Mechanistic Study of Cationic Dye Interactions with Clay-Polymer Dispersions via Metachromatic Effect, Aggregation, and Surface Charge

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ABSTRACT: Interactions for a series of aqueous dispersions of a clay, Laponite, and nonionic difunctional triblock copolymer, Pluronic L62, with two cationic dyes, crystal violet and brilliant green, are studied using UV–vis spectroscopy, dynamic light scattering (DLS), and electrophoretic mobility (EPM) to better understand the adsorption mechanisms. Different concentrations for clay, 0.1–2.0 g/L, mixed with polymer, 0.125–0.5 g/L to produce an organoclay, were tested with a fixed dye concentration, 2.0×10^{-5} mol/L. The aggregation states of the cationic dyes interacting with the clay–polymer dispersions were characterized by UV–vis absorbance. The dyes changed aggregation states from monomer to dimer and higher aggregate states upon addition to varying Laponite–polymer dispersion concentrations. DLS was used to understand the adsorbed polymer and dye interactions on the clay particle showing longer relaxation times for the largest aggregates observed from UV–vis absorbance. The EPM was used to characterize the surface charge of the clay relative to the polymer–dye interactions, which showed that the surface charge approached zero as the dyes interacted with clay–polymer dispersions. The most significant changes occurred with a reduction in light scattering intensity and longer relaxation decay at 0.1 g/L Laponite and 0.5 g/L Pluronic L62 concentrations in the presence of cationic dyes. The study of the clay–polymer–dye interactions help to better understand and design chemical templates for removal of contaminates in waste-water treatment. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40141.

INTRODUCTION

There are numerous studies that show the biological effects of polycyclic aromatic hydrocarbons (PAHs) which have adverse toxic and mutagenic effects at concentrated levels.[1–4] Therefore, removal of PAHs in water treatment facilities is a growing concern.[5–8] One current avenue to remove organic contaminants, such as PAHs whether in industrial water treatment facilities or consumer product water purification systems is through organoclay composites.[9] Dyes and active pharmaceutical compounds are just some examples of PAHs. Dyes are typically cationic or anionic in nature, while pharmaceuticals are zwitterionic and/or nonionic.

There have been many sorbents studied and used to remove PAHs and two choices to consider in PAH removal are clays and surfactants.[10,11] Clays synergistically interact with surfactants, to give organoclays, which display unique colloidal and rheological properties. Organoclays are known to improve PAH removal compared to just the clay alone.[12,13] The challenges with organoclays include the limited removal efficiency for PAHs, unclear mechanism for removal, and cost.

Laponite has a high aspect ratio, size, and processability. It is in the class of smectites and has two tetrahedral silicates sandwiching one octahedral plate.[14] An advantage of Laponite is its small particle size, ~25 nm long and 1 nm thick. Another advantage of Laponite is its large scale production with precise reproducibility of material for use in a wide range of applications. The processing alone of different clay materials generates variability leading to conclusions that are process dependent. Laponite geometry and size allows for fast equilibrium and kinetics with dye interactions as compared to other smectites.[15]

Clays can be modified with block copolymers of ethylene oxide-propylene oxide (EOPO, commercially available from BASF as Pluronics).[16] The clay–polymer composites display unique thermal and mechanical properties. There are only a few studies that have examined Pluronic adsorption onto clays. Some highlights of these studies include the adsorption of selected pluronics onto saponite, segments of pluronics adsorbed to laponite as a function of molecular weight and geometry, and intercalation of low and medium sized molecular weight
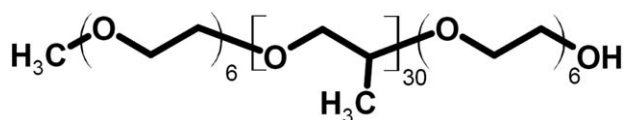
Figure 1. General molecular structure of Pluronic L62.

polyethyleneoxide (PEO) into clays.[16–19] Another study investigated dilute high molecular weight PEO to characterize the adsorbed layer onto Laponite.[20] These studies are fundamental in clay polymer interactions, but dye interactions with the clay–polymers have not been investigated as much.

These dye interactions with clay–polymers can be studied by looking at metachromic effects, light scattering changes, and surface charges. Metachromatic effect is a UV–vis phenomenon that is a departure from Beer's Law where a decrease in absorbance of the dye's monomer (α) band and appearance of newer bands at different wavelengths occurs upon an increase of dye concentration. This is an indication of the formation of different aggregate states present for the dye. This effect can be used to study the mechanism of absorption of dyes with clay–polymer composites.[21,22] Metachromatic effects have been successfully used to semiquantify and detect sub ppm levels of montmorillonite, illite, and kaolinte in aqueous suspension.[23] Metachromasy can also provide insight into designing organoclays with optimal properties for the removal of a wider range of PAHs, i.e. cationic, anionic, zwitterionic, and nonionic PAHs.[24] Some dyes have been studied by displaying metachromasy in an aqueous environment with Laponite.[25] In our studies we expect to see metachromic effects at lower concentrations upon the incorporation of Pluronic L62, since the polymer will adsorb onto the Laponite therefore modifying the aggregation of the dye.

For this work, direct characterization is performed of cationic dye interactions with clay–polymer dispersions. UV–vis absorbance is used to explore the metachromatic effects of crystal violet (CV) and brilliant green (BG) with a series of Laponite-Pluronic L62 dispersions. Dynamic light scattering (DLS) is used to characterize light scattering changes with the clay–polymer–dye interactions. DLS gives insight into the relative size of the dispersion, especially for formation of larger aggregates. Electrophoretic mobility (EPM) gives insight into how the surface charge of the Laponite changes in relation to Pluronic L62 and dye interactions. It is important to tailor the combine clay–polymer surface interactions for dye absorption to define the optimal loading and lead to higher PAHs removal.

EXPERIMENTAL

Materials

The general chemical structure of Pluronic L62 is a difunctional triblock copolymer PEO-polypropyleneoxide (PPO)-PEO with a
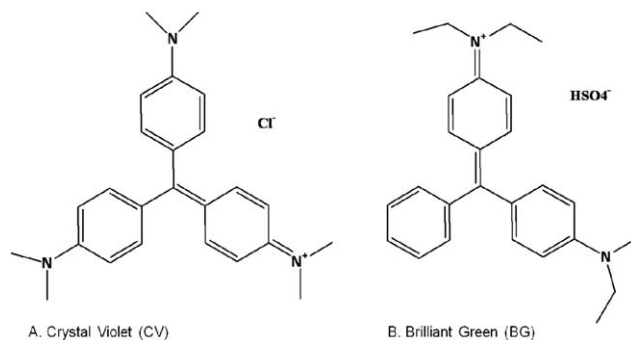

Figure 2. Molecular structure of two dyes used in the study: (A) CV and (B) BG.

M_w of 2500 g/mol (Figure 1). Table I shows some general chemical properties for Pluronic L62. Our measured critical micelle concentration (cmc) for Pluronic L62 in water was 5.6×10^{-4} g/L using a Whilhelmy Plate technique with 500 μL dosimeter (SCAT form Future Digital Scientific, NY). The surface tension for a 0.1% Pluronic L62 dispersion was 44.9 mN/m in deionized water. The cationic dyes CV and BG were from Sigma-Aldrich and the structures are shown in Figure 2. Some physical properties for CV and BG are shown in Table II. The clay used was Laponite XLG (Southern Clay Products), a synthetic 2 : 1 smectite with a particle diameter of approximately 25 nm (Figure 3). Chemical formula, surface area, and critical exchange capacity are given in Table III.

The order of addition for the dispersion is important and the following order was maintained for the dispersion series. First, Laponite XLG was added to deionized water and stirred for 24 h. The series of Laponite concentrations ranged from 0.1 to 2.0 g/L. Next, the appropriate polymer amount was added to the Laponite dispersion and this was allowed to mix for 24 h. Polymer concentrations ranged from 0.125 to 0.5 g/L. Finally, the dye was added and stirred for 24 h. The dye concentrations were 2.0×10^{-5} mol/L. All dispersions were stored from light when not in use and the pH remained at ~9.2 for all the dispersions.

Characterization

The techniques used to directly characterize the absorption mechanisms were UV–vis absorbance (aggregation of the dye onto the organoclay), DLS (particle size of the organoclay and dye), and EPM (surface charge of the organoclay and dye). UV–vis spectroscopy was performed on the dye solutions and dispersions using a MultiSpec 1501 (Shimadzu Corp.) scanning range from 200 to 1000 nm at 25°C. Deionized water was used as the background. DLS and EPM were performed as well for

Table I. Physical Properties of Pluronic L62

Polymer	Molecular weight (g/mol)	Surface tension (mN/m) at 298 K	Cmc (g/L) at 298 K	HLB
Pluronic L62	~2500	43	5.6×10^{-4}	3–7

Table II. Physical Parameters of Crystal Violet and Brilliant Green

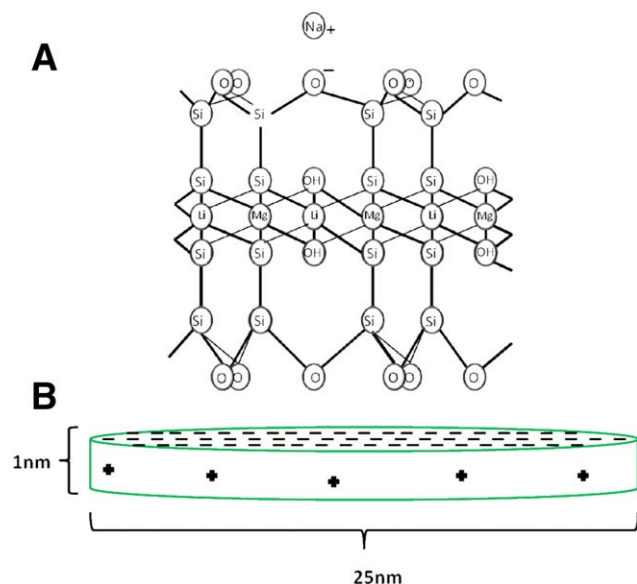| Dye	Chemical formula	MW (g/mol)	Solubility (mg/L)	pK_a	UV–vis (λ_{max}, nm)
Crystal violet	$C_{25}H_{30}N_3Cl$	408.00	10,800	1.6	~590
Brilliant green	$C_{27}H_{33}N_2HO_4S$	482.64	100,000	4.33	~625

Figure 3. A: General chemical structure for Laponite and (B) Laponite dimensions and charge. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the dispersions using a Zeta PALS (PALS Zeta Potential Analyzer Software and 90Plus Particle Size Analyzer Software, Brookhaven Instruments). The angle, temperature, viscosity, dielectric constant, and refractive index of water and Laponite XLG used were 90°, 298K, $\eta = 0.890$ cPs, $\varepsilon = 78.54$ and $n_w = 1.33$, $n_L = 1.44$, respectively, for both DLS and EPM. Sample count rate was adjusted and maintained between 100 and 1000 kcps for DLS and EPM. A total of 10 sample runs for 5 min was used for DLS. A total of 10 sample runs with 30 cycles per run was used for EPM. A wavelength of 660 nm and 600 nm were used for EPM and DLS, respectively.

RESULTS AND DISCUSSION

UV–Vis Spectroscopy

Metachromatic effect is a UV–vis phenomenon that is understood to be a departure from Beer's Law where a decrease in absorbance of the dye's monomer (α) band occurs along with an appearance of bands at different wavelengths upon a change in dye concentration. There are two types of aggregation associated with metachromasy. At lower wavelengths, face-to-face aggregation of the π electrons (H-aggregates) occurs and at higher wavelengths, head-to-tail aggregation (J-aggregates) occurs due to dipole attraction. UV–vis spectroscopy was run for CV and BG in the presence of Laponite only [Figure 4 (A,B)], to further investigate the properties of Laponite and interactions with the dyes. The major absorbance was the α aggregate for both dyes. For CV only [Figure 4(A1) no Laponite, no Pluronic L62], the peak assignments for the monomer (α) and dimer (β) are at 590 and 550 nm, respectively. Higher aggregates (μ) (trimers and tetramers) begin to appear as a broad absorbance maximum near 480 nm as Laponite is added to the dye. This agrees with previously reported values for metachromasy of CV and BG in aqueous solutions.[26,27] The dose response of Laponite (0.1–2.0 g/L) with no Pluronic L62

on the CV absorbance [Figure 4(A)] shows an overall reduction of absorbance with the addition of Laponite to the dye. This is an indication of the strong interaction between the dye and dispersion. At 2.0 g/L of Laponite, the cationic character of CV is electrostatically attracted to the negative silicate surface. All Laponite concentrations have a surface charge density greater than the CV dye concentration. Any shift in absorbance is due to the steric effect from the dye interacting with Laponite. This steric effect shifts the aggregates from α to β and μ aggregates. As the Laponite concentration decreases from 0.25 to 0.1 g/L, the aggregates shift from monomer to dimer and higher aggregates. This can be seen from a reduction in absorbance of the α-aggregate at 590 nm and the appearance of the μ aggregation. This shift can be associated with the flocculation due to the destabilization of the dispersion. When a higher amount of Laponite is added (2.0 g/L), there is also a reduction of the β aggregate for CV. For CV with Laponite, a blue shift from 588 to 581 nm was observed for the α-aggregate. This agrees with CV and Laponite dispersions as reported by others.[25] Another report shows a similar finding with methylene blue (MB) and Laponite RD.[15] The blue shift is a face-to-face aggregation (H-aggregation) for CV adsorbed on Laponite.

Figure 4(B) shows a similar trend of absorbance changes and corresponding aggregate shifts for BG. Initially there is a large monomer (α) peak for BG that gradually decreases then increases with addition of Laponite. Additionally, the absorption maxima shifts as well for BG in the presence of Laponite, showing a red shift from 624 to 631 nm for the α-aggregate. This has been observed as well with Toluidine Blue O (TBO) and Laponite.[24] The red shift indicates head-to-tail aggregation (J-aggregation). The differences between CV (blue shift) and BG (red shift) molecules lie in functional moieties and symmetry. Both CV and BG are triphenyl moieties but CV has three methyl groups symmetrically surrounding N atoms giving it more symmetry compared to BG that has two ethyl groups leading to less symmetry and more steric hindrance. These attributes lead to the differences observed in the presence of Laponite for CV to H-aggregate and BG to J-aggregate.

In Figure 4(C), it is observed that the addition of Pluronic L62 to CV only results in a reduction of absorbance of the monomer but no change into higher aggregates. However in Figure 4(D), for BG, higher amounts of Pluronic L62 shows an increase in absorbance compared to BG alone but no changes in aggregation. For both dyes, this demonstrates that the only interaction of higher order aggregates for CV and BG is from the interactions with the Laponite and Laponite-Pluronic L62 dispersions. Previous reports have shown that Pluronic F-127 does not micellize dyes of TBO and MB at the cmc.[24] This indicates that Pluronics in general do not adversely affect the UV–vis

Table III. Laponite Properties

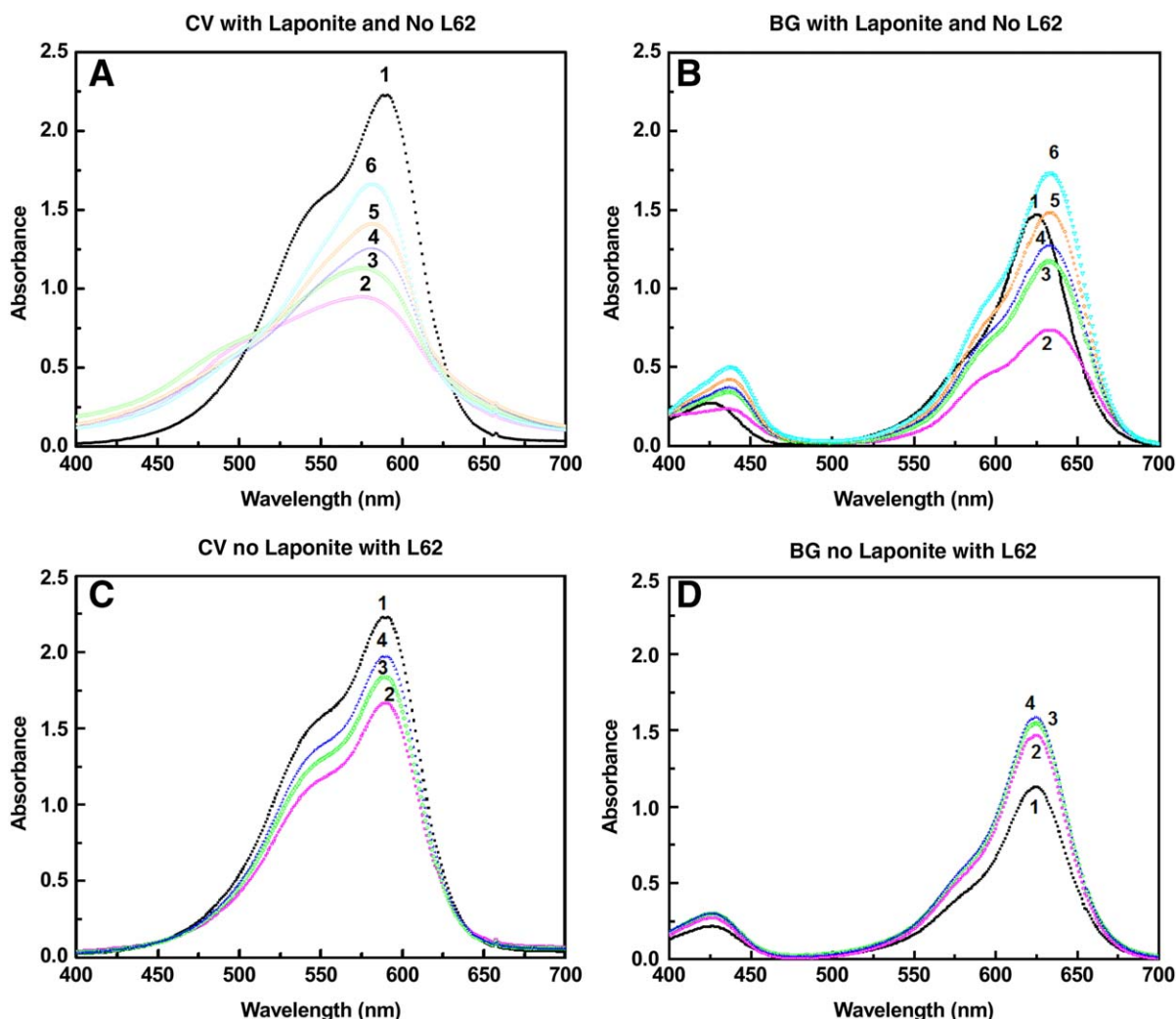| Name	Empirical formula	Surface area (m^2/g)	CEC (meq/100 g)
Laponite	Na$_{0.7}$[(Si$_8$Mg$_{5.5}$Li$_{0.3}$) O$_{20}$(OH)$_4$]$^{-0.7}$	300–450	50–75

Figure 4. UV–vis absorption at 2.0×10^{-5} mol/L of (A) CV and (B) BG with a dose response of Laponite (1, 0 g/L; 2, 0.1 g/L; 3, 0.25 g/L; 4, 0.5 g/L; 5, 1.0 g/L; 6, 2.0 g/L) and no Pluronic L62. C: CV and (D) BG at 2.0×10^{-5} mol/L with dose response of Pluronic L62 (1, 0 g/L; 2, 0.0125 g/L; 3, 0.025 g/L; 4, 0.05 g/L) and no Laponite. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

characteristics of the dyes, i.e. aggregation changes at these concentrations. Change to higher aggregation is due to the interaction with Laponite-Pluronic L62 dispersion.

Figure 5(A) shows that there is no shift from monomer to dimer and higher aggregation for CV with 2.0 g/L of Laponite as the Pluronic L62 concentration increases. Figure 5(B) shows a similar effect for BG, there is no metachromatic effect for BG, only absorbance is affected. However, when the Laponite concentration is decreased there is a shift from monomer to dimer and higher aggregates by a change in wavelength indicating interaction between the dye and Laponite–Pluronic L62 dispersions as illustrated in Figure 5(C,D). More specifically, the CV is beginning to aggregate preferentially within the Laponite–Pluronic L62 dispersion. In Figure 5(C), the increase of Pluronic L62 with the Laponite–Pluronic L62–CV dispersions results in CV forming more β and μ aggregates. Figure 5(C) shows that for CV with 0.1 g/L Laponite with Pluronic L62, there is reduction in absorbance characteristics and change in aggrega-

tion compared to 2.0 g/L Laponite [Figure 5(A)]. A significant shift in structure from α-aggregate as the major absorbance for 0.1 g/L Laponite with no Pluronic L62 to the μ-aggregate occurs with the addition of Pluronic L62. With 0.05 g/L of Pluronic L62 [Figure 5(C), line 4], peptization (formation of a colloidal solution) has occurred since there is an increase in absorbance maxima, an indication that saturation of absorbance has occurred and dispersion restabilizes the suspension.[24,28]

