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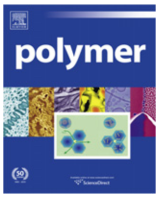

Microstructure and rheological properties of thermo-responsive poly (N-isopropylacrylamide) microgels

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ABSTRACT

The microstructure and rheological properties of thermo-responsive poly(N-isopropylacrylamide) (PNIPAM) microgels cross-linked with methylenebis-acrylamide (BA) were examined by dynamic light scattering and rheological techniques. As the temperature was increased from 10 to 50 °C, the particles diameter decreased by approximately two times near the volume phase transition temperature, T_v of between 30 and 35 °C. The addition of salt to the microgel dispersion provides competition for the water molecules hydrating the PNIPAM chains thus weakening the PNIPAM–H_2O hydrogen bonds and the microgel progressively deswelled. The validity and limitation of the semi-empirical approach to model charged soft microgel particles developed previously were tested on this thermo-responsive system. A variable specific volume, k was introduced to convert the mass concentration to effective volume fraction. With increasing concentration, inter-particle repulsive force was enhanced, which overcame the osmotic force inside the soft particle, resulting in the expulsion of solvent from the swollen particles, and the particle shrank. The viscosity data for PNIPAM microgels at varying solution temperatures and ionic strength showed excellent agreement with the modified Krieger–Dougherty (K–D) model.

1. Introduction

Thermo-responsive colloids based on latex particles are ideal model system in the field of soft condensed matter due to their relatively simple molecular structure and ability to alter their swelling and shrinkage almost reversibly in response to an external temperature. First synthesized by Pelton and co-workers [1], PNIPAM microgel is one of the most frequently studied thermo-responsive systems that possess a lower critical solution temperature (LCST) in water of 32 °C, at which point the microgel reversibly deswells from a fully swollen particle [1–3]. At room temperature, the gels have high water content, a low refractive index difference with water, and small amounts of electrically charged groups on the chain ends. By contrast, at elevated temperatures the particle volume is 10-times less; the density of electrically charged groups is higher and the refractive index difference with water is enhanced [2]. Hence, the effective volume fraction φ_{eff} can be easily controlled by temperature changes while the mass concentration and the particle number density is kept constant. These are attractive features for applications that require 'switchable' or 'intelligent' material responses to environmental stimuli, including drug delivery [4], temperature sensitive optical filters [5] and microreactors [6]. Hoare and Pelton have successfully broadened the applicability of such 'intelligent' microgels by incorporating functional groups such as amines [7] and carboxylic acid [8–11] within the PNIPAM microgel matrix, which has significant impact on the swelling [8] and electrophoretic behaviors.[11] In addition, they developed models to predict both chain and radial functional group distributions and explained key differences in observed microgel swelling according to the different functional group and cross-linker distributions in the functionalized microgels [2–15].

Another characteristic feature that makes PNIPAM microgels extremely important is their capacity to change the flow properties of microgel dispersions by tuning the degree of swelling of the particles [16–21]. At a low degree of swelling, the dispersions are viscous fluids that behave very much like conventional particulate suspensions [16]. At a high degree of swelling, the microgels are in contact and pack into a continuous elastic network that behaves like a weak solid [16,20]. Upon application of a sufficiently high stress, the particles can flow past one another, and the elastic network is disrupted, making the dispersion strongly shear-thinning [6,18].

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This unique property is widely exploited to impart solid-like behavior to formulations that are used extensively in a range of industries, such as coatings, inks, personal care products, and foods [22]. When the concentration is sufficiently high, PNIPAM microgels are good model systems for studying the inverse thermoreversible gelation process from changes in viscoelastic properties, such as the storage modulus G′ and loss modulus G″ since it circumvents several problems, such as chain entanglements and phase separation, normally occurring in a gelling process [23,24].

In the last 15 years, significant progress was made, where theoretical and semi-empirical models were developed and extended to various stimuli responsive microgels including PNIPAM microgels [16–19,25–32]. The major contribution in the field of modeling of thermo-responsive microgels can be attributed to the pioneering work of Ballauff and Richtering [16–20], They reported that the ϕ_{eff} of microgels can be determined using the Batchelor's equation, $\eta_0/\eta_s = 1 + 2.5\phi_{eff} + 5.9\phi_{eff}^2$ at dilute regime, where φ_{eff} is substituted with the term kc [33]. Here η_0 is the viscosity of the suspension and η_s the viscosity of the medium (or solvent), c is the mass concentration and k is the specific volume, which is a constant, and also the only adjustable parameter. The Richtering group also investigated inter-particle interactions in more concentrated dispersions where PNIPAM microgels with differing degrees of cross-linking and particle diameters behaved as hard spheres up to ϕ_{eff} of 0.35 [29]. At higher φ_{eff} values, interpenetration of the less cross-linked outer regions of the microgels and significant particle compression were observed resulting in strong deviation from hard sphere behavior where the plateau modulus, G_P revealed typical soft sphere behavior. Berli and Quemada adopted similar concept and predicted the rheological behavior of dilute and concentrated microgel suspensions on the basis of the effective volume fraction of particles, using the Krieger–Dougherty equation, $\eta_0/\eta_s = (1 - \phi_{eff}/\phi_m)^{-2}$, where ϕ_m is the maximum volume fraction [26,27]. The effective volume fraction of the disperse phase is defined according to $\phi_{eff} = \phi(1 + CS)$ where ϕ is the volume fraction of the swelled particles, C is the "compactness factor" and S is the structural variable [26,27]. In contrast to suspensions of rigid hard spheres, the overall particle size and the distance between the internal polymer networks of PNIPAM microgels decreased with concentration revealing the increasing compression of the spheres as reported by Stieger and Richtering by employing rheology and small-angle neutron scattering (SANS) [29]. Very recently, the same group investigated the phase behavior of charged cross-linked PNIPAM microgesls for a wide range of concentrations using static and dynamic light scattering methods. These microgel dispersions exhibited a short-range liquid order at low concentration (<0.03 wt%), a face centered cubic (FCC) crystalline order at intermediate concentrations (0.03–0.3 wt%) and a possible coexistence of body centered cubic (BCC) and FCC phases at higher concentration (~0.35 wt%) which revealed that the interaction potential between the microgel particles corresponded to the screened Coulomb repulsive type within these concentration ranges. At higher concentration (~0.57 wt%), DLS method confirmed the disordered state of the soft microgel particles to be glassy [34,35].

By evaluating the published data of Ballauff and Richtering, Tan et al. reported that the specific volume, k determined at dilute solution regime could not account for the prevailing physics of soft colloidal particles at moderate to high concentrations. Instead they proposed that k should decrease with increasing concentration until it approached the hard sphere limit, and based on this principle, a variable specific volume, k was introduced to convert c to ϕ_{eff} [30–32]. The values of k were determined from the mathematical fitting of the data to the form of the modified Krieger–Dougherty equation,

$$\eta_0/\eta_s = (1 - kc/\phi_m)^{-[\eta]\phi_m} \tag{1}$$

where the intrinsic viscosity, [η] is 2.5 and maximum volume fraction, ϕ_m is 0.63 for hard spheres [30–32]. The relationship between the specific volume, k and concentration of particles, c can be written as,

$$k - k_{min}/k_0 - k_{min} = \left[1 + (c/c_0)^2\right]^{-m} \tag{2}$$

with k_{min} describes the limiting condition when the soft particles are compressed to the hard sphere equivalent volume at high concentration. The constant c_0 denotes the critical concentration at which the concentration of free counter-ions in the solution is large enough to induce an osmotic deswelling of the soft particle, resulting in a smaller k. The decrease in k with particle concentration is described by the parameter m, which can also be obtained from the slope of the $k - k_{min}/k_0 - k_{min}$ versus c curve on a log–log plot. Depending on the nature of soft particles and surrounding environment, the rate of reduction in k with volume fraction varies. Eq. (2) permits the determination of k, once the parameters c_0, m, and k_0 are known for a given system. The ϕ_{eff} of microgels at various particle concentrations can be determined from Eq. (3) by substituting Eq. (2) into $\phi_{eff} = k\ c$,

$$\phi_{eff} = k_{min} + (k_0 - k_{min})\left[1 + (c/c_0)^2\right]^{-m} {*c} \tag{3}$$

where this expression corrects for changes in the volume fraction of soft particles to that of equivalent hard sphere. Tan et al. observed excellent agreement with the modified K–D model, $\eta_0/\eta_s = (1 - \phi/\phi_m)^{-[\eta]\phi_m}$ for moderate to high volume fraction, where a master curve was obtained when the viscosity data of methacrylic acid-co-ethyl acrylate (MAA-EA) microgels were plotted using the modified ϕ_{eff} determined from Eq. (3) [30,31]. This strongly suggests that the semi-empirical approach is appropriate for understanding the rheological behavior of soft, deformable particles. Moreover, Eq. (1) can be used to predict the relative viscosities of concentrated aqueous microgel solutions by taking account of the corrected volume fraction (Eq. (3)) due to particle compression.

In this present study, we examined the validity and limitation of the semi-empirical approach on a different soft particulate system, i.e. stable dispersions of thermo-responsive PNIPAM-based microgels that possess negatively charged groups at the surface arising from the initiators during the polymerization process. The PNIPAM system was colloidally stable at elevated temperatures in contrast to conventional uncharged PNIPAM microgel particles that flocculate at temperatures above the volume phase transition [36]. Such systems are excellent soft particle models since the particle size (hence the volume fraction) can be readily controlled by temperature. We manipulated the characteristics of particles and their corresponding interaction potential by varying the solution temperature and ionic strength of the solvent environment.

2. Experiment

2.1. Materials

NIPAM (Kodak) was purified by recrystallization from toluene, hexane mixtures. BA was recrystallized from methanol. Potassium persulfate, KPS (BDH, analytical grade) and sodium dodecyl sulfate (SDS) (Aldrich) were used without further purification. All solutions were made with water obtained from Milli Q (Millipore Corp.) treatment of distilled water.

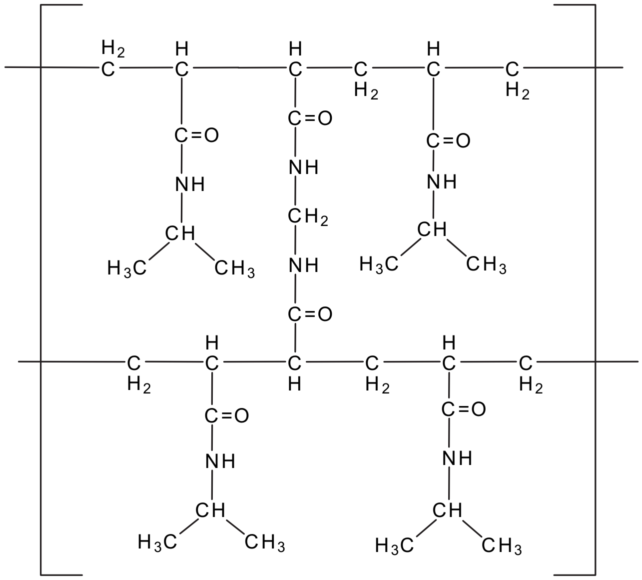

Fig. 1. Chemical structure of model thermo-responsive poly(N-isopropylacrylamide) (PNIPAM) microgel cross-linked with methylenebis-acrylamide (BA).

2.2. *Polymer synthesis*

Stable aqueous colloidal dispersions of cross-linked PNIPAM were prepared as previously reported using aqueous dispersion copolymerization of NIPAM and BA in the presence of SDS [36]. The reaction was conducted in a 1-L glass polymerization reactor fitted with a condenser, a glass stirring rod with a Teflon paddle, a reflux condenser and a nitrogen bubbling tube. The reactor was immersed in a water bath set at 70 °C. In a typical experiment 470 ml of Milli Q water, 7 g NIPAM, 0.7 g BA and 0.094 g SDS were added to the reactor. The solution was stirred at 200 rpm for 30 min with a nitrogen purge to remove oxygen. Initiator, KPS (0.28 g) dissolved in 30 ml water was added and the reaction was stirred for 4 h. The solid product was cooled and filtered through a 200-mesh nylon cloth and the final solid content was approximately 10% by weight.

Latexes were purified to remove SDS and other impurities by four successive centrifugations (Beckman L7 Ultracentrifuge, 10 000–50 000 rpm for 60 min), decantations and dispersions in Milli Q water. The conductivity of the fourth supernatant was typically 2 μS/cm. The chemical structure of the cross-linked PNIPAM microgel is schematically shown in Fig. 1.

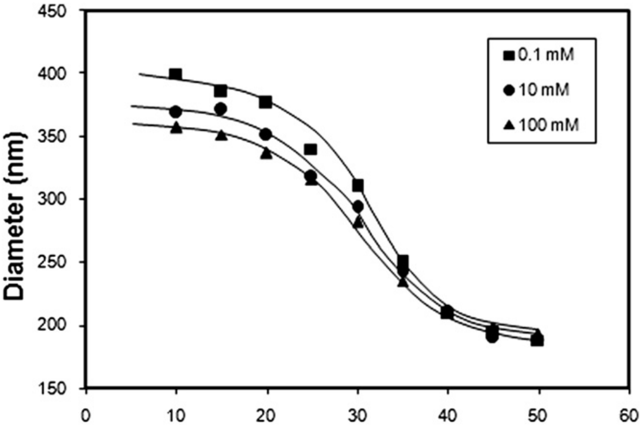

Fig. 2. Dependence of diameter on temperature for cross-linked PNIPAM microgels in three different concentrations of NaCl solutions, i.e. 0.1 mM, 10 mM and 100 mM.

