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Solubilization in micellar systems. Analytical and environmental applications

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Abstract: Surfactant-based separation techniques largely exploit the solubilization power of micelles and other amphiphilic aggregates towards a great variety of hydrophilic and hydrophobic solutes. Micellar extraction, based on the cloud-point phenomenon, and micellar ultrafiltration have been succesfully applied for preconcentration and removal of organic and inorganic analytes of environmental concern from aqueous media. In particular, the recent development of chelating surfactant aggregates allows to perform very selective demetallation treatments. The factors which control the separation efficiencies of these methods are examined and discussed.

INTRODUCTION

Surfactant organized assemblies have great potential application in analytical chemistry as well as in separation science and technology (1-10) since these microheterogeneous systems can solubilize and compartmentalize ionic and neutral solutes in different regions of the aggregate structure, drastically altering the chemical equilibria and the reactivity of the bound substrates. The solubilization capacity of micellar systems, expressed as moles of solutes dissolved per mole of surfactant generally follows the order: nonionics > cationics > anionics for amphiphiles with the same hydrophobic moiety.

Very interesting for practical purposes is that aqueous micellar solutions can replace in some cases the more dangerous and toxic organic solvents, allowing to perform the fractionation and concentration of environmental and biological samples under mild conditions.

The main applications of surfactants in chemical separations include micellar chromatography, capillary electrophoresis, transport across liquid membranes, foam-based concentration, liquid-liquid extractions using reversed micelles, micellar extractions based on thermal phase transition (cloud-point extractions) and micellar-enhanced ultrafiltration (MEUF). Among these techniques, the last two have captured the growing interest of researchers since they have simultaneously a great potential utility either as separation-preconcentration methods applied during the analysis and as environmental treatments. In fact, they allow to perform the efficient and selective removal of organic and inorganic pollutants from aqueous streams by simply adding a more safe, cheap and versatile component (the amphiphile), followed by the application of a physical phase-separation procedure.

The aim of this overview is to summarize and update the recent progress on this topic, with particular attention devoted to the examination of the behavior and properties of highly selective ligand micelles, recently developed for the recovery and/or removal of metal ions.

MICELLAR EXTRACTIONS BASED ON THE CLOUD-POINT PHENOMENON

Aqueous solutions of several nonionic and zwitterionic surfactants, when heated or cooled, become turbid over a narrow temperature range due to the diminished solubility of the amphiphile in water (11), This critical temperature, called "cloud point" depends on the amphiphile nature and concentration. A lower (or higher) consolute boundary is present in the corresponding phase diagram, depending on the nature of the surfactant used.

When nonionic surfactants are employed, the solution separates into two isotropic liquid phases above the cloud point (see Fig.1).

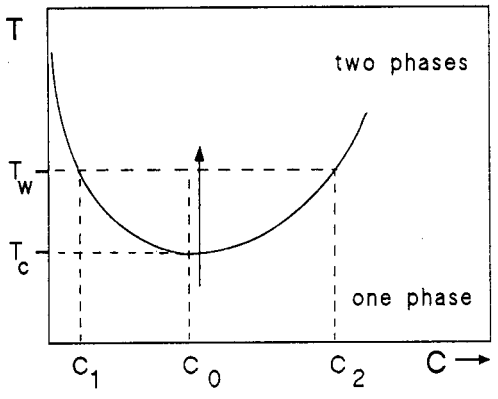


Fig.1. Typical phase diagram of an aqueous solution of a polyoxyethylene alkyl ether.

Starting from a solution at a given surfactant concentration (C_0) at room temperature and heating above the cloud point (T_C) up to T_W, phase separation occurs. The composition of the surfactant-rich liquid, where the hydrophobic solutes are accumulated, is given by C_2, whereas C_1 is the (very low) surfactant concentration in the aqueous-rich phase. The phase separation occurs spontaneously at the working temperature but, since the densities of both liquids are generally not very different, centrifugation is usually used to speed up the process.

The concentration factor is fixed by the volume fraction of each phase, which in turn depends on surfactant concentration. Working with alkyl- and arylpolyoxyethylene surfactants in the concentrantion range 0.5-2% w/v, the typical volumes of the extracting phase represent about 1-10% of the initial volume. Thus, concentration factors from 10 to 100 can be easily achieved. Of course, these factors are very sensitive to the surfactant type and structure.

Cloud-point extraction of organic compounds

The cloud-point procedure has been applied for preconcentration and removal of several organic pollutants, including pesticides, aromatic hydrocarbons, PCB's, phenols and chlorophenols from aqueous samples (see Table 1). The percent extraction achieved is in most cases comparable to those obtained using classic extraction systems and, moreover, sensitized determinations (i.e., fluorimetric, phosphorimetric, potentiometric,etc.) of the analytes can be directly performed in the enriched surfactant solution.

The cloud-point approach can also be applied to treat contaminated environmental phases, especially soils and water streams. In fact, nonionic surfactant solutions have been proposed to wash contaminated soils (12-16), merely exploiting their solubilization capability and their interfacial tension lowering power. The successive disposal or reuse of the (dilute) wash solution could be adequately conducted after a cloud-point separation step.

Another interesting application of micellar solutions is in the storage of aqueous samples prior to the analysis, in order to avoid the loss of the organic hydrophobic analytes due to their sorption on the container walls (17,18). Also in this case, the use of proper nonionic surfactants could be furtherly combined with a direct cloud-point extraction step. A more extended examination of the theoretical basis and applications of the cloud-point technique can be found in ref. 19.

For organic pollutant molecules, the extraction efficiency can be adequately related to the binding constant solute-micelle, in turn dependent on the substrate hydrophobicity. The binding constant (K_B) of a solute S, in the presence of a large excess of surfactant, is given by the equation:

$$K_B = [S]_m/[S]_w C_D \quad (1)$$

where the subscripts m and w indicate the micellar and aqueous phase, respectively, and C_D is the concentration of the micellized surfactant ($C_D = C_{tot}$ - cmc). According to the two pseudophases approach (23), the binding constant is related to the partition coefficient (P) through the equation:

$$K_B = (P - 1)V' \quad (2)$$

where V' is the partial molar volume of the surfactant. These partition parameters can be

TABLE 1. Cloud-point extractions of some organic pollutants.

Compounds extracted	Surfactant system	Rec.	Ref.
Pesticides:			
Endrin, Lindane, DDT, Aldrin, Chlordane, BHC, Methoxychlor, Chloropyrifos	PONPE-7.5	QR	17
Parathion	Triton X-114	QR	20
2,4-D, 2,4,5-T	$C_{12}E_8/C_{12}E_{4.2}$	PR	21
Phenols:			
Phenol	$C_{12}E_8/C_{12}E_{4.2}$	PR	21
4-t-butylphenol	IGEPAL CA 520	QR	22
Aromatic hydrocarbons:			
Benzo[a]pyrene, Fluoranthene, Pyrene, Benzo[e]pyrene, Fluorene	IGEPAL CO-630	QR	17
Chloroaromatic compounds:			
4-chlorophenol, 3,5-dichlorophenol	$C_{12}E_8/C_{12}E_{4.2}$	PR	21
2,4,5-trichlorophenol, 3-chloro-biphenyl, 3,3'-dichlorobiphenyl, 2,2,4,5-tetrachlorophenol, penta-chlorophenol		QR	

PR: partial recovery; QR: quantitative recovery (>95%). PONPE-7.5: polyoxyethylene(7.5)nonyl phenyl ether; IGEPAL CA-520: polyoxyethylene(5)octyl phenyl ether; IGEPAL CO-630: polyoxyethylene(9-10)nonyl phenyl ether; Triton X-114: t-octylphenoxy polyoxyethylene(7-8) ether; $C_{12}E_8$: polyoxyethylene(8)dodecyl ether; $C_{12}E_{4.2}$: polyoxyethylene(4.2)dodecyl ether.

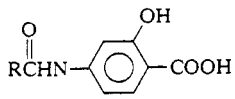
independently evaluated using different experimental techniques (24), or estimated from the hydrophobic contributions of the chemical groups present in complex molecules (25).
Since the extraction system is composed by a water phase containing a low percentage of dissolved surfactant and a highly hydrated surfactant-rich phase, the condition of complete non-miscibility of the two liquids is rarely fulfilled. Consequently, the P values of lipophilic solutes in micellar solutions are much lower than those measured in traditional water-organic solvent systems.

As a general rule the cloud-point extractions are more effective when the target solutes are uncharged, although hydrophobic ionized compounds can also be extracted. A systematic study performed on chlorophenols (21) indicated that there is a threshold value of the binding constant ($K_B \cong 1000\ M^{-1}$) which ensures the quantitative recovery of the analyte in the low-volume surfactant-rich phase. Other compounds, such as the polycyclic aromatic hydrocarbons, exhibit very high binding constants to common nonionic micelles (26) and can be effectively removed from aqueous wastes using the cloud-point approach (27).

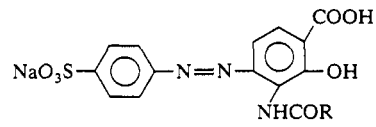
Cloud-point extraction of ionic species

Most investigations in this field were centered on the extraction of metal ions as sparingly water-soluble chelate complexes. The first described procedure concerned the separation of Ni(II)-TAN (1-(2-thiazolylazo)-2-naphthol) complexes in Triton X-100 micellar solutions at temperatures above ca.70°C (28). Other cloud-point extractions of transition metals using similar ligands (PAR, PAN) and other polyoxyethylene-type nonionic surfactants were successively reported in literature (29-37).
More recently, increasing efforts were devoted to the development of reactive mixed micelles formed from common (unreactive) ionic or nonionic surfactants and suitable amphiphilic ligands. These ligands, which contain selective chelating groups and usually have a tuned hydrophobicity, are ideal candidates for more selective extractions of the target metals,
A systematic study was performed on a series of acyl derivatives of 4-aminosalicylic acids (PAS--C_n) dissolved in mixed micelles of Triton X-100 (t-octylphenoxy polyoxyethylene(9-10) ether) and $C_{12}E_{4.2}$ (polyoxyethylene(4.2)dodecyl ether), used as model systems for the extraction of

iron(III) (38). These ligands (see formulas below) can spontaneously form-micelles when present in aqueous alkaline solution (39), but in order to avoid hydrolysis of the metals, they have been employed in acidic media as mixed aggregates with other surfactants.



PAS-C_n



Y-PAS-C_n

Kinetic and equilibria studies (38,40) clearly indicated that the hydrophobicity of ligands and complexes are the fundamental factors which regulate the extraction efficiency. For example, the ligand PAS-C_4 ($K_B \cong 500\ M^{-1}$ in Brij 35) is largely bound to nonionic micelles, whereas the positively charged 1:1 iron(III)-PAS-C_4 complex exhibits a lower K_B value (ca. 70 M^{-1}) and, thus, cannot be quantitatively extracted in the nonionic surfactant-rich phase after clouding.

The complex formation constants in micellar solutions are generally different from those measured in homogeneous solutions and are largely dependent on the extent of complex-micelle binding ($K_{B(C)}$). In some cases, as for the above reported metal-chelate, the determination of the apparent formation constant at different micellized surfactant concentrations ($C_D = C_{tot}$ - cmc) allows the estimation of $K_{B(C)}$ through the very simple equation (40):

$$K_{f(mic)}/K_{f(homog)} = 1 + K_{B(C)}C_D \qquad (3)$$

Since the stoichiometry of the metal chelates can also vary passing from homogeneous to micellar solutions, a preliminary study of the behavior of the extraction system is essential before to start with any practical application.

When different lipophilic ligands, having similar binding constants to the micelles, form stable chelates of the same stoichiometry with the target metal ion, the system originating uncharged complexes is preferred. This condition was clearly evidenced in studies performed with some sulfonated azo-derivatives of 4-alkylamidosalicylic acids (Y-PAS-C_n ligands), which also form 1:1 complexes with Fe(III) and exhibit nearly the same K_B values as the corresponding PAS-C_n compounds (19). The amount of Fe(III) extracted after clouding from aqueous saline solutions of Triton X-100 and $C_{12}E_{4.2}$ is about 90% using Y-PAS-C_4 ($K_B = 360\ M^{-1}$ in $C_{12}E_8$), whereas it is only about 55% using PAS-C_4 ($K_B = 350\ M^{-1}$ in the same surfactant) which forms a positively charged 1:1 complex with Fe(III).

Table 2 reports some examples of cloud-point extractions of metal chelates using nonionic polyoxyethylene-type surfactants.

TABLE 2. Cloud-point extractions of metal ions using hydrophobic and amphiphilic ligands

Metal ion extracted	Nonionic surfactant	Ligand	%E	Ref.
Zn(II)	PONPE 7.5	PAN	~100	28
Zn(II),Ni(II), Cd(II), Cu(II)	PONPE 7.5	PAMP	~100	29-32
Fe(III), Ni(II)	Triton X-100	TAC		33,34
U(VI)	Triton X-114	PAN	98	35
Fe(III), Cu(II), Zn(II)	PONPE 7.5	SCN^-	72-97	36
Fe(II), Ni(II), Cd(II), Zn(II)	PONPE 7.5	TAC	~100	37
Fe(III)	Triton X-100/ $C_{12}E_{4.2}$	PAS-C_2	30	38
		PAS-C_4	55	
		PAS-C_8	95	
		PAS-C_{10}	~100	

TAC: 2-(2-thiazolyl-azo)-4-methylphenol; PAN: 1-(2-pyridylazo)-2-naphthol; PAMP:2-(2-pyridylazo)-5-methylphenol.

It must be noted that the kinetics of complex formation is another crucial parameter, since the micellar effects on reaction rates are usually relevant. Kinetic studies performed on the extraction systems are, thus, very important and recent contributions to the knowledge of metal ion separations using chelating aggregates extensively concern the kinetic aspects of these processes (41,42).

MICELLAR-ENHANCED ULTRAFILTRATION

The technique has been introduced some years ago by Scamehorn et al.(43). It has been applied either to remove organic and inorganic solutes of environmental concern from aqueous wastes, as well as peculiar preconcentration step in some analytical determinations.
The separation procedure is based on the association of solutes to added micellar aggregates, successively removed from the bulk solution through an ultrafiltration membrane (see Fig.2). The membrane pore-size has to be small enough to block the aggregates (and their guest solutes) in the retentate, and large enough to allow acceptable flux rates in the system.

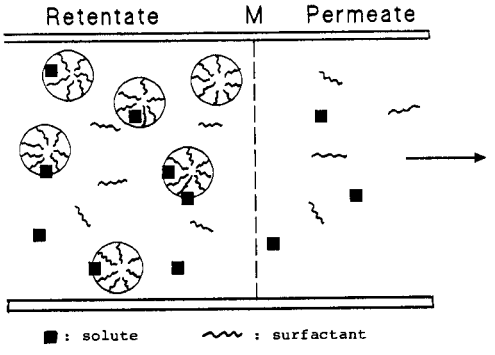


Fig. 2. Simplified scheme of MEUF.

A detailed description of the basic theory and features of this separation method is given in literature (43-45).
When the micelles are completely retained, the permeate contains only low amounts of surfactant (near the critical micellar concentration limit) and the concentration of solutes in this phase depends on the extent of binding to the micelles. The efficiency of ultrafiltration is measured by the rejection factor, defined as: $R = C_P/C_0$, where C_P and C_0 are the solute concentrations in the permeate and in the initial solution, respectively.

Separation of organic pollutants using MEUF.
Several organic compounds of environmental interest, present at the ppm or sub-ppm level in aqueous streams, have been concentrated and removed using the MEUF approach. They include aromatic hydrocarbons (46), alkylphenols (43), