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Electrochemical Study of Core-Shell Microgels

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Summary

Core and core-shell microgels are synthesized by aqueous free radical precipitation polymerization and their solvent release effects characterized. Dynamic light scattering (DLS) reveals hydrodynamic radii (Rh) decrease sharply at lower critical solution temperature (LCST) of 32°C. Electrochemical properties of microgels were also investigated using cyclic voltammetry (CV) and chronoamperometry (CA) with electroactive probes: $Fc(MeOH)_2$, uncharged and $Ru(NH_3)_6Cl_3$, positively charged. By measuring the effect of temperature change on the diffusion coefficients, I estimated the electrostatic interactions in varying solutions: aqueous (without migrogels), 25% core microgel and 25% core-shell microgel solution systems. The diffusion coefficient of uncharged ferrocenedimethanol $Fc(MeOH)_2$ was found to increase as temperature increases, in both core or core-shell solutions. Positive charged $Ru(NH_3)_6Cl_3$ shows a different behavior in both 25% core and 25% core-shell systems. In aqueous solution, increasing temperature brings increased diffusion coefficients. With the addition of core and core-shell microgel solution systems, diffusion coefficients fall sharply above LCST. This suggests that there is some amount of electrostatic interactions between negatively charged core and core-shell microgels and positively charged $Ru(NH_3)_6Cl_3$.

Introduction

Stimuli-sensitive microgels continue to find utility in a wide variety of applications. The most widely researched temperature responsive polymers are the poly alkylacrylamides, of which the best known and studied is poly N-isopropylacrylamide (pNIPAm) [1-4]. pNIPAm is composed of the monomer N-isopropylacrylamide (NIPAm), and has a volume phase transition temperature, also known as a lower critical solution temperature (LCST) of ~31-32 °C. Other polymers have also been shown to have similar behavior [2, 5-8], but pNIPAm is unique in that the phase transition occurs in an experimentally useful temperature range; namely body temperature. Temperature responsive hydrogels composed of pNIPAm have been utilized for various applications such as actuators [9], modulated drug delivery [10-13], protein release [14], chemical separations [15-17], and metal ion and biomolecule detection [18-19].

In such applications, the knowledge of solute molecular mobility in microgels before and after volume phase transition is of great importance. Transport properties of ions and molecules via polymeric gels are of interest for the characterization of biological fluids and ion-exchange membranes [20-23]. Core and core-shell microgels can be treated as model systems and can be used to mimic properties of a wide range of polyionic microgels characterized by various charge densities. Strong, long-distance, electrostatic interactions between the polyion and the counterion suppress transport counterion [24-27].

Here, we examine the electroanalytical properties of core and core-shell microgels. The core and core-shell microgels were synthesized by aqueous free radical precipitation polymerization. The hydrodynamic radii (R_h) of the microgel particles were characterized with dynamic light scattering (DLS) over a temperature range of 25°C to 40°C. The diffusion coefficients of electroactive probes of $Fc(MeOH)_2$ and $Ru(NH_3)_6Cl_3$ were obtained by using cyclic voltammetery (CV) and chronoamperometry (CA) with a Pt microdisk as a function of temperature in aqueous, 25% core, 25% core-shell microgel solution systems. These diffusion coefficient values were used to explain the solvent release from polymeric network of microgels and electrostatic interactions between microgles and electroactive probes.

Experimental

Materials

All chemicals were obtained from Sigma Aldrich unless otherwise stated. *N*-Isopropylacrylamide (NIPAm) was recrystallized from hexane (J. T. Baker) prior to use. *N,N′*-Methylenebis(acrylamide) (BIS), ammonium persulfate (APS), anhydrous acrylic acid (AAc; Fluka), $Fc(MeOH)_2$, $Ru(NH_3)_6Cl_3$, lithium chlorate ($LiClO_4$), sodium dodecyl sulfate(SDS) were used as-received from Sigma.

Core and Core-Shell Microgel Synthesis and Characterization

Synthesis of the pNIPAm core: pNIPAm core microgel particles were prepared via free radical polymerization using the method reported by Daoji Gan et al [28]. Polymerization was performed in a 500 mL reaction vessel equipped with a mechanical stirrer, reflux condenser, thermometer, and N_2 gas inlet. 0.5665 g (88.7 %) of NIPAM, 0.0193 g (3.0 %) of BIS, 0.0242 g (3.8 %) of SDS were dissolved in 74 mL of water and this solution heated to 70°C while being purged with nitrogen gas and stirred vigorously for about 1 h. After 1 h, polymerization was initiated with 0.0288 g (4.5 %) of APS dissolved in 1 mL of water. This continued for 4 h under a nitrogen stream. Following synthesis, the particles were purified by centrifuging the particle solution.

Synthesis of the pNIPAm core / AAc Shell: The first batch of microgel particles (core) served as the nuclei in a second stage of polymerization for shell addition. Here, 5 mL of crude microgel core and SDS (0.007g) was dissolved in 15 mL of water and heated to 70°C with stirring under nitrogen gas stream. 0.048 g of AAc and 0.0017 g of BIS were dissolved in 5 mL of water, degassed under nitrogen and added to crude microgel core solution. This solution was kept at 70°C under a stream of nitrogen. Polymerization was then initiated by the addition of 0.0009 g of APS dissolved in 1 mL of water and carried out for 5 h for polymerization. Ciszkowska *et.al.* has successfully characterized such a system before demonstrating that the acrylic monomer is successfully bonded to the core [29]. The core-shell hydrogel was subjected to seven centrifugation cycles (1hr/cycle) at 22000 RPM to minimize the presence of any monomer that may distort the result of the experiment.

Electrochemical measurements: Voltammetric measurements were carried out in a jacketed glass cell by using CHI potentiostat and controlled via a personal computer with a three electrode system consisting of an Ag/AgCl reference electrode, a Pt wire as counter electrode, and Pt microdisk as working electrode (radius of 10.0 μm). The average current signal from at least 5 measurements was used to calculate the corresponding diffusion coefficient at scan rate of 100 mV/s. The chrono-amperometric parameters were as follows: $E_{\text{initial}} = -0.2$, $E_{\text{final}} = +0.4$ for $Fc(MeOH)_2$, $E_{\text{initial}} = -0.4$, $E_{\text{final}} = +0.2$ for $Ru(NH_3)_6Cl_3$. For 25% core and core-shell microgels solution systems, 1.5 mL of $Fc(MeOH)_2$ solution (2.0 mM) with 0.1M $LiClO_4$ as the supporting electrolyte was added to 0.5 mL of 10 %(v/v) core or core-shell microgel solution, and 1.5 mL of $Ru(NH_3)_6Cl_3$ (2.0 mM) solution with 0.1M NaCl as the supporting electrolyte was added to a 0.5 mL aqueous 10 %(v/v) core or core-shell microgel.

Dynamic light scattering (DLS) :The thermoresponsive behavior of the microgels used in this investigation was confirmed by DLS (Protein Solutions, Inc.) in the 10 mM solutions in pH 3.0, and 6.5 buffer systems (formate and phosphate) from temperatures 25°C to 40°C.

Results and Discussions

Figures 1 (a) and (b) show typical phase transition behavior of core microgels in pH = 7.0 buffer solution and core-shell microgels in pH = 3.0 and pH = 6.5 buffer solutions as a function of temperature. From the data shown in Figure 1(a), it was deduced that the core microgels have an average R_h of 103 nm at 25°C which decreases significantly at the lower critical solution temperature (LCST) of 32°C. Figure 1(b) shows a comparison of hydrodynamic radii of core- shell microgels in pH = 3.0 and pH = 6.5 buffer solutions over the temperature range of 25°C to 40°C. The core-shell microgels have an average radii of 110 nm at acidic pH values below the pKa of acrylic acid (pKa = 4.25). Therefore, the shell AAc groups are almost fully protonated and make hydrogen bonds between the hydrophilic group and water. When the temperature is increased above the LCST, these hydrogen bonds are weakened requiring water molecules to diffuse out resulting in a reduction in radii of the particles. In contrast, at pH =6, the hydrodynamic radii of microgels undergo only small changes in radii because of coulombic repulsion between carboxylate anions as the temperature is scanned from 25°C to 40°C.

The representative voltammograms for the core system obtained in the swollen and shrunken states at approximately neutral pH are shown in Figure 2. Additionally, Figure 3 shows the temperature dependence of the diffusion coefficients of $Fc(MeOH)_2$ and $Ru(NH_3)_6Cl_3$ in core, core-shell microgel and aqueous solution. The diffusion coefficient D, of an electroactive probe was obtained from the following equation at microelectrode [30]: $D= I_s/4nFCr_d$ where, I_s is the diffusion limited steady state current at a disk microelectrode as shown in Figure 2, C is the concentration of an electroactive probe, r_d is the radius of the microelectrode, n is the number of

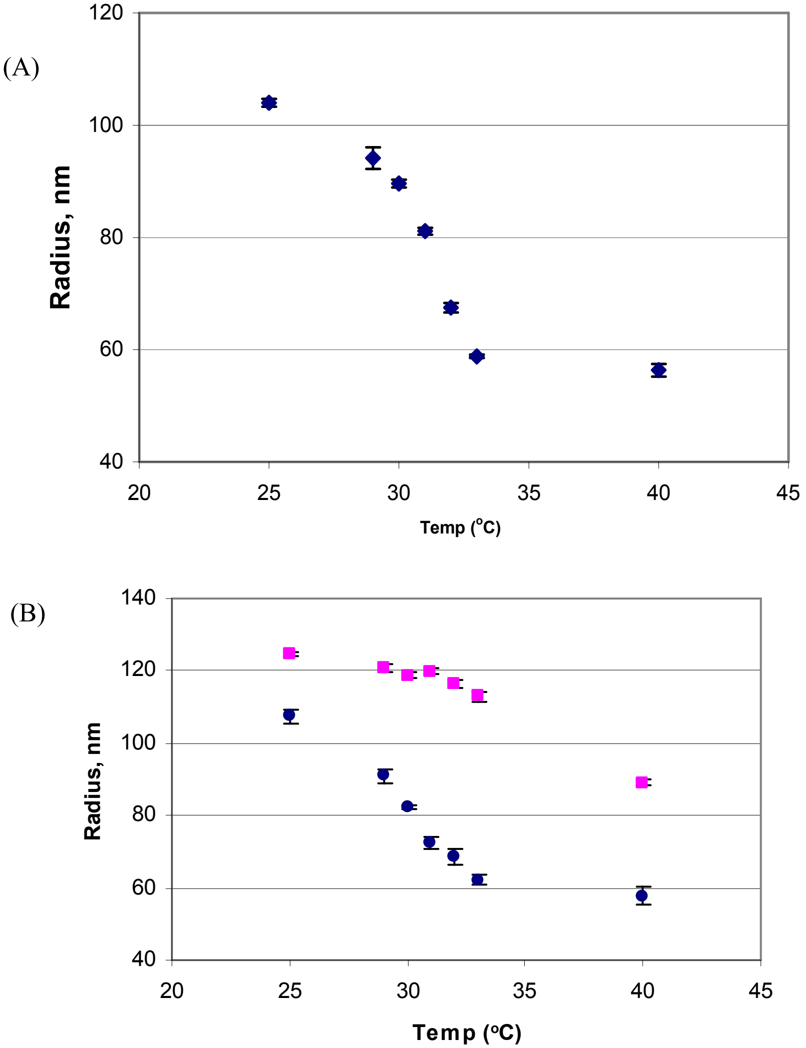

Figure 1. Volume phase change curves taken from photon correlation spectroscopy for the core microgels at pH 7 (a) and core /shell microgels (b) at pH 3.0 (circles) and pH6.5 (squares). Error bars represent standard deviation over an average of five measurements.