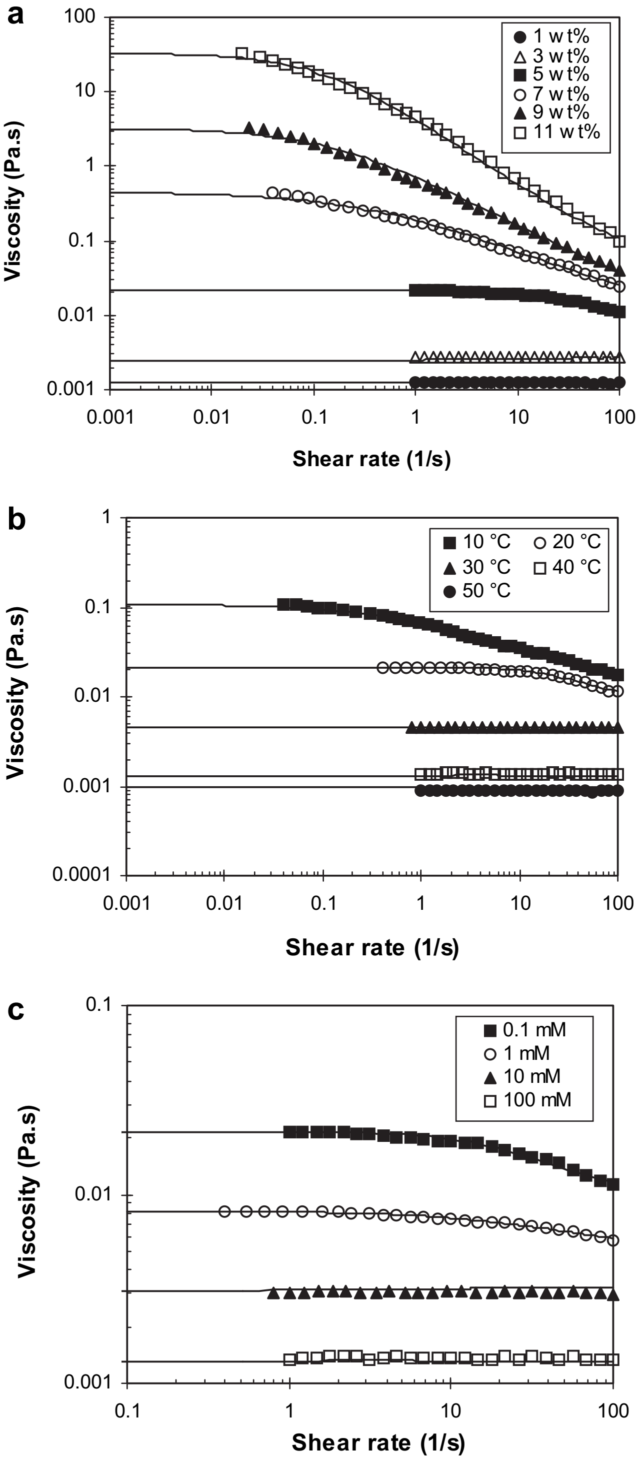

Fig. 3. Viscosity versus shear rate of model PNIPAM particles at three different conditions; (a) varying concentration (wt%) of microgel particles in 0.1 mM NaCl and solution temperature of 25 °C (b) 5 wt% microgel particles in 0.1 mM NaCl at varying solution temperature and (c) 5 wt% microgel particles in varying salt concentration (mM NaCl) and solution temperature of 25 °C. The solid lines denote mathematical fittings according to Eq. (4).

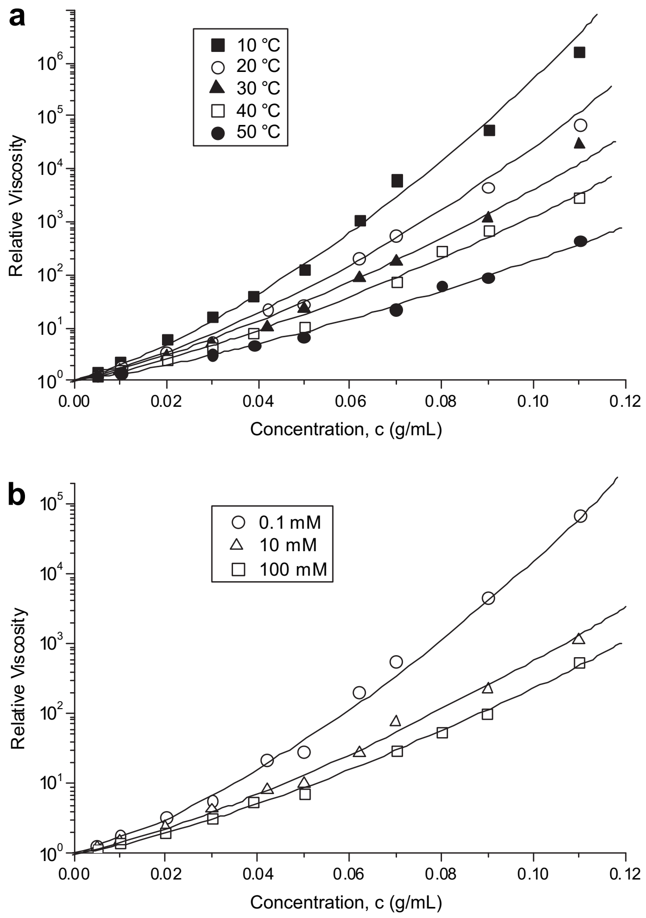

Fig. 4. Relative viscosity versus concentration of microgel particles at two different conditions; (a) varying solution temperature and (b) varying salt concentration (mM NaCl). The solid lines are to guide the eye.

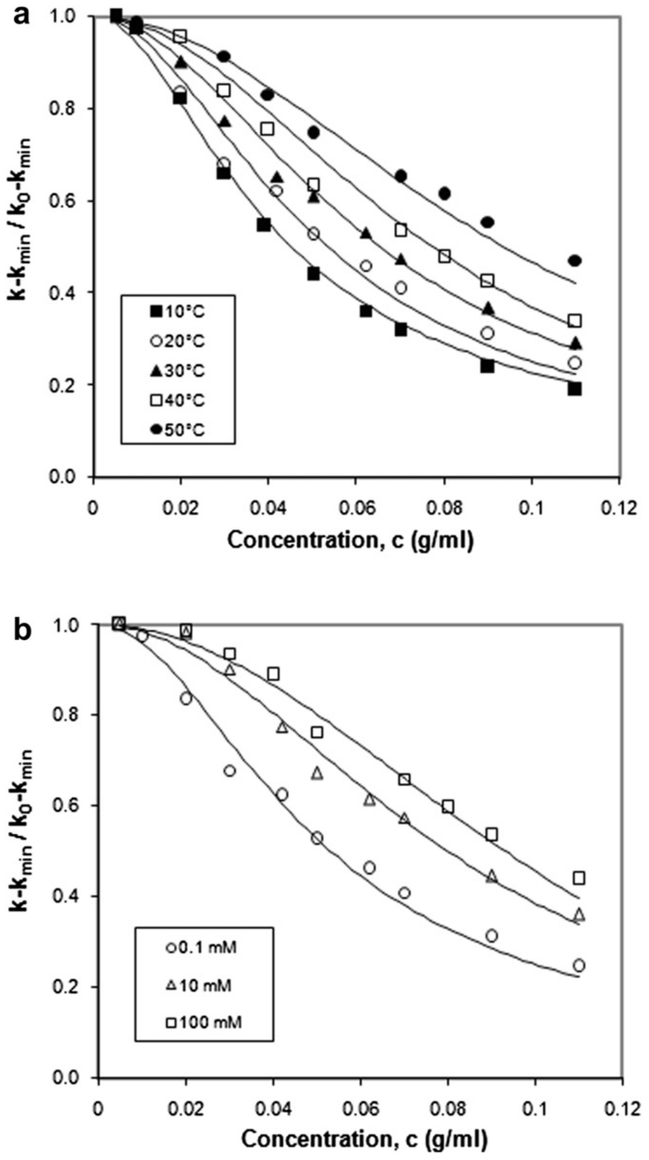

Fig. 5. Specific volume, k as a function of concentration of PNIPAM particles at two different conditions; (a) varying solution temperature and (b) varying salt concentration (mM NaCl). The solid lines denote mathematical fittings according to Eq. (2).

2.3. *Physical characterization*

Rheological studies of semi-dilute to concentrated solutions were carried out using the Carri-Med CSL500 controlled-stress rheometer and Contraves LS40 controlled rate rheometer. Cone and plates with (40 mm, 2°), cup and bob geometry were employed to measure high and low viscosity solutions respectively. All experiments were conducted under the temperature of 25 ± 0.1 °C, and at other preset temperatures ranging from 10 to 50 °C. The steady shear viscosity measurements were performed under equilibrium viscosity conditions.

The particle size of 0.1 wt% PNIPAM latex as a function of temperature was determined by dynamic light scattering (DLS) using a fixed angle NICOMP 370 sub-micrometer particle sizer (Pacific Scientific). The sample was allowed to equilibrate until the desired temperature was reached before the data were sampled. Intensity averaged particle sizes are reported based on Gaussian analysis using Version 3.70 of the NICOMP software.

3. Results and discussion

3.1. *Swelling and rheological behavior*

The PNIPAM particles were characterized in 0.1 wt% solution using the DLS system for temperatures ranging from 10 to 50 °C and in salt concentration ranging from 0.1 to 100 mM NaCl. As illustrated in Fig. 2, the latex particles were swollen with water at 10 °C in 0.1 mM NaCl solution. As the temperature was increased, the particle diameter decreased from an initial size of 400 nm to approximately 190 nm at 50 °C. Over this temperature range, the average particle diameter decreased by about 2 times, which represents an effective volume change of 8 times. The greatest change in diameter occurred at the volume phase transition temperature, T_v which was in the temperature range of 30–35 °C. Above 40 °C, the diameter decreased more slowly with increasing temperature as the particles were already in the collapsed state.

Swelling was reduced when salt concentration was increased as depicted in Fig. 2. When [NaCl] was increased from 0.1 to 100 mM, the diameter decreased from ∼400 to ∼360 nm at 10 °C. The swelling behavior of microgels in all the three salt concentrations was identical, where the particle diameter decreased with increasing temperature and the greatest change in diameter occurred at T_v. Studies by Saunders and Vincent have shown that the addition of NaCl to the continuous phase caused deswelling of

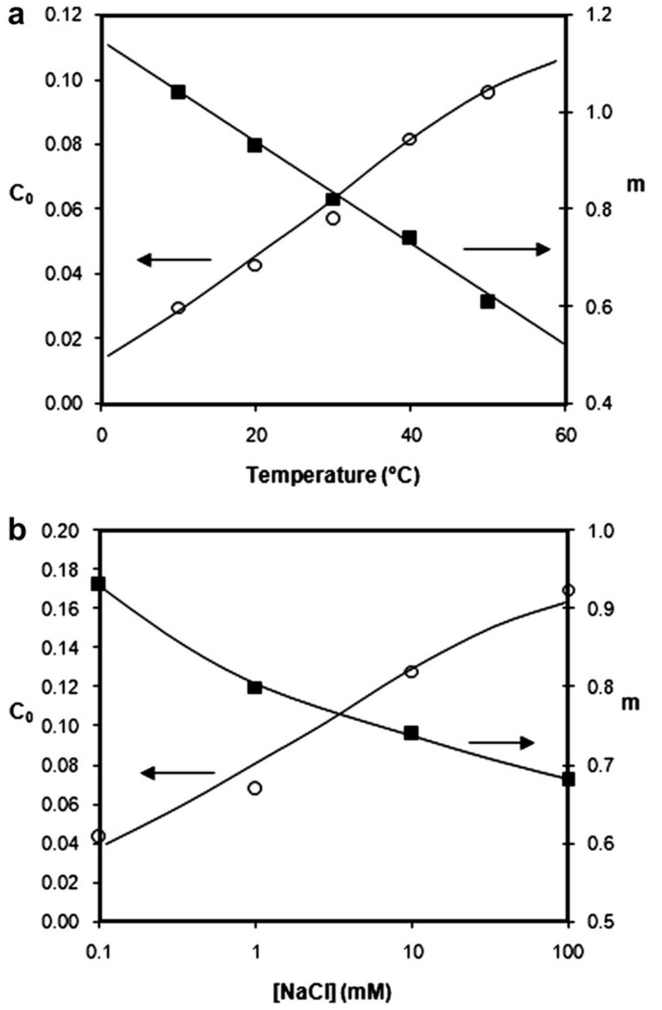

Fig. 6. c_0 (open symbol) and m (filled symbol) of PNIPAM particles as a function of (a) temperature and (b) salt concentration (mM NaCl). The solid lines are to guide the eye.

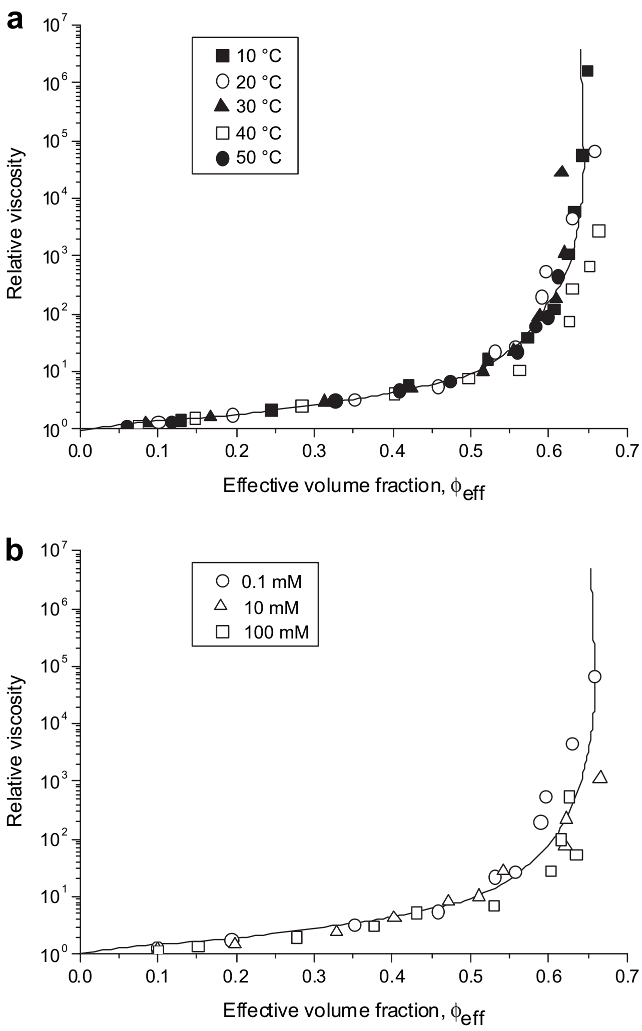

Fig. 7. Relative viscosity versus φ_{eff} of PNIPAM particles at two different conditions; (a) varying solution temperature and (b) varying salt concentration (mM NaCl). The solid lines denote the modified K–D model.

PNIPAM microgels [37–42]. It is well established that the hydration of PNIPAM results from the formation of cage-like water structures surrounding the hydrophobic groups of the polymer to produce stable structures at room temperature. As the temperature and electrolyte concentration increased, PNIPAM–H_2O hydrogen bonds decreased, the hydrophobic interactions became dominant and the microgel progressively deswelled [39–42]. The thermal energy (entropic contribution) eventually overcame the favorable enthalpy changes associated with the formation of hydrogen bonds between polymer and solvent. Furthermore, the addition of salt to the dispersion provided competition for the water molecules hydrating the PNIPAM chains [39–42].

Fig. 3(a) to (c) display the flow properties of the PNIPAM particles at three different conditions, namely; (a) varying particle concentration, c (wt%); (b) varying solution temperature and (c) varying salt concentration [NaCl]. At low c, high temperature (>30 °C) and high salt environment, the samples displayed a Newtonian behavior with a low shear viscosity close to that of water. The effective volume of the microgels in solution was small due to insignificant degree of swelling caused by the disruption of PNIPAM–H_2O hydrogen bonds [39], resulting in an almost constant viscosity-shear rate relationship. At high c, (c > 5 wt%), low temperature (<30 °C) and low salt environment, the enhanced osmotic pressure inside the polymeric network caused an increase in the effective volume occupied by the particles. Such increase decreased the inter-particle distance, where the interaction forces between the swollen particles increased sharply, resulting in the observed shear-thinning behavior. When a shear force was applied to the latex dispersion, the particles tend to flow and align themselves in the direction of shear. As the shear force was increased further, more particles were aligned in the shear direction resulting in a drop in the viscosity of the latex (shear-thinning effect) as particles can be deformed more readily by the higher shear stress. As can be seen from Fig. 3, the extent of shear-thinning decreased with decreasing particle concentration, increasing temperature and increasing salt concentration respectively, and became almost independent of shear rate because the equilibrium position of the particles was less perturbed even at high shear rates. The low shear viscosity changed by two orders of magnitude with increasing temperatures, for example microgel at 5 wt% particle concentration in 0.1 mM NaCl possessed a low shear viscosity of ~0.1 Pa s at 10 °C and it decreased to ~ 0.001 Pa s at 50 °C (Fig. 3b). Similar shear rate dependent viscosity behavior has been observed for various thermo-responsive PNIPAM microgel systems [16,17,29]. The low shear rate viscosity plateau, η_0 was determined from a regression fit to the Cross model [43],

$$\eta/\eta_0 = 1/1 + (\kappa\cdot\gamma)^b \tag{4}$$

which is known to provide a good description of the viscosity of colloidal suspension [16–20]. The fits according to Eq. (4) are represented by the solid lines in Fig. 3.

