MARCOSCOPIC AND MICROSCOPIC MOTION OF IRON OXIDE MAGNETIC NANOPARTICLES STABILIZED PICKERING EMULSION: MAGNETOPHORESIS AT LOW FIELD GRADIENT

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by

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LIST OF ABBREVIATIONS

ATR-FTIR	Attenuated total reflectance-Fourier transform infrared spectroscopy
CMC	Critical micelle micellization
CTAB	Cetrimonium bromide
DLS	Dynamic light scattering
HGMS	High gradient magnetic separation
HLB	Hydrophilic-lipophilic balance
IONP	Iron oxide Nanoparticle
IONP-PSS	Poly (sodium 4-styrenesulfonate) coated iron oxide nanoparticle
IONP-PSS-CTAB	Cetrimonium bromide and poly (sodium 4-styrenesulfonate) coated iron oxide nanoparticle.
LDV	Laser Doppler velocimetry
LGMS	Low gradient magnetic separation
MPE	Magnetic Pickering emulsion
O/W	Oil in water
PSS	Poly (sodium 4-styrenesulfonate)
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
W/O	Water in oil
UV-Vis	Ultraviolet-visible light
VSM	Vibrating sample magnetometer

LIST OF SYMBOLS

B	Magnetic flux density/magnetic field
B_r	Remanence flux density
∇B	Magnetic flux density gradient/magnetic field gradient (dB/dz)
D	Diameter of emulsion droplet
D_t	Diffusion coefficient
d	Diameter of nanoparticles (TEM)
d_h	Hydrodynamic diameter
η	Viscosity
F_{drag}	Viscous drag force
F_{mag}	Magnetophoretic force
ΔG_d	Free energy of desorption
$\gamma_{o/w}$	Oil-water interfacial tension
$\gamma_{s/o}$	Solid particle-oil interfacial tension
$\gamma_{s/w}$	Solid particle-water interfacial tension
H	Height of bar magnet
H_c	Coercitivity
H_m	Magnetic field strength/ magnetic field
H_{cm}	Height of cylindrical magnet
k_B	Boltzmann constant

L	Length of bar magnet
M_p	(Mass) magnetization
M_r	Remanent Magnetization
M_s	Saturation Magnetization
m_p	Total mass of IONPs
μ	Magnetic dipole moment
μ_{AB}	Reduced mass of A and B
n_A	Number density of species A
n_B	Number density of species B
R	Radius of emulsion droplet
R_m	Radius of cylindrical magnet
r	Hydrodynamic radius
T	Absolute temperature
T_c	Temperature in celcius
θ	Contact angle
v	Relative velocity
v_T	Terminal velocity
W	Width of bar magnet
x	Distance travelled
Z_{AB}	Collision frequency of species A and B
z	Distance from magnet

PENGERAKAN MAKROSKOPIK DAN MIKROSCOPIK EMULSI PICKERING BERMAGNET YANG DISTABILKAN OLEH NANOZARAH BESI OKSIDA: MAGNETOFORESIS BERKECERUNAN RENDAH

ABSTRAK

Emulsi Pickering Magnet (MPE) yang mempunyai responsif magnetik telah distabilkan oleh nanozarah besi oksida (IONP) salutan dengan poli(natrium 4-stiresulfonat) dan setilmonium bromida (CTAB) serta molekul CTAB bersebelahan. Dalam projek ini, MPE, IONP, IONP-PSS dan IONP-PSS-CTAB disintesiskan and dikajikan dengan siri karakterisasi bagi kelakuan kimia, fizikal dan magnetik. MPE ini dikajikan pada kedu-dua skala, iaitu (1) skala makroskopik dan (2) skala mikroscopik untuk pengerakan MPE. Dalam kajian makroskopik, imej bagi ubah kekeruahan MPE dirakamkan oleh kamera digital dengan intervalometer. Manakalanya, mikroskop optik medan terang telah digunakan untuk mengkaji sifat mikroskopik MPE. Semua imej terdapat dalam eksperimen dianalisiskan oleh teknik Image J. Pada skala makroscopik, keberkesanan pemisahan magnetik untuk MPE pada 90 % telah dicapai dalam masa 30 minit.bagi semua keadaan. Walaubagaimanapun, kestabilan berkoloid bagi MPE dalam pH 10 adalah paling rendah berbanding dengan keadaan pH 3 dan air ternyaion. MPE dalam pH 10 memerlukan jangka masa yang singkat untuk mencapai keefisienan pemisahan yang tertinggi. Oleh sebab itu, MPE dalam pH 10 mengalami magnetoforesis secara berkerjasama apabila pengelompokan satu arah (tidak berbalik) terdapat dalam MPE semasa magnetoforesis. Selain itu, MPE tidak mengalami pemecahan bawah medan magnetik, B dengan nilai 0.26 T~0.66 T dan kecerunan medan magnetik (dB/dz), ∇B, dengan nilai 52.07 T/m ~ 95.74 T/m sewaktu kajian skala makroscopik. Pada pandangan mikroscopik, titisan-titisan MPE dengan diamater yang berbeza (2.5 μm ~7.5 μm) dihijrahkan bawah kecerunan medan magnetik

(dB/dz), ∇B dengan nilai 98.38 T/m. Titisan-titisan MPE yang terbesar memerlukan jangka masa yang singkat untk mencapai halaju terminal yang tertinggi. Tambahan pula, analisis magnetoforesis dapat menyimpulkan bahawa lapisan tunggal (monomolekuler) nanozarah magnetik (komposit IONP-PSS-CTAB) telah terjadi pada semua titisan-titisan MPE yang berbeza saiz. Magnetoforesis juga menunjukkan liputan permukaan bagi MPE bersesuaian dengan potensi zeta MPE yang positif tinggi. Hal ini berpunca daripada CTAB molekuler meliputi bilangan yang tinggi pada permukaan titisan-titisan emulsi di samping IONP-PSS-CTAB. Kejayaan magnetoforesis MPE yang baru disintesis ini juga menyumbangkan prospek yang baik untuk perolehan minyak supaya mengelakkan pembaziran sumber tenaga.