electron transferred, and F is the Faraday constant. The corresponding diffusion coefficients calculated from an averaged current (n = 5) and concentrations of electroactive probes ($[Fc(MeOH)_2]$ = 2.0 mM, $[Ru(NH_3)_6Cl_3\ ]$ = 2.0 mM). As shown, the diffusion coefficients of $Fc(MeOH)_2$ and $Ru(NH_3)_6Cl_3$ increased with a temperature in aqueous solutions. Also, the diffusion coefficient of uncharged $Fc(MeOH)_2$ probe increased in core, core-shell microgels solutions with 0.1 M $LiClO_4$ as temperature increased. The diffusion coefficients of $Fc(MeOH)_2$ with microgel solution systems calculated from averaged currents and concentration of $Fc(MeOH)_2$ are close in value to those obtained in the aqueous system as shown on Table 1. The transformation that takes place at the LCST was expected to yield a denser network,

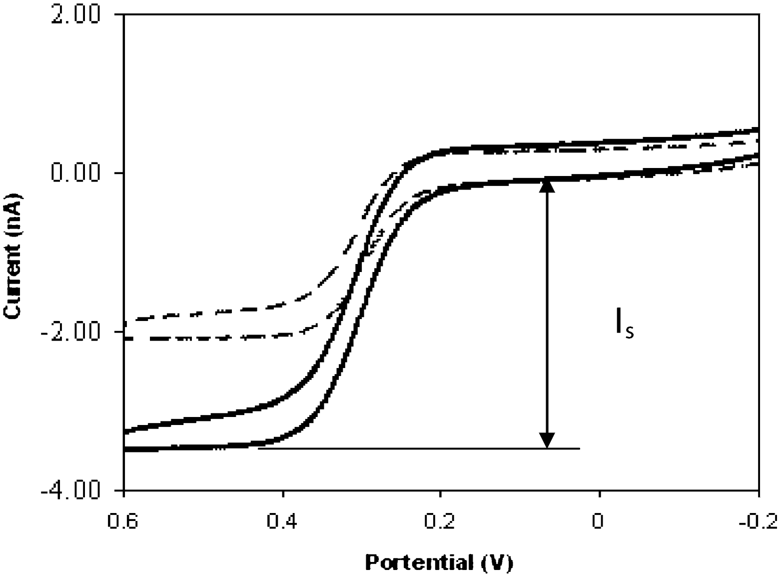

Figure 2. Cyclic Votammogram of the oxidation of 2 mM $Fc(MeOH)_2$ in core microgel solution system at 25°C (----) and 50°C (——).

which would be characterized by a decrease in diffusion coefficient. In contrast, the data suggested that the permeability of the thin film increases with temperature both below and above the LCST. Since $Fc(MeOH)_2$ has no electrostatic interaction with the microgel, the increase in permeability may be due not to the reduction in the size of the microgel, but instead, the newly acquired shape of the gel. Since the study was conducted with a micro-electrode another possibility is that the increase in the density of the microgel was not significant enough to impede the rate of movement of the probe towards the relatively small electrode surface. In figure 3(b), the diffusion coefficients of the positively charged $Ru(NH_3)_6Cl_3$ probe dropped significantly about the LCST of microgels. As seen in Table 1, the diffusion coefficient just above LCST temperature in core system is about 50% smaller than that at 25°C. The diffusion coefficient just above the LCST temperature in core-shell system is decreased by 75% of that at 25°C. The observed decrease of the diffusion coefficient in the microgels above LCST temperature can be due to strong electrostatic interaction between positively charged $Ru(NH_3)_6^{3+}$ and collapsed polyanionic microgels. The diffusion coefficient of $Ru(NH_3)_6Cl_3$ in the core-shell microgel solution decreased more than in the core microgel solution because of high total charge density in core-shell microgel. As a result, the diffusion movement of $Ru(NH_3)_6^{3+}$ in this system is slowed by electrostatic interactions.

Chronoamperometry (CA) was applied to measure the diffusion coefficient of electroactive probes in core, core-shell microgel and aqueous solutions because CA is independent of concentration (unlike CV). This is ideal since an accurate determination of the concentration of the probe in the microgel system is not necessary in order to conduct exact diffusion coefficient analysis as is warranted by CV (29). The diffusion coefficients can be obtained from the slope of I_t / I_s versus $t^{-1/2}$, based on chronoamperometric equation [31]: $I_t/I_s = 1+ (2\ r_d/\ D^{1/2}\ t^{1/2}\ \pi^{\ 3/2})$, where I_t is

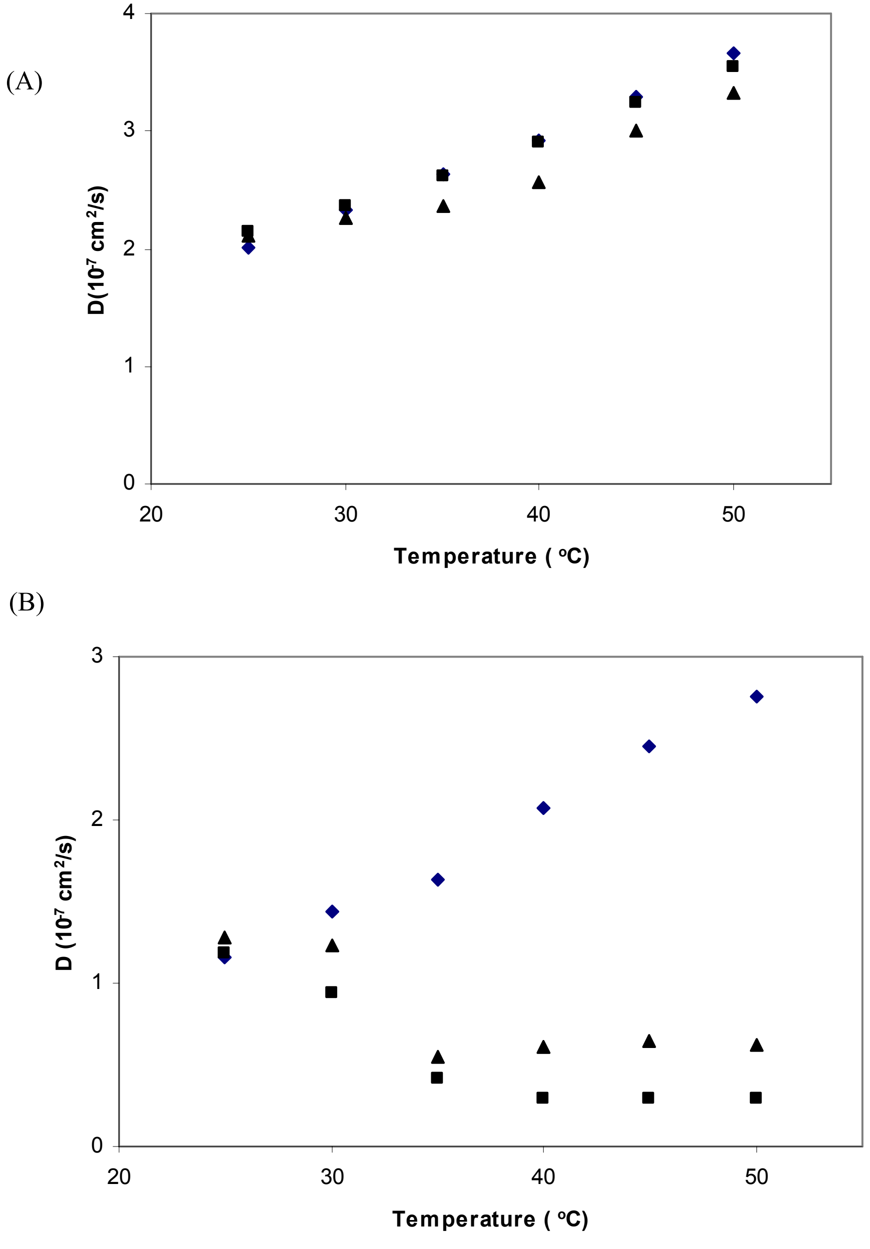

Figure 3. Temperature dependence of the diffusion coefficients of a) $Fc(MeOH)_2$ in aqueous(♦), core microgel solution system (■), and core/shell microgel solution system (▲), b) $Ru(NH_3)_6Cl_3$ in aqueous (♦), core microgel solution system (■) , and core/shell microgel solution system(▲) measured by CV.