Fig. 4 depicts the low-shear relative viscosity, η_r or η_0/η_s versus the concentration of particles, c for two different systems of PNIPAM microgels, namely; (a) varying temperature; and (b) varying [NaCl]. We observed that the viscosity increased continuously as microgel concentration was increased from 0 to 11 wt%, where PNIPAM particles at 10 °C and 0.1 mM NaCl solution exhibited the largest viscosity increase. At lower temperature and [NaCl], the particles exhibited significantly larger swelling, which reduced the inter-particle distance. Hence, for a fixed microgel concentration, stronger inter-particle interaction was observed with PNIPAM at 10 °C and 0.1 mM NaCl solution compared to PNIPAM at 50 °C and 100 mM NaCl solution.

Here we extended the semi-empirical approach developed previously to predict the viscosity of dilute and concentrated soft particles where the specific volume, k, which describes the volume change of microgel particles, is inversely proportional to volume fraction [30–32]. The values of k were determined from the mathematical fitting of the data to the form of Eq. (1). Figs. 5(a) and (b) show the specific volume, k as a function of concentration of particles, c for two different systems of the PNIPAM microgels, namely; (a) varying temperature; and (b) varying [NaCl]. The solid lines in Fig. 5 denote the mathematical fittings according to Eq. (2) [30–32]. In the dilute solution regime, inter-particle interaction was absent and k was almost a constant. Microgels were highly swollen at low temperature and low [NaCl], thus with increasing concentration, the inter-particle distance between microgels was reduced resulting in stronger inter-particle interaction between the soft particles.[16,30] Increasing inter-particle interactions caused the microgel to shrink, thus exhibiting strong dependence of k on c, where (k/k_0) decreased from 1.0 to 0.2.

Figs. 6(a) and (b) summarize the dependence of c_0 and m at varying temperature and varying [NaCl] respectively of the PNIPAM microgels determined from the mathematical fitting of the data to Eq. (2). When the temperature and [NaCl] were reduced, strong temperature and ionic strength dependence in c_0 and m can be seen which is caused by the swelling of the microgels. The critical concentration, c_0 at which the soft particle began to deswell decreased and the degree of deswelling, m increased, because the enhanced osmotic pressure of the microgels decreased the inter-particle distance resulting in an increase in the interaction forces between the swollen particles. Richtering and co-workers demonstrated that the softness of the microgels was enhanced with increasing volume fraction and strong deviation from the hard sphere behavior occursed [16,29]. In our current investigation, the deviation of our microgel systems from the hard sphere behavior was reflected in the parameters c_0 and m, which agreed well with our previous findings on the ionic strength dependence of flow behavior of pH-responsive microgels [30,31].

The ϕ_{eff} of our model core-shell series at various particle concentrations can be determined from Eq. (3) where this expression corrects for changes in the volume fraction of soft particles to that of equivalent hard sphere. Excellent agreement with the modified K–D model, $\eta_0/\eta_s = (1-\phi/\phi_m)^{-[\eta]\phi_m}$ was observed for moderate to high volume fraction where a common curve was obtained when the viscosity data were plotted using the modified ϕ_{eff} determined from Eq. (3) (Fig. 7(a) and (b)). This strongly suggests that the semi-empirical approach is able to capture the physics of soft PNIPAM particles and the form of Eq. (3) has the capability of predicting the relative viscosity of this microgel system.

Note that we have also demonstrated previously the good agreement between our semi-empirical approach with the modified K–D model for other soft sphere systems, such as the cross-linked anionic and cationic microgels [30–32]. The validity of our semi-empirical approach is further enhanced when tested on these soft thermo-responsive PNIPAM systems.

4. Conclusions

The validity and limitations of the semi-empirical approach to predict the viscosity of dilute and concentrated soft sphere systems were examined for PNIPAM microgels by varying the solution temperature and ionic strength of the solvent environment. Excellent agreement was obtained when the viscosity data was compared with the modified Krieger–Dougherty (K–D) model, where a common master curve was obtained.

Acknowledgements

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