CHAPTER 1

Introduction

In this chapter a brief description is provided of the properties of the components of the systems investigated in the present thesis.

1.1 Gold

Gold (atomic number $Z = 79$ and atomic mass 197) holds a special position among the metals owing to its unique characteristics. For at least three millennia, it has been known as “king of the metals” or the most noble of the metals referring to its resistance behind most corrosive forces. Many application of gold rely on its low chemical reactivity. Besides this, the nobility of gold causes problems in the study of its properties. Whereas chemically extremely robust, it is yet mechanically ductile and malleable. It has been treasured by man since antiquity because of its pretty colour, glittering appearance and rarity. This property makes it an ideal construction material for objects of cult and art, for jewellery and coinage. In more recent periods, besides its main use in jewellery and investment, because of its high electrical and thermal conductivity with outstanding resistance to corrosion, gold plays an important role in industrial application for the electrical and then electronics industry, especially telecommunications and information technology. Gold’s electrical conductivity is surpassed only by copper and silver, but unlike these metals gold does not tarnish. Where resistance to tarnish or corrosion is essential, gold becomes the most reliable of conductive metals. The latest generations of electronic equipments, which are developed thanks to gold include, for instance, microcircuits and switching
devices. Gold coating and plating is used in aerospace equipment, radiation inhibiting window panels, and solar-energy collectors.

Gold and its compounds are also employed in medicine and dentistry as a consequence of its biocompatibility. The earliest recorded medical use of gold was by the Chinese in 2500 BC. Since then, numerous cultures have utilized gold-based medicinal preparations for the treatment of various diseases including small pox, skin ulcers and measles. Throughout most of the 20th century gold compounds were investigated for a range of ailments, with the aim to understand the chemistry involved so that intelligent design of more effective and less toxic gold drugs could be undertaken. Recent years have seen a resurgence of interest in gold compounds in the treatment of cancer, with many prominent academic and industrial labs active in the field (Dou and Milacic, 2009). Gold(III) compounds generally exhibit significant cytotoxicity effects on cancer cells. In vitro pharmacological studies point out that some of these novel gold(III) complexes are highly cytotoxic toward cultured human tumor cell lines and are able to overcome resistance to platinum. In spite of uses in chrysotherapy, it has been found that gold drugs do accumulate in the kidney, liver, spleen and the hypothalamus. Concentration in the kidney can have particularly serious medical effects, and in animal studies excess concentration in hypothalamus is found to lead to obesity, hyperphagia, and brain damage.

Catalysis is another field where gold and its complexes are deeply involved (Stephen et al., 2006; Arcadi, 2008; Carabinerio and Nieuwenhuys, 2009). Gold compounds are often used to modify the properties of other catalysts. Gold metal is not usually regarded as a good catalyst, in contrast to its neighbour platinum in the periodic table. Indeed, it is often added to other noble metal catalysts to reduce their reactivity and thereby improve the selectivity of reaction.

As mentioned earlier, recently, the industrial demand of gold is increasing, and very recently also the private demand is showing an abrupt increase. Note that, in contrast to the increase of gold applications, mine production of gold is
considerably decreasing. Therefore, extraction and recovery of gold from scraps and waste promises to constitute an important and convenient activity (Akita, 1996; Shen, 2007).

Figure 1.1 shows in form of a diagram the distribution of the gold use. It should be noticed that, in recent years, the use of gold in electronics has reached the same level of the gold employment in investment. Well over 300 tons of gold are used annually only for electronic components such as ICs contacts and bonding wires, but, differently from gold employed in other uses, gold employed in electronics is in big part lost. Hence, the recovery of the metal from dumps offers an important recycling potential for the secondary supply of gold. With gold concentration 300-350 g/t for mobile phone and 200-250 g/t for computer circuit boards, this urban mine is significantly richer than that available in primary ores (Hagelüken and Corti, 2010).

![Figure 1.1 Distribution of gold applications 2006. Source cashforgold.to](image)

The booming growth in sales of electronic devices has led to a substantial net increase in gold demand over recent years (GFMS Ltd, 2010, Gold Survey 2010, London www.gfms.co.uk). Mobile phones and computers are a good example in this context (Table 1) (Hagelüken and Corti, 2010).
Table 1 Content of gold and other metals in mobile phones and computers in relation to total demand from these appliances and world mine production

<table>
<thead>
<tr>
<th></th>
<th>Mobile phones (a)</th>
<th>PC and laptops (b)</th>
<th>World mine prod. (c)</th>
<th>% from (a+b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>0.25g/unit = 325 t</td>
<td>1g/unit = 300 t</td>
<td>21000 t/a</td>
<td>3%</td>
</tr>
<tr>
<td>Au</td>
<td>0.024g/unit = 31 t</td>
<td>0.22g/unit = 66 t</td>
<td>2400 t/a</td>
<td>4%</td>
</tr>
<tr>
<td>Pd</td>
<td>0.009g/unit = 12 t</td>
<td>0.08g/unit = 24 t</td>
<td>220 t/a</td>
<td>16%</td>
</tr>
<tr>
<td>Cu</td>
<td>9 g/unit = 12,000 t</td>
<td>500 g/unit = 15,000 t</td>
<td>16 Mt/a</td>
<td>&lt;1%</td>
</tr>
</tbody>
</table>

Generally, gold recovery is performed from industrial waste by hydrometallurgical processes, involving chloride media. After dissolution (frequently in aqua regia (Cui, 2008)), several separation techniques, such as chemical precipitation (Marsden, 2006), ion exchange (Iglesias, 1999; Cortina, 2004), adsorption (Cox, 2005; Farag, 2007) or solvent extraction (Hilson, 2006; Narita, 2006; Shen, 2007) are used for gold recovery. Solvent extraction has been the most widely employed for the recovery of gold and other precious metals from chloride media solutions (Bock, 1950; Ichnicose, 1971; Das, 1976; Baghalha, 2007). However, growing demand for safety concern requires clean and efficient procedures. In recent years the research on metal extraction based on micelles, as nano-reactors, indicates that these particles can provide a useful tool for the development of new technologies suitable for the separation, extraction and recovery of metal-ions.

In most of its compounds gold has oxidation states (I) or (III). It is known that gold(I) compounds usually have linear stereochemistry and gold (III) compounds square planar stereochemistry. The +3 valence state produces species which are generally more stable than the +1 state. In aqueous solution, \( \text{AuCl}_4^- \) forms different gold(III) species depending on pH and chloride ion concentration. Bjerrum showed that the first two chlorides were displaced very rapidly but that the last two required time to dissociate from metal (Bjerrum, 1948). A sequence of mixed species \( \text{Au(OH)Cl}_3^- \), \( \text{Au(OH)}_2\text{Cl}_2^- \), \( \text{Au(OH)}_3\text{Cl}^- \) and
Au(OH)$_4^-$ can form from AuCl$_4^-$ on raising the solution pH. Unfortunately, the situation is more complicated than described, since it has been shown that also the Au(OH)$_3$ hydroxide can form from AuCl$_4^-$ on raising the solution pH and, eventually, precipitates. The state diagram of Figure 1.2 shows the conditions of predominance of the various gold(III) species in a solution containing Cl$^-$ ions (Baes, 1976).

![Figure 1.2 Predominance diagram of Au(III)—OH—Cl$^-$ species.](image)

1.2 Surfactants
The term surfactant is derived from SURFace ACTive AgeNT. A surfactant is a substance that reduces the surface tension of the medium in which it is dissolved. By lowering the interfacial tension between two media or interfaces the surfactant plays a key role in the removal and suspension of dirt.

Surfactants may be either of natural or synthetic origin. Surfactants from natural origin (vegetable or animal) are known as oleo-chemicals and are derived from sources such as plant oils or animal fats. They include, for instance, the lipids which are surfactants based on glycerol. Surfactants from synthetic origin are known as petro-chemicals and are derived from petroleum.
A surfactant molecule has a hydrophilic head and a long hydrophobic tail and for this reason it is often regarded as an amphiphilic molecule (Figure 1.3). Many of the physico-chemical properties of these molecules in solution stem from this ambivalency. However, small changes in the architecture of the surfactants, which alter the balance between hydrophobic and hydrophilic properties, can result in dramatic changes in their behaviour in solution.

![Figure 1.3 Structure of a generic surfactant.](image)

Surfactants can be categorized, according to the charge present in the hydrophilic portion of the molecule after dissociation in aqueous solution, in four main types: anionic, cationic, non-ionic and amphoteric/zwitterionic. The molecular structure of surfactants means that they have unusual properties, leading to both widespread and highly specialized applications. They can interact with water in a variety of ways, each of which disrupts or modifies the hydrogen bonding network of water. Surfactants are versatile molecules and they can be also classified, depending on their applications technology, as wetting, foaming, dispersing or deflocculating, emulsifier and detergent agents. The properties of surfactants fall into two broad categories: adsorption and self-assembly. The adsorption properties mean that surfactant molecules usually locate themselves at the interface between oil and water phase or water and air phase. This molecular property leads to the macroscopic properties of wetting, foaming, detergency and emulsion formation. Self-assembly is the tendency for surfactant molecules to organize themselves into extended structures in water.
1.2.1 Association of surfactant molecules
Surfactant molecules can associate in aqueous solution to form large aggregates, which, depending on the specific surfactant and solution conditions, can adopt a variety of shapes. This includes the formation of micelles, bilayers and vesicles (Figure 1.4). This remarkable phenomenon can be rationalized in terms of the tendency of apolar groups to avoid contact with water, while simultaneously the polar parts display a propensity to be strongly hydrated. The primary tendency for aggregation results from the hydrophobic effect (Tanford, 1978). The origin of this effect arises from the fact that hydrocarbon-water interactions are unfavorable compared to the “like-to-like” interactions of both hydrocarbon and water.

![Figure 1.4 Forms of surfactant aggregates: a) spherical micelles, b) rod like micelle, c) vesicle, d) bilayer.](image)

Surfactant molecules undergo cooperative association into aggregates of definite size and shape. The hydrophobic effect dictates a lower limit to the size of the aggregate because a minimum number of surfactant monomers have to be united in one aggregate before a sufficiently effective elimination of the hydrocarbon-water interface could be achieved. On the other hand, the existence of an opposing force to the hydrophobic effect, located at the hydrocarbon-water interface, prevents the aggregate from growing into larger assemblies. This repulsive force originated mainly from the electrostatic head-group repulsions (Patist et al.; 2002). The delicate balance between repulsive and attractive forces, which are coupled to specific regions in the molecule, leads to directional bonding and, therefore, to the formation of aggregates of a definite size and morphology. It should be noted that surfactant aggregation is
not limited to water and it exists in polar non-aqueous solvents too (Sjoberg and Warnheim, 1997).

1.3 Micelles
A spherical micelle is the simplest surfactant aggregate formed in aqueous solution. Micelles are small aggregates with a size of few nanometers. They are formed in such a way that their hydrophilic head groups are exposed to the water medium and their hydrophobic tails form a water free core. However, even after this organization some of the hydrophobic chain can be exposed to water. Extensive discussions have focused on the conformation of the alkyl chains in the interior (Dill, 1985; Gruen, 1985; Menger, 1985). It has been demonstrated that the alkyl chains of micellized surfactant are not fully extended. As a result, the methyl group of the surfactant molecules can be located near the surface of the micelle, and it has even been suggested that it is able to protrude into the aqueous phase (Clifford, 1965). They are definitely not all gathered in the centre of the micelle as is often suggested in pictorial representations. NMR studies have indicated that the hydrocarbon chains in a micelle are highly mobile, comparable to the mobility of a liquid alkane (Walderhaug, 1984).

Another topic of intense debate is the extent of water penetration into the hydrocarbon interior. Small-angle neutron scattering studies have resolved this matter by indicating that significant water penetration into the micellar core is unlikely (Dill et al., 1984; Tabony, 1984). However, at the interface, extensive contact between water and the hydrocarbon chain segments definitely occurs. The head-groups of the micelle are extensively hydrated. For ionic micelles, a large fraction of the counterions are located in the vicinity of the head-groups. These counterions normally retain their first hydration shell. The part of the surfactant that contains the head-groups and a variable fraction of the counterions is called the Stern region. This region has an important role in solubilization. Micelle solutions can solubilize an insoluble organic material by incorporating it either at the surface or in the inner core. This property gives
micellar solutions an important role in chemistry in terms of ability to solubilize materials, catalyze reactions, and extract metal, as it will be reviewed in the next sections.

Although spherical micelles are the most popular, they can also exist as ellipsoids, discs, elongated rods or lamellar in shape (Figure 1.4), depending on the properties of the solution and on the nature of the monomer surfactant. Israelachvili et al. (1976) have introduced the concept of “packing parameter”, allowing prediction of the type of aggregate formed by considering the cross-sectional head-group area and the length and volume of the non polar part of the amphiphile molecules. Surfactants containing a single alkyl chain usually form micelles when dissolved in water.

Micelles are also formed in non-polar solvents, where the amphiphiles cluster around small water droplets present in the system form an assembly containing the head group in the core. Such an assembly is known as a “reversed micelle”. The structures of a spherical and a reversed micelle are schematically represented in Figure 1.5.

![Figure 1.5](image_url)  
*Figure 1.5 Normal micelle (a) and reversed micelle (b).*

The concentration at which micelles start to form is called the critical micelle concentration (CMC). Micellisation is usually driven by an increase in entropy, resulting from the liberation of the water molecules from the hydrophobic hydration shells of the monomeric amphiphile molecules, whereas the enthalpy change is generally close to zero (Lindman and Wennerstroem, 1980).
Micelles are often depicted as static structures of orientated surfactant molecules; however, they are very dynamic aggregates. Actually they breakdown and reform rather rapidly. Ultrasonic, stopped-flow, temperature and pressure jump techniques have been employed to study the rates and the mechanism of the formation/dissociation process. In particular, these studies showed that there are two relaxation effects involved in the micelle formation process (Lang et al., 1975; Aniansson et al., 1976; Tondre and Zana, 1978). The first, in the order of microseconds, is associated with the exchange of monomers between micelles and the surrounding bulk phase. The second effect, in the milliseconds range, is attributed to the micelle formation and dissolution process. Due to this dynamic character, the size and shape of micelles are subject to appreciable structural fluctuations. The so-called aggregation number $n$, represents the number of surfactant monomer in a micelle. Average aggregation numbers are typically in the range of 40 - 100. Spherical micelles have aggregation number of less than 100 while cylindrical or lamellar micelles have aggregation number of several hundreds.

### 1.3.1 Critical micelle concentration

The concentration of surfactant at which micelles first appear in solution is called the critical micelle concentration or CMC. Above the CMC, the concentration of free surfactant is essentially constant, while the micelle concentration increases approximately linearly with the total surfactant concentration. The concentration at which micelles first become detectable depends on the sensitivity of the experiments used to determine the CMC. At this concentration, abrupt changes in several physical properties take place. Actually, the CMC can be experimentally determined from the discontinuity or inflection point in the plot of a physical property of the solution as a function of surfactant concentration (Patist, 2001), as shown in Figure 1.6. A wide variety of techniques involving the measurement of physical properties have been used to determine CMC values such as surface tension, electrical conductivity, light scattering, refractive index and viscosity. In the laboratory where this thesis has
been made the CMC values of sodium dodecylsulphate (SDS) and dodecyltrimethylammoniumchloride (DTAC) have been measured by conductivity and light scattering methods.

**Figure 1.6** Changes in some physical properties for an aqueous solution of sodium dodecyl sulphate (SDS) in the neighborhood of the CMC.

Many factors are known to affect the CMC value in aqueous media. Among these are (Patist, 2001):

- **Surfactant structure.** As the hydrophobic chain length increases, the CMC decreases. In contrast, increasing hydrophilicity of the polar parts will increase the CMC. Moreover, the introduction of branching, double bonds or polar functional groups to the alkyl chain leads to a CMC increase.
- **Electrolytes.** The higher the ionic strength, the lower the CMC becomes. Therefore, adding an electrolyte causes a decrease in the CMC, the effect being more pronounced for ionic surfactants.
- **Organic additives.** The addition of polar organic molecules (like medium chain length alcohols), which are adsorbed mainly in the outer portion of the micelles (at the surface), lowers the CMC. Hydrocarbons that dissolve into the inner core of the micelles slightly lower the CMC.
• Temperature. The effect of temperature on the CMC is rather complicated. Anyway, it does not influence much the CMC value. For non-ionic surfactants, the CMC decreases with increasing temperature. For ionic surfactants, the CMC decreases to a minimum value and then increases, displaying a U-shaped behavior.

• Pressure. Typically, the lower the pressure, the lower the CMC becomes.

• pH. Where surfactant molecules contain ionisable groups, the dissociation degree of the polar group will be very dependent on pH. In general, the CMC will be high at pH values where the group is charged and low when uncharged.

1.3.2 Solubilization

One of the most important characteristics of micelles is their ability to take up all kinds of substances. Actually a number of solutes, which would normally be insoluble or slightly soluble in water, dissolve extensively in the presence of micelles. Binding of these compounds to micelles is generally driven by hydrophobic and electrostatic interactions. Solubilization is usually treated in terms of the pseudo-phase model, in which the bulk aqueous phase is regarded as one phase and the micellar pseudo-phase as another. This allows the affinity of the solubilize for the micelle to be quantified by a partition coefficient, P. Several definitions of P can be found in the literature, differing in their description of the micellar phase; when dealing with catalysis by micellar aggregates it is more convenient to express P as a ratio of concentrations. Solubilization is believed to occur at a number of different sites in the micelle (Rosen, 1989) and the nature of the solubilize largely determines its position in the aggregate. Saturated hydrocarbons show a preference for the core of the micelle (Reinsborough, 1982). In contrast, solubilizes that contain hydrophilic substituents, such as alcohols or amines, prefer to stay at the surface, where the hydrophilic groups can remain largely hydrated (Porter, 1994). Note that a micelle offers several binding sites for relatively apolar molecules. These include the hydrophobic core and
hydrophobic binding sites located in the Stern region. The latter region is particularly flexible in binding molecules as it contains the highly hydrophilic surfactant head groups and hydrophobic domains due to backfolding of the surfactant tails as well as water molecules (Gruen, 1985). In the case that the solubilizate has an amphiphilic character itself, the apolar parts generally are directed towards the centre of the micelle and its orientation in the aggregate resembles that of the surfactant molecules. However, since microenvironments available for solubilization change continuously, due to the dynamic nature of micelles, any attempt to situate the solubilized molecule in specific sites of the micelle could be difficult.

1.3.3 Micellar Catalysis
Concerning reactive processes, it has been recognized for long time, that the reaction medium plays an important role in controlling the mechanism and rates of chemical reactions. Recently, the influence of organized assemblies, such as micelles, has attracted increasing attention. The chemical reactivity exhibited by molecules and ions organized around these assemblies is often very different from their reactivity in pure water. Actually, chemical reactions can be influenced in three main ways: by an increase or decrease of rate reaction, by an alteration in the reaction pathway and by an alteration in the reaction stereochemistry. Most of the research has focused primarily on the kinetics of the reactions involved. In the early 1970’s, the Russian school of Berezin (Berezin et al, 1970; Martinek et al, 1977) attempted to rationalize the effect that micelles had on reaction rates in solution (Figure 1.7). In the presence of ionic surfactants some reaction rates were dramatically enhanced over a narrow concentration range near the CMC to fall off more gradually with increasing surfactant concentration (Figure 1.7, curve (a)). In other reactions, the observed rates rose more gently to plateau in enzyme-like fashion (Figure 1.7, curve (b)). A further series of reactions displayed the opposite behaviour beyond the CMC, considering that the reaction rates decreased (Figure 1.7,
curve (c)). Usually, rate inhibition occurred, as with the enhancement effects, over a narrow surfactant concentration range.

**Figure 1.7** Effect of surfactants on reaction rates. Curves (a) and (b) represent micellar catalysis while curve (c) is a typical example of micellar rate inhibition.

The phenomenon of the rate enhancement is known as “micellar catalysis”. The fact that the surfactant is not consumed in the reaction and that the surfactant concentration required to bring about marked effects is usually very low, justifies the use of the term “micellar catalysis”. On the other hand, in many instances, the micelles bring about considerable shifts in equilibrium constants; therefore the term “micellar catalysis” is somewhat incorrect (Romsted and Bunton, 1997). The interest in micellar catalysis phenomenon came from many areas. The industry was interested for example in searching for quicker and more efficient routes to synthesize important organic compounds. The efficiency of micellar catalysis relies on two principal factors. First, there is the effect of the micellar environment on the rate-controlling step in the reaction mechanism. The relative free energies of the reactant(s) and/or the transition state can be altered when the reaction takes place in the micellar phase instead of the bulk water (Romsted, 1976). However, further studies have shown that
this effect is often rather small and cannot account for the very large rate changes in many micellar systems. A more important consideration is the localization of the reacting species in the relatively small volume of the micelles compared to the bulk solution. This leads to a large increase in the effective concentration and the observed rate increases accordingly. An important conclusion is that rate enhancements of bimolecular and higher order reactions are not due to large change in kinetic rate constants but instead are a consequence of the localized concentration of reactants at the micelle-solution interface. The simplest case of micellar catalysis applies to unimolecular reactions where the catalytic effect, according to the above considerations, will depend on the efficiency of binding of the reactant to the micelle and on the differences in the reactivity of the reagent in the bulk aqueous and micellar environments. For more complicated bimolecular or higher-order reactions, the rate of the reaction will be affected also by the local concentration of the reacting species in or at the micelle.

The kinetic data analysis of chemical reactions in micelles generally involves the use of the well-known pseudo-phase model (Shinoda and Hutchinson, 1962; Menger and Portnoy, 1967), which assumes the micellar solution as consisting of two separate phases. The reaction may take place in both the aqueous and micellar pseudo-phases and the overall reaction rate is the sum of the rates in each pseudo-phase. A rate promotion occurs when both reactants are preferentially located in the micelles, while a rate decrease follows if only one of the reactants has been incorporated into the micelles, since in the latter case the two reaction partners are separated.

The pseudo phase model has been applied to a wide variety of reactions (Bunton, 1979); however, modifications have been proposed to account for the competitive counterion binding of reactive and inert counterions (Romsted et al, 1991). From the applications standpoint, potential problems with micellar catalysis include the competitive binding between reactive and non reactive counterions, which can greatly reduce the rate of reaction, and the fact that the surfactant must be ionic and opposite in charge compared with water soluble
reactants. For instance anionic micelles inhibit the reactions of organic substrates with anions by incorporating the substrate and (at least partially) excluding the anions. On the contrary, cationic micelles incorporate both nonionic and anionic reagents and increase rates of anionic nucleophilic reactions.

1.4 Micellar Extraction
Micellar systems have attracted considerable attention in the last few years as potential extracting media and continue to have a broad appeal for extraction applications. Solutes that bind to micelles in solution are extracted to different extents, depending on the micelle-solute binding interactions. Hydrophobic compounds are favorably partitioned in the non-polar microenvironment, while metal ions can bind electrostatically to the polar head of the surfactant, or can be extracted by complexation with a ligand soluble into the micellar pseudo-phase, thus being preferentially in form of metallic chelates. The whole process resembles conventional extraction, where the organic phase has been replaced by a micellar pseudo-phase acting as a receiving phase for solutes. The replacement of the organic phase by pseudo-phases built up with surfactants offers an attractive alternative to classical solvent extraction. Micellar media, indeed, provide a number of potential advantages over water/organic solvent two phase systems. Firstly, the extraction occurs in a medium which is essentially aqueous so that this system is environmentally acceptable. Secondly, the micelles are nanometer-sized droplets uniformly dispersed through the aqueous medium so that no stirring is required since the system is single phase and homogeneous. Thirdly, micelles act as micro-reactors, able to concentrate the reagents and enhance the reaction rate. Finally, extracting agents (or ligands), have often limited solubility in water, but this is considerably enhanced in micellar solutions. For effective metal recovery, the separation of the micellar pseudo-phase from the aqueous phase has to be achieved. It can be carried out by means of ultrafiltration (Micellar Enhanced Ultrafiltration or Ligand Modified Micellar Enhanced Ultra Filtration).
1.4.1 Micellar-Enhanced Ultrafiltration/Ligand-Modified Micellar-Enhanced Ultrafiltration

A large number of studies have demonstrated that the separation of the micellar pseudo-phase from the aqueous phase can be achieved by ultrafiltration using membranes with pore diameter smaller than the size of the micelle (Scamehorn and Harwell, 1988). Ultrafiltration is a membrane separation process aimed at dissolved or dispersed particles, which have size ranging from 1 to 100 nm. As a consequence, the pore size is too large to reject small molecules (below $10^3$ Da). Micellar Enhanced Ultrafiltration (MEUF) is a surfactant-based separation process in which surfactants are added to a waste stream to promote the removal of small molecules. MEUF has been widely used to remove metal ions (Li et al, 2006; Juang et al., 2003; Scamehorn et al., 1994; Liu and Li, 2005) and organic contaminants (Douilia and Xiarchos, 2007; Zaghbani et al., 2007; Kim et al., 1998; Dunn et al., 1989) from dilute aqueous solution. Concerning the metals, in which we are mainly interested, the basis of the MEUF technique is the specific binding force between surfactants and metals. Multivalent metal ions have been successfully recovered through MEUF using surfactants having opposite charge. Usually micelles of anionic surfactants (one such typical surfactant is sodium dodecyl sulphate) have been used for the removal of metal ions which will be attracted by the negatively-charged micelle surface. The micelle solution is subsequently passed through an ultrafiltration membrane with pore sizes small enough to retain the micelles and the associated metal ions. As a result, the permeate (which passes through the membrane) will contain very low amounts of unattracted metal and surfactant, while the retentate will have high concentrations of both metal and surfactant and will be much smaller in volume than the initial solution. One advantage of MEUF is that organics and heavy metal ions can be removed simultaneously, provided that the micelles have a charge opposite to the target metal ions (Lee et al., 2005; Baek and Yang, 2004; Witek et al., 2006). On the other hand a disadvantage is that there is little selectivity in removing ionic species from solution, except on the basis of charge. Actually, Scamehorn et al.
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(1994) removed divalent cadmium, zinc, copper and calcium ions and their mixtures with an efficiency of at least 96%. The trapping of metal ions on the micellar pseudo-phase can be achieved also by specific complexation with an amphiphilic ligand bound to the surface or solubilized into the core of the micelle. The extent of the metal ion binding depends on the stability constant of the metal-ligand complex and the use of extractants able to selectively bind the target metal ion can be very important for selective metal separations. In this case the process is referred to as Ligand Modified-Micellar Enhanced UltraFiltration (LM-MEUF). By using a cationic surfactant in an LM-MEUF process, the micelle will reject the cations which are not specifically bound to the solubilized ligand, into permeate. The result is that certain target ions can be highly concentrated in the retentate, while ion expulsion causes the noncomplexed metal ions to become concentrated in the permeate. For instance, Klepac et al. utilized N-n-dodecyliminodiacetic acid in combination with cetylpyridinium chloride (Keplac et al., 1991) for the selective rejection of copper, while europium(III) was determined in cetyltrimethylammonium bromide micelles by LM-MEUF using a series of extractants derived from 5-pyrazolone (Hebrant et al., 2001). Theoretical models able to explain and predict the performances of MEUF/LM-MEUF have been proposed (Scamehorn et al., 1994; Dharmawardana et al.; 1992). Moreover, a systematic comparison between solvent extraction and MEUF for the removal of copper from aqueous solutions demonstrated that when the volume ratios organic/aqueous or micellar pseudophase/aqueous phase have similar values, the two extraction techniques are equally efficient (Hebrant et al., 1998). On the other hand, a comparative economic analysis of copper removal from water by ligand-modified micellar-enhanced ultrafiltration and by conventional solvent extraction indicates a 17% higher capital and a 43% higher operating cost for the LM-MEUF process compared to the solvent extraction process (Filippi et al., 1998). Since the MEUF techniques has been developed there have been a lot of applications on the removal of cationic metals, such as Cu$^{2+}$, Co$^{2+}$, Ni$^{2+}$ and Cd$^{2+}$ (Akita et al, 1996), some on the removal of anionic pollutants (Fe(CN)$_6^{3-}$, CrO$_4^{2-}$,
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(NO\textsuperscript{3−}) (Baek et al., 2003) and a few studies have been conducted on the removal of precious metals (Akita et al., 1997). However, not much attention has been given so far to the problem of metal recovery after ultrafiltration. If MEUF or LM-MEUF permits efficient metal concentration, there still exists the problem of subsequent metal recovery from the micellar solution (retentate). Some authors (Reiller et al. 1996) investigated the possibility of metal release by changing ligand and medium conditions (i.e. pH or ligand concentration). Akita et al. (1996) limited themselves to observing that salt addition depresses metal retention and that this characteristic could be useful for the recovery of metal ions from the retentate solution, while Liu and Li (2005) employed an electrolysis process to recover copper.

1.5 Mechanism of ligand substitution at square-planar complexes

The knowledge of the equilibria and mechanisms of metal interaction with the extractant can be of great relevance for the optimization of the extraction and recovery of metal ions based on the LM-MEUF. It is therefore useful at this point to summarize the main aspects of the mechanism of ligand substitution at square planar metal complexes since the structures of the precious metals, when they react with PADA in LM-MEUF, are those of chloro complexes, i.e. PdCl\textsubscript{4}−, PtCl\textsubscript{4}− and AuCl\textsubscript{4}−.

The general features of the mechanism of metal complexes formation in solution have been known since the beginning of the sixties (Basolo and Pearson, 1967) when intensive kinetic studies on ligand substitution at platinum(II) have been undertaken mainly by the schools of Basolo, Tobe and Cattalini.

Tetracoordinated complexes of Pd(II), Pt(II), Au(III), and in some cases of Ni(II) and Cu(II) as well, display a square-planar geometry. Concerning the mode of ligand replacement on the coordination shell of these metals, the Pt(II) complexes, beside being the first to be examined (as outlined above), are also the most intensively investigated. Studies on ligand replacement at other metals are more limited and more recent, since, owing to the rapidity of some
of the processes involved, rate measurements on ligand binding to metals other than platinum(II) could be performed only after that the apparatuses for fast reaction studies were commercialized.