In Figure 5(D), a similar trend is observed with the BG series upon addition of Pluronic L62. Only the β-aggregate is the dominant species observed for BG. In either case for BG or CV with the Laponite-Pluronic L62 dispersion, the spectra show there is a shift from monomeric to larger aggregates. This has also been observed with Pluronic F127-Laponite RD and TBO/MB dispersion.[24] This may indicate that one can achieve a similar absorbance spectra to that of 0.1 g/L Laponite with 0.0125 g/L Pluronic L62 by loading the clay up to 2.0 g/L Laponite with a much higher Pluronic L62 concentration.
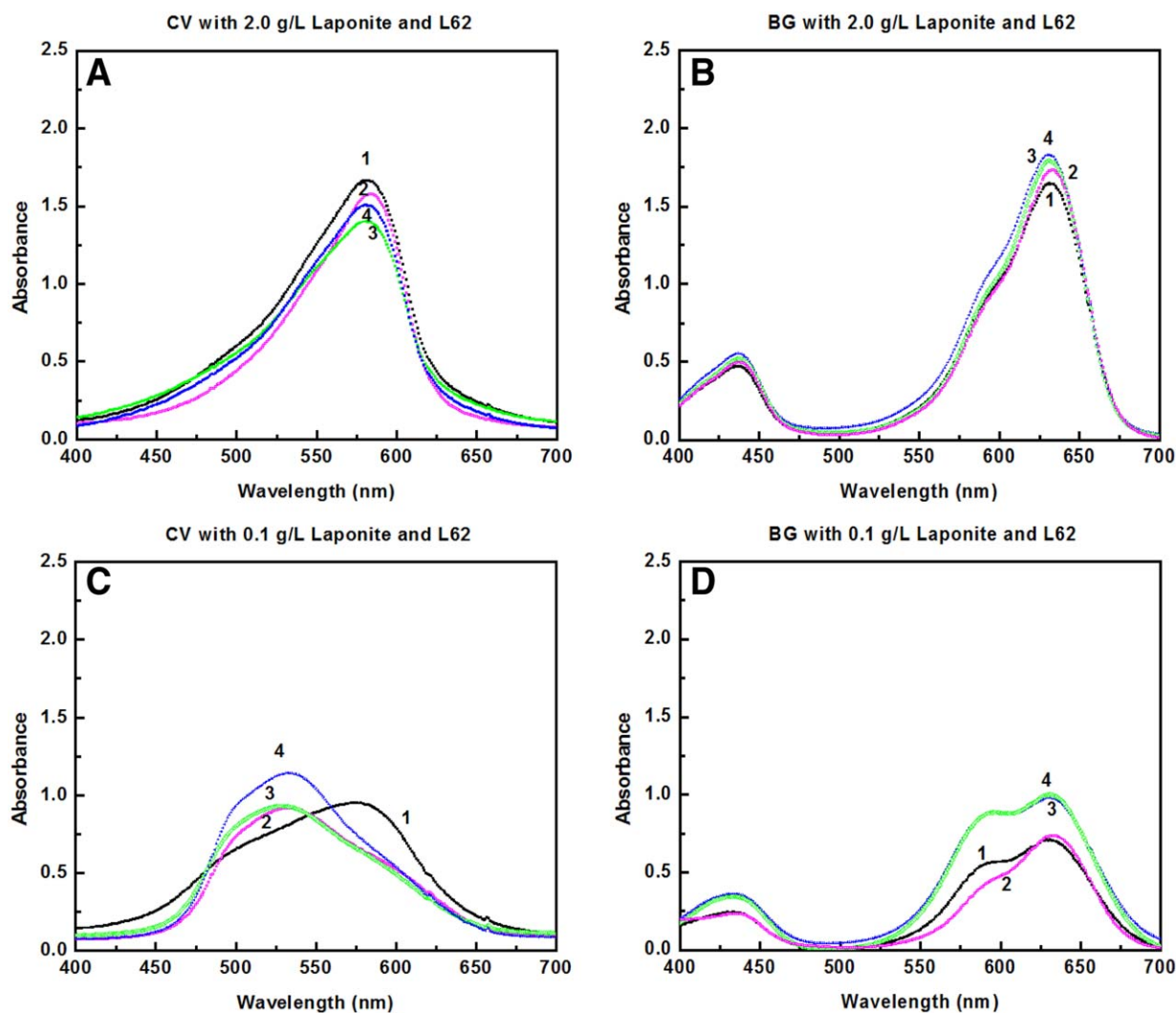
Figure 5. UV–Vis absorption at 2.0×10^{-5} mol/L of (A) CV and (B) BG with 2.0 g/L Laponite at dose response of Pluronic L62 (1, 0 g/L; 2, 0.0125 g/L; 3, 0.025 g/L; 4, 0.05 g/L). C: CV and (D) BG at 2.0×10^{-5} mol/L with 0.1 g/L Laponite at dose response of Pluronic L62 (1, 0 g/L; 2, 0.0125 g/L; 3, 0.025 g/L; 4, 0.05 g/L). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Surface Charge

