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Aqueous stability and mobility of C₆₀ complexed by sodium dodecyl benzene sulfonate surfactant

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ABSTRACT

Surfactant complexation may have significant effects on the environmental behavior of nano-particles. In order to understand the ecological exposure of nano-materials, it is important to determine the stability and mobility of surfactant-complexed nano-materials in aqueous systems. In this study, the aggregation and transport of C₆₀ complexed by the surfactant sodium dodecyl benzene sulfonate (SDBS) were investigated. It was found that SDBS-complexed C₆₀ had a ζ-potential of −49.5 mV under near-neutral pH conditions and remained stable during an aging period of 15 days. It had a critical coagulation concentration of 550 mmol/L for NaCl, which was higher than common natural colloids and many kinds of raw nano-materials, and was comparable to those of many kinds of surface-modified nano-materials. SDBS enhanced the stability of C₆₀ colloid; however, at the same time, it also enhanced the colloidal particle aggregation rate. Much higher mobility was found for SDBS-complexed C₆₀ than C₆₀ colloid. Increase in ionic strength, Ca²⁺ concentration or Al³⁺ concentration decreased the mobility. In general, SDBS-complexed C₆₀ had high stability and mobility.

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Introduction

Among many kinds of nanomaterials developed, C₆₀ (Fullerene) was a landmark discovery for carbon nanomaterials and has attracted wide attention since its discovery. C₆₀ has a spherical cage-like molecular structure and its discovery has led to the equally significant subsequent discovery of other fullerenes, including carbon nanotubes (CNTs) (Chen and Elimelech, 2006). C₆₀ is a classical engineered material with potential applications

in the areas of biomedical technology, electronics, optics, etc. C₆₀ is highly hydrophobic, tends to aggregate and is not readily dispersed in the aqueous phase. However, the complexation of C₆₀ with manufactured surfactants may enhance the aqueous stability and thus enhance its mobility in environmental media. The complexation of C₆₀ with surfactant to enhance aqueous stability may occur in two main ways, i.e., (1) the complexation of C₆₀ discharged into the environment with residual surfactants discharged to the environment by human activities; and (2) the complexation

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of C_{60} with surfactants in industrial processes to enhance the aqueous solubility of C_{60} .

Surfactants are a diverse group of chemicals that are best known for their wide use in detergents and other cleaning products. Annual production of surfactants worldwide has risen to 12.5 million tons (Tan et al., 2010). No doubt this figure will grow with the ever growing detergent and cosmetic industries. After being used, residual surfactants are discharged into sewage systems or directly into surface waters. Most of them finally disperse in different environmental compartments such as soil, water or sediment (Ivankovic and Hrenovic, 2010). Although most surfactants are readily biodegradable, the existence of surfactants in the environment is obvious in many regions due to the continual discharge (Sanderson et al., 2006; Ying, 2006). For example, the concentration/mass fraction of one of the most common surfactants, linear alkylbenzene sulphonic acid (LAS), reached 1.1 mg/L in sewage effluents (Holt et al., 1998) and 30.2 g/kg dry mass of treated sludge (Berna et al., 1989). Up to 0.4 mg/L of LAS was measured in surface waters (Fox et al., 2000). The elevated levels of surfactants in the environment can greatly affect the transport and fate of environmental pollutants in the environment. With the possible discharge of C_{60} into the aqueous environment, the complexation of C_{60} in the aquatic environment with residual surfactants may enhance the stability and mobility of C_{60} .

On the other hand, in the application of nano-materials, it is often required that C_{60} be debundled and made hydrophilic in order to be solubilized in the aqueous phase. In these cases, surfactant treatment is usually employed to modify C_{60} . Solubilizing C_{60} by attaching surfactants to the surface through non-covalent interactions is an important approach to enhance the hydrophilic properties for solubilization. For example, C_{60} can be solubilized in water after being wrapped with triptycene-based surfactants (Torres et al., 2011). Surfactants such as Tween 20, Tween 60, Tween 80, Triton X-100, polyoxyethylene (10) lauryl ether, *n*-dodecyl trimethylammonium chloride, myristyl trimethylammonium bromide and sodium dodecyl sulfate can be used to solubilize C_{60} to facilitate its biomedical application (Hammershøj et al., 2012).

In previous investigations, the environmental aspects of raw carbon nano-materials (Prylutskyy et al., 2013; Wang et al., 2014) and oxidized carbon nano-materials (Li and Huang, 2010) have been documented. Recently, the stability and mobility of surfactant complexed carbon nano-materials have become the concern of several researchers. The aggregation and transport of one kind of carbon nano-materials, single-walled carbon nanotubes, after surfactant complexation were investigated (Bouchard et al., 2012). Due to the fact that surfactant complexation may increase the aqueous stability and mobility of C_{60} , which may subsequently facilitate the transport of environmental pollutants and cause enhanced harm to organisms, it seems necessary to understand the fate of surfactant-complexed C_{60} in the natural environment. Wang et al. (2012a) also investigated the effect of different kinds of surfactants on the mobility of C_{60} .

In this investigation, the stability and mobility of surfactant-complexed C_{60} was studied as affected by electrolytes.

1. Experimental

1.1. Materials

The C_{60} used in this study, which was claimed to have a purity of 99.9% by the producer, was purchased from Nanjing Jicang Nano-Material Company (Nanjing, China). It was used as received without further purification. Surfactant sodium dodecyl benzene sulfonate (SDBS) of analytical grade was provided by Sinopharm Chemical Reagent Co. Ltd. Tetrahydrofuran (THF) of HPLC grade was purchased from Dikma Technologies INC, USA. Glass beads with an average diameter of 1.0 mm were employed as the porous media. Before being used, the beads were soaked in 0.01 mol/L NaOH for 24 hr and then in 0.01 mol/L HNO_3 for 24 hr. After being washed with ultra-pure water, the beads were dried at 105°C for 12 hr and stored in a closed desiccator. Ultra-pure water was used throughout the experiments.

1.2. Characterization and concentration measurement

The ζ -potentials of SDBS-complexed C_{60} dispersions were determined at various pH values, and the pH values of the dispersions were adjusted using either HCl or NaOH. The C_{60} concentration was analyzed spectrophotometrically using a Hach DR-5000 UV-visible spectrophotometer at 800 nm using matched 10 mm quartz cells. It was observed that SDBS had no absorbance at 800 nm, and there was a good correlation between the absorbance at this wavelength and the C_{60} concentration. A similar phenomenon was also observed by Lin et al. (2009), who found a good correlation between the absorbance and the concentration of multi-walled carbon nanotubes (MWCNTs) at 800 nm in the presence of tannic acid.

1.3. Preparation of SDBS-complexed C_{60}

Before the preparation of SDBS-complexed C_{60} colloid, C_{60} colloid was prepared employing the method of Fortner et al. (2005) with modifications. 0.02 g C_{60} was added to 400 mL THF and N_2 was sparged to remove oxygen. Then the bottle was sealed to prevent contact with air. Sonication was employed for the solubilization of C_{60} and a sonication time of 15 min was employed. After sonication, the mixture was filtered using a 0.45 μ m nylon membrane, and a transparent pink liquid was obtained. Then 400 mL water was added to the solution and a yellow solution was obtained. A three-step evaporating procedure using a rotary evaporator was then employed for removal of THF from the mixture, with an evaporating temperature of 75°C. First, the obtained 800 mL liquid was evaporated to 350 mL. Then 100 mL water was added and the obtained 450 mL liquid was evaporated to 350 mL. Finally, 100 mL water was added, the liquid was evaporated to 400 mL and the obtained liquid was cooled to room temperature and employed as C_{60} colloid in subsequent study. For the preparation of SDBS-complexed C_{60} colloid, a prescribed amount of SDBS was added to the C_{60} colloid, stirred for 12 hr and stored at room temperature for later use. Every time before being used, the C_{60} colloid was sonicated for 10 min.

1.4. Dynamic light scattering

The dynamic light scattering (DLS) measurements were performed on a CGS-3 dynamic light scattering apparatus (ALV, Langen, Germany). The DLS instrument was operated under the following conditions: temperature 25°C, detector angle 90°, and laser wavelength 632.8 nm. For the DLS measurement, SDBS-complexed C_{60} suspension with C_{60} concentration of 12.0 mg/L was employed. To induce aggregation, a predetermined amount of electrolyte solution, which was filtered through a 0.1 μm filter, was added to 2.5 mL of the above-mentioned suspension contained in the sampler holder. The mixture was immediately sealed, mixed by hand and placed on the DLS apparatus, and then DLS measurements were initiated.

1.5. Aggregation kinetics

During the initial aggregation period, i.e., the time period from the start of aggregation to the time when the measured particle radius (r_H) reaches 1.50 $r_{H,initial}$, the aggregation rate constant (k_a) is proportional to the initial rate of increase in r_H with time (Eq. (1)) (Bouchard et al., 2012).

$$k_a \propto \frac{1}{N_0} \left(\frac{dr_H(t)}{dt} \right)_{t \rightarrow 0} \quad (1)$$

where N_0 (mg/L) is the initial particle concentration. The attachment efficiency, α , ranging from 0 to 1, is the probability of an irreversible attachment resulting from the collision of two colloidal particles. It can be calculated by normalizing the measured k_a by the diffusion-limited aggregation rate constant $k_{a,fast}$ (Eq. (2)) (Bouchard et al., 2012).

$$\alpha = \frac{k_a}{k_{a,fast}} = \frac{\left(\frac{dr_H(t)}{dt} \right)_{t \rightarrow 0}}{\left(\frac{dr_H(t)}{dt} \right)_{t \rightarrow 0,fast}} \quad (2)$$

Therefore, for given particle concentrations and DLS experimental parameters, the attachment efficiency can be obtained by measuring the change of hydrodynamic radius as a function of time.

1.6. Porous media column study

A column setup, which consisted of a constant-flow pump and a cylindrical Plexiglas column (height of 15.0 cm and inner diameter of 3.0 cm), was employed in the column study. The column was tightly packed with cleaned glass beads and the porosity of the packed column was measured to be 0.39. The column study was carried out employing an upflow mode with a flow rate of 1.5 mL/min, which was provided by the constant-flow pump. Before each column experiment, at least 10 pore volumes of background solution with the same pH and electrolyte concentration as the SDBS-complexed C_{60} suspension were introduced into the column to compact and saturate the glass bead bed. The effluent C_{60} concentration, C (mg/L), was monitored to obtain the breakthrough curve, which was plotted as C/C_0 (C_0 (mg/L) was the C_{60} concentration introduced into the column) as a function of the number of pore volumes passing through the porous medium. A C_0 value of 12.0 mg/L was employed in the column study.

In this study, clean-bed filtration theory was employed to interpret the steady-state effluent concentration data according to Yao et al. (1971), Liu et al. (1995) and Lecoanet et al. (2004). Particle mobility in porous media was expressed in terms of the distance in a homogeneous porous medium that the nano-particles would have to traverse to reduce their concentration to an arbitrary fraction of that initially present (designated as L_0). L_0 values were calculated using Eq. (3) (without detailed deduction):

$$L = k \ln(C/C_0). \quad (3)$$

By fitting the experimental plateau C/C_0 value and the column length to Eq. (3), the k value can be calculated. Then at a given arbitrary C/C_0 value, the distance that the nano-particles would have to traverse to reduce their concentration to the arbitrary C/C_0 value can be calculated for evaluating the migration potential. In this study, an arbitrary C/C_0 level of 0.001 or a 3-log reduction in C_{60} concentration was adopted.

2. Results and discussion

2.1. Aqueous stability

The stability of colloids is closely related to their electrokinetic characteristics. The electrokinetic characteristics of SDBS-complexed C_{60} were measured and the ζ -potential as a function of pH is shown in Fig. 1. It was shown that, in the pH range of 4.2 to 9.2, SDBS-complexed C_{60} was highly negatively charged and the ζ -potential ranged from -39.3 to -58.3 mV, which is much higher than that of C_{60} . In the near-neutral pH range, a ζ -potential value of -49.5 mV was measured. It is interesting to compare the ζ -potential of SDBS-complexed C_{60} with that of natural colloids, which have been of concern because of their high negative charge, and thus transport easily in porous media and facilitate aqueous pollutant transport. For example, it has been documented that colloids from a river site had a ζ -potential of -42 mV (Kaplan et al., 1995); dispersible

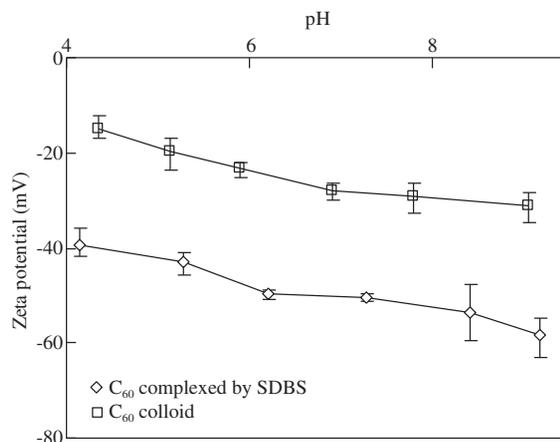


Fig. 1 – ζ -Potential of C_{60} and SDBS-complexed C_{60} as a function of pH (SDBS concentration for SDBS-complexed C_{60} system was 0.03%).