the current at the time t, I_s is the steady state current similar to that obtained from the CV acquired at scan rate of 100 mV/s. Figure 4 shows the transition current I_t as a function of $t^{-1/2}$. The diffusion coefficients of the electroactive probes obtained using

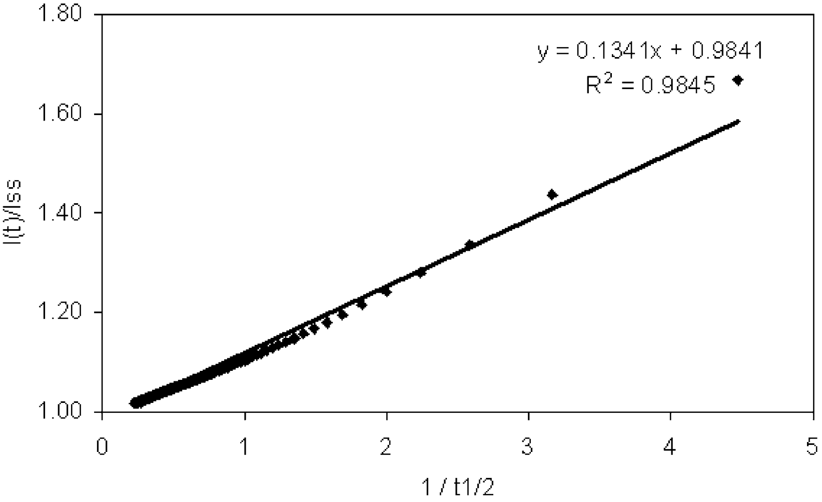

Figure 4. Plot of the experimental I_t/I_s vs t-1/2 for oxidation of $Fc(MeOH)_2$ in core/shell microgel at 25°C.

Table 1. Temperature dependence of the diffusion coefficients of $Fc(MeOH)_2$ and $Ru(NH_3)_6Cl_3$ by CV. (The diffusion coefficients (cm/s^2) were calculated by using the average of five time CV measurements.)

	$Fc(MeOH)_2$			$Ru(NH_3)_6Cl_3$		
	Aqueous	25% core	25% core-shell	Aqueous	25% core	25% core-shell
25	2.02 x10^{-7}	2.15 x10^{-7}	2.10 x10^{-7}	1.16 x10^{-7}	1.28 x10^{-7}	1.18 x10^{-7}
30	2.33 x10^{-7}	2.36 x10^{-7}	2.26 x10^{-7}	1.44 x10^{-7}	1.23 x10^{-7}	0.94 x10^{-7}
35	2.64 x10^{-7}	2.62 x10^{-7}	2.36 x10^{-7}	1.64 x10^{-7}	0.54 x10^{-7}	0.41 x10^{-7}
40	2.91 x10^{-7}	2.90 x10^{-7}	2.57 x10^{-7}	2.07 x10^{-7}	0.61 x10^{-7}	0.30 x10^{-7}
45	3.29 x10^{-7}	3.23 x10^{-7}	3.01 x10^{-7}	2.45 x10^{-7}	0.64 x10^{-7}	0.29 x10^{-7}
50	3.66 x10^{-7}	3.55 x10^{-7}	3.32 x10^{-7}	2.75 x10^{-7}	0.62 x10^{-7}	0.29 x10^{-7}

Table 2. Temperature dependence of the diffusion coefficients of $Fc(MeOH)_2$ and $Ru(NH_3)_6Cl_3$ by CA. (The diffusion coefficients (cm/s^2) were calculated by using the average of five time CA measurements.)