EPM is used to characterize surface charge of clays in solution. Surface charge of clays changes in the presence of polymers and dyes and aids in understanding the dispersion stability in relation to the charge of the clay.[28–30] For instance, addition of PEO polymers onto Laponite has been characterized for Laponite systems using EPM, small angle neutron scattering (SANS), and rheology.[31,32] Very stable dispersions have strong, or high, charges, either positive or negative. The strong charge stabilizes the particle by resisting aggregation. As the particle approaches zero charge, instability of the particle occurs which leads to coagulation. Commonly, zeta potential (ζ) is calculated from the EPM (μ) determined at a given temperature. In this study, $k\alpha \gg 1$, where k is the Debye–Huckel parameter and α is a calculated particle radius. The Smoluchowski relationship was used:

$$\zeta = \eta\mu/\varepsilon \tag{1}$$

where η is the viscosity of the medium, μ is EPM of the particle, and ε is the dielectric constant of the medium. Laponite is known to have a very negative charge on its surface. In this study, EPM is used to give a more representative value, since these dispersions are not ideal. Figure 6 shows surface charges of the dispersions as a function of Laponite and Pluronic L62 concentration. In Figure 6 the surface charge of the Laponite–CV complex increases with increasing Laponite concentration with no Pluronic L62 as a result of the EPM magnitude of Laponite increasing with Laponite concentration. The stability of the dispersion increases with increasing Laponite concentration. Upon addition of Pluronic L62 the surface charge from the Laponite–CV complex is maintained for each Laponite concentration, showing a stable Laponite–Pluronic L62–CV dispersion is maintained. There is a general trend in surface charge magnitude observed for 1.0 g/L of Laponite with CV as Pluronic L62 increases showing an increase in stability. From DLS and SANS, it is known that Laponite has a small particle size and can be stabilized by PEO polymer and Pluronic adsorption.[32]
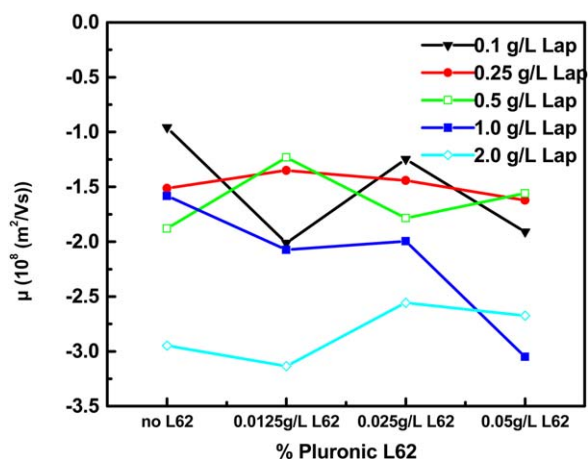
Figure 6. Electrophoretic mobilities for Laponite with CV vs. Pluronic L62 concentration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Dynamic Light Scattering

DLS aids in understanding the interactions of the clay–polymer–dye interactions. DLS characterizes how particles are dispersed in liquids, by the relaxation of scattered light from a spherical particle in a liquid medium, giving a hydrodynamic property. Polymer adsorption of PEOs onto Laponite has been studied to determine hydrodynamic polymer thickness.[20] Since Laponite is not a spherical particle that can generate a true value of particle size with both dye and polymer added, a more valuable approach would be to look at the autocorrelation function relaxation time. For DLS, there are two general points to qualitatively characterize. First, the relaxation time for each dispersion is different for each concentration effect in Laponite and Pluronic L62. In Figure 7(A), as the concentration of Laponite increases the relaxation times generally increase. Quick relaxation times occur for the 0.1 g/L and 0.25 g/L Laponite concentrations with CV. Higher Laponite concentrations have a longer relaxation time. Secondly, differences occur from the
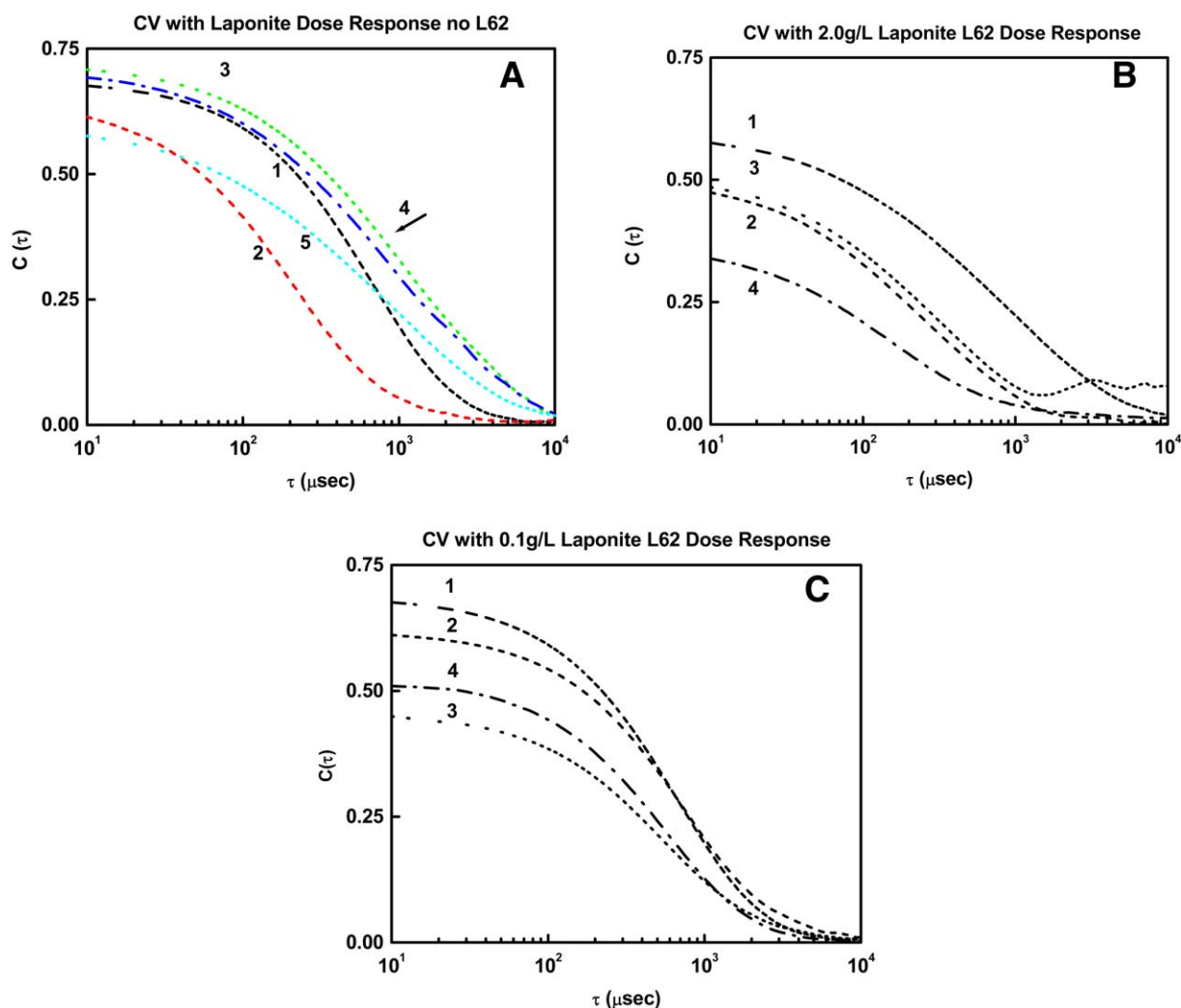