MACROSCOPIC AND MICROSCOPIC MOTION OF IRON OXIDE MAGNETIC NANOPARTICLES STABILIZED PICKERING EMULSION: MAGNETOPHORESIS AT LOW FIELD GRADIENT

ABSTRACT

A magnetic responsive of magnetic Pickering emulsion (MPE) was synergistically stabilized by the iron oxide nanoparticles (IONPs) coated by poly(sodium 4-styrenesulfonate) (PSS) and cetrimonium bromide (CTAB) as well as the adjacent CTAB molecules. In this project, MPE, IONPs, IONPs-PSS and IONP-PSS-CTAB were synthesized with their chemical, physical and magnetism properties thoroughly characterized. The synthesized MPE was studied under two main scales: (1) macroscopic and (2) microscopic experiment for the motion of MPE. For macroscopic experiment, the changing of turbidity of the MPE suspension was recorded by a digital camera using intervalometer. Whereas, a bright field optical microscope was employed to study the microscopic behavior of the Pickering emulsion. All images analysis were performed by standard technique using Image J. At the macroscopic scale, the magnetic separation efficiency of MPE at 90 % was achieved within 30 minutes for all condition. However, the colloidal stability of MPE at pH 10 was the lowest as compared to pH 3 and deionized water conditions. MPE at pH 10 required the shortest time for achieving the highest separation efficiency. Hence, MPE at pH 10 experienced cooperative magnetophoresis as it could be irreversible flocculated during magnetophoresis. Besides that, the MPE didn't deform and coalescence under the magnetic field, B of 0.26 T~0.66 T and magnetic field gradient (dB/dz), ∇B of 52.07 T/m~ 95.74 T/m during macroscopic study. At the microscopic scale, different diameters (2.5 µm~7.5 µm) of emulsion droplets of MPE were

migrated under magnetic field gradient (dB/dz), ∇B of 98.38 T/m. The largest droplets (7.5 µm) required the shortest time to achieve the highest terminal velocity. Moreover, magnetophoresis analysis also concluded that monolayer of magnetic nanoparticles (IONPs-PSS-CTAB composites) was formed for the all sizes of emulsion droplets. Magnetophoresis analysis also showed that the surface coverage of IONPs composites on the emulsion droplets was coincided with the high positive zeta potential of MPE. This is because the CTAB molecules occupied the other large proportions of the surface of emulsion droplets in addition IONPs-PSS-CTAB. The successful of magnetophoresis of new synthesized MPE also contributed a great prospect for the oil recovery to prevent the loss of energy source.

CHAPTER ONE

INTRODUCTION

First of all, this chapter will introduce the topics that are relevant to the project. Hence, the magnetic Pickering emulsion (MPE) and magnetophoresis of MPE will be elaborated. Besides, this chapter also comprise the problem statements of the project, main objectives for the research and study scope of the project. Eventually, this chapter will be ended with introduction of the whole thesis's organization.

1.1   Magnetic Pickering emulsion (MPE)

Emulsion is a heterogeneous system which consists of at least two immiscible liquids, mainly water and oil, one is uniformly dispersed as fine droplets in another liquid as a continuous phase. Generally, there are two main types of emulsion to be formed which are oil-in-water emulsion and water-in-oil emulsion. Emulsion with oleaginous as internal dispersed phase and aqueous as external continuous phase is the oil-in-water emulsion (O/W), on the contrary, emulsion with aqueous as internal dispersed phase and oleaginous as external continuous phase is the water-in-oil emulsion (W/O). Emulsion is a thermodynamically unstable system but it can be stabilized for certain period of time by implementation of energy barrier. Emulsifier is the substance which is required to stabilize the emulsion by reducing the interfacial tension between the two layers of the liquids.

At the beginning of 20th century, Ramsden (Ramsden, 1903) and Pickering (Pickering, 1907) discovered and described respectively that the colloidal-sized solid

particles adsorb on the liquid-liquid interface to form the emulsion. This type of emulsion was named after S.U. Pickering, so it is usually known as Pickering emulsion. The unique feature of Pickering emulsion, in comparison to the conventional emulsion, is Pickering emulsion use the solid particle as emulsifier whereas conventional emulsion use molecular surfactant or polymer as emulsifier. In the recent years, the application of Pickering emulsion draws a strong research interest from the scientific community (Yang *et al.*, 2017), mainly due to its interesting colloidal behavior and its versatility to create multimodal functionalities depends on the physical/chemical properties of particles used to stabilize Pickering emulsion . To fulfill the innovative application of Pickering emulsion, the responsive of the emulsion has been studied extensively (Tang *et al.*, 2015). By stabilizing the Pickering emulsion with magnetic nanomaterials, it is possible to impart the magnetic responsiveness to the Pickering emulsion and this colloidal system with its transport behavior can be controlled by an externally applied magnetic field (Kaiser *et al.*, 2009).

Magnetic Pickering emulsion (MPE) is a kind of emulsion which has the magnetic properties and it is normally stabilized by the superparamagnetic iron oxide nanoparticle (IONP) (Lin *et al.*, 2016). IONP has a small size with diameter between 1 nm to 100 nm. However, due to its smaller size, iron oxide nanoparticle has a high ratio of surface area to volume and it is resulting to the high surface energy (Woo *et al.*, 2004). IONPs will aggregate to each other to minimize the surface energy. To solve the aggregation of IONPs, the surface functionalization of nanoparticle has been utilized to modify the surface properties of nanoparticles (Yeap *et al.*, 2012). The surface of nanoparticle is normally treated with the physical adsorption of the polymer or surfactant. The aggregation of unstable IONPs will cause the MPE to be flocculated and creamed in the short period of time. To enhance the stability of MPE, the IONPs

will be physically adsorbed by surfactants (Almahfood and Bai, 2018) or polymers (ShamsiJazeyi *et al.*, 2014) to create the steric barrier to slow down the flocculation of emulsion.

1.2 Magnetophoresis of magnetic Pickering emulsion (MPE)

Magnetophoresis is a migration process in which magnetic materials move towards a region with highest magnetic field gradient (magnetic field sources) whilst its motion relative to the surrounding fluid (Zborowski *et al.*, 1999). The motion of the magnetic responsive object is actually caused by the magnetophoretic force. The magnetic dipole moment of the magnetic material will induce the magnetophoretic force for magnetic material under an applied magnetic field. In engineering application, magnetic separation is achieved by the process of magnetophoresis of the magnetic material, such as iron (Lim *et al.*, 2014a), nickel (Benelmekki *et al.*, 2011), cobalt (Suwa *et al.*, 2008), etc. Meanwhile, the magnetic separation is also widely used for environmental treatment (Zhou *et al.*, 2011) and biological separation (Winoto-Morbach *et al.*, 1995) besides their application in separation of mineral ore tailing.