	$Fc(MeOH)_2$			$Ru(NH_3)_6Cl_3$		
	Aqueous	25% core	25% core-shell	Aqueous	25% core	25% core-shell
25	1.24x10^{-7}	1.29x10^{-7}	8.68x10^{-8}	2.28x10^{-8}	6.27x10^{-8}	6.50x10^{-8}
30	1.67x10^{-7}	1.31x10^{-7}	9.39x10^{-8}	4.15x10^{-8}	7.80x10^{-8}	7.80x10^{-8}
35	1.96x10^{-7}	1.52x10^{-7}	9.14x10^{-8}	5.69x10^{-8}	1.60x10^{-8}	7.53x10^{-9}
40	1.82x10^{-7}	1.68x10^{-7}	1.03x10^{-7}	6.07x10^{-8}	1.94x10^{-8}	3.91x10^{-9}
45	2.05x10^{-7}	1.62x10^{-7}	1.38x10^{-7}	1.19x10^{-7}	1.90x10^{-8}	3.43x10^{-9}
50	2.07x10^{-7}	1.58x10^{-7}	1.55x10^{-7}	1.17x10^{-7}	1.63x10^{-8}	3.17x10^{-9}

CV and CA are summarized in tables 1 and 2, respectively. The diffusion coefficients of $Fc(MeOH)_2$ increased with an increase in temperature from 25°C to 50°C in core, core-shell microgel and aqueous solutions. The diffusion coefficients of $Fc(MeOH)_2$ in core, core-shell microgel systems are 24% and 25 % smaller then that in aqueous solution system at 50°C, respectively. These reductions in diffusion coefficients results from the higher density of both core and core-shell system compared to the aqueous solution. When the positively charged probe was used, the diffusion coefficients of $Ru(NH_3)_6^{3+}$ increased as temperature increased in aqueous solution, but sharply decreased in the core and core-shell microgel solution systems. These results are consistent with those obtained from CV. The diffusion coefficients of $Ru(NH_3)_6^{3+}$ at 50°C were decreased by 98 % and 96 % of that 25°C in core, core-shell microgels systems, respectively. The observed large decreases of the diffusion coefficients in microgels systems above LCST temperature is due to strong electrostatic interaction as well as release of solvent from polymeric network. Based on the calculated reduction in diffusion coefficient, about 74-71 % of the decrease was be due to electrostatic interaction and 25-24 % due to solvent release of microgels. A comparison of the two electro-analytical methods show that the diffusion coefficients of $Ru(NH_3)_6^{3+}$ obtained from CA above LCST temperature in core, and core-shell system is decreased by 75 % and 90 %, respectively, compared to that of CV. As such, CA may prove a better method for diffusion coefficient measurement in microgel systems because this method is independent of concentration of electroactive probes. For the first time a comparison is been made between the diffusion coefficients in core and core-shell microgels systems.

Conclusions

In this investigation, the core and core-shell microgels were synthesized and the hydrodynamic radii (R_h) of microgels were characterized with dynamic light scattering. The hydrodynamic radii changes were obtained with a function of temperature in buffer solutions. Two electroanalytical methods, CV and CA were used to measure the diffusion coefficients of $Fc(MeOH)_2$ and $Ru(NH_3)_6Cl_3$ in aqueous, core, core/shell microgel solution systems with a platinum microelectrode. The diffusion coefficients of $Ru(NH_3)_6^{3+}$ at 50°C decreased by almost 100 % compared to that at 25°C in both core and core/shell systems. A greater depression was observed in the core/shell system, which may be attributed to the high total charge density associated with this system. Based on the two electroanalytical method, the diffusion coefficients of $Ru(NH_3)_6^{3+}$, obtained via CA above the LCST in core and core/shell systems, diminished by 75 % and 90 % respectively in comparison to the values obtained using cyclic voltammetry. These results show the strong dependence of the transport of counterions in microgel solution system. This indicates that this methodology can be used to study the molecular properties of microgels in terms of charge density. Also, this method may be applied to study the transport properties of electroactive probes in various solvents and biological polyelectrolytes.

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