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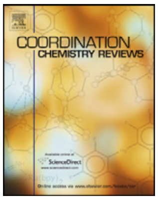

Review

Metal ion extraction in microheterogeneous systems

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ABSTRACT

Metal ion extraction in microheterogeneous systems (micelles, vesicles and polymeric micelles) research works are reviewed taking into account both the studies of the extraction equilibrium and the extraction kinetics. Dealing with the extraction equilibrium, beyond the principles governing its implementation and potential applications, light is thrown on two particular points: (i) the comparison of the means by which the pseudophases separation may be carried out and (ii) the stoichiometries of the complexes formed in the micelles. Kinetics studies are reviewed with the purpose of describing the specificities brought by microheterogeneous systems in the field of metal ion extraction, a focus being made on the specific interaction the surfactant molecules may have with one of the reacting species.

Abbreviations: APG, alkylpolyglycoside; Brij35, (dodecyloxy)polyethoxyethanol; BuOH, n-butanol; CDBA, cetyl dimethyl benzyl ammonium chloride; $CDBA^+$, cetyl dimethyl benzyl ammonium cation; CPC, cetyl pyridinium chloride; CPE, cloud point extraction; CTAB, cetyl trimethyl ammonium bromide; D2EHPA, di-2-ethylhexyl phosphoric acid; D3T2A, di-dodecyl-diethylene-triamine-triacetate; DPC, dodecyl pyridinium chloride; DBP, di butyl phosphate; DODAB, dioctadecyldimethylammoniumbromide; DHAB, dihexadecyldimethylammoniumbromide; HBTMPP, bis(2,4,4-trimethyl) phosphinic acid; HL-10-HL, 1,12-bis(1′-phenyl-3′-methyl-5′-pyrazolone-4′)-1,12-dodecanedione; HL-4-HL, 1,6-bis(1′-phenyl-3′-methyl-5′-pyrazolone-4′)-1,6-hexanedione; HNPMOBP, 1-*p*-nitrophenyl-3-methyl-4-*p*-octylbenzoyl-5-pyrazolone; HPMBP, 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone; HPMLP, 1-phenyl-3-methyl-4-lauroyl-5-pyrazolone; K100, Kelex 100, an undecyl alkylated hydroxyquinoline; MWCO, molecular weight cut-off; PADA, pyridine-2-azo-p-dimethylaniline; SDS, sodium dodecyl sulfate; TAN, 1-(2-thiazolyazo)-2-naphtol; TAR, 4-(2-thiazolyazo)-2-resorcinol; TX-114, Triton X-114 (p-t-octylphenoxy)polyethoxyethanol $C_{14}H_{21}O(C_2H_4O)_nH$ with $n = 8.1$ (mean average); TX-100, TX-114 analog with $n = 9.6$ (mean average); UF, ultrafiltration; VBAC, poly-2-vinyl-N-benzyl-trimethylammonium chloride; TBP, tri butyl phosphate.

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1. Introduction

1.1. Selected terms to focus on a small area of a vast field

The IUPAC recommends to restrict the use of the word "micelle" to the systems in which surfactants, surface active substances, form aggregates of colloidal dimensions (*i.e.* particles dispersed in a medium that have at least in one dimension, a length between 1 nm and 1 μm). The "surfactant" has to be in equilibrium with the aggregate it forms. The surface active substance may be a classical natural or synthetic molecular amphiphile or a "block type" copolymer. The aggregates may be either micelles, oil in water microemulsions or reversed micelles (water in oil micelles). Vesicles may only be considered if one assumes that a metastable state can be seen as a kind of equilibrium state during a restricted experimental time, nevertheless they are valuable tools in the domain considered here. Polymeric micelles are not exactly aggregates when the microscopic hydrophobic domains are formed with only one coiled macromolecule. Innovations were performed in metal extraction using this kind of micelle. This is why this review considers microheterogeneous systems rather than micelles.

A "ligand" is an atom or a group of atoms joined to the central atom usually metallic to form a "coordination entity" (the recommended term instead of "complex"). The term "extractant in microheterogeneous systems" has been preferred to "ligands in micelles" since it excludes both hydrophilic and amphiphilic ligands in reversed micelles, which allow metal separation from bulk water but with metal complexes mainly solubilised in the aqueous core of the reversed micelles or in the organic continuous phase.

1.2. Conditions necessary to extract metal ion from water

When the colloidal suspension is in thermodynamic equilibrium, the system is not truly heterogeneous since the microscopic domains do not constitute a separated phase. It is nevertheless practical, by analogy with biphasic systems, to distinguish two pseudophases, one being the continuous part of the suspension the other the sum of the dispersed domains.

To separate two pseudophases the thermodynamic equilibrium has to be broken. This is the condition to perform true extraction. The experimental methods which allow the separation and their advantages and drawbacks will be discussed in a part of this paper. To extract a metal from water the formed coordination entity has to be located in the microheterogeneous phase. This can be obtained using different strategies:

- A Lewis base can be covalently bound to the colloidal particles in the case of polymeric micelles. Some naturally occurring molecules interacting with metal ion are sometimes referred to as micellar extraction [1]. Neither the structure nor the aggregation state of those molecules is clearly stated. In some cases also, interaction with metal ions is studied with polyelectrolytes [2–4] exhibiting no particular hydrophobic microscopic domains, the status of the macromolecule (coiled or uncoiled) not being clearly stated. This review will only take into account partially hydrophobic polymer covalently grafted with complexing functions.
- The metal complex can be much better solvated in the particles than in the water continuum, as in the case in classical solvent extraction. Obviously, the most direct way to fulfil this condition is to consider a hydrophobic ligand solubilised in the oily core of the aggregates. It is noticeable that, contrary to what is observed in macroscopic biphasic systems, in microheterogeneous systems the hydrophobic interaction can be modulated by electrostatic interactions in the extracting pseudophase, depending on the sign of the electric charge of the colloid.
- Nothing resembles more a surfactant molecule than an amphiphilic molecule like a Lewis base bearing an alkyl chain. The third strategy consists in auto-aggregating extracting agents and/or coordination entities. If the metal complex aggregates, it may be named metallosurfactants [5]. Almost the same strategy is followed by researchers aiming at dispersing in micellar state a transition metal complex having catalytic properties, the specific keyword being then tenside ligands [6]. The metallosurfactants and tenside ligand domains will be thus only cited with a very specific eye in this review, the metal extraction.

Finally the author wishes to stress that a given extractant molecule, namely CnNHMePyr, initially designed to mimic metalloenzymatic esterolysis in metallomicelles [7], has been considered in Cu(II) micellar extraction in $C_{12}EO_6$, SDS and CTAB micelles [8], appears also in a review devoted to tenside ligand [6]. This clearly indicated that all tenside ligand, metallosurfactants may be seen as potential extracting agent in micellar systems. Bearing in mind that metallomesogens [9] might also "be dispersed in micelles", the reviews published in all these fields illustrate well the great variety of molecules already described which would deserve, would they be available and cost-effective, to be considered in micellar specific metal ion extraction.

1.3. Previously published reviews

Some reviews dealing with the metal ion extraction in microheterogeneous systems have already been published. They aimed at comparing solvent extraction and micellar extraction [10], or at reviewing the usefulness of organized assemblies for the on-line spectrometric determination [11] or as tools for preconcentration in metal analysis [12,13]. The only review which take into account both the kinetics and the thermodynamics of surfactant base colloidal particles was published in 2000, by Tondre [14]. Instead of attempting to reach exhaustiveness, this paper mainly aims at compiling recently published works, or not already reviewed particular aspects of former works.

2. Metal ion extraction in micro-heterogeneous systems

2.1. Applied aspects of micellar extraction: means and goals

Depending on the phenomenon leading to phase separation, three ways can be distinguished in the different published studies to separate metal ion from water: (i) the cloud point extraction (CPE) *i.e.* the loss of stability of the zwitterionic or non-ionic micellar aggregates induced by increasing the temperature, (ii) ultrafiltration (UF) which consists in bringing enough energy to the system to overcome the osmotic pressure and to concentrate the micelles and (iii) the third possibility is the phase separation induced by the metal ion complexation itself.

