CHAPTER II

THEORY AND LITERATURE REVIEWS

Basic principle of solid-phase extraction, knowledge of silica and sol-gel process are described in this chapter. The functionalization of this material and the characterization of adsorbent are next explained. Finally, the information on doping molecules (HPMSP) and related literature reviews are given in details.

2.1. Solid-phase extraction (SPE)

Despite the selectivity and sensitivity of analytical techniques, there is a crucial need for the preconcentration of trace elements before their analysis due to their frequent low concentrations in numerous samples especially water samples [1]. Additionally, since high levels of non-toxic components usually accompany analytes, a clean-up step is often required. Liquid–liquid extraction (LLE) is a classical method for preconcentrating metal ions and matrix removal. Solid phase extraction is another approach that offers a number of important benefits. It reduces solvent usage and exposure, disposal costs and extraction time for sample preparation. Consequently, in recent years SPE has been successfully used for the separation and sensitive determination of metal ions, mainly in water samples.

2.1.1. Basic principle of solid-phase extraction

SPE method always consists of three to four successive steps [2]. First, the solid sorbent should be conditioned using an appropriate solvent, followed by the same solvent as the sample solvent. This step is crucial, as it enables the wetting of the packing material and the solvation of the functional groups. In addition, it removes possible impurities initially contained in the sorbent or the packaging. Also, this step removes the air present in the column and fills the void volume with solvent. The nature of the conditioning solvent depends on the nature of the solid sorbent. Care must be taken not to allow the solid sorbent to dry between the conditioning and the sample treatment steps, otherwise the analytes will not be efficiently retained and poor recoveries will be obtained. If the sorbent dries for more than several minutes, it must be reconditioned. The second step is the percolation of the sample through the solid sorbent. Depending on the system used, volumes can range from 1 ml to 1 litre. The sample may be applied to the column by gravity, pumping, aspirated by vacuum or by an automated system. The sample flow-rate through the sorbent should be low enough to enable efficient retention of the analytes. During this step, the analytes are concentrated on the sorbent. Even though matrix components may also be retained by the solid sorbent, some of them pass through, thus enabling some purification (matrix separation of the sample). The third step may be the washing of the solid sorbent with an appropriate solvent, having a low elution strength, to eliminate matrix components that have been retained by the solid sorbent, without displacing the analytes. The final step consists on the elution of the analytes of interest by an appropriate solvent, without removing retained matrix components. The solvent volume should be adjusted so that quantitative recovery of the analytes is achieved with subsequent low dilution. In addition, the flow-rate should be correctly adjusted to ensure efficient elution. It is often recommended that the solvent volume be fractionated into two aliquots, and before the elution to let the solvent soak the solid sorbent.

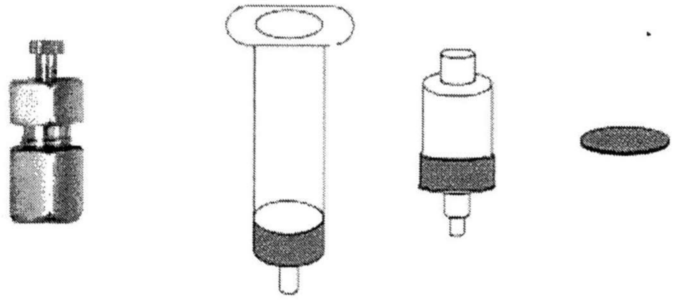
2.1.2. Sorbents

Sorbents are important in SPE. The nature and properties of the sorbent are of prime importance for effective retention of metallic species [3]. Careful choice of the sorbent is thus crucial to the development of SPE methodology. In practice, the main requirements for a solid sorbent are: (1) the possibility to extract a large number of trace elements over a wide pH range along with selectivity towards major ions; (2) the fast and quantitative sorption and elution; (3) high capacity; (4) regenerability; and (5) accessibility.

The sorbents used for SPE are similar to those used in liquid chromatography. Examples of favorite sorbents are silica, polystyrene-divinylbenzene based sorbents, and carbon sorbents. Among these materials, silica is the most popular packing materials since it presents the advantages of mechanical, thermal and chemical stability under various conditions.

2.1.3. Sorbent containers

The sorbent may be packaged in different formats such as filled micro-columns, syringe barrels, cartridges and disks as shown in Figure 2.1 [1].



Micro-column Syringe barrel Cartridge Disk

Figure 2.1 Disposable sorbent containers [1]

2.1.3.1. Micro-columns

The use of a micro-column is a common procedure for extraction of trace elements from various samples. It affords the opportunity of packing the column with the desired sorbent. In addition, the size of the column (i.e. the sorbent weight) may be adapted to the sample volume. In particular, it allows larger sample volumes, thus enabling the concentration of metal ions at very low concentration level.

2.1.3.2. Disposable cartridges and syringe barrels

The most frequently used design in off-line SPE is the cartridge or the syringe barrel. They are usually made of polypropylene or polyethylene and filled with packing materials having different functional groups. The solid sorbent is contained between two 20 mm polypropylene frits (in some cases they may be made of glass). Cartridges vary from as little as 100 mg to 1 g or more. Syringe barrels range in size from 1 to 25 ml and packing weights from 50 mg to 10 g. Solvent reservoirs may be used at the top of the syringe barrels to increase the total volume (50 – 100 ml).

2.1.3.3. Disks

The use of flat disks with a high cross-sectional area may largely prevent all the problems encountered with columns, cartridges and tubes. The packing material is usually embedded in an inert matrix of polytetrafluoroethylene (PTFE) microfibrils, with a typical composition of 90% w/w sorbent and 10% w/w PTFE fibers.

2.1.4. Mechanisms in SPE

There are four mechanisms in SPE depends on the nature of the sorbents [1].

2.1.4.1. Reverse phase

Reverse phase separations involve a polar or moderately polar sample matrix and a nonpolar stationary phase. The analyte of interest is typically mid to nonpolar. Retention of organic analytes from polar solutions onto these SPE materials is due primarily to the attractive forces between the carbon-hydrogen bonds in the analyte and the functional groups on the silica surface. To elute an adsorbed compound from a reverse phase SPE tube or disk, use a nonpolar solvent to disrupt the force that bind the compound to the packing.

2.1.4.2. Normal phase

Normal phase SPE procedures typically involve a polar analyte, a mid to nonpolar matrix and a polar stationary phase. Retention of an analyte under normal phase conditions is primarily due to interactions between polar functional groups of the analyte and polar groups on the sorbent surface. A compound adsorbed by these mechanisms is eluted by passing a solvent that disrupts the binding mechanism. Usually a solvent that is more polar than the sample's original matrix.

2.1.4.3. Ion exchange

Ion exchange SPE can be used for compound that are charged when in a solution (anionic (negatively charged) compounds and cationic (positively charged) compound). The primary retention mechanism of the compound is based mainly on the electrostatic attraction of the charged functional group on the compound to the charge group that is bonded to the silica surface. In order for a compound to retain by ion exchange from an aqueous solution, the pH of the sample matrix must be one at which both the compound of the interest and the functional group on the bonded silica are charged.

2.1.4.4. Adsorption

Compound of interests are usually adsorbed on solid phases through van der Waals forces or hydrophobic interaction. More recently, reversed polymeric phases have appeared, especially the styrene-divinylbenzene copolymer. Elution is usually performed with organic solvents, such as methanol or acetonitrile. Such interactions are usually preferred with online systems, as they are not too strong and thus they can be rapidly disrupted. However, because most analyte species are ionic, they will not be retained by such sorbents.

2.1.5. <u>Adsorption isotherms</u>

Adsorption is often described in terms of isotherms which show the relationship between the concentration of adsorbate remaining in solution at equilibrium and its adsorbed extent at a constant temperature [10-12]. A number of isotherm models have been proposed to describe adsorption process but the most frequently uses are (a) linear sorption isotherm, (b) Langmuir isotherm and (c) Freundlich isotherm (Figure 2.2).

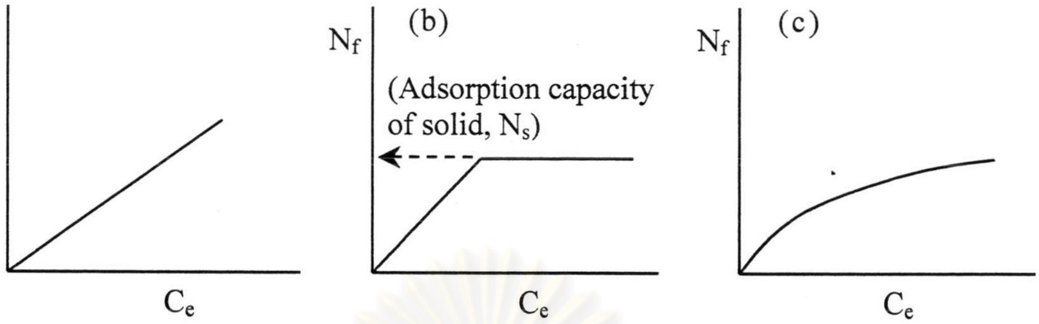


Figure 2.2 The adsorption isotherms: (a) linear sorption isotherm (b) Langmuir isotherm (c) Freundlich isotherm.

If the sorption isotherm is linear, the amount adsorbed, N_f, (mg/g) is directly proportional to the concentration of metal at equilibrium, C_e, (mg/L) and the slope of the isotherm is referred to the distribution coefficient, K_d. The linear sorption isotherm is expressed as:

$$N_f = K_d C_e \tag{2.1}$$

In the Langmuir model, the adsorption increases linearly with the increasing of solute concentration at low C_e values and approaches a constant value at high concentration. The adsorbed concentration approaches a constant value because there are limited numbers of adsorption sites in solid sorbent. The Langmuir equation can be described mathematically with equation 2.2.

$$N_f = \frac{K_L N_S C_e}{1 + K_L C_e} \tag{2.2}$$

Where N_f is the amounts of metal adsorbed at equilibrium (mg/g), K_L is the equilibrium constant for the adsorption reaction, N_S is the number of sorption sites (maximum amounts of metal adsorbed) (mg/g) and C_e is the concentration of metal at equilibrium (mg/L). After linearization of the Langmuir isotherm, we obtain:

$$\frac{C_e}{N_f} = \frac{C_e}{N_S} + \frac{1}{K_L N_S} \tag{2.3}$$

The plot of C_e/N_f versus C_e gives a straight line with a slope equal to $1/N_S$ and an intercept equal to $1/K_L N_S$. The values of N_S and K_L are then calculated from the slope and intercept of the Langmuir plot, respectively.

If the number of adsorption sites is large relative to the number of metal ions, it is possible to use the Freundlich isotherm:

$$N_f = K_d C_e^{N} \tag{2.4}$$

Where N_f is the amounts of metal adsorbed at equilibrium, K_d is the distribution coefficient, C_e is the metal concentration at equilibrium and N is a chemical-specific coefficient. The linear form of Freundlich model derived from equation 2.4 is expressed in the following equation.

$$\log N_f = \log K_d + N \log C_e \tag{2.5}$$

The plot of log N_f versus log C_e yields a straight line with a slope equal to N and an intercept equal to log K_d.

2.1.6. Application of SPE for metal extraction

The use of SPE for metal extraction has been growing in the past few year due to their advantages offered for trace element determination: ease of automation and possible on-line coupling to instrumental techniques.

For solid-phase extraction of metal, the amounts of metal ions on the adsorbents and the distribution ratio of the metal were calculated according to the following equations.

$$q = (C_i - C_e) \times L/W \tag{2.6}$$

$$D = q/C_e \tag{2.7}$$

Where q is the amount of metal on the adsorbents ($\mathrm{mol/kg_{adsorbent}}$), D is the distribution ratio of the metal ($\mathrm{L/kg_{adsorbent}}$), C_i is the initial metal concentration in the aqueous solution (mol/L), C_e is the metal concentration in the aqueous solution at equilibrium (mol/L), L is the volume of the aqueous solution (L), and W is the weight of the adsorbents (kg).

2.2. Silica

2.2.1. General

Silica is an inorganic polymer with the general structure formula of $SiO_2 \cdot xH_2O$. Silica has a porous structure and can be classified in three types dependent on its pore size.

1. Microporous silica with pore diameter smaller than 2 nm.
2. Mesoporous silica with pore diameter between 2 and 50 nm.
3. Macroporous silica with pore diameter larger than 50 nm.

Silica is used in most chromatographic applications [13]. The primary advantages of silica are its availability in a wide range of well defined surface area and pore size as well as its relative low cost. Furthermore, the silica is the most widely used solid support due to its high thermal, chemical and mechanical stability properties compared to other organic and inorganic supports.

Amorphous silica with a porous structure consists of three kinds of silanol (Si-OH) on the surface: isolated, germinal and vicinal. The surface also contains siloxane bonds (Si-O-Si). The silanols are hydrophilic while siloxanes are hydrophobic. The surface of amorphous silica is depicted in Figure 2.3.

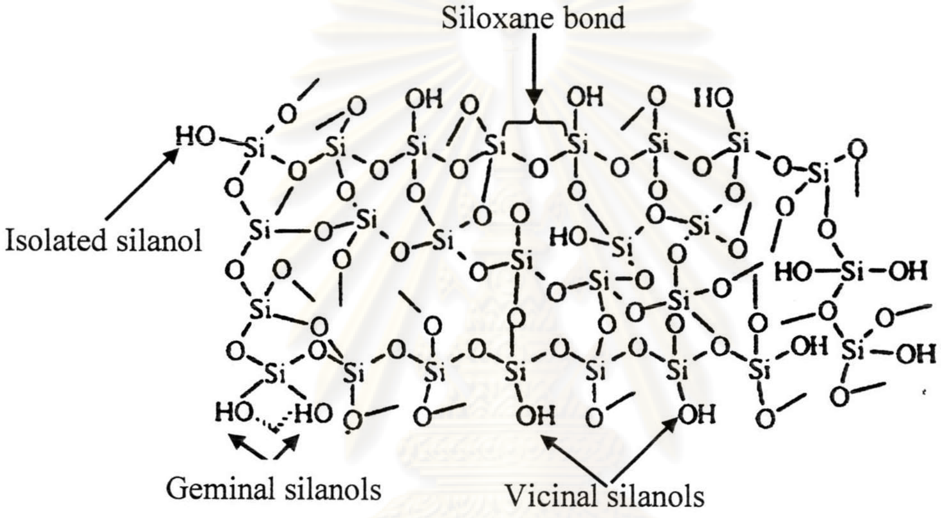


Figure 2.3 Structure of a silica gel showing siloxane bond, isolated silanol, germinal silanol and vicinal silanol [3].

Two parameters are usually used to characterize the ability of silica to act as an ion-exchanger: the pK_a value of the ion-exchange site and point of zero charge (pzc). Most chemical properties of silica are due to surface silanols. The silanol groups form strong hydrogen bonding with water molecules. These adsorbed water molecules can be removed by heating at 150°C under vacuum for several hours. The hydroxyl groups on the porous silica surface have also an acidic character. The pK_a value of the reaction

$$\equiv Si\text{-}O\text{-}H \rightleftharpoons Si\text{-}O^{-} + H^{+} \qquad (2.8)$$

is about 6.8 (± 0.5) [13]. The acidic character of surface silanols confirms some ion-exchange properties on porous silica. At pH = 7, silica consists of negative charge in solution. For this reason, the silica is known to act as inorganic ion exchanger, but its application to the extraction of ionic species is not so popular because the interaction between many metal ions and the silica surface is weak and non-selective. Therefore, it is essential to increase the selectivity of extraction of silica by functionalization process.

The point of zero charge (pzc) where the surface charge is zero and the isoelectric point where the electrical mobility of silica particles is zero have been measured by many methods. The pzc of silica have been variously reported to be from pH 0.5 to 3.7 according to a review of the literature [14]. However, a pH of around 2 ± 0.5 appeared to be an average for various types of silica ranging from purified ground quartz to colloidal silica. Some variation may be expected, depending on whether the surface is crystalline or amorphous, possibly on particle size, and especially on the presence of impurities.

2.2.2. Sol-gel process

The sol-gel process involves the evolution of inorganic networks through the formation of a colloidal suspension (sol) and gelation of the sol to form a network in a continuous liquid phase (gel) [15]. The precursors for synthesizing these colloids consist of a metal or metalloid element surrounded by various reactive ligands. Metal alkoxides are the most popular precursor because they react readily with water. The most widely used metal alkoxides are alkoxysilanes, such as tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS). However, other alkoxides such as aluminates, titanates, and borates are also commonly used in the sol-gel process, often mixed with TEOS.

At the functional group level, three reactions are generally used to describe the sol-gel process: hydrolysis, alcohol condensation, and water condensation. This general reaction can be described in terms of two separated reactions as shown below.

Hydrolysis:

$$\equiv\text{Si-OR} + H_2O \rightleftharpoons \equiv\text{Si-OH} + \text{ROH} \qquad (2.9)$$

Alcohol condensation:

$$\equiv\text{Si-OR} + \text{HO-Si}\equiv \rightleftharpoons \equiv\text{Si-O-Si}\equiv + \text{ROH} \qquad (2.10)$$

Water condensation:

$$\equiv\text{Si-OH} + \text{HO-Si}\equiv \rightleftharpoons \equiv\text{Si-O-Si}\equiv + H_2O \qquad (2.11)$$

The hydrolysis reaction occurs when an amount of water is added to the silicon alkoxide. Intermediates obtained as a result of this reaction include alcohol, which corresponds to the alkoxide used. In the condensation or polymerization reactions alkoxide groups (-SiOR) react with hydroxyl groups (-SiOH), which are formed during the hydrolysis step, to yield siloxane bonds (-Si-O-Si). Both hydrolysis and condensation reactions of the alkoxide precursor are occurred by acid or base catalyst.

However, the characteristics and properties of a particular sol-gel inorganic network are related to a number of factors that affect the rate of hydrolysis and condensation reactions such as pH, temperature and time of reaction, reagent concentrations, catalyst nature and concentration, H_2O/Si molar ratio, aging temperature and time, and drying. Of the factors listed above, pH, nature and concentration of catalyst, H_2O/Si molar ratio, and temperature have been identified as most important. Thus, by controlling these factors, it is possible to vary the structure and properties of the sol-gel-derived inorganic network over wide ranges.

2.2.3. Functionalization of materials

Chemical immobilization, impregnation technique and chemical doping are technologies used to immobilize chemical reagent in porous support [4]. The same classes of matrix modification are used for organic and inorganic supports. Chemical immobilization is the direct chemical bonding of organic reagents to materials. This technique has found many applications in chromatography due to the high stability of chemical bond. However, this type of encapsulation is very specific, so the reaction conditions and precursors have to be specially tailored for each case. Impregnation technique is another method used to immobilize organic molecules in materials. The organic reagents are physically adsorbed, chemisorbed or physically encased in porous supports. Typical impregnation procedures are carried out by exposing the porous support to a concentrated solution of the reagent in organic solvent, which after drying gives a support coated in reagent. The technology is highly versatile and the same solvents, manufacturing apparatus and impregnation protocol can be used to immobilize difference reagents in a variety of organic and inorganic matrices. However, the adhesion of the reagent to the support is rather weak and short life time. Otherwise, application of impregnation is restricted to disposable or renewable devices. Chemical doping is the direct encapsulation of organic reagents by using sol-gel process. This method is gaining popularity for immobilization of organic compounds in organic and inorganic matrices due to its high versatility. This technique is simplicity in its preparation and low temperature process. In general, the modified material using this chemical doping method has better mechanical properties and chemical durability as compared to impregnated materials. The doping method has found applications in various kinds of field such as catalysis, sensors, and separation [5, 6, 16, 17].

2.2.4. Mesoporous silica

Mesoporous silica was first synthesized by a group of researchers at Mobil Corporation in 1992 [18]. This material is characterized by narrow pore size distributions, turnable from 1.5 to 10.0 nm. The extremely high surface areas (>1000 m^2/g) and the precise tuning of pore sizes are among the many desirable properties that make such materials the great interest. This research group proposed later a Liquid Crystal Templating (LCT) mechanism to explain the formation of mesoporous structure [19]. For this mechanism, the silicate condensation is not a dominant factor in the formation of mesoporous structure, but the whole process of two possible pathways shown in Figure 2.4 is. For pathway 1, hexagonal crystal mesophases form prior to the addition of silicate species. While for pathway 2, the silicate species added to the reaction mixture influence the order of isotropic rod like micelles of the desired liquid crystal phase, i.e. hexagonal mesophase. Therefore, the mesophase is structurally and morphologically directed by the existence of liquid crystal micelles and mesophases.