clays from surface or near-surface sediment possessed a ζ -potential of about -25 mV (pH 7–10) (Ryan and Gschwend, 1994); the ζ -potential of colloids from a coastal plain was measured to be -41 to -18 mV (Kaplan et al., 1993). As compared to these naturally occurring colloids, SDBS-complexed C_{60} has higher negative charge, which may enhance its mobility and facilitate its transport. Recently, the electrokinetic characteristics of several kinds of modified nano-materials have been of concern and were documented. Previous investigation showed that oxidized multi-walled carbon nanotubes (MWCNTs) had negative ζ -potentials in the range of -31.0 to -49.5 mV in the pH range 2.6–6.5, and a ζ -potential value of -49.5 mV was measured under near-neutral pH conditions (Peng et al., 2009). The ζ -potential value of oxidized single-walled carbon nanotubes (SWCNTs) reached -45 mV (Li et al., 2008). That of natural organic matter (NOM)-modified C_{60} was documented to reach -42 mV (Wang et al., 2012b). The value measured in this investigation seemed to be quite comparable to those of other kinds of modified nano-materials in previous investigations.

The stability of C_{60} colloid and SDBS-complexed C_{60} was investigated using a sedimentation test and the results are shown in Fig. 2. It can be seen from this figure that SDBS-complexed C_{60} has higher stability than C_{60} colloid. It has been reported that oxidized and surfactant-modified CNTs have relatively high stability in the aqueous phase. SWCNTs modified by low-concentration surfactant were documented to have high stability. The suspended mass and ζ -potential potential varied by $<5\%$ over a 17-day period (Bouchard et al., 2012). Oxidized MWCNTs were reported to have a concentration decrease of only 15% even after 30-day aging (Peng et al., 2009). It is shown in Fig. 2 that the C_{60} concentration remained almost constant during an aging period of 15 days, which indicated that SDBS-complexed C_{60} had rather high stability. The stable dispersion of SDBS-complexed C_{60} may make it a potential pollutant after being discharged into water bodies.

The high stability of SDBS-complexed C_{60} is mainly due to three mechanisms. The first one is that the surfactant coating enhanced the dispersive properties of C_{60} through providing an increased electrostatic repulsion. In the aqueous phase, the electrostatic repulsive forces between the negative surface

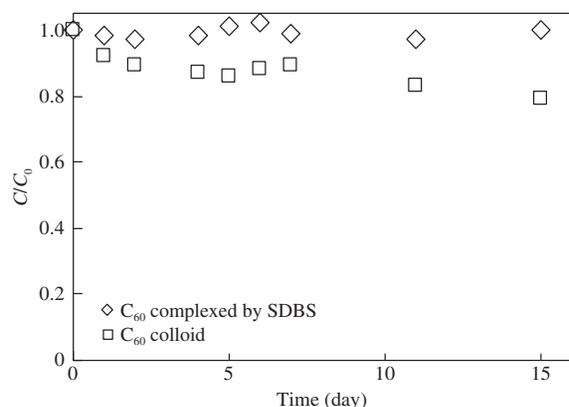


Fig. 2 – C_{60} concentration versus aging time in SDBS-complexed C_{60} dispersion (SDBS concentration for SDBS-complexed C_{60} system was 0.03%).

charges of the surfactant coated on C_{60} surfaces led to the stability of C_{60} , and the SDBS-complexed C_{60} formed a stable dispersion in water. The second is that the surfactant coating reduced the surface hydrophobicity, which facilitates aggregation. In the investigation of enhanced stability of SWCNTs by surfactants, Bouchard et al. (2012) suggested that surfactant adsorbed on the SWCNT surface reduced the exposure of pristine surface to the aqueous phase and thus enhanced SWCNT stability. This mechanism can also be employed for the explanation of the high stability of SDBS-complexed C_{60} . The pristine carbon surface, which was highly hydrophobic, facilitated the aggregation and reduced the colloid stability. However, after surfactant was adsorbed on the surface, a chemically heterogeneous surface was created and the hydrophobic surface was partially shielded. This also enhanced the stability. The third mechanism is the steric repulsion between C_{60} caused by the adsorbed SDBS.

2.2. Aggregation kinetics

The aggregation kinetics of SDBS-complexed C_{60} was studied over a NaCl concentration range of 100 to 1000 mmol/L at pH 6.5, and an SDBS concentration of 0.015% was adopted for the colloid preparation. The aggregation experiments were carried out in duplicate and the results showed good reproducibility. Fig. 3 shows the aggregation profiles. It was indicated that, under very low electrolyte concentrations (NaCl concentration ≤ 100 mmol/L), no obvious aggregation was observed. However, when the NaCl concentration increased to 200 mmol/L, the growth of the hydrated particle radius became observable. The positive correlation of the aggregate size of SDBS-complexed C_{60} with ionic strength is in accordance with other kinds of nano-particles (Conway et al., 2015). With the further increase in NaCl concentration from 200 to 550 mmol/L, the $\frac{dr_H(t)}{dt}$ value increased rapidly, which

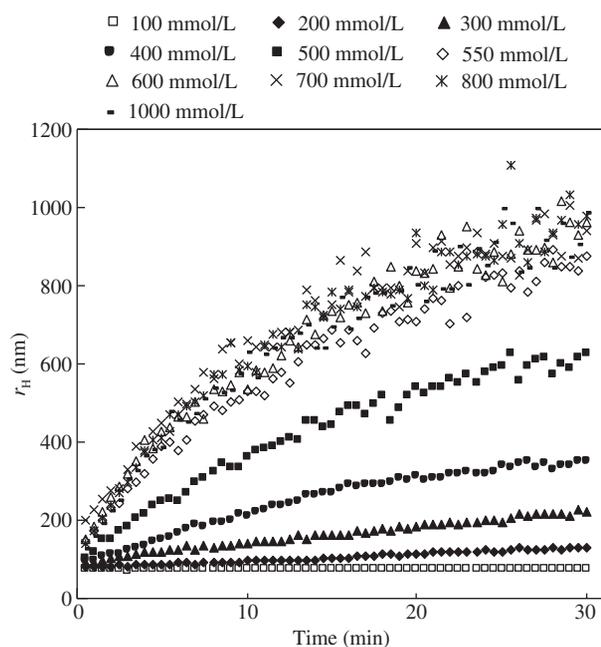


Fig. 3 – Aggregation kinetics of SDBS-complexed C_{60} over a NaCl concentration range of 100 to 1000 mmol/L at pH 6.5.

meant an increasing degree of aggregation with increasing electrolyte concentration. After that point, the $\frac{dr_H(t)}{dt}$ value remained constant, indicating the occurrence of fast aggregation. The measured kinetics was in accordance with the two regimes typical of colloidal systems, in which the aggregation kinetics can be explained by DLVO theory. Under low electrolyte concentration conditions, attachment efficiency increased due to the screening of particle surface charge and the reduction of the energy barrier to aggregation. This was called the reaction-limited regime or slow aggregation regime and the attachment efficiency was governed, in part, by electrostatic repulsive interactions. With the further increase in electrolyte concentration, the surface charge of particles was completely screened, the energy barrier was eliminated, and the $\frac{dr_H(t)}{dt}$ value reached 1.0 and remained constant. The aggregation was no longer governed by electrostatic repulsive interactions but by the diffusion of particles. This is known as the diffusion-limited regime. The increasing aggregation with increasing electrolyte concentration indicated that electrostatic repulsion played an important role in the stabilization.

Fig. 4 shows the attachment efficiency of SDBS-complexed C_{60} as a function of salt concentration. The SDBS concentration adopted was also 0.015%. The critical coagulation concentration (CCC) values were obtained by determining the intersection point between the reaction-limited regime and the diffusion-limited regime. The CCC value of NaCl for SDBS-complexed C_{60} obtained from this investigation, as shown in Fig. 4, was 550 mmol/L at the near-neutral pH value employed. The magnitude of CCC values for natural colloids, nano-materials and modified nano-materials has been of concern due to the fact that their stability will facilitate their transport in the environment. It was documented that two kinds of natural colloids, montmorillonite and illite, had CCC values of 5 and 34 mmol/L NaCl, respectively (Lagaly and Ziesmer, 2003; Jiang et al., 2012). Although much higher values have been documented for specific kinds of natural colloids, for example, a CCC value of 137 ± 24 mmol/L NaCl has been measured for quartz (Jiang et al., 2012), most natural colloids were reported to have CCC magnitudes of tens of mmol/L NaCl or lower. Generally, though several kinds of man-made nano-materials have lower CCC values, most man-made nano-materials seem to have higher CCC values

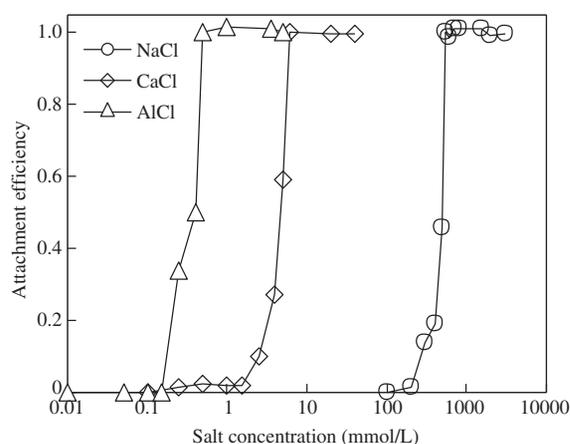


Fig. 4 – Attachment efficiency of SDBS-complexed C_{60} as a function of salt concentration.

than natural colloids. It has been documented that GeO_2 nano-particles had a CCC value of 34 mmol/L KCl (Li et al., 2011). That of SWCNTs was reported to be 20 mmol/L NaCl (Saleh et al., 2010). However, those of pure magnetite sol, C_{60} and boron nano-particles reached 120, 160 and 200 mmol/L, respectively (Illés and Tombácz, 2006; Chen and Elimelech, 2007; Liu et al., 2010). Surface modification of colloidal particles can significantly enhance their stability. After the modification process of oxidation, CCC values for SWCNTs and MWCNTs reached 160 mmol/L (Li and Huang, 2010) and 185 mmol/L (Peng et al., 2009), respectively. That of surfactant-complexed SWCNTs varied in the range of 121–871 mmol/L, depending on the surfactant concentration adopted (Bouchard et al., 2012). It has also been shown that, even at high NaCl concentration, humic acid-complexed C_{60} showed very slow aggregation kinetics (Chen and Elimelech, 2007). The measured CCC value of 550 mmol/L NaCl for surfactant-complexed C_{60} seemed to be higher than natural colloids and many kinds of raw nano-materials, comparable to those of surface-modified nano-materials and lower than that of extremely stable systems, such as humic acid-complexed C_{60} .

Generally, the valence of electrolyte cations has a significant effect on the aggregation of colloids. The attachment efficiencies of SDBS-complexed C_{60} as a function of $CaCl_2$ and $AlCl_3$ concentration are also shown in Fig. 4, and CCC values for $CaCl_2$ and $AlCl_3$ were determined to be 6 mmol/L and 0.5 mmol/L, respectively. The ratio of the CCC values for NaCl, $CaCl_2$ and $AlCl_3$ was 1100:12:1, different from the ratio of 729:11.4:1 predicted by the Schulze–Hardy rule. The difference between the experimental data and the Schulze–Hardy rule maybe was due to the fact that salts not only acted as electrostatic screening electrolytes for surfactant complexed C_{60} colloids, but also reacted with the surfactant in the aqueous solution to form surfactant micelles.

The aggregation of SDBS-complexed C_{60} under varying surfactant concentration as a function of NaCl concentration was also investigated. The results showed that the CCC values of SDBS-complexed C_{60} under surfactant concentrations of 0.001%, 0.005%, 0.010%, 0.015% and 0.050% (the critical micelle concentration of SDBS under the experimental conditions was 0.052%) were 450, 500, 550, 600, 700 and 800 mmol/L NaCl, respectively, which indicated that the stability of C_{60} increased with the increase in surfactant concentration. This is different from fulvic acid- and bacillus subtilis exudate-complexed nano-particles, in which case adsorption of organic molecules onto nano-particles can enhance aggregation via colloidal bridging and/or charge neutralization, or with more complete surface coverage, can diminish aggregation via electrostatic repulsion and/or steric hindrance (Duster and Fein, 2014). Moreover, the $(\frac{dr_H(t)}{dt})_{t \rightarrow 0, fast}$ values obtained under surfactant concentrations of 0.001%, 0.005%, 0.010%, 0.015% and 0.050% were 12.2, 18.3, 27.9, 43.8 and 59.7 nm/min, respectively, which indicated that SDBS in the aqueous phase enhanced the colloidal particle growth rate. Similar results were also obtained under electrolyte concentrations below the CCC values. For example, for NaCl concentration of 400 mmol/L, the $(\frac{dr_H(t)}{dt})_{t \rightarrow 0}$ values obtained under SDBS concentrations of 0.001%, 0.005%, 0.010%, 0.015% and 0.050% were 5.3, 8.2, 10.3, 13.8 and 35.7 nm/min, respectively, which also indicated that surfactant in the aqueous phase enhanced the colloidal particle growth rate. The increase in colloidal particle

growth rate with the increase in SDBS concentration was due to the fact that electrolyte reacted with the surfactant in the aqueous solution and surfactant micelles formed, which combined with C_{60} colloidal particles and enhanced the colloid growth rate.

2.3. Transport in porous media

Breakthrough curves of SDBS-complexed C_{60} (0.015% SDBS) under various ionic strength conditions are presented in Fig. 5, which show the normalized effluent C_{60} concentration (C/C_0) as a function of the cumulative number of pore volumes passing through the porous media. An ionic strength range of 5.0 to 100.0 mmol/L NaCl was employed for the investigation. Before the investigation, the DLS data were recorded to determine the stability of the dispersions under the employed dispersion conditions for transport investigation. The results showed that, during the 10 hr aging, there was no obvious aggregation. As a comparison, breakthrough curves of C_{60} were also studied and the results are presented in Fig. 6. It was shown that, under the same ionic strength conditions, SDBS-complexed C_{60} had a much higher plateau C/C_0 value than C_{60} , which indicated that surfactant complexation significantly enhanced the mobility. This is in accordance with Yang et al. (2013) and Wang et al. (2012), who found that oxidation or complexation by stabilizing agents enhanced the mobility of carbon nano-materials, due to increased electrostatic repulsion. The particle mobility in porous media is generally dependent on two main processes. One is the Brownian diffusion process, which determines the transport of particles from fluid to the media surface. Another is the deposition of particles on the media surface. It can be argued that the enhancement of C_{60} mobility by complexation with SDBS was due to the fact that surfactant complexation, which significantly enhanced particle surface charge, decreased the deposition. The deposited particles on the media surface, which were negatively charged, excluded the immediate vicinity of the collector surface from subsequent deposition. This surface exclusion phenomenon has been termed blocking (Liu et al., 1995). Compared with C_{60} , SDBS-complexed C_{60} had enhanced blocking properties due to the enhanced surface charges.

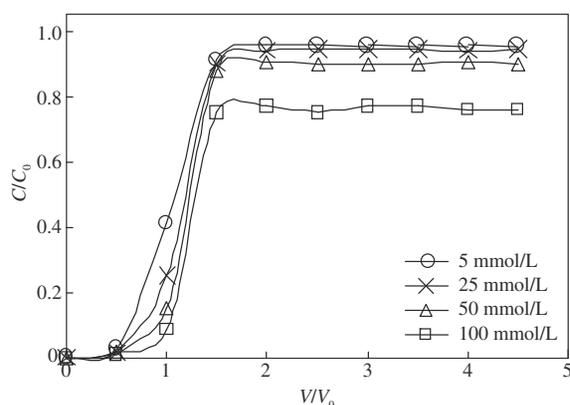


Fig. 5 – Breakthrough curves of SDBS-complexed C_{60} under various NaCl concentrations.

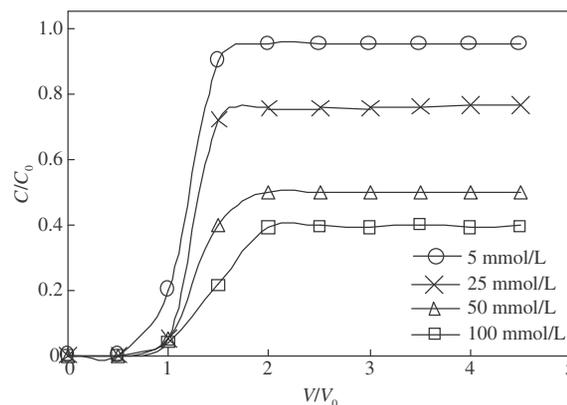


Fig. 6 – Breakthrough curves of C_{60} under various NaCl concentrations.

The calculation of the L_0 values showed that, under the near neutral pH value and low ionic strength (5 mmol/L NaCl) conditions, SDBS-complexed C_{60} had an L_0 value of 22.25 m. Generally, surface oxidation using a strong oxidant will also introduce negative surface charges on the surface of carbon nano-materials, which will be capable of enhancing their stability and mobility. It is interesting to compare the mobility of SDBS-complexed carbon nano-materials with that of surface-oxidized carbon nano-materials. In our previous investigation, MWCNTs oxidized by concentrated nitric acid for 12 hr, which had a ζ -potential of -45 mV, had an L_0 value of 7.69 m under dispersion conditions of $I = 5$ mmol/L NaCl and $pH = 6.5$ (Peng et al., 2011). However, in this investigation, under similar dispersion conditions, it was found that SDBS-complexed C_{60} , which had a similar ζ -potential of -49.5 mV, had a much higher L_0 value. This result indicated that surface complexation by surfactants may facilitate the mobility of carbon nano-materials more than oxidation does. It can also be seen clearly that ionic strength had an obvious effect on the mobility of SDBS-complexed C_{60} , and an increase in ionic strength decreased the mobility of SDBS-complexed C_{60} . L_0 values under ionic strength of 5.0, 25.0, 50.0 and 100.0 mmol/L NaCl were calculated to be 22.25, 18.32, 9.94 and 3.78 m, respectively.

The effect of divalent and trivalent cations, Ca^{2+} and Al^{3+} , on the transport was also investigated and the results are shown in Fig. 7. Before the investigation, the DLS measurements also showed that, under the divalent and trivalent cation concentrations employed, there was no obvious aggregation during the time period of the transport investigation. Ca^{2+} and Al^{3+} in the dispersion significantly decreased the mobility. The L_0 value calculation showed that an increase in Ca^{2+} concentration from 0.05 to 0.15 mmol/L resulted in a decrease in L_0 value from 17.85 to 3.88 m. An increase in Al^{3+} concentration from 0.02 to 0.05 mmol/L resulted in a decrease in L_0 value from 15.62 to 5.06 m.

3. Conclusions

In this study, the aggregation and transport of C_{60} complexed by the surfactant sodium dodecyl benzene sulfonate (SDBS) were investigated. It was found that SDBS-complexed C_{60} had

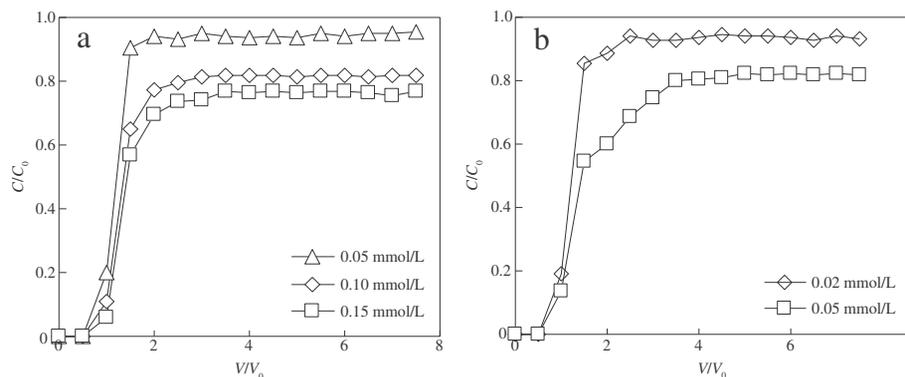


Fig. 7 – Breakthrough curves of SDBS-complexed C_{60} under various $CaCl_2$ (a) and $AlCl_3$ (b) concentrations.

a ζ -potential of -49.5 mV under near-neutral pH conditions, which indicated that SDBS-complexed C_{60} had higher negative charge compared to the naturally occurring colloids and comparable negative charge to other kinds of modified nano-materials. SDBS-complexed C_{60} had rather high stability and remained stable during an aging period of 15 days. It had a critical coagulation concentration (CCC) of 550 mmol/L for NaCl, which was higher than common natural colloids and many kinds of raw nano-materials, and comparable to those of many kinds of surface-modified nano-materials. SDBS enhanced the stability of C_{60} colloid; however, at the same time it enhanced the colloidal particle aggregation rate. Surfactant complexation significantly enhanced the mobility of C_{60} , and SDBS-complexed C_{60} had much higher mobility than C_{60} colloid. Increase in ionic strength, Ca^{2+} concentration or Al^{3+} concentration decreased the mobility of SDBS-complexed C_{60} . An increase in ionic strength from 5.0 to 100.0 mmol/L resulted in a decrease in L_0 value from 22.25 to 3.78 m; an increase in Ca^{2+} concentration from 0.05 to 0.15 mmol/L resulted in a decrease in L_0 value from 17.85 to 3.88 m; and an increase in Al^{3+} concentration from 0.02 to 0.05 mmol/L resulted in a decrease in L_0 value from 15.62 to 5.06 m.

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