The nature of magnetic separation can be crudely classified into two domain, e.g. high gradient magnetic separation (HGMS) and low gradient magnetic separation (LGMS). HGMS has been practically used in most industrial applications as it can have high throughput and can be used to separate huge range of size of particles (Moeser *et al.*, 2004). As compared to HGMS, LGMS is low cost and low energy consumption, so it has a great potential to be implanted and replaced the work of HGMS (Toh *et al.*, 2012). In 2006, Yavuz *et al.* have published their seminal work on the possibility of using LGMS for nanomaterials separation in *Science* magazine

(Yavuz *et al.*, 2006). It reported that the 12 nm magnetic nanoparticle under low gradient magnetic field (< 100 T/m) originated by a handheld permanent magnet can be re-harvested by from an aqueous environment (Yavuz *et al.*, 2006). It also showed that the critical size range of magnetic material separated by LGMS is close to the HGMS.

Typically, superparamagnetic IONP is the magnetic material that is frequently implemented in the magnetic separation for environmental treatment and biological separation. The IONP is used as magnetic carrier and dispersed in the solution containing the targeted compound. To adsorb the specific binding of the targeted compound, the surface of the IONP is modified and functionalized with polymer or surfactant (El-Boubbou, 2018). The composite of targeted compound and IONP will be extracted by external magnetic field. There are plenty of researches have demonstrated the successful separation of different compounds using IONP under low field gradient such as separation of microalgae (Chai *et al.*, 2015), separation of heavy metal (Yavuz *et al.*, 2006), separation of tumor cell (Xu *et al.*, 2011), etc.

In spite of renewable energy is progressed, oil and gas are still the main energy sources for our industries and developments. Enhancement of oil separation and recovery technique by using chemicals are still the main concern for petroleum industry (Gbadamosi *et al.*, 2019). Recently, there are many researches that stabilize the desired dispersed phase (oil or water) with different kinds of nanoparticles to form stimuli responsive Pickering emulsion droplets under an external force field (Tang *et al.*, 2015). Magnetic Pickering emulsion (MPE) is one of the stimuli responsive Pickering emulsion developed due to its magnetophoretic property. The magnetic properties of MPE is originated from the IONPs adsorbed on the surface of emulsion (Zhou *et al.*, 2011). Due to its magnetic properties, magnetic separation technique has

been implemented to separate the MPE (Figure 1.1) (Kaiser *et al.*, 2009). Magnetophoresis arises as the strength of magnetic force acting on MPE under non-uniform external magnetic field. The stabilized and monodisperse MPE will allow the researchers to study the fundamental of magnetophoresis of MPE under external magnetic field (Krebs *et al.*, 2013). Due to the complex interplay of various factors, such as (i) flux-closure effects, (ii) particles-to-particles interaction effects, (iii) mobility of particles at liquid-liquid interface, etc, the underlying transport behavior of MPE undergoing magnetophoresis is ill understood.
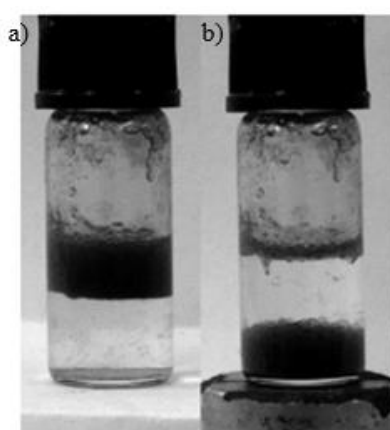
Figure 1.1. (a) The magnetic capsules was creamed at the top of aqueous phase because of lower density of oil in the magnetic capsule. (b) The magnetic capsules was attracted downward by the external magnetic field. [Reprinted with permission from (Kaiser *et al.*, 2009). Copyright © 2009 American Chemical Society]

1.3   Problem statements

In the 21st century, the recovery of oil is highly demand in the oil and gas industry due to the oil depletion is getting serious as the development of globalization requires high quantities of energy sources. The chemical enhanced oil recovery is improved by the nanotechnology. The formation of Pickering emulsion is the one of the technique which is using the nanoparticles fluid as solid emulsifier. To achieve the

separation of Pickering emulsion, the magnetic responsive of Pickering emulsion is attained by the adsorption of magnetic nanoparticles to form MPE.

However, the stability of MPE is lower as the variation of magnetic field from weak to strong (Melle *et al.*, 2005). To manipulate and separate the MPE without breaking and coalescence, LGMS will be a choice to be used instead of HGMS. Since, high field gradient can easily impose a translational magnetophoretic forces that ripping-off the IONPs from the liquid-liquid interface and leading to the complete breakdown of the entire emulsion structure. However, there were still some limited reviewed research works could destabilize the emulsion droplets with low magnetic field gradient. Lin *et al.* and Yang *et al.* used the permanent magnet of 1T and 0.4T to destabilize the magnetic Pickering emulsion (Lin *et al.*, 2015; Yang *et al.*, 2018). Hence, the nature of rupture such as the magnetic sheering effect is unclear. It is the interesting question and should be pursued in future study before it is applied in the separation process even it is the LGMS method. To maintain the stability of MPE against the low gradient magnetic field, there were some researchers using a composite of two nanoparticles with chemical differences as the emulsifier of the emulsion such as composite of graphene oxide-iron oxide nanoparticles and composite of iron oxide nanoparticles-cellulose nanocrystal (Lin *et al.*, 2015; Low *et al.*, 2017). Besides improving the stability of emulsion, the composite of two nanoparticles also provides the multi responsive of the emulsion which is useful in the future application in engineering or industry (Xie *et al.*, 2017). There were also many researches that used the nanoparticles and surfactant mixtures (Zhao *et al.*, 2018) or nanoparticles and polymer mixtures (Lai *et al.*, 2016) to achieve the synergism effect on stabilizing Pickering emulsion. On the other hand, the nanoparticle which was grafted by polymer in order to reduce the interfacial tension of two liquid phases, by adsorbing on the oil-

and-water interface of the emulsion, has also been developed (Kaiser *et al.*, 2009). In spite of the benefit in tailoring the wettability of nanoparticles for stabilization of Pickering emulsion, there are also some drawbacks, such as the strong electrostatic and steric repulsion found within composite of nanoparticles and polymers (Yeap *et al.*, 2012). In previous researches, Binks *et al.* and Tambe *et al.* made various studied on aggregation of silica and concluded that the large weak flocculated particles with the size up to 100 nm were more efficient emulsifiers of Pickering emulsion(Binks and Whitby, 2005; Tambe and Sharma, 1994). To solve the weakness that is appeared in all the aforementioned systems above, here I proposed the combination of three building blocks, which is nanoparticle-polymer-surfactant ternary system for the emulsion stabilization. Previously, there were some studies found that nanoparticle-polymer-surfactant system could produce the synergistic effect on the stabilization of emulsion (Saigal *et al.*, 2015). They concluded that the complexation interaction might form between the surfactant and polymer-grated nanoparticles causing the Pickering emulsion to be more stable. Subsequently, the almost monodisperse and stable magnetic Pickering emulsion (MPE) is the ideal emulsion for fundamental study of transport phenomena under external magnetic field so it is required to mitigate the problems above and design a mixture to fulfill the study's requirement.

LGMS is a new challenge to the magnetic separation technique. Compared to conventional industrial scale magnetic separation technique such as HGMS, LGMS based on motion of emulsion droplets or nanoparticle is still not well understood (Lim *et al.*, 2014b). LGMS is the well choice for the manipulating and separating MPE. Beyond the chemical enhanced stability of MPE for direct usage in LGMS technique, the mechanistic evaluation under aspect of time and space is required for the magnetophoresis of MPE under low gradient magnetic field. There is very limited

number of published researches on the magnetophoresis of MPE. The most relevant works were done by Suwa *et al.* and Zhao *et al.* Suwa *et al.* used the paramagnetic manganese (II) chloride droplet in organic medium as the materials for the magnetophoretic behavior study (Suwa and Watarai, 2001). Meanwhile, Zhao et al. employed microsphere coated by surfactant and IONPs for magnetophoresis study (Zhao and Helseth, 2007). Previously, there were also some researchers produced the high stability MPE with composite of two chemical differences of nanoparticles with different focuses (Lin *et al.*, 2015; Low *et al.*, 2017). Hence, it requires the alternative methods to study the transport phenomena of MPE under magnetic field in both macroscopic and microscopic scale. The results from both scales of experimental work may provide separation efficiency and magnetophoretic mobility of MPE under low gradient field. For the macroscopic study of separation of MPE, most of the studies were lack of kinetic study (Wang *et al.*, 2015; Choi *et al.*, 2018). Thus, it requires the motion of MPE respect to time. Besides, magnetic field gradient can be declined under the influence of distance (Lim *et al.*, 2014b). The effective range of distance for applying magnetic separation will be investigated by the magnetophoretic analysis of MPE. The separation efficiency and magnetophoretic mobility MPE under aspect of time and space respectively rather than controlling parameter will become the important direction for the design of a new low gradient magnetic separator. Hence, the development of low gradient magnetic separator based on the transport rather than equilibrium will be possible. It will be high efficient and scalability for LGMS to operate on the basis of the mobility of different size of emulsion droplets of MPE under low gradient of magnetic field (Zborowski *et al.*, 1999).

1.4   Research objectives

The primary goal of the researches is to study the motion of MPE under low gradient magnetic field. Thus, the specific objectives are listed below:

I.   To prepare and characterize a new MPE stabilized by nanoparticle-polymer-surfactant mixture.

II.   To design alternative analytical methods for studying the kinetic profile of MPE under low gradient magnetic field at macroscopic and microscopic scale.

III.   To investigate the particle size effects and pH of surrounding environment on influencing the magnetophoresis and colloidal stability of MPE.

IV.   To analyze quantitatively for the motion paths of emulsion droplets of MPE under low gradient magnetic field.

1.5   Scope of study

In this project, it focused on the effect of magnetic field on the motion of emulsion. To produce a type of emulsion possessing magnetic properties, the emulsion required some kind of magnetic materials such as IONPs (Wang *et al.*, 2015). Hence, the first step of the work was to synthesis IONPs by the method of co-precipitation. IONPs has low stability without the coating of organic compounds (Ghosh *et al.*, 2011; Demangeat *et al.*, 2018). To enhance the stability of IONPs, IONPs was coated with PSS and CTAB via post coating technique to form IONPs-PSS-CTAB. IONPs-PSS-CTAB was eventually used to adsorb on the emulsion droplets and the organic solvent was dodecane. This emulsion was called as MPE.

Two main scales of magnetophoretic motion study for MPE which were macroscopic and microscopic motion. The colloidal stability of emulsion could be affected by few parameters, such as pH, temperature, ionic strength, size of emulsion etc (Laplante *et al.*, 2005; Goodarzi and Zendehboudi, 2018). The pH conditions of the suspension was the main parameter in the macroscopic motion of MPE. This is because the surfactant and polymer interaction could be affected by the pH (Petkova *et al.*, 2013). Besides, the characterizations were based on the surface analysis, size measurements and magnetic properties of the samples. The pH suspensions could affect the zeta potentials of the bare IONPs, IONPs composite and MPE because the layer of PSS and CTAB owned negative charge group and positive charge group respectively. Hence, a series of measurement of zeta potential of bare IONPs, IONPs composites and MPE were conducted on range of pH values from 3 to 11. Moreover, the effect of pH on the sizes of IONPs-PSS-CTAB and MPE would be examined.

For the macroscopic motion, MPE was diluted with 50 times and prepared in a cuvette. Real time image capturing of digital camera by intervalometer was employed to record the transport phenomena of MPE under the influence of low gradient magnetic field (magnetophoresis) and no low gradient magnetic field (creaming). The macroscopic motion of MPE was also conducted at the condition of pH 3, pH 10 and deionized water. Then, the kinetic profile of these two process (creaming and magnetophoresis) were plotted and analyzed. Besides, the creaming rate and magnetophoresis rate were compared to analyze the effect of creaming on the magnetophoresis.

The size of magnetic materials would affect the magnetophoretic forces of magnetic materials (Leong *et al.*, 2016). For the microscopic motions, MPE was diluted to 50000 times and dropped on the microscope slide. Real time video recording

of camera (at monochromatic scale) equipped on the optical microscope was applied to record the transport phenomena of MPE under an in-plane low gradient magnetic field. Motions graphs of emulsion droplets were plotted and analyzed. Besides, the effect of size of emulsion droplets on the magnetophoresis was observed and analyzed. Mathematical analysis was applied on the magnetophoretic behavior of emulsion droplets which could evaluate the number of nanoparticles on the emulsion droplets.

1.6   Organization of thesis

There are five main chapters in this thesis. All of this five chapters are introduced and summarized here. Chapter one introduces magnetic Pickering emulsion and magnetophoresis of magnetic Pickering emulsion under magnetic field technique that is available nowadays. Besides, chapter one also will show the problem statements for the direction of research, main objectives of the research and study's scope

In the following chapter, literature reviews on published researches related to this research topic is done in detail. The chapter two consists into three main sections such as iron oxide nanoparticles, Pickering emulsion and magnetic separation. In the first section, the unique of property of IONPs and functionalization of IONPs are first to be emphasized. The factors that are included in the aggregation and dispersion of IONPs and IONPs composites will also be discussed. Besides, the wetting properties of Pickering emulsion, stabilization of Pickering emulsion and stimuli-responsive of Pickering emulsion for application are reviewed in the next section. In the last section, LGMS and HGMS were introduced and reviewed. In addition, the theoretical background of magnetophoresis is presented in detail. Moreover, the trend of study of

magnetic separation of MPE in microscopic and macroscopic and even its challenges are appraised in the final sub section of section three.

Chapter three discusses the detail on the procedure to prepare MPE and alternative of analytic method used in this project. In this chapter, it begins to show the research flow chart and the material to be used in the whole projects. Then, the methods to functionalize the IONPs with PSS and CTAB and preparation of MPE are explained in detail. Subsequently, the characterization of all samples with FTIR, DLS, zeta potential measurement, TEM, VSM, TGA and optical microscope will be described. The alternative of analytic methods for observing physical motion of MPE under low gradient magnetic field in macroscopic scale and microscopic scale are delineated in the next section. This chapter is end with presenting the use of image J for the analysis of the image capturing and video recording from the experiment.

Chapter four shows all the qualitative and quantitative results obtained from the research. There are six sections in this chapter four. The results of surface properties of bare IONPs, coated IONPs and MPE will be discussed and shown in the first section. Next, the size measurement of bare IONPs, coated IONPs and MPE at different pH are presented. Moreover, magnetic properties of IONP and fraction of iron oxide content in composites IONPs are determined and discussed. With the aid of images J, the profile graphs of macroscopic study of magnetic separation and creaming of MPE are shown and analyzed in the following section. Besides, the motion of the emulsion droplets is also analyzed by Image J for the microscopic study. Eventually, the estimation of surface coverage of IONPs on the emulsion droplets of MPE are discussed and calculated with aid of certain results above during magnetophoresis analysis.

In the last chapter, this project is end with the conclusion and recommendations. The conclusion is made with all the findings accordance with the objective of researches. Furthermore, some recommendations are listed for the future investigation and development of this project.

CHAPTER TWO

LITERATURE REVIEW

There are three main sections in this chapter and they are closely associated to the nature of this work. The three main sections are iron oxide nanoparticles (IONP), Pickering emulsion and magnetic separation. In every sub sections, examples are given on published information and research works with reasons given to justify the main direction of this project. Initially, the research activities are starting from the synthesis of bare IONP followed with surface functionalization of IONP, emulsification of magnetic Pickering emulsion (MPE) and eventually the magnetic separations of MPE.

2.1   Iron oxide nanoparticle (IONP)

Iron oxides are the compounds which are widely distributed in nature and synthesized in the laboratory and industry. 16 types of iron oxides are found around us (Cornell and Schwertmann, 2003). The iron oxides are consisted of Fe together with O and/or OH and they mostly are in trivalent state. The three common forms of iron oxide are magnetite, maghemite, and hematite. Among these three iron oxides, hematite is the lowest magnetization while magnetite is the highest magnetization (Dar and Shivashankar, 2014). Hence, magnetite will be the first choice as the magnetic carrier for the engineering applications. Magnetite is very sensitive to oxygen so maghemite is the product which is oxidized from the original magnetite under room temperature (Laurent *et al.*, 2008). Hence, most of the IONPs that used and stored for application or research will contain a mixture of two types of magnetite or maghemite with different proportions as the time proceeds (Bumb *et al.*, 2008).

Comparison between most of the mineral oxides nanoparticles, the unique property of IONP is its superparamagnetic property. The magnetization of IONPs is zero when the magnetic field is absent. While, the IONPs can possess large saturation of magnetization under an applied magnetic field (Faraudo and Camacho, 2009). In short, the IONPs is said to be superparamagnetic as they do not show hysteretic behavior within its M-H_m curve (Hatch and Stelter, 2001). Besides, the diameters of IONPs range from 1 to 100 nm. From colloidal perspective, its nano-sized offers a high surface area-to-volume ratio for the physical adsorption of other molecules (Laurent *et al.*, 2008). Combining its unique magnetic property and large surface area, IONP is widely used for engineering application. For instance, removal of heavy metal and organic solvent for water treatment (Yavuz *et al.*, 2006), a contrast agent for Magnetic Resonance Imaging MRI (Javed *et al.*, 2017), oil recovery by forming Pickering emulsion (Wang *et al.*, 2015), a recyclable catalyst of a chemical reaction (Bhalkikar *et al.*, 2015), etc.

There are few methods which are used to synthesize IONPs. All these methods can be categorized into two main approaches which are bottom-up approach and the top-down approach. The top-down approach consists of methods to reduce the size of macro magnetic materials such as magnetite high pure ore to the nanometer size. The methods categorized as top-down approach are wet grinding (Jung *et al.*, 2015), milling (Dutz *et al.*, 2007), ultra-sonication (Yang *et al.*, 2005), etc. However, the narrow size range of IONPs in nanometer is difficult to be obtained through the tough physical crushing of macro size materials (Biehl *et al.*, 2018). Although it may be produced in high quantity, it will take high energy and resources to have highly irregular shape and polydisperse particles from the mineral ore or micro powders. Besides, the top-down approach may cause the defection of the structure of the crystal

of core IONPs so it may affect much on the desired magnetic properties from the product of magnetite ores (Dutz *et al.*, 2007).

Meanwhile, the bottom-up approach is the most favorable among industries and research fields. The bottom-up approach is using more chemical synthesis methods than physical methods. In the bottom-up approach, the promising methods are co-precipitation (Che *et al.*, 2014b), high-temperature decomposition (Lassenberger *et al.*, 2017), micro-emulsion synthesis (Chin and Yaacob, 2007), hydrothermal method (Takami *et al.*, 2007) and others. Among the methods above, high-temperature decomposition and hydrothermal method achieved better size control of the synthesized IONPs with narrow size distribution (Zhu *et al.*, 2018). However, both methods above consume long synthesis time, the expensive and high thermal energy required (Zhu *et al.*, 2018). Moreover, the micro-emulsion synthesis and high-temperature decomposition methods will produce IONPs dispersed in organic solvents (Chin and Yaacob, 2007; Lassenberger *et al.*, 2017). If they were used for water treatment purposes by targeting low fraction organic solvent in an aqueous medium with the aim of forming an emulsion, IONPs dispersed in the organic solvent will not be the primary choice. In overall, co-precipitation is the most favorable and simple chemical method to prepare the IONPs from the precursor of salts aqueous solution in alkaline pH. It is low cost, low energy and high productivity of IONPs for both research and industrial applications (Zhu *et al.*, 2018). Although the IONPs produced from co-precipitation consist of the broad size range in nanometer, several modifications in the past had done to control the size of the IONP cluster (Zhu *et al.*, 2018). The IONPs produced by co-precipitation has satisfied magnetic property which is useful for magnetophoresis study in this project.

2.1.1. Stabilization and surface functionalization of bare IONP

Bare IONP has a large has large surface-to-volume ratio, hence, bare IONP will favor aggregation to minimize the surface energy of nanoparticles in the suspension. The aggregated IONPs will settle down under the gravitational pulling since thermal displacement alone is insufficient in dispersing them and eventually to have a strong colloidal stability of suspension. . Bare IONPs with low colloidal stability are not favorable for the engineering applications and research activities. Several stabilization strategies for increasing the colloidal stability of IONPs are reviewed in this section.
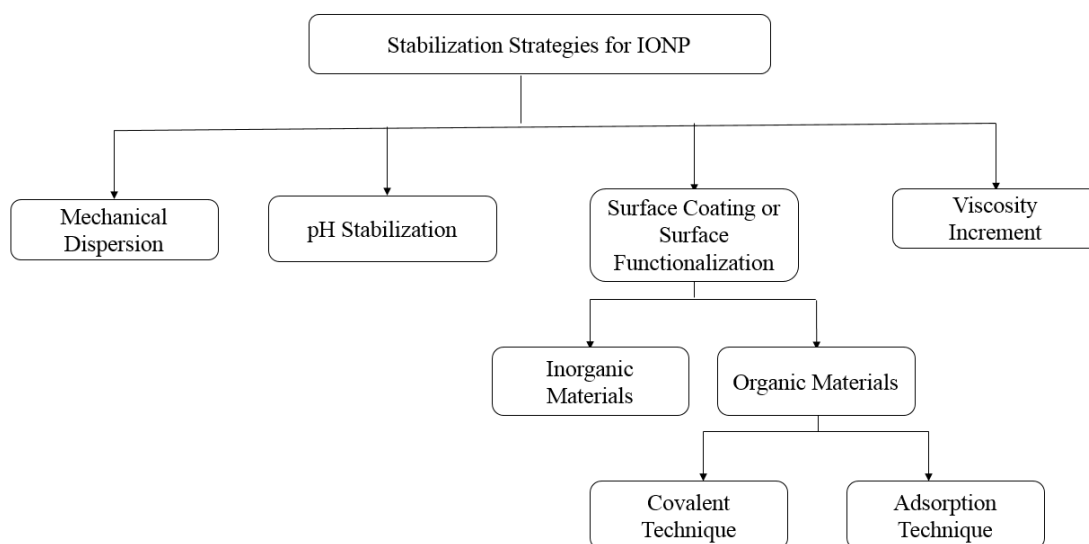
Figure 2.1. Summary of stabilization strategies reviewed for the bare IONPs.

Such as shown in Figure 2.1, there are four main strategies used in common research and engineering applications. For instance, mechanical dispersion by ultra-sonication (Yang *et al.*, 2005), pH stabilization (Faiyas *et al.*, 2010), surface coating (Yeap *et al.*, 2012) and viscosity increment (Comba and Sethi, 2009). Among four strategies, ultra-sonication and pH stabilization are a simple way to enhance the colloidal stability of IONPs. For the ultra-sonication, Yang *et al* found that 10 minutes

of ultra-sonication of IONPs will gain particles with diameters in the range of 100 - 200 nm (Yang *et al.*, 2005). On the other hand, pH stabilization can increase the colloidal stability of IONPs. Faiyas *et al.* and Yang *et al.* found that the average sizes of IONPs produced by co-precipitation can be further reduced by subjecting them to extreme acidic or alkaline pH (Yang *et al.*, 2014; Faiyas *et al.*, 2010). After undergoing pH treatment the particle size can be reduced to below 10 nm. Nevertheless, bare IONP is easily oxidized in the air so it will eventually lose magnetization (Laurent *et al.*, 2008). Surface coating on bare IONPs will provide protection layer(s) to the hydroxyl group of IONPs to slow down the oxidation process (Wu *et al.*, 2015). Besides, bare IONPs will have limited applications for instance the bare IONPs have no functional groups which can be attached to biomolecules so it was low biocompatibility (Lin *et al.*, 2008).

For the viscosity increment, some researchers have stabilized the magnetic nanoparticles using xanthan gum and guar gum (Comba and Sethi, 2009; Sakulchaicharoen *et al.*, 2010). This method provides dual outcome, in which by increasing the suspension's viscosity: (1) decrease the collision frequencies of the nanoparticles by slowing down the Brownian motions and (2) also slow down the settling time so the particles stayed dispersed in prolonged hours. However, the magnetic separation of magnetic nanoparticles will take longer time as the viscosity of suspensions increase.

Meanwhile, the surface coating is the most suitable and promising method for stabilizing the IONPs. Many research outcomes have justified the advantages of the surface coating (Biehl *et al.*, 2018). Two types of materials have been used to form the outer shell of IONP. These two types of materials are inorganic nanoparticles and organic molecules. Inorganic nanoparticles such as gold nanoparticles can be coated

onto the core magnetic core of IONPs by reducing agent (Yan and Sun, 2014). The coating of gold nanoparticles or silver nanoparticles on the IONPs is also assisted by the surfactant or polyelectrolyte layer (Lim *et al.*, 2010; Du and Jing, 2011). This is also one of the layer-by-layer techniques. However, inorganic nanoparticles such as gold and silver materials are an expensive noble metal, it is not suitable to be used in the water treatment. Besides, most of the inorganic nanoparticles categorized as a heavy metal group and it will cause heavy metal pollutions to the environments.

Comparing to inorganics shell of IONPs, organic molecules are the optimal choice for the surface coating of IONPs. There are a variety of choices of organic materials to be used for the surface coating which are both biocompatible and environmentally friendly. Next, the surface coating of IONPs was separated into two main techniques which are covalent technique and adsorption technique (Biehl *et al.*, 2018). These two techniques are commonly used in the research and engineering application for stabilization of nanoparticles. For the covalent technique, it requires the nanoparticles to possess own functional group prior to the grafting of long chains polymers onto the surface of nanoparticles. For example, IONPs functionalized with the initiators (triethylammonium bromide) were subjected to atom transfer radical polymerization (ATRP) to form layer(s) of poly (carboxybetaine methacrylate) from its monomers - carboxybetaine methacrylate (Zhang *et al.*, 2011). The grafting polymer on the IONPs will provide steric repulsion among nanoparticles. On the other hands, the adsorption technique will be much easier than covalent techniques. Adsorption technique mostly driven by the electrostatic attraction between the nanoparticles and the adsorbed organic molecules, such aspolyelectrolyte (Yeap *et al.*, 2012). It involves less steps in surface modification and also required the deposition of either anionic or cationic molecules on the surface of nanoparticles. The

polyelectrolytes attached on the surface of IONPs will produce electrostatic and steric repulsion between nanoparticles.

The surface coating of IONPs by inorganic materials and organic materials is the stabilization strategy which can functionalize the IONPs for the engineering application. For the inorganic outer shell of nanoparticle, the composites of silver-iron oxide nanoparticles were used for the catalytic agent, antibacterial agent and biomedical device (Amarjargal *et al.*, 2013; Satvekar *et al.*, 2015). For the organic outer shell of nanoparticles, grafting polymer on the nanoparticle could form linkage and capture N-linked glycopeptides (organic molecules) in the application of bio-separation (Yeh *et al.*, 2012). Furthermore, polyelectrolyte PSS adsorbed on the
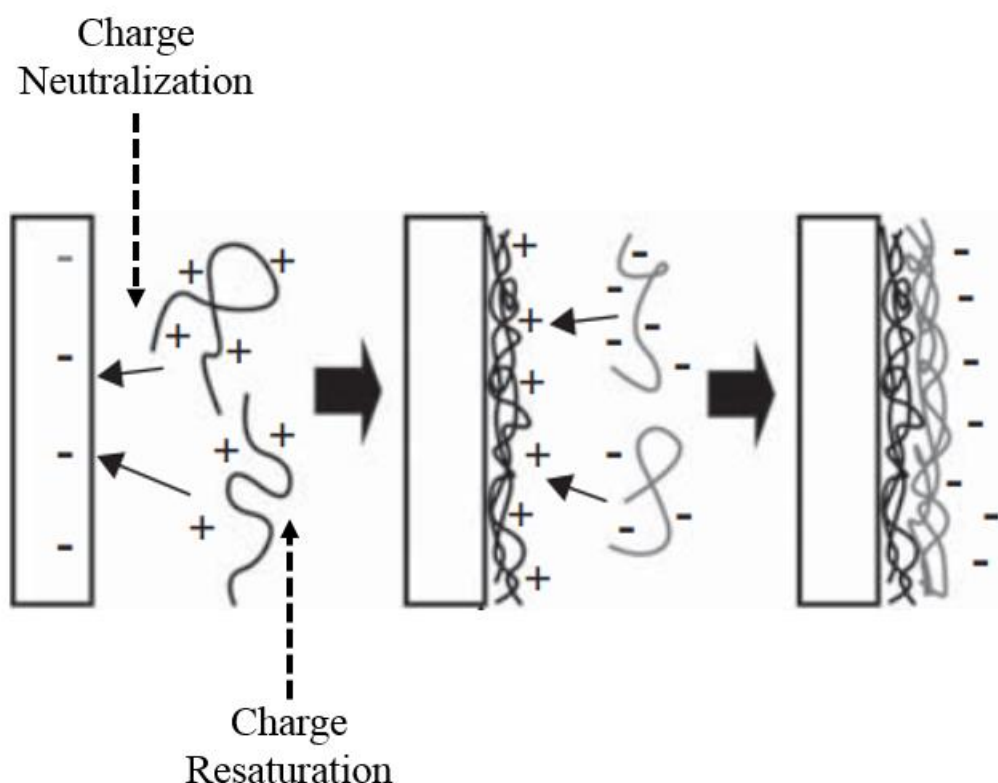

Figure 2.2 Schematic diagram of layer by layer assembly of polyelectrolytes on the surface of material. The effective charge of material based on the charge neutralization and charge resaturation. [Reprinted with permission from (Ariga *et al.*, 2011) Copyright © 2011 Taylor & Francis Online]

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IONPs could be assembled by another layer of polyelectrolyte poly (diallyl-dimethylammonium) chloride (PDADMAC) during post modification shown in Figure 2.2 (Wong *et al.*, 2008). Layer by layer assembly of polyelectrolytes on the nanoparticle surfaces was achieved by the adsorption of polyelectrolytes under the effect of electrostatic interaction (Berndt *et al.*, 1992). This interaction was driven by two phenomena, charge neutralization and charge resaturation (Ariga and Lvov, 2003). It eventually cause the charge reversal for the surface of material during the subsequent of adsorption of polyelectrolytes (Ariga *et al.*, 2011).