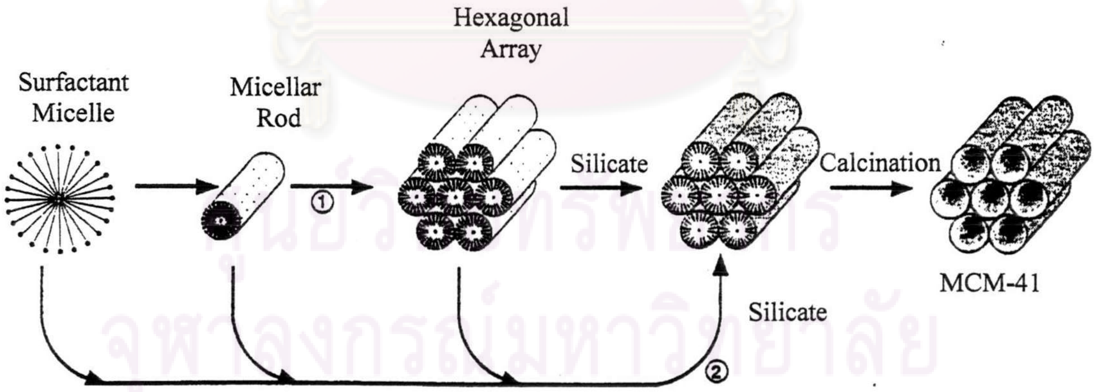


Figure 2.4 Schematic model of liquid crystal templating mechanism via two possible pathways [19].

Chen *et al.* [20], carried out an *in situ* ^{14}N-NMR spectroscopy to investigate the mechanism of the formation of MCM-41 and summarized the inexistence of hexagonal liquid crystal during the MCM-41 synthesis. So, this hexagonal phase could not be the structure-directing agent for the synthesis of mesoporous materials. This conclusion was in agreement with the already proposed mechanism through route 2. The randomly ordered rodlike organic micelles interacted with silicate species to yield two or three monolayers of silica around the external surface of micelles. Subsequently, these composite species spontaneously formed the long-range order. The mechanism is illustrated in Figure 2.5.

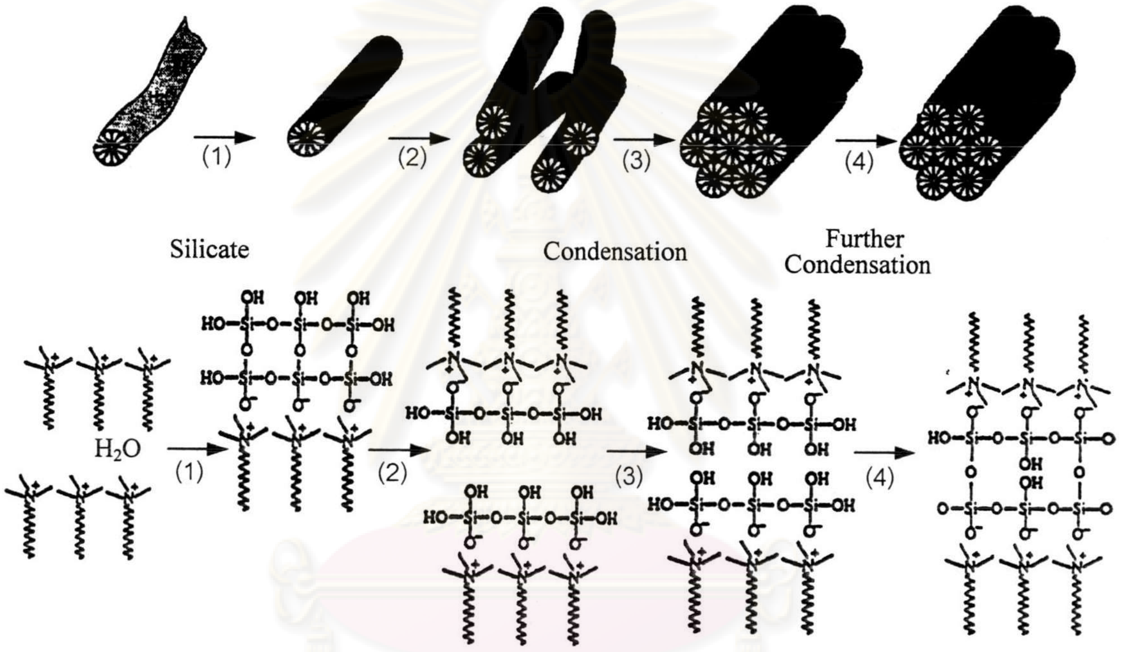


Figure 2.5 Assembly of silicate-encapsulated rod [20].

Huo *et al.* [21] developed a model that made use of the cooperative organization of inorganic and organic molecular species into three dimensionally structured arrays. A micellar solution of CTAB transformed to a hexagonal phase in the presence of silicate anions were shown : this was consistent with the effect of electrolytes on micellar phase transitions. The silicate anions ion-exchanged with the surfactant halide counterions, to form a silicatropic liquid crystal (SLC) phase that involved silicate-encrusted cylindrical micelles as shown in Figure 2.6. The SLC phase exhibited behavior very similar to typical lyotropic systems, except that the surfactant concentrations were much lower and the silicate counterions were reactive.

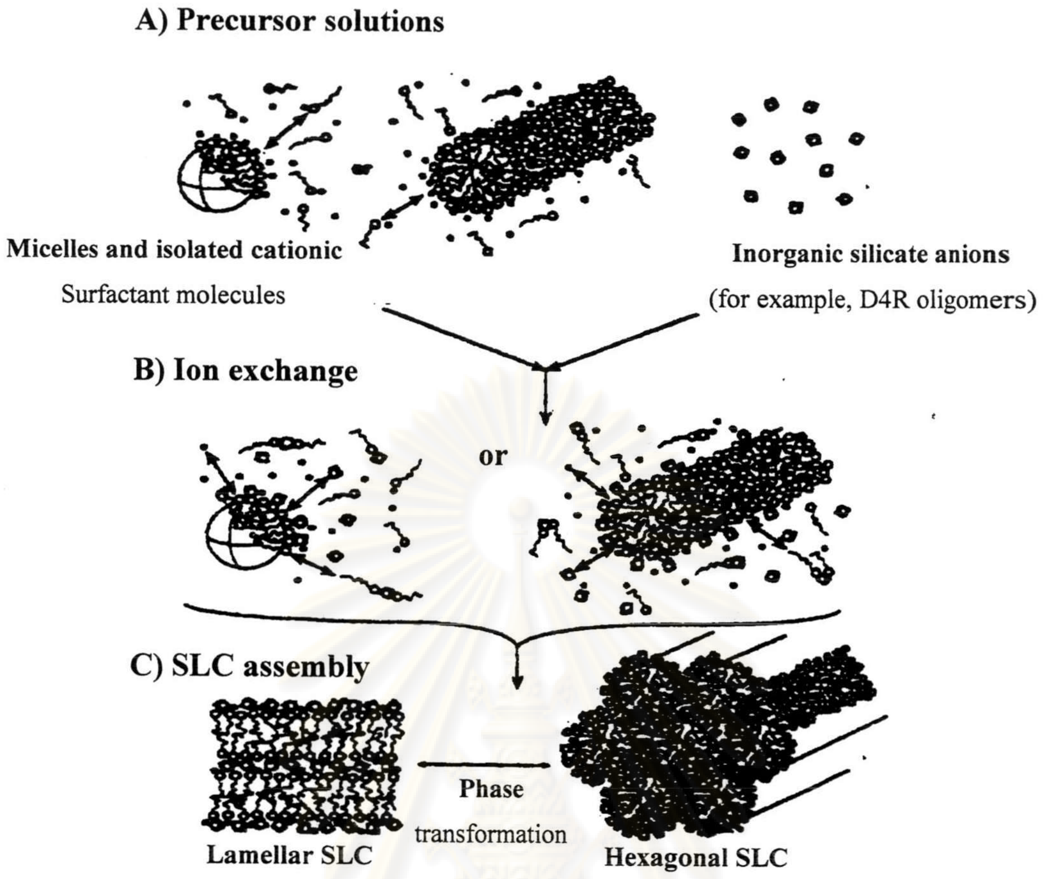


Figure 2.6 Formation of a silicatropic liquid crystal phase [21]