Figure 7. Autocorrelation Functions, $C(\tau)$, of (A) CV at 2.0×10^{-5} mol/L with a dose response of Laponite (1, 0.1 g/L; 2, 0.25 g/L; 3, 0.5 g/L; 4, 1.0 g/L; 5, 2.0 g/L), (B) CV at a concentration of 2.0×10^{-5} mol/L and Laponite at 2.0 g/L with a dose response of Pluronic L62 (1, 0 g/L; 2, 0.0125 g/L; 3, 0.025 g/L; 4, 0.05 g/L) and (C) CV at a concentration of 2.0×10^{-5} mol/L and Laponite at 0.1 g/L with a dose response of Pluronic L62 (1, 0 g/L; 2, 0.0125 g/L; 3, 0.025 g/L; 4, 0.05 g/L). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

shape and curvature of relaxation for the dispersions. For 0.1 g/L and 0.25 g/L Laponite concentrations, the curves are substantially different with a sharper slope as compared to higher concentrations. The slope differences suggest aggregation kinetics between particles are relatively fast, or monodisperse. The ionic character of the dispersion is attributed from the dye. Similar effects have been reported for simple salts.[28] This data suggests that the Laponite concentration below 0.25 g/L with CV do not aggregate. The autocorrelation function measures the change in scattered light intensity, $C(\tau)$. In Figure 7(B), CV with 2.0 g/L Laponite shows an immediate reduction in relaxation above an autocorrelation function of 0.5. As Pluronic L62 content increases, $C(\tau)$ reduces with broad relaxation times due to the formation of large aggregates. In Figure 7(C), for the 0.1 g/L Laponite and L62 dose response, a similar trend is seen where incremental polymer addition reduces $C(\tau)$ intensity and increases relaxation time.

Laponite–Pluronic L62–Dye Interactions

Utilization of UV–vis absorbance, DLS, and EPM helps to understand how to design organoclays with higher loading capacities of PAHs onto clays. The Laponite–Pluronic dispersions maintained its high surface charge while improving its organophilicity. The organophilicity was demonstrated by the dramatic change in UV–vis absorbance of the cationic dyes, monomer to higher order aggregates, with the Laponite–Pluronic dispersions. The dye–laponite–polymer complexes increased in aggregation relative to the laponite–dye and laponite–polymer interaction alone. There was a reduction in charge as the dyes changed from monomer aggregates to higher order aggregates upon higher loading of the Pluronic L62, leading to larger particles observed by DLS and a reduction in surface charge from EPM. The metachromatic effect seen for the dyes was supported by both DLS and EPM in regards to the aggregate states of the dye to the Laponite–Pluronic L62 dispersions.

A mechanism can be proposed for the action of a Laponite–Pluronic L62 system in the removal of cationic dyes from water. Initially, there is the formation of the adsorbate by the interaction of Pluronic L62 with Laponite to increase its organophilicity with minimal change to surface charge. Next the dye loads onto the surface and forms a complex that changes in aggregation of dye–clay–polymer, surface charge of clay and size of complex. This cationic dye interacts with the organophilic surface while the surface charge changes. This dye–clay–polymer interaction is indicated by a change in decay and intensity of the light scattering profile. This interaction leads to the loading impact for removal of the PAH. These techniques can be used to define an optimal range of Pluronic L62 to Laponite for the interaction with a cationic dye that can ultimately lead to higher PAH removal in water treatment.

Additional work is needed to evaluate Pluronic hydrophilic-lipophilic-balance (HLB) ratios with similar molecular weight. This would change the hydrophobicity leading to aggregation and particle size changes with the Laponite-polymer composite. Also work would include how this composite behaves with anionic, zwitterionic, and nonionic PAHs to demonstrate increased PAH sorption onto the composite.