Many studies of metal ion extraction by a ligand solubilised in micelles are not reported as such, since the phase separation is not performed in these studies. This happens for instance in analytical spectrophotometric protocols [15]. Nevertheless one can reasonably forecast that any hydrophobic complexing agent would extract metal ion if the phase separation was carried out.

Zwitterionic surfactants (alkyl-β-alanine) known to form micelles and to complex copper into the micelles [16] form liquid crystal structures if the ratio copper/surfactant is too high [17]. Coacervate phase separation of lauric acid has been described as a useful mean to pre-concentrate Cd^{2+} and Zn^{2+} prior to their atomic absorption analysis [18]. It is an euphemism to say here that this way of effecting metal ion extraction, i.e. phase separation driven by complexation, has been explored more or less intentionally and many examples are not described as such and may been hidden in the literature. It may be noticed also that, on the contrary, very happy chemists synthesized complexing surfactants that form micelles and maintain their properties upon metal ion binding [19].

2.1.1. Ultrafiltration

Ultrafiltration has been combined with macromolecular complex [20,21] or emulsified liquid ion exchanger [21] selectively binding a metal before being associated with micellar metal extraction. The reason why micellar enhanced ultrafiltration developed more than the process using polymer may be attributed to the huge versatility of surfactants, their lost cost, and the relative simplicity to obtain them pure. Controlling the reactivity of the system is indeed not obvious in polymeric systems. For instance with VBAC, a cationic polymer, Ni^{2+} was unexpectedly extracted due to remaining non-quaternary alkylated amino functions [22].

Pore size indications of the ultrafilters are usually given as MWCO, the molecular weight cut-off, the weight above which at least 90% of the molecules are retained. Typical cut-off that have been used are ranging from 5 to 30 kDa. Relation between MWCO and particle diameter is not straightforward. Diameters from 25 to 80 Å have been proposed for ultrafilters depending on the MWCO and on the nature of the membrane (inorganic Zr/Ti oxide) or polymeric [23].

Membranes pores up to 0.1 or even 0.2 μm have been considered for the retention of fatty acids (C16 or C18 alkyl chains) aggregates [24]. Whatever the exact pore diameter is, the retention of micelles is a peculiar fact: a lab scale ultrafiltration experiment usually needs 10–20 min whereas the surfactant molecule typical lifetime in the micelle is of the order of 0.1 ms, and the micelle lifetime is in the order of 1 s for classical surfactants [25]. One could imagine that the micelles would be able to pass through the filter as fragments (much smaller than the MWCO), and rebuilt after the filter. This is not what is observed, the micelles are effectively retained, concentrated until the surfactant forms a viscous gel. The solution passing through the filter contains about the CMC of surfactant along the ultrafiltration experiment. The permeate surfactant concentration logically increases if the retentate approaches the viscous gel state, either locally by adsorbing the surfactant on the membrane and forming a so-called polarisation concentration layer, or simply when almost all of the water has been filtered. Salt, pH effects on UF flux, permeate content have been investigated during tangential UF of micellar solutions of CPC, SDS and TX-100 with mineral Zr–Ti oxide membranes [26] and frontal UF with regenerated cellulose membrane of CPC, CTAB, SDS micelles [27] or CTAB, APG, SDS micelles [28].

Metal ion extraction selectivity in a UF process considering cationic micelles was initially demonstrated using a N-n-dodecyl iminodiacetic acid as the “copper specific ligand” solubilised in CPC micelles [29]. The iminodiacetic acid moiety is not a very selective complexing agent since it strongly complexes many transition metal ions. The term “specific” is only meaningful when comparing ligand assisted micellar extraction with metal ion extraction resting on electrostatic interaction. Indeed, in anionic micelles, any metal cation (including alkaline and alkaline earth cations) having a better affinity for the micellized surfactant polar head is extracted. In cationic micelles solubilising an extractant, the uncomplexed metal ions may be expelled by Donnan effect. Moreover, in many cases the amount of extractant that may be solubilised in the micelles is limited. This may be seen as a limitation of the micellar extraction, the other side of the coin being that only the metal forming the most stable complex may be extracted.

Anionic surfactants are selected if selectivity toward cationic metallic species is not the main objective. 96% of 100 mg/kg of Cr^{3+} ions were extracted in SDS micelles [30]. Anionic micelles solubilising PADA were successfully used to extract 10^{-4} M of Cd(II) [31]. SDS micelles solubilising D2EHPA gave no selectivity between Co(II) and Ni(II) [32]. Mixtures of anionic (SDS) and non-ionic (TX-100) surfactants have been considered, allowing the extraction of cadmium at low SDS and with reduced surfactant loss in the permeate [33]. D3T2A allows one to extract more than 99% of a 52 ppm solution of Cr(III) [34].

Using electrostatic interaction renders possible the removal of anionic metal species such as chromate by ultrafiltration of aqueous streams, a cationic surfactant being required in this case [35].

Recently the simultaneous removal of TBP the extractant used in reprocessing of nuclear fuel, and DBP, the main degradation product of TBP, together with the residual uranyl ions was performed using SDS [36]. In this case no synergistic effect was obtained by considering together the extracting agents and the metal ions. Indeed, the extraction of the TBP and DBP molecules seems to rest only on their hydrophobic partitioning and the extraction of uranyl ions on the electrostatic interaction with the anionic polar heads of SDS.

Progress in membrane technology rendered possible the scale up of the micellar ultrafiltration for the removal of Th, $UO_2{}^{2+}$, Ru from aqueous effluents at industrial scale [37]. MEUF feasibility was investigated to treat washing effluent of heavy metal contaminated soil using EDTA and CPC micelles [38]. Removal of arsenate ions by MEUF may be considered as a feasible process using CTAB or CPC micelles in comparison with other solid adsorbent based processes [39].

Despite the fact an ultrafiltration device is an open system, with at least a continuous outflow of filtered solution, ultrafiltration results may be treated using the same equilibrium way of modelling as in semi equilibrium dialysis experiments [40]. A common implicitly used approximation is to neglect the extraction equilibrium shift that may occur during the UF process.

Only the slowest reaction allows one to perform the UF experiment within the extraction reaction time. To obtain such a slow reaction a direct microemulsion system CTAB/BuOH/salt/C_{11}HQ was formulated to separate cobalt and nickel on a kinetic basis [41].

Back extraction and recycling of the micellar aggregates is sometimes studied. When an acidic chelating agent is involved, adding acid allows one to back extract the metal [42]. By adding a strong complexing hydrophilic agent, copper and cadmium have been back-extracted from SDS micelles [43]. Continuous recycling of SDS micelles by copper reduction has been performed [44]. Copper(II) reduction was not possible in a CTAB/BuOH/HQ microemulsion [45]. The effects of Mg^{2+}, Na^+ and H^+ were investigated for the recovery of Cd^{2+} from PADA-SDS micelles [31].

2.1.2. Cloud point extraction

With zwitterionic or non-ionic surfactants, the loss of solvation of the hydrophilic part of the surfactant molecule when raising the temperature leads to a phase separation into a surfactant rich viscous phase and a mainly aqueous phase containing small amounts (nearly the CMC) of surfactant. This is the so-called cloud point phenomenon. If an hydrophobic complexing agent is solubilised into the micelles before reaching the cloud point, it is extracted in the surfactant rich phase. If some metal ions are complexed to these ligand molecules, there are extracted at the same time. No quantitative study reports the exact ratio of the metal complexed to the micellized extractant toward the quantity of metal ion extracted, in other words the stability variation of metal complexes during the cloud point phenomenon is not described. From the practical point of view of metal ion extraction, the main difference between UF and CPE is that in UF the concentration factor (the metal concentration ratio in the retentate or surfactant rich phase to the one in the initial solution) is an adjustable parameter whereas it is imposed by the surfactant nature and initial concentration in CPE.

