary electrophoresis (CE) has been

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The final authenticated version is available online at: https://doi.org/10.15583/jpchrom.2017.013
examined [8-10]. Anionic SDS was used to disperse SWCNT in an aqueous solution through the hydrophobic interaction, and negative charge is provided to SWCNT [3,8]. The dispersed SWCNTs were resolved by CE [8]. Since SWCNT is relatively large molecules compared with the size of the anionic micelle, the partition to the micelle is not applied. The anionic surfactant adsorbs on the surface of the CNTs. The CNTs are apparently anionic, and they electroforetically migrate in the separation capillary. In the study [8], several sharp peaks were obtained in the electropherogram, and they were assigned to CNT by the Raman detection, although a tailing broad signal was not mentioned [8]. Separation of bundled and individual CNT was examined by CE coupled with Raman detection with SDS suspensions or with polyvinylpyrrolidone stabilization [9]. The electropherograms showed that sharp signals were detected on top of a broad background signal. Intensity ratio of the Raman spectrum, 267 cm\(^{-1}\) against 234 cm\(^{-1}\) (radial breathing mode with diameter-dependent) was monitored, where the former wavenumber represents the bundled CNT and the latter the isolated CNT. Raman intensity at 267 cm\(^{-1}\) was strong with the shot signals region, and that at 234 cm\(^{-1}\) was strong at the broad signal region. The results suggested that the shot signals are of aggregated CNT and they are separated from individually isolated CNT [9]. Reproducibility of the signals in the electropherogram was also reported [10]. When SDS is present in the separation buffer, the reproducibility of the signals was wrong. Therefore, CNT was dispersed in a sample solution containing SDS and hydroxylpropyl methyl cellulose and CE separation was made with ammonium acetate buffer and hydroxylpropyl methyl cellulose; SDS was not used in the CE separation [10]. Ionic liquid of 1-butyl-3-methylimidazolium tetrafluoroborate was used to unbundle the CNTs in an anionic micellar solution by encapsulation, and the dispersion was monitored by CE [11].

Dispersion of CNT in an aqueous solution was further examined with an aromatic and anionic dispersant, 2,3,6,7,10,11-hexakis (carboxydecyloxy) triphenylene aiming at chiral separation and size separation [12,13]. Dispersed CNT was photometrically detected as a broad signal, and fractionation was also made with a sheath flow. Although some of the fractions contained a certain chiral CNT, the chiral CNTs dispersed in various fractions and the CE separation was expected to be diameter dependent [12].

Oxidized CNTs, as well as surfactant coated CNTs, are stable in an aqueous solution, and they are used as pseudo-stationary phase in electrokinetic chromatography (EKC) [14,15]. Carboxylic SWCNT was used for the EKC separation of caffeine and theobromine [16], pyrimidine bases [17], as well as DNA fragments [18]. Surfactant coated CNT or micellar nanotubes were used as an EKC modifier for the separations of chlorophenols [19], penicillins [19], nonsteroidal anti-inflammatory drugs [19], and antibiotics [20]. Micro-emulsified CNT was prepared with SWCNT, SDS, and 2-butanol, and the micro-emulsion was used for the separation of polyphenols including catechin analogues [21].

Although SDS is popularly used in the CE separation of CNT and in the EKC modification with CNT, the dispersion of CNT in an aqueous surfactant solution was not discussed sufficiently. In this study, electrophoretic migration of CNT has been examined in the presence of an anionic surfactant and water-soluble nonionic polymer. The dispersion of CNT is discussed from the signal shape of the electropherograms. Broad peak in the electropherogram is attributed to the dispersed CNT possessing wide variety of the dimensions, while irreplicable shot signal is attributed to the bundled or condensed CNT. Migration behavior of the dispersed CNT is also discussed from the electrophoretic mobility and the theoretical number of plates.

2. Experiments
2.1. Reagents

Single-walled carbon nanotube was purchased from Sigma-Aldrich (St. Louis, MO, USA; preparation note: electric arc discharge method, bundle dimensions of 2–10 nm diameter and 1–5 µm length). Sodium tetraborate decahydrate (borax) was from Kanto Chemical (Tokyo, Japan), and it was used as a separation buffer component. Surfactants of sodium dodecyl sulfate (SDS) and sodium dodecybenzenesulfonate (SDBS) were from Kanto Chemical and Wako Pure Chemical, respectively. Water-soluble nonionic polymers used were polyethylene glycol (PEG; average molecular weight of 10,000, from Merck, Darmstadt, Germany), polyvinylpyrrolidone (PVP; average molecular weight of 8,000 and 24,500, from Alfa Aesar, Lancashire, UK and Nacalai Tesque, Kyoto, Japan, respectively), and polyvinyl alcohol (PVA; molecular weight range of 13,000–23,000, from Sigma-Aldrich). Other reagents were of analytical grade. Water used was purified by Milli-Q Gradient A10 (Merck Millipore, Billerica, MA, USA).

2.2. Apparatus

An Agilent Technologies (Waldbronn, Germany) 3DCE was used as a CE system, equipped with a photodiode array detector. A fused silica capillary with its inner diameter of 50 µm was purchased from GL Sciences (Tokyo, Japan). It was cut to a length of 64.5 cm and attached to the system after making a detection window by burning a small portion of the polyimide coating. The dimensions of the capillary were 64.5 cm in total length and 56 cm from the injection end to the detection window. An Elma-Hans Schmidbauer
Transsonic T310 was used for the ultrasonic radiation (35 kHz, 45 W, Singen, Germany).

2.3. Procedure
A surfactant solution was prepared with SDS or SDBS at the concentration of 20 mmol dm$^{-3}$ to dissolve the SWCNT. An aliquot of 0.5 mg of SWCNT was dissolved in an aliquot of 0.25 mL of the surfactant solution; the concentration of the SWCNT was 2.0 mg mL$^{-1}$. Ethanol was also added in the SWCNT solution at 1%(v/v) to monitor the electroosmotic flow. The SWCNT solution was sonicated in an ultrasonic bath for 5 min. The solution was used for the CE analysis after standing for more than 24 h to precipitate possible carbon substances except SWCNT.

Separation buffers were prepared with SDS or SDBS with its pH adjusted at around 9 with 4 mmol dm$^{-3}$ borax. When PVA was involved, 4 mmol dm$^{-3}$ CHES-NaOH buffer (pH ~ 9) was used instead. An aliquot of water-soluble polymer was also added in the separation buffer.

Anodic and cathodic buffer vials were filled with the separation buffer as prepared, and they were set in the CE system. The capillary was filled with a separation buffer by applying a pressure to an anodic vial. The SWCNT solution was then injected into the capillary by applying a pressure to a sample vial at 50 mbar for 5 s. After injecting the sample solution, a DC voltage of 20 kV was applied to the capillary for the electrophoresis, and the SWCNT was photometrically detected at 420 nm. A photometric detection was simultaneously made at 200 or 220 nm to detect the electroosmotic flow (EOF) with the ethanol. The temperature of the capillary cassette was controlled at 25 °C through the experiment by circulating thermostat air.

3. Results and discussion
3.1. CE separation of carbon nanotube with surfactant
Carbon nanotubes easily condense in an aqueous solution through the van der Waals attraction and hydrophobic interaction forming bundle structures. There are two major methods to disperse CNT in an aqueous solution as mentioned in the introduction section; oxidation with strong acids forming carboxylated CNT, and coating with anionic surfactant. The first CE separation used SDS to give anionic charge to CNT and to disperse CNT in an aqueous solution [8]. Shot signals were obtained in the electropherograms by the study [8], but the shot signals were found to be still bundled CNT through the Raman spectra [9]. Therefore, it is not clearly described what type of signals would be obtained with the dispersed/unbundled graphene.

In this study, a SWCNT was dissolved in a micellar solution of SDS or SDBS under ultrasonic radiation. The supernatant solution was analyzed by CE. Since CNTs absorb the wide range of visible light, the SWCNT was photometrically detected at 420 nm. Electropherograms of the SWCNT are shown in Fig. 1. Both a broad peak and shot signals were detected in the electropherograms. While the broad peak was reproducibly detected, the shot signals were not reproducible neither in the number of the

Fig. 1. Electropherograms of SWCNT in the presence of anionic surfactant in the separation buffer. Surfactant used in both the dissolution and the CE: A, SDS; B, SDBS. Concentration of the surfactant: (a), 10 mmol dm$^{-3}$; (b), 20 mmol dm$^{-3}$; (c), 40 mmol dm$^{-3}$; (d), 60 mmol dm$^{-3}$; (e), 80 mmol dm$^{-3}$. Arrows indicate the migration time of the EOF. CZE conditions: 20 kV applied voltage, 420 nm detection wavelength, 25 °C capillary temperature, and 250 mbar·s sample injection.
signals and in the migration time of the signals.

When an MEKC separation was examined with graphene, a different type of carbon material, SDBS was found to be a good surfactant to disperse graphene in an aqueous solution [22]. Both a broad peak and shot signals were detected with graphene in the electropherograms. Since graphene is composed of wide variety of the 2-dimensional structure, the dispersed graphene is detected as continuous signals of individual graphene successively detected [22]. The shot signals were suppressed at SDBS concentrations of around 20 mmol dm$^{-3}$ [22]. It was concluded that low concentrations of SDBS is not enough to dissolve the graphene, and high concentration of SDBS or salts promote the aggregation of graphene in an aqueous solution [22,23]. Therefore, the broad peaks in Fig. 1 would also be attributed to the molecularly dispersed SWCNT, and the shot signals are to the bundled and condensed SWCNT. Although broad signals including the tailing were detected in the electropherograms in the precedent studies, the continuity of successive CNT was not addressed [8,9].

In the comparison of the surfactants between SDS and SDBS, the broad peak was detected with the SWCNT in the wide concentration range of SDS; SDS is a better surfactant than SDBS to disperse CNT in an aqueous solution, while SDBS is better with graphene [22]. The predominance of SDBS on dispersion of graphene was explained by the π-π interaction between the benzene ring in SDS and the graphene plane [22]. On the other hand, CNTs possess curved surface, and therefore, the benzene ring in SDBS would not be effective on the dispersion of the SWCNT.

3.2. Effect of addition of water-soluble nonionic polymer

Water-soluble polymer of polyvinylpyrrolidone was found to solubilize SWCNT in an aqueous solution through helical wrapping [24]. Therefore, four types of water-soluble nonionic polymers were examined in this study in addition to SDS to improve the dispersion of SWCNT in the separation buffer, i.e., to reduce the shot signals in the electropherogram. The polymers used were: PEG (M.W. ~10,000), PVP (M.W. ~8,000 and ~24,500), and PVA (M.W. 13,000~23,000). The concentration of SDS in the separation buffer was set at 20 mmol dm$^{-3}$, and the polymer was added in the separation buffer in the concentration range from 0% (v/v) to 6% (v/v). Typical electropherograms are shown in Fig. 2, where the PVP was added in the separation buffer. In Fig. 2, the number of the shot signals got smaller by the addition of the PVP. Shot signals are well suppressed with PVP concentration at 4% (v/v) as in Fig 2(d), and the electropherogram has been reproducible. The RSD values of the migration time of the broad signal (peak top) and the peak height are 1.1% and 11%, respectively (n = 3). The results suggest that PVP is helpful on the dispersion of CNT in the micellar solution [24]. When the PEG or the PVA was added in the SDS solution, the broad signal of SWCNT got smaller with increasing concentration of the polymer. The two polymers were not useful for the reduction of the shot signals.

![Fig. 2. Electropherograms of SWCT in the presence of SDS and PVP (MW ~ 8,000). Surfactant: 20 mmol dm$^{-3}$ SDS. Concentration of the PVP in % (v/v): (a), none; (b), 1.0; (c), 2.0; (d), 4.0; (e), 6.0. CZE conditions are the same as in Fig. 1. Arrows indicate the migration time of the EOF.](image)

3.3. Changes in the electrophoretic mobility of the broad peak by the addition of the polymer

The net charge of the SWCNT solubilized with SDS would change by the addition of the surfactant, as well as the polymer. Changes in the effective electrophoretic mobility of the SWCNT, the broad peak, are shown in Fig. 3. The migration time of the peak top was used for the analysis. The SWCNT is negatively charged by the solubilization with the surfactant. When the concentration of the surfactant was increased, the effective electrophoretic mobility increased a little (Fig. 3). Net charge of the SWCNT would be increased with higher concentrations of the surfactant by the adsorption to the SWCNT.

The effective electrophoretic mobility of the SWCNT, however, decreased with increasing concentrations of the polymer added in the separation buffer (Fig. 4). Although the viscosity of the separation buffer changes by the addition of the polymer, the change is not so much significant to discuss the effective electrophoretic mobility. Because the velocity of the electroosmotic flow is not so decreased. By the addition of the polymer, the effective electrophoretic mobility got sufficiently small as little as close to zero, and the polymer would competitively replace
the SDS on the SWCNT surface; the net charge of the SWCNT would be decreased. The degree of the decrease is significant with the PVA and the PEG. Too much replacement of SDS would prevent the dispersion of the SWCNT in an aqueous solution, and therefore, the broad signal would have got smaller at high concentrations the polymers.

Fig. 3. Changes in the effective electrophoretic mobility of the broad peak of SWCNT with increasing concentrations of the surfactant. Surfactant: ○, SDS; ●, SDBS.

Fig. 4. Changes in the effective electrophoretic mobility of the broad peak of SWCNT with increasing concentrations of the polymer. Polymer: ○, PVP 8,000; ●, PVP 24,500; □, PEG; ■, PVA. Concentration of SDS: 20 mmol dm$^{-3}$.

3.4. Changes in the theoretical number of plates of the broad peak by the addition of the polymer

It is also noted in the electropherograms in Fig. 1 that the broad peak of SWCNT got broader with increasing concentrations of the surfactant. To examine the peak broadening quantitatively, the theoretical number of plates was calculated in an ordinary manner from the migration time and the half width of the peak. The result is shown in Fig. 5. The theoretical number of plates decreased with increasing concentrations of the surfactant. The decrease in the number of plates would suggest that the coverage ratio of the surfactant, i.e. apparent charge/mass ratio of the SWCNT, comes to be wide range. Or, high concentration of salt, the surfactant, would have promoted the aggregation/dissolution of the SWCNT in the separation buffer, as observed with graphene oxide [23].

Effect of the additional polymer on the theoretical number of plates was also examined, where the concentration of SDS in the separation buffer was set at 20 mmol dm$^{-3}$. The results are shown in Fig. 6. The number of plates tended to increase with increasing concentrations of the polymer, while the increase is little with PVP 8,000. This result agrees with the changes in the apparent charge of the CNT is decreased. From the view

Fig. 5. Changes in the theoretical number of plates of the broad peak with increasing concentrations of the surfactant. Surfactant: ○, SDS; ●, SDBS.

Fig. 6. Changes in the theoretical number of plates of the broad peak with increasing concentrations of the water-soluble polymer. Surfactant: 20 mmol dm$^{-3}$ SDS. Polymer: ○, PVP 8,000; ●, PVP 24,5000; □, PEG; ■, PVA.
point of electrophoretic mobility. PEG and PVA are more likely to replace the surfactant on the CNT, and the dispersion of the dispersion of the SWCNT in the surfactant solution, the competitive replacement of the surfactant is not desirable.

4. Conclusions
Carbon nanotube was successfully dispersed in the surfactant solution with SDS. Both a broad signal and shot signals were obtained with the SWCNT in CE. The broad signal is attributed to the dispersed SWCNT in the surfactant solution, while shot signals are to the aggregated/bundled SWCNT. Migration behavior of the broad peak was examined with the effective electrophoretic mobility and the theoretical number of the plates. On the dispersion of the SWCNT in the surfactant solution, moderately broad peak and moderately anionic charge is preferable.

Acknowledgement
This study was supported by JSPS KAKENHI Grant Number 17K05903.

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