CONCLUSIONS

A relationship was found between the aggregation of the cationic dyes with the surface charge and particle size when Pluronic was included in the Laponite dispersion. The dye changed to larger aggregate forms upon addition to the Laponite–Pluronic dispersion relative to Laponite alone. The surface charge can be tuned by optimizing the polymer content. Surface charge magnitude increased at higher Laponite concentrations. When the polymer content increased, the surface charge magnitude was maintained while increasing organophilicity of nanocomposite. Aggregate size was dependent upon the polymer and clay content with CV and BG as seen from the metachromic shifts in UV–vis. The size of the complex was smallest for the low content Laponite with marginal differences from polymer content. The size of the complex was larger at higher concentrations of Laponite. The results obtained showed that the Laponite Pluronic L62 can be used successfully as an effective sorbent to remove CV and BG from aqueous solution.

REFERENCES

1. Daughton, C.; Ternes, T. *Environ. Health Perspect.* **1999**, *107*, 907.

2. Guo, Y.; Wu, K.; Huo, X.; Xu, X. *J. Environ. Health* **2011**, *73*, 22.

3. Halling-Sorensen, B.; Nielsen, S.; Lanzky, P.; Ingerslev, F.; Lutzhoft, H.; Jorgensen, S.E. *Chemosphere* **1998**, *36*, 357.

4. Environmental Protection Agency. Guidelines for Carcinogen Risk Assessment, Risk Assesment Forum; Environmental Protection Agency: United States of America, **2005**.

5. Beall, G. W. *Appl. Clay Sci.* **2003**, *24*, 11.

6. Dutta, P. K. *Indian J. Environ. Prot.* **1994**, *14*, 443.

7. Haro, M.; Cabal, B.; Parra, J. B.; Ania, C. O. *Adsorp. Sci. Technol.* **2011**, *29*, 467.

8. World Health Organization Guidelines for Drinking Water Quality, First and Second addenda, 3rd ed., World Health Organization Press: Geneva, Switzerland, **2008**; Vol. *1*.

9. Neumann, M. G.; Gessner, F.; Schmitt, C. C.; Sartori, R. *J. Colloid Interface Sci.* **2002**, *255*, 254.

10. Alkaram, U. F.; Mukhlis, A. A.; Al-Dujaili, A. H. *J. Hazardous Mater.* **2009**, *169*, 324.

11. Lee, S. M.; Tiwan, D. *Appl. Clay Sci.* **2012**, *59–60*, 84.

12. Changchaivong, S.; Khaodhiar, S. *Appl. Clay Sci.* **2009**, *43*, 317.

13. Swartzen-Allen, S. L.; Matijević, E. *Chem. Rev.* **1974**, *74*, 385.

14. Brindley, G. W.; Brown, G. Crystal Structure of Clay Minerals and their X-ray Identification; Mineralogical Society: London, **1980**.

15. Jacobs, K. Y.; Schoonheydt, R. A. *Langmuir* **2001**, *17*, 5150.

16. De Lisi, R.; Lazzara, G.; Milioto, S.; Muratore, N. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3994.

17. Hecht, E.; Hoffmann, H. *Tenside Surf. Deterg.* **1998**, *35*, 185.

18. Bujdák, J.; Hackett, E.; Giannelis, E. P. *Chem. Mater.* **2000**, *12*, 2168.

19. Loyens, W.; Jannasch, P.; Maurer, F. H. *J. Polymer* **2005**, *46*, 915.

20. Nelson, A.; Cosgrove, T. *Langmuir* **2004**, *20*, 10382.

21. Bujdak, J.; Komadel, P. *J. Phys. Chem.* **1997**, *101*, 9065.

22. Maupin, P. H.; Gilman, J. W.; Harris R.H., Jr.; Bellayer, S.; Bur A. J.; Roth, S. C.; Murariu, M.; Morgan, A. B.; Harris, J. D. *Macromol. Rapid Commun.* **2004**, *25*, 788.

23. Lofaj, M.; Bujdák, J. *Phys. Chem. Miner.* **2012**, *39*, 227.

24. Yurekli, K.; Conley, E.; Krishnamoorti, R. *Langmuir* **2005**, *21*, 5825.

25. Yariv, S.; Nasser, A. *J. Chem. Soc. Faraday Trans.* **1990**, *86*, 1593.

26. Braswell, E. *J. Phys. Chem.* **1968**, *72*, 2477.

27. Schuber, M.; Levine, A. *J. Am. Chem. Soc.* **1955**, *77*, 4197.

28. Bergaya, F.; Theng, B. K. G.; Lagaly, G. Handbook of Clay Science Developments in Clay Science; Elsevier Ltd., Amsterdam, **2006**; Vol. *1*.

29. Barron, W.; Murray, B. S.; Scales, P. J.; Healy, T. W.; Dixon, D. R.; Pascoe, M. *Colloids Surf. A* **1994**, *88*, 129.

30. Delgado, A.; Gonzalez-Caballero, F.; Bruque, J.M. *J. Colloid Interface Sci.* **1985**, *113*, 203.

31. Morariu, S.; Bercea, M. *J. Chem. Eng. Data* **2009**, *54*, 54.

32. Nelson, A.; Cosgrove, T. *Langmuir* **2005**, *21*, 9176.