The extraction of 10^{-5} M Ag(I) in non-ionic polyoxyethylated alkylphenol micelles solubilising TAR is limited by the distribution

Table 1
Specificities of CPE and UF.

UF	CPE
Easy scale up, using tangential UF and high surface membrane area modules	Cloud point temperature depending on the salt nature and amount
Ionic surfactants allowed	Properties depending on the nature and amount of extracted species and on the purity of the surfactant constituting the micelles
Concentration factors chosen	Low CMC of non-ionic surfactants
Continuous flow	Concentration factors imposed by the surfactant nature and its initial concentration
Electrolysis after pre-concentration in concentrated micelles may be possible	No specific device required
Relatively high surfactant (*i.e.* the ionic surfactant CMC) amount leaking through the filter	Viscous surfactant rich phase obtained
Donnan membrane effect with ionic surfactants [50]	

of the Ag:TAR complex whereas Ag:TAN allows an extraction yield >99% in the same conditions [46].

For ionic extractants, a temperature change (a decrease in this case) can also induce a separation at the Kraft temperature. In this case the surfactant rich phase is in a state close to the solid crystalline state. It seems that this has only been explored in few cases. The formation of an ion pair between the metal ion or a cationic metal complex and the micellized surfactant allows one to successfully remove Cu, Ni, Zn, Pd(II), Pt(II) amine complexes from water by decreasing the temperature below the Kraft point of SDS in these experimental conditions [47]. Using the same principle but with opposite electric signs Pt(II), Pt(IV) and Pd(II) anionic chloro-complexes were extracted by CPC in solutions also containing copper, zinc and iron [48,49].

Chemists have a great talent to transform drawbacks into advantages. Thus the features of CPE and UF methods outlined in the table below may be seen as both, advantages or drawbacks, depending on the circumstances (Table 1).

Acetyl lysine chelating group grafted on the tip of a non-ionic surfactant extracts uranyl nitrate by CPE. This illustrates that the non-ionic surfactant behaviour may be kept with complex entities having at least a partial ionic character [51]. In another study a diamide chelating group grafted on a $C_{12}E_5$ or $C_{10}E_8$ micelles allows one to extract to uranyl ions from 4 M $LiNO_3$ solution [52]. To our knowledge these works are the unique examples of effective metal micellar extraction using a solvating extractant instead of an acidic one. The influence of the counter ion nature would deserve an evaluation.

HQ solubilised in TX-114 solution was used to extract efficiently lanthanum and gadolinium by CPE whereas K100, an hydrophobic derivative of HQ in the same system was inefficient. The same team showed that CPE by TX-114 without any extractant molecule allows one to extract non-negligible quantities of Gd and La [53] and even allows one to reach 100% yield of extraction of UO_2^{2+} [54].

These CPE experiments revealed an interaction of non-ionic surfactants with the metal ion in conditions in which the cloud point phenomenon occurs. This ligandless CPE has been exploited for various metal species pre-concentration before spectrometric determination (Cr(III), Pb(II), Cu(II), Ni(II), Bi(III), Cd(II) with Tween 80 and Bi, Cd, Ni, Cu, Pb, Zn, Co, Ge, Cr with TX-114 or PONPE 7.5 [[55] and ref. cited therein]. The interaction between non-ionic surfactant (PONPE with 10–15 ethylene oxide unit) and metal ion was only reported with gold in UF experiment [56]. This might indicate that special solvation effect might occur in cloud point condition.