Four pathways were presented in the synthesis of mesostructured surfactant-inorganic biphasic arrays as shown in Figure 2.7 [22]. In the two direct pathways, cationic surfactants S^+ were used for matching with negatively charged, inorganic species I^- to form S^+I^- mesostructure and anionic surfactants (S^-) were employed for cationic inorganic species (I^+) to form S^-I^+ mesostructure. Organic-inorganic combinations with identically charged partners are possible. In the two mediated pathways, the formation of the mesostructure was mediated by the counter charged ions which must be present in stoichiometric amount, i.e. $S^+X^-I^+$ (X^- was a counter anion), and $S^-M^+I^-$ (M^+ was a metal cation). In cases where the degree of condensation of the oligomeric ions which form the walls is low, the removal of the template leads to the collapse of the ordered mesostructure. It would then be of both fundamental and practical interest to develop new synthetic routes which allow the template to be more easily removed.

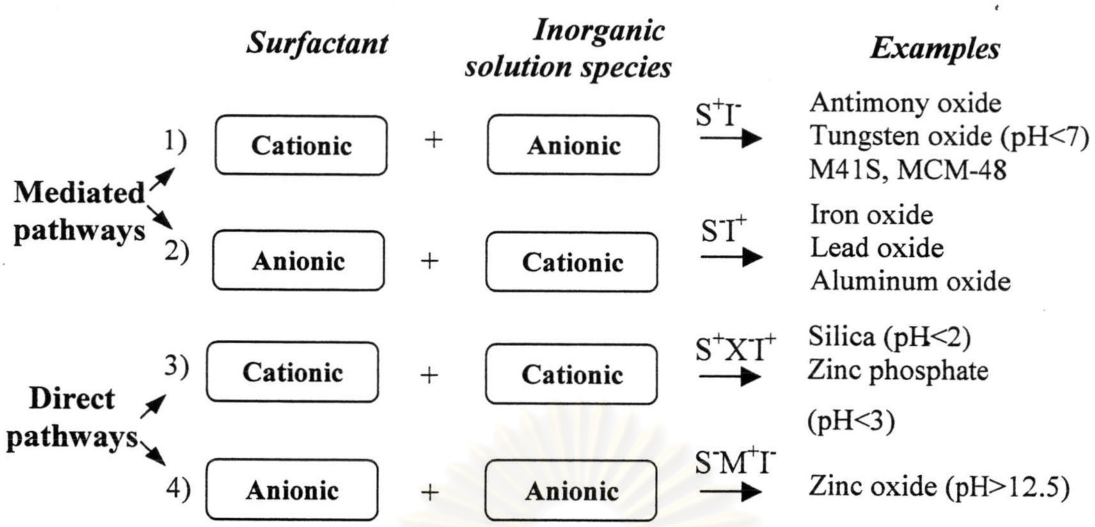


Figure 2.7 A general scheme for the self-assembly reaction of different surfactant and inorganic species [22].

2.3. Characterization of materials

2.3.1. Characterization of adsorbents

2.3.1.1. Classification of pores

Adsorbents of high surface area are generally porous. There are many different kinds of rigid and non-rigid pore structures and an adsorbent is likely to contain a range of pores of different size and shape. A convenient classification of pore according to their effective width, adopted by IUPAC is as follow [23]:

1. Micropores have widths not exceeding about 2 nm.
2. Mesopores have widths between 2 nm and 50 nm.
3. Macropores have widths exceeding about 50 nm.

Pores can be closed, blind, or through. Each pore can be isolated or, more frequently, connected to other pores to form a porous network (Figure 2.8).

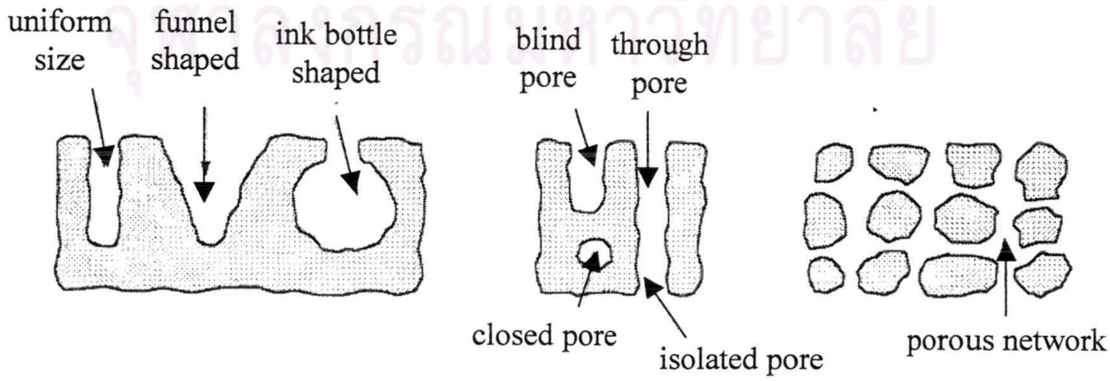


Figure 2.8 Type of pores [23].

2.3.1.2. Classification of adsorption isotherms

The first stage in interpretation of physisorption isotherm is the identification of isotherm type and hence the nature of the adsorption process. The physisorption isotherm may be grouped into the six types as shown in Figure 2.9.

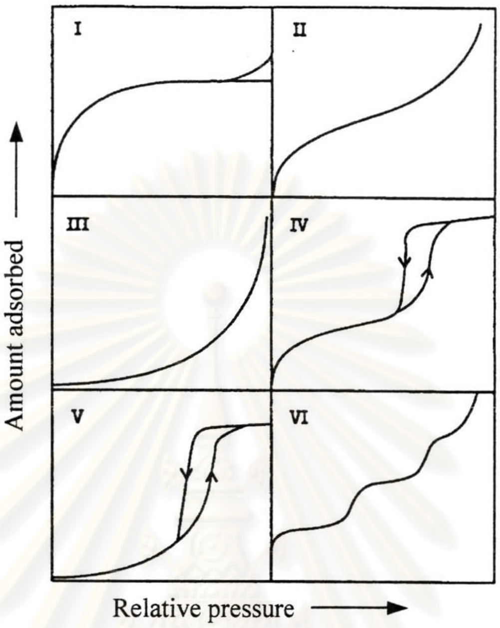


Figure 2.9 Types of adsorption isotherms [23]

The Type I isotherm is given by a microporous solid (e.g. zeolites, active carbon) having a relatively small external surface. In contrast, the Type II isotherm represents unrestricted monolayer-multilayer adsorption on a non-porous or macroporous adsorbent. The characteristic features of the Type IV isotherm are its hysteresis loop and the limiting uptake at high p/p_0. These features are associated with capillary condensation taking place in mesopores. Type VI represents stepwise multiplayer adsorption on a uniform non-porous surface, whereas Types III and V are Associated with weak adsorbent-adsorbate interactions.

2.3.1.3. Adsorption hysteresis

Capillary condensation/evaporation usually gives rise to hysteresis in the multiplayer region of the physisorption isotherm. Four characteristic types of hysteresis loop are shown in Figure 2.10. Type H1 loop is given by porous materials having narrow distribution of mesopore size and shape. Many porous oxides tend to give Type H2 loops, but in these systems the distribution of pore size and shape is not well defined and the broadness of the loop appears to be associated with pore blockage effects. Type H3 and H4 loops are usually found on solid consisting of aggregates or agglomerates of particles forming slit shaped pore (plates or edged particles like cubes), with uniform (H4) or non-uniform (H3) size and/or shape. If no hysteresis, this is the case of blind cylindrical, cone-shaped and wedge-shaped pores.

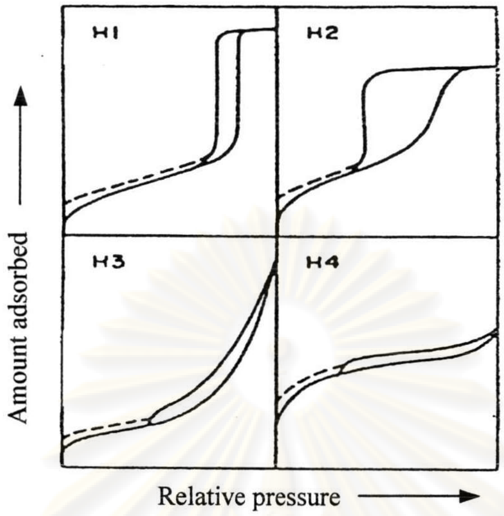


Figure 2.10 The four hysteresis shapes of adsorption isotherm usually found by nitrogen adsorption [23].

2.3.1.4. Determination of surface area

The Brunauer-Emmett-Teller (BET) method is still the most widely used procedure for the determination of the surface area of finely-divided and porous materials. The BET equation is usually expressed in the linear form.

$$\frac{p}{n(p_o-p)} = \frac{1}{nC} + \frac{(C-1)}{n_m C}\frac{p}{p_o} \tag{2.12}$$

where n is the amount adsorbed at the relative pressure p/p_o and n_m is the monolayer capacity. According to the theory, C is a constant which is related exponentially to the heat of adsorption for the first layer.

The second stage in the application of the BET method is the calculation of the surface area from the monolayer capacity, n_m. This requires a knowledge of the average area, a_m, occupied by the adsorbate molecule in the complete monolayer. Thus,

$$A(BET) = n_m . l . a_m \tag{2.13}$$

where A(BET) is the surface area of the adsorbent and l is the Avogadro constant.

2.3.1.5. Mesopore volume and mesopore size distribution

The mesopore size is usually calculated with the methods proposed by Barrer, Joyner and Halenda (BJH method). The model is simple. In the capillary condensation region ($p/p_o>4$), each pressure increase causes an increase of the thickness of layer adsorbed on pore walls and capillary condensation in pores having a core size r_K defined by Kelvin equation.

$$r_K = \frac{2\,\gamma\, v_L}{RT \ln (p_o/p)} \tag{2.14}$$

where p/p_o is the relative pressure at which condensation occurs, r_K is the radius of a hemispherical meniscus, γ is the surface tension and v_L is molar volume of the liquid condensate.

2.3.2. X-Ray Diffraction technique

X-ray diffraction is a typical technique for the investigation of structure and crystallinity of materials [24]. In common with other types of electromagnetic radiation, interaction between the electric vector of X-rays and the electrons of the matter through which it passes results in scattering. When an X-ray beam strikes a crystal surface at some angle θ, a portion is scattered by the layer of atoms at the surface. The unscattered portion of the beam penetrates to the second layer of atoms where again a fraction is scattered, and the remainder passes on to the third layer (Figure 2.11). The cumulative effect of this scattering from the regularly spaced centers of the crystal is diffraction of the beam in much the same way as visible radiation is diffracted by a reflection grating.

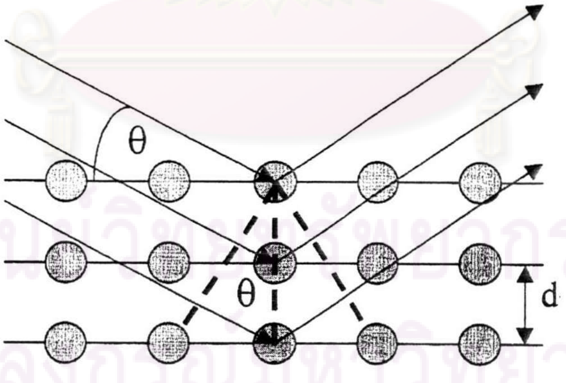


Figure 2.11 Diffraction of X-ray by a crystal [24]

The relationship between wavelength, atomic spacing (d) and angle was solved as the Bragg equation.

$$n\lambda = 2d \sin\theta \tag{2.15}$$

This equation is a fundamental relationship in X-ray diffraction analysis, as it permits the interplanar distance, d, to be calculated from the measured diffraction angle, θ, for a known wavelength of the primary radiation. Quantity, n, corresponds to the diffraction order.

2.3.3. Fourier-transform infrared (FT-IR) spectroscopy

The infrared spectroscopy is generally regarded as one of the technique to study the characteristic property of a compound [24-26]. All molecules are made up of atoms linked by chemical bonds. The movement of atoms and chemical bonds can be likened to that of a system comprised of springs and balls in constant motion. Their motion can be regarded as being composed of two components, the stretching and bending vibrations. The frequencies of these vibrations are not only dependent on the nature of the particular bonds themselves, but are also affected by the entire molecule and its environment. The vibration of bonds which accompany electric vibrations will increase their amplitude if an electromagnetic wave (infrared beam) strikes them. The difference between a molecule and the spring-ball system is that the vibrational energy levels of the former are quantized. Therefore, only the infrared beam with a frequency exactly corresponding to that required to raise the energy level of a bond will be absorbed. The amplitude of the particular vibration is increased suddenly by a certain amount and not gradually. When the sample is irradiated by an infrared beam whose frequency is changed continuously, the molecule will absorb certain frequencies as the energy is consumed in stretching or bending different bonds. The transmitted beam corresponding to the region of absorption will naturally be weakened and thus a recording of the intensity of the transmitted infrared beam versus wavenumbers or wavelength will give a curve showing absorption bands. This is the infrared spectrum.

In FT-IR spectrometer, the signal “seen” by the detector is termed an interferogram. The region of maximum signal in the interferogram is called the centerburst and corresponds to the point when the moving and fixed mirrors in the interferometer are equidistant from beam splitter. The interferogram is transfered mathematically by the Fourier transform to produce a single beam spectrum. The Fourier transform takes the data recorded as a function of mirror movement in distance and produces data as a function of frequency in cm^{-1} (wave number). The principle of the Michelson interferometer is shown in Figure 2.12.

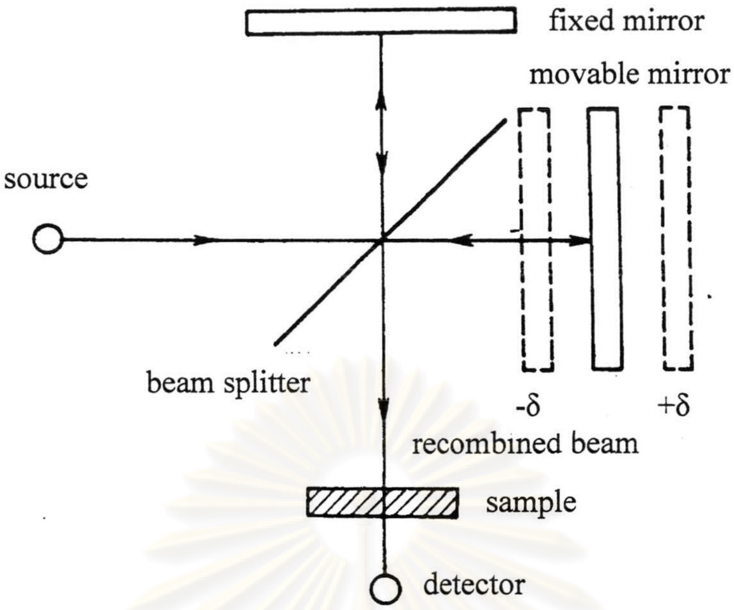


Figure 2.12 A diagram of the Michelson interferometer [25].

2.3.4. Particle size measurement

Malvern laser diffraction technique is one of a method for the determination of particle size of material [27, 28]. Laser diffraction works by measuring the light scattered from particles as they pass through a laser beam. Depending on their size, the particles scatter light at different angles. The laser diffraction method is based on the Mie theory, which predicts the scattering intensities for all sphere particles of varying size. Light scattering theory may be categorized in terms of two theoretical frameworks. One is the theory of Rayleigh scattering that is applicable to small, dielectric and spherical particles. The second is the theory of Mie scattering that encompasses the general spherical scattering solution without a particular bound on particle size. Hence, Mie scattering has no size limitations and converges to the limits of geometrical optics for the large particles. Mie theory, may be used for describing most sphere particle scattering systems, including Rayleigh scattering.

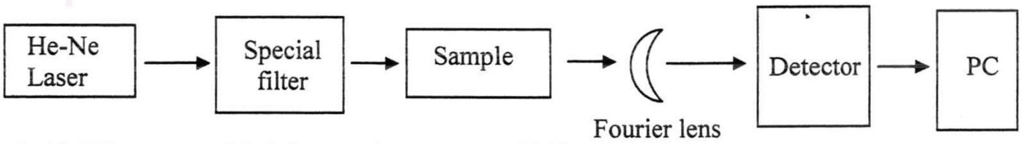


Figure 2.13 Diagram of Malverns instrument [28]

Figure 2.13 illustrates the diagram of Malverns instrument. The Helium-Neon laser of wavelength 632.8 nm is used as a light source, which illuminates the dispersed particles in the measuring zone. During the laser diffraction measurement, the particles are passed through a focused laser beam. These particles scatter light at an angle that is inversely proportional to their size. The angular intensity of the scattered light is then focused by a Fourier lens to a detector, which consists of a large number of photosensitive elements radiating outward from the center. A novel property of a Fourier lens is that it collects the scattered light from an ensemble of particles, and overlays the common angles of scattering on the detector array. The intensity of the scattered light is measured and an optical model (Mie theory) is used to calculate the scattering pattern and a mathematical deconvolution procedure. A volumetric particle size distribution is calculated until it is close to the measured pattern.

2.3.5. Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) is considered as a micro-analytical technique which is able to image or analyze materials that can not be observed with the resolution offered by other visible techniques [24]. In light microscopy, a specimen is viewed through a series of lenses that magnify the visible-light image. Whereas, the scanning electron microscope (SEM) does not actually view a true image of the specimen, but rather produces an electronic map of the specimen that is displayed on a cathode ray tube (CRT).

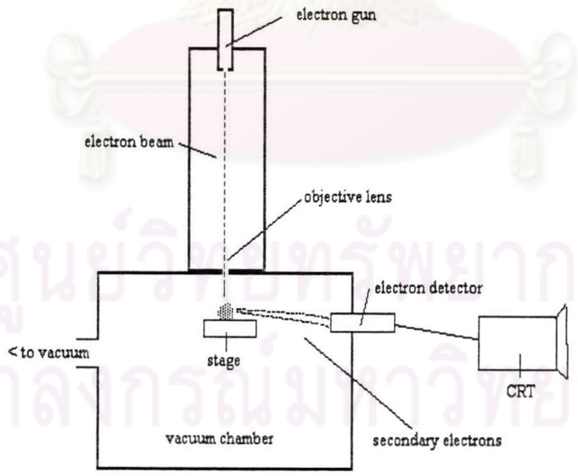


Figure 2.14 Schematic of a SEM [24]

The figure above shows a schematic for a generic SEM. Electrons from a filament in an electron gun are beamed at the specimen in a vacuum chamber. The beam forms a line that continuously sweeps across the specimen at high speed. This beam irradiates the specimen which in turn produces a signal in the form of either x-ray fluorescence, secondary or backscattered electrons. The SEM has a secondary electron detector. The signal produced by the secondary electrons is detected and sent to a CRT image. The scan rate for the electron beam can be increased so that a virtual 3-D image of the specimen can be viewed. The image can also be captured by standard photography.

2.4. Doping molecules (HPMSP)

1-Phenyl-3-methyl-4-stearoylpyrazol-5-one (HPMSP), a β-diketone whose structure is shown in Figure 2.15, can be easily synthesized and is widely used in liquid-liquid extraction. Indeed, HPMSP has a potential to form different types of coordination compound due to its several electron-rich donor centers and the tautomeric effect of enol form and keto form. HPMSP has thus been used as an advantageous metal extractant or a chelating agent especially in the spectroscopic determination of trace metals. Various metals such as Cd(II), Co(II), Cu(II), Ni(II) and Zn(II) are the examples of metal that can be form stable complexes with the HPMSP molecules [7, 8, 29-31].

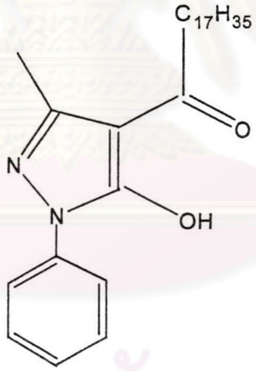


Figure 2.15 Structure of 1-phenyl-3-methyl-4-stearoylpyrazol-5-one (HPMSP)

2.5. Literature review

Since the development of an ordered mesoporous silicate using a surfactant templating by a team of scientist from Mobil, this kind of materials has aroused enormous interest among researchers in various fields on account of their potential application [18, 32-34]. There are several researches relating to the synthesis of such materials. Some works were described below.

Mokaya [35] studied the restructure of mesoporous silica by performing the secondary synthesis in which the calcined MCM-41 silica is used as a silica source.

The factors investigated are (1) the time allowed for hydrothermal recrystallisation at 150°C, (2) the amount of amorphous silica available during the recrystallisation and (3) the use of large pore MCM-41 as a silica source. The results had shown that the increase in the time allowed for recrystallisation had little effect on the basal spacing but resulted in a gradual and considerable increase in the pore wall thickness. The pore size therefore decreased slightly while both pore volume and surface area undergone more significant reduction. These textural changes were accompanied by restructuring of the particle morphology from the small sphere shaped particles of the original MCM-41 to much larger particles that were both elongated and sheet (plate)-like.

Pang and colleagues [36] prepared mesoporous silicas with different morphologies from an aqueous reaction mixture consisting of an inexpensive silica source, template (CTAB) and NaOH solution. The narrow distribution of mesopores and high specific surface area of the mesoporous silica was obtained when using TEOS as silica precursor. The molar ratio of TEOS/CTAB and the stirring were the significant parameter which affected the shape transition of the silica.

For the researches concerning the functionalization of silica by chemical doping, Jeronimo and coworkers [17] prepared a 4-(2-pyridylazo)resorcinol (PAR) doped silica thin film to be used as an optical sensor for a determination of Zn(II) in insulin. Several parameters such as type of precursor, catalyst and concentration of ligand were studied. The optimum performance of the sensor was obtained when using tetraethoxysilane (TEOS) and 3-amynopropyltriethoxysilane (3-APTES) as silica precursors, NaOH as catalyst and 3.0×10^{-2} M of ligand.

Ghiasvand and colleagues [37] presented a successful route to prepared bis(2-hydroxyphenylamino) glyoxime doped octadecyl silica membrane disks and applied this material to separate and concentrate ultra trace amounts of Cu(II) ions contained in aqueous samples. The maximum capacity of the membrane disks modified with 25 mg of ligand was found to be 280 ± 32 μg of Cu(II). Also, the desorption of Cu(II) ions was achieved using 0.2 M nitric acid solution as eluent.

For the researches related to the potential pyrazolone ligand, Tong and colleagues [30, 38] prepared the HPMSP impregnated microporous silica to be used as a sorbent for the preconcentration of Cu(II), Co(II) and Ni(II). These metal ions were quantitatively retained on the proposed sorbent above pH 4. The adsorptioncycle were repeated ten times with no observable decline in the efficiency of such sorbent. The preconcentration factor of this microporous material was found to be 40. The method was successfully applied to sodium chloride solution and tap water samples. The satisfactory results were also obtained when using this sorbent for the extraction of Fe(III), Mn(II), Pb(II) and Zn(II) from environmental samples.

The functionalization of microporous silica by HPMSP molecules using doping technique was firstly introduced by Intasiri [9]. Various synthesis parameters such as speed of drying, temperature and gelation time were studied. The results had shown that a significant factor was the speed of drying. The physical and the Cu(II) extraction properties of the sorbent were also examined. The auther concluded that the Cu(II) adsorption capacity of the sorbent depended mainly on its surface area. The Cu(II) extractability of the sorbent obtained by batch method was found to be 0.04 mol/kg. The sorption behaviors of this HPMSP doped microporous sorbent towards Co(II) and Ni(II) ions were also studied and the adsorption capacity was found to be 0.03 and 0.04 mol/kg, respectively. Furthermore, this sorbent was successfully applied to the preconcentration of Cu(II) ions from tap water.

The same research group [29] proposed also the preparation of the HPMSP doped mesoporous silica to be used as a sorbent. This HPMSP modified support was found to be better than the same functionalized microporous material in terms of facility, rapidity and reproducibility of the synthesis. In addition, the Cu(II) sorption capacity of the mesoporous silica was approximately 5 times greater than that of microporous silica. The influence of parameters on the synthesis of HPMSP doped mesoporous silica was also investigated [39]. These parameters were the concentration of NaOH used as catalyst and the amounts of functionalized molecules. The author concluded that the appropriate concentration of NaOH for the synthesis should be 0.1 M. For the extent of functionalized molecules, the author recommended the number 0.06 as the mole ratio of HPMSP/TEOS used for the synthesis since higher extent of HPMSP would result to the difficulty in dissolution of these molecules. Then, the extraction properties of the HPMSP doped mesoporous silica synthesized with the mole ratio of HPMSP/TEOS equal to 0.06 was examined by batch method. The target metal ions were Co(II), Cu(II) and Ni(II) and the parameters studied were pH of metal solution, initial metal concentration and the presence of foreign ions in metal solution. The sorbent had shown a high adsorption capacity to the extraction of Cu(II) even at low pH. For the adsorption of Co(II) and Ni(II), the pH of metal solution should be higher than 4 to reach the maximum capacity of material. Moreover, the sorption capacity of this sorbent was enhanced with the presence of foreign ions in the metal solution. The complete elution of metal ions from the sorbent were achieved by 1 M HNO_3.

The arrangement of surfactant (CTAB) and ligand (HPMSP) in the HPMSP doped mesoporous silica was later investigated by ^1H HRMAS NMR [40]. From this research, the surfactant molecules in the modified silica could be classified into two types: the bound CTAB and the free CTAB. The bound CTAB is the templating surfactant which is bonded by electrostatic interaction to the silica surface whereas the free CTAB interacts with the encapsulated HPMSP molecule by electrostatic and hydrophobic interactions to form ion pairs at the same ratio.

According to the literature mentioned above, most researches were focused on only some parameters which affected the synthesis of the HPMSP doped mesoporous silica. Furthermore, the study of its metal extraction behavior was limited on some metal ions and the extraction method was performed only by batch experiment. Thus, in this work, much more crucial synthesis factors including the type of silica precursor and the amounts of surfactant molecules should be clarified in order to attain the optimum parameter for the preparation of such effective sorbent. In addition, the role of other extraction factors on the metal extractability of the HPMSP modified silicas determined by both batch and column methods is also a subject of interest with the aim of achieving the maximum efficiency and using this sorbent to the removal of different metals from various industrial wastewater samples.

2.6. Research objectives

2.6.1. To investigate the influence of parameters on the synthesis of HPMSP doped mesoporous silica.

2.6.2. To study the physical properties and to determine the effect of parameters on the metal extraction efficiency of HPMSP doped mesoporous silica.

2.6.3. To apply the HPMSP doped mesoporous silica to the removal of metal ions from industrial waste water samples.