Besides, polyelectrolyte coated nanoparticles were also being used to form complexation with surfactant molecules (Chiappisi *et al.*, 2013). In general, the complexation of polyelectrolyte and surfactants are governed by parameters, such as (1) concentration of surfactants and polyelectrolyte, (2) molecular weight of polyelectrolyte, (3) stiffness of polyelectrolyte and (4) charge density of polyelectrolyte (Chiappisi *et al.*, 2013). For example, the increment of surfactant concentration will change the structure of polyelectrolyte by the formation of micelle during the interaction of polyelectrolyte and surfactant (Fundin, 1994). As the concentration of surfactant increased, the polyelectrolyte and surfactant complex would be precipitated out from the solution (Zhou and Chu, 2000). Hence, the previous research study of complex polyelectrolyte and surfactant complex would contribute a new insight for functionalization of IONPs by binding surfactants onto the polyelectrolytes coated IONPs.
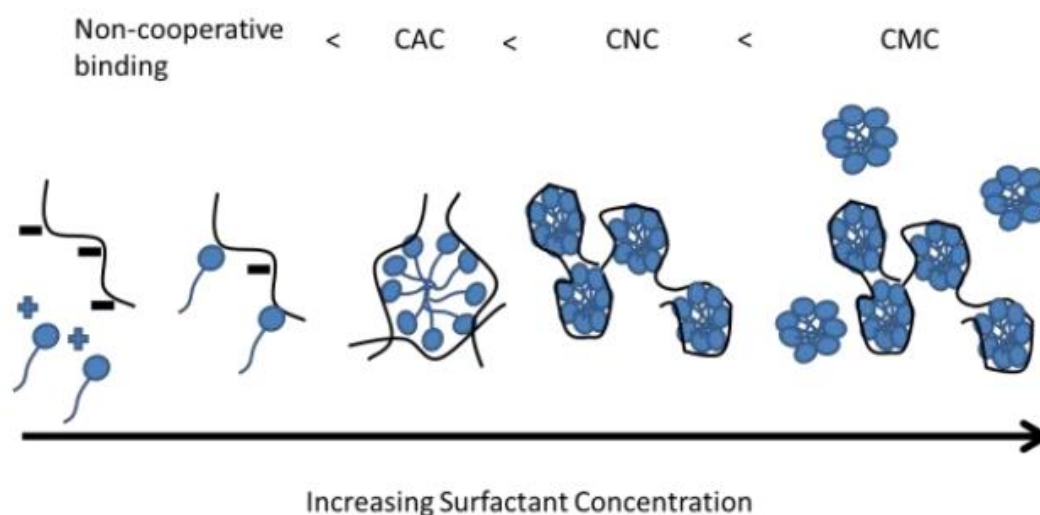
Figure 2.3. Schematic diagram of the evolvement of micelle like the structure of surfactants on the polyelectrolyte with increasing surfactant concentration. [Reprinted with permission from (Khan and Brettmann, 2018). Copyright © 2018 by the Nasreen Khan and Blair Brettmann. Licensee MDPI, Basel, Switzerland

2.1.2. Colloidal stability of IONPs and IONPs composites (aggregation and dispersion)

Aggregation and dispersion of nanoparticles was a challenge for successful manipulation of nanoparticles in the engineering application. By referring to a review article on IONPs, the colloidal stability is mainly determined by the collision frequency and collision efficiency of IONPs (Champagne *et al.*, 2018). The collision frequency of IONPs is caused by the Brownian motion, concentration of IONPs and hydrodynamic flow. Meanwhile, collision efficiency of IONPs is originated by particle interaction forces such as van der Waals force, electrostatic force, steric force, magnetic force and hydration force.

Brownian motion of IONPs is arisen by the random movement of IONPs in a fluid which can cause the collisions between IONP (Einstein, 1905). As the diameters of IONPs are smaller than 1 μm, the Brownian motion effect is dominant for the whole

suspension (Zhang *et al.*, 2012). The IONPs will undergo diffusion due to the Brownian motion. Hence according to Stoke-Einstein equation, the diffusion coefficient of IONP, D_t can be described as follow:

$$D_t = \frac{k_B \text{T}}{3\pi\eta d_h} \qquad (2.1)$$

where k_B is the Boltzmann constant, T is the absolute temperature, η is the suspension's viscosity and d_h is the hydrodynamic diameter of IONPs. From equation 2.1, diffusivity of IONPs is affected by the size, viscosity, and temperature. When the sizes of IONPs are reduced to less than 100 nm, the diffusion of IONPs will increase and thus collision of the frequency of IONPs will eventually increase. The aggregation rate of IONPs will be higher due to the smaller hydrodynamic diameters of IONPs. The collision frequency, Z_{AB} of particles is calculated from the equation (Chai *et al.*, 2015):

$$Z_{AB} = n_A n_B (r_A + r_B)^2 \sqrt{\frac{8\pi k_B \text{T}}{\mu_{AB}}} \qquad (2.2)$$

where n_A and n_B are the number density of species A and B, r_A and r_B are the species' hydrodynamic radii, k_B is Boltzmann constant and μ_{AB} is both species' reduced mass. From the Equation 2.2, the concentration of IONPs is one of the experimental parameters which can affect the collision frequency. A high concentration of IONPs will increase the aggregation of IONPs by increasing the probability of collisions (He *et al.*, 2007).

For the interaction forces of nanoparticles, electrostatic and steric forces are the repulsion forces between nanoparticles to enhance the colloidal stability of suspension (Champagne *et al.*, 2018). Van der Waals force is the main attraction force

among two nanoparticles (Israelachvili, 2011). It is always occurred between nanoparticles by depending on radius and distance as the natural material of nanoparticles is controlled as IONPs. Meanwhile, the ultimate fate of IONPs either aggregated or dispersed, are relying on the balance between repulsive electrostatic force and steric force and attractive van der Waals force. Surface coating is the primary strategy to enhance the steric force and electrostatic force. For instance coating of polyelectrolytes onto the surface of IONPs, the nanoparticles exhibited strong electrostatic and steric repulsions although the collision frequency is increased due to the low hydrodynamic diameter (Yeap *et al.*, 2012). The surface charge of polyelectrolytes coated IONPs can be affected by the two main parameters pH of suspensions and ionic strength of suspensions. The pH suspension could induce the changing of conformation of weak polyelectrolyte, poly (acrylic acid) (PAA) adsorbed on the IONPs and it will weaken the colloidal stability of IONPs composites (Ghosh *et al.*, 2011). Furthermore, ionic strength of suspension could also be shielding the electrostatic forces from the organic matters (chitosan) coated on the IONPs and resulted in low colloidal stability to the whole IONPs composites (Saleh *et al.*, 2008). However, PSS is a strong polyelectrolyte, Yeap *et al.* found out that that PSS coated IONPs was strong colloidal stability regardless of changing of pH (Yeap *et al.*, 2012). In this project, PSS complexation with surfactant will give a new challenge for the PSS coated IONPs although the PSS charge is independent to pH effect. As the new challenge is concerned, the binding of surfactant on the PSS would change the conformation of PSS during the formation of the micelle structure (Fundin, 1994; Khan and Brettmann, 2018).