2.2. *Stoichiometry of the complexes in micro-heterogeneous systems*

The continuous variation methods, resulting in the so-called Job plots, is used to determine the stoichiometry of the complex formed [57,58]. Such Job plots allow one to postulate a 4:1 complex stoichiometry for the Iron(III)–Morin complex micelles of different surfactants types (including ionic or non-ionic micelles) [59]. The continuous variation method allowed also to show that the Beryllium complex formed with chromazurol S and chromazurol B have different stoichiometries in non-ionic micelles (2:1) and in aqueous solution (1:1 stoichiometry). In this case the difference rests on the local high concentration of the complexing agent in the micellar oily core, concentrations that cannot be attained for solubility reasons in aqueous medium [60]. On the contrary PADA forms 1:1 complex with Pd(II) in both water and DTAC micelles [61].

Experimental curves of yields of ultrafiltration versus pH allow one to propose the most plausible stoichiometry of pyrazolones derivatives complexes of europium. EuL_3 (3:1) was formed with HPMBP and HPMLP. Two bolaform extractants, thus bearing two acidic functions, were studied in the same work, the complex Eu_2L_3 (3:2) was formed with HP-10-HP whereas $Eu(L_2H)$ (2:1 with one remaining proton on one ligand) was described with HP-4-HP [62]. This clearly illustrate that a small oily micellar core may accommodate a big complex. The same group using the same methodology showed that the stoichiometry of copper–HQ complex is the same (*i.e* 2:1) in micelles or in biphasic system [50].

The classical log–log plot method allows one to postulate a stoichiometry 1:1:1 for the mixed complex Ag:TAR:DP, explaining the increase of the extraction yield in presence of small amounts of DPC. The added DPC concentration has to be small enough so as the mixed DPC/non-ionic surfactant micelles still give rise to the cloud point phenomenon [40]. In this particular case and owing to the very particular interaction of silver with chloride, such an interesting result would have been reinforced by using dodecyl pyridinium nitrate for instance. The metal:chromazurol S:CTA^+ (or $CDBA^+$) ternary complexes are described on the basis of spectrophotometric investigations. In this study the surfactant concentrations are lower than the complexing agent one, the surfactant cation role is described as the one of “a simple cation” [63]. Aside from kinetic studies these are the only explicit examples of ternary complexes including a surfactant molecule, though they are often encountered in the biphasic extraction experiments [64].

On the basis of log–log plots, HBTMPP a phosphinic derivative solubilised in TX-100 micelles forms two different complexes with Eu^{3+} and Yb^{3+} depending on the extractant concentration ($M(HL)_2L$ at low HL concentration, $M(HL_2)_3$ at higher concentrations, the uncomplexed ligand being in dimeric form in the micelles) [65].

Cu(II) UF extraction by 1-(2′-hydroxy-5′-alkylphenyl)-1-alkanone oxime occurs in more acidic medium in $C_{12}E_6$ micelles than in CTAB micelles [66]. The same finding was reported for the couple $C_{11}HQ$/Cu(II) [50]. Based on the shape of the yield versus pH curves a 2:1 complex was proposed in both cases. This illustrates that a given hydrophobic complex may be better solvated in micelles of shorter alkyl chain surfactant.

Tartaric acid based ligands forms coexisting neutral, anionic and cationic binuclear complexes with Cu(II) in Brij58 micellar solution. Ultrafiltration experiments demonstrated that anionic complexes may be associated to the micelles and allows copper extraction [67].

In most other cases the stoichiometry is still ill defined, or postulated by analogy with homogeneous or biphasic systems. Nevertheless there is some evidences that the stoichiometry and the stability constant of metal complexes may be dramatically changed when comparing a true biphasic system and micellar system: C_{16}NHMePyr proved to be an efficient extracting molecule in

CTAB and $C_{12}EO_6$ micelles whereas it was unable to extract copper in true hexadecane biphasic system [68,50].

Kinetic studies mainly take into account 1:1 complexes. This does not indicate that the selected extracting agent for kinetic studies only form 1:1 complexes but that the elementary kinetically limiting step of the complex formation is the departure of a first water molecule from the solvation sphere of the metal ion as in homogeneous systems [69].

3. Kinetic aspects of micellar metal extraction

3.1. Metal ion extraction kinetics in micellar systems

Micelles are well known to affect the rates of chemical reactions by selectively sequestering the reagents by means of electrostatic and/or hydrophobic interactions.

The first studies in this field described the complexation rate increase when both the ligand and the metal ion are concentrated in the anionic micelles instead of being spread over the whole volume of the solution. The reaction kinetics of PADA with Ni(II) in SDS micelles were the first described in this field [70]. A comparison of apparent rate constant for benzoyl acetone reacting with copper in either SDS or DTAC, $C_{12}E_8$ or $C_{12}E_{25}$ micelles may be found in references [71,72].

In the metal extraction kinetic studies, the micelles are often used to mimic the interface of true biphasic systems in order to understand the reaction rate limiting step in real biphasic systems [73,74] or the site where the complexation really does take place [75].

Such studies are also able to bring information in other domains: simultaneous determination of nickel and cobalt by 5 octyloxymethylquinol based on their kinetic rate of reaction in TX-100 has been reported for instance [76].

Metal ion kinetics data obtained in micellar systems are systematically treated using the pseudophases' model. This model is often attributed to Berezin et al. [77] even if some of its basics may be found in the work Menger and Portnoy [78]. More generally, to our knowledge only one group proposed to use another model to treat micellar effect in kinetics, and not on metal ion complexation [79]. Briefly, in the so-called pseudophases' model, the complexation reaction occurs in both the micellar and aqueous pseudophases. The fractions of the reaction occurring in each phase, thus the resulting observed rate constant, are given by the molar fraction of the reacting and formed species localised in the micellar and aqueous pseudophases. Distribution of the reactants is considered to be very rapid compared to the complexation reaction. Nevertheless, the extent of the distribution of the extractant, depending on its hydrophobicity greatly influences the extraction rate [80]. Distinguishing an interfacial area and a hydrophobic core was necessary to describe the PAN/Ni(II) complexation kinetics in SDS [81].

Some problems face the chemist who uses this model:

- As most of the complexation reactions are involving the proton, one has to define its molarity in both pseudophases. It is often assumed that the molarity of the proton is the same at the non-ionic micelle surface and in water. With ionic micelles, the Poisson Boltzmann equation (considering a uniformly charged sphere) may be used to take into account the attractive or repulsive potential of the micelles surface toward the proton [82].
- Since they constitute a dynamic pseudophase and not a true separate phase, the definition of the micelles volume cannot be rigorous. Is it the oily core of the micelles or the whole volume occupied by the surfactant? This point is in direct relation with the preceding one: how to define a molarity of the proton, or of one other species, without knowing the volume in which it exists? Often the molar volume of the surfactant is taken as the micellar volume occupied and available for reaction in a solution containing one mole of surfactant. This geometrically corresponds to a shell surrounding the micelles (assumed to be spherical) and having a thickness of about 25% of the micelle radius.
- These problems induce also questions about the meaning of the values of the rate constant in the micelles. Clearly, rate constants can only be compared together bearing in mind how the micellar volume and the local concentrations have been defined.

Despite these difficulties, since micelles are essentially interfacial objects, kinetic studies in micellar systems are very useful tools to discuss essentially interface catalysed reactions such as the metal ion extraction [83]. The fraction of the reaction occurring in the micelles may be negligible, especially in the case of cationic micelles from which the metal ions being electrostatically repelled and are in low concentration "in the micelles". In these cases the reaction is assumed to occur only or mainly in water, implying that the extractant has to partition in the aqueous pseudophase to react with the metal ion [84].

Variation of the electrostatic potential was performed by varying the composition of $C_{12}E_6$/CTAB micelles and the resulting effect on the apparent rate constant of 5-alkoxypyridine aldoximes complexation by Ni(II) was evaluated [85].

The apparent complexation rates of Cu(II) by C_{16}NHMePyr were determined in polymeric undec-10-enyltrimethyl ammonium bromide micelles [86]. The comparison with the results obtained in CTAB micelles did not allow one to demonstrate an effect of the dynamic exchange of the surfactant molecule between the surrounding water and the micelles on the extraction reaction rates.

The partial hydrolysis of the metal was taken into account to describe the kinetic of reaction of iron(III) by 4-((alkylcarbonyl) amino)-2-hydroxybenzoic acid solubilised in Brij35 micelles [87]. The path involving the hydroxo species $PdCl_3OH^{2-}$ reacting with PADA is about 10 times faster than the other paths in DTAC micelles, whereas only $PdCl_4^{2-}$ and $Pd(H_2O)Cl_3^-$ need to be considered in water [61].

Most of the kinetics studies are performed with the stopped flow technique, which can be considered as a concentration jump perturbation technique. The T-jump perturbation technique may also be used [88].

In the following, focus is made on the specific role eventually played by the surfactant in the reaction kinetics.

3.2. Specific interaction of the surfactant with one of the reactant

The comparative study in TX-100 micelles and water toluene real biphasic system of the kinetics of formation and dissociation of the complexes of HPMBP or HPMCP with Pr^{3+}, Eu^{3+}, Tb^{3+}, Ho^{3+}, Yb^{3+} allow one to show (i) interfacial catalysis of the extraction by Arsenazo III occurs in the biphasic system but is not significant in micelles. (ii) The adduct between the 3:1 complex and the TX-100 molecule occurring in both system does not alter the dissociation kinetic constant rate [75].

The kinetics of complexation of Ni^{2+} by PADA in anionic mixed micelles of fluorinated-hydrogenated surfactants have shown synergistic PADA solubilisation [89], but a lower solubilisation ability for the pure fluorinated micelles (for a same micellar volume). Pure fluorinated micelles were considered in the study of kinetics of water replacement in the palladium complex of tetraethyldiethylenetriamine by monoalkylthioureas [90]. In this case the fluorinated micelles better solubilise the alkylthioureas than the hydrogenated ones. This was attributed to a difference in the solubilisation sites.

The counterion (chloride or nitrate or bromide) of CTA^+ has an interaction with Cu(II) or Co(II) during the complexation by the hydrophobic C_{11}HQ extractant whereas no influence of the micelle counterion was observed for HQ [91].

The complexation rate of copper by diC_{12}NHMePyr in DODAB and DHAB vesicles is influenced by the melting of the surfactant alkyl chains ($L_\beta \rightarrow L_\alpha$ transition) [92]. The influence of the state of the DODAB vesicle bilayer has an influence on the distribution of the ligand PADA between the bilayer and the bulk aqueous water and thus on the complexation kinetics. In the same work the nickel(II) complexation by PADA in 6-SLABS anionic vesicles occurs on two time scales: a short one, relative to the ligand located in the outer leaflet of the bilayer and a longer one relative to the ligand solubilised in the inner leaflet which necessitate that the reactant diffuses through the bilayer to react [93]. Aside this slow diffusion phenomenon, the extraction rates are very comparable to those determined in micelles.

The effect of the solvent nature (heptane or toluene) in microemulsion CTAB-butanol-solvent is of secondary influence on the rate of HPMLP, HNPMOBP with lanthanum and lutetium [94].

4. Perspectives

Dealing with applied aspects, solvent free processes are promising for great development in a near future. In this view, replacing a large volume of organic solvent with a small amount of surfactant in a process allows one obviously to decreases the impact of human activities on the environment. It is now established that metal ion extraction in micelles offer a way to remove heavy metal from waste effluents. To go further, biodegradable surfactants would have to be used, biological amphiphiles (although not pure and some time ill defined at the molecular level [95]) not requiring any organic synthesis may be a trail to be followed. Environment would gain in any improvements of the micellar UF process allowing to decrease the surfactant loss in the effluent.

Among the academically rising research fields, the extraction kinetics by solvating extractants is not described at this time. On the margin of the microheterogeneous media domain, micelles trapped into mesoporous materials (silica, titanium oxide) may offer food for thought to those intending to describe and to understand kinetics and thermodynamics of metal ion extraction in such media.

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