The general kinetic behaviour of planar square complexes towards ligand replacement at the metal coordination shell has lead to the formulation of a common mechanism as described below.

The replacement of a ligand X, coordinated to a metal in a planar structure, by a nucleophilic ligand Y, is shown in the reaction scheme of Figure 1.8 were L and T are generic ligands which remain coordinated on the central metal and are not directly involved in the ligand substitution process. Note that T is in trans-position with respect to the leaving ligand X.

\[ Y + \left[ \begin{array}{c} L \\ X \\ L \end{array} \right] \xrightarrow{L,T} \left[ \begin{array}{c} L \\ X \\ L \end{array} \right] \xrightarrow{L,Y} \left[ \begin{array}{c} Y \\ L \\ L \end{array} \right] + X \]

**Figure 1.8** Mechanism of the reaction of ligand replacement in square-planar complexes.

The reaction rate of the process depicted in Figure 1.8 is in most cases expressed by the two term equation (1.1)

\[ \text{Rate} = -d[ML_2TX]/dt = (k_1+k_2[Y])[ML_2TX] \] (1.1)

The reaction path corresponding to \( k_1 \) (not shown in the reaction scheme) refers to the parallel solvent attack to the central atom while the pathway corresponding to \( k_2 \) refers to the attack of the entering group Y. In the experiments conducted in the excess of Y the pseudo first-order rate constant, \( k_{obs} \), is a linear function of the concentration of Y and depends on the individual rate constants according to equation (1.2).
It has been shown that the formation of the transition states of both pathways $k_1$ and $k_2$ do involve an expansion of the metal coordination number from 4 to 5. Such an expansion implies that the transition states do assume the configuration of a trigonal bipyramid or that of a square pyramid. It has been suggested, however, that both geometries can be consecutively developed in the course of the replacement (McAuley, 1979). The reaction product is anyway a square-planar complex as the reactant.

Many of the kinetic studies performed in the sixties, (mainly on ligand substitution at Pt(II)) were concerned with the search of factors that could affect the reaction rates, as, for instance, the role of the entering group, the role of the leaving group, the role of ligands that, although bound to the metal, are not directly involved in the reaction pathway, and, finally, the role of the solvent (Cattalini, 1970; Basolo and Pearson, 1967; Langford and Gray, 1965). If simple dependence of the rate constant on the entering ligand concentration (equation (1.2)) is displayed by substitution reaction at Pt(II), it will be shown in this work that substitution at Au(III) follows a more complex kinetic behaviour.

1.6 The acid dissociation constants of week acids in the presence of surfactants

The hydrogen ion concentration in water (bulk solution) generally differs from the value on the micelle surface. For instance, in the presence of SDS micelles, the negatively charged surface will attract protons resulting in an increase in the proton concentration at the surface with a consequent decrease in the pH. Hartley and Roe (1940) showed that the surface pH$_s$ is related to the bulk pH$_w$, at 25 °C, by the following equation:

$$\text{pH}_s - \text{pH}_w = 59.2$$  (1.3)
where $\Psi$ is the surface potential of the micelle expressed in mV. The high surface potential of the SDS micelle ($\Psi = -120$ mV) leads to a decrease in the local pH at the surface which, according to equation 1.3, is equivalent to about two units. This result shows that $[H^+]_s/[H^+]_w \approx 100$, i.e. the proton concentration on the micelle surface is one hundred times higher than in water. On the contrary, for a cationic surfactant (such as DTAC) the repulsion towards the positive hydrogen ions makes the pH on the micelle surface higher with respect to the bulk solution pH.

The measured $pK_A$ of a ligand with weak acid characteristics, which is located on the micelle surface, is also shifted. Actually, the major influence on the $pK_A$ shift is attributed to the increased proton concentration close to the micelle surface, rather than an effect on the intrinsic $pK_A$ of the ligand, arising from the change in environment (James and Robinson, 1978). Again following Hartley and Roe (1940), at 25°C the surface $pK_A$, $(pK_A)_s$, is related to the bulk $pK_A$, $(pK_A)_w$, by equation 1.4.

$$(pK_A)_s - (pK_A)_w = - \frac{\Psi}{59.2}$$

Based on the above considerations any evaluation of data obtained for micellar systems requires the knowledge of the surface $pK_A$, $(pK_A)_s$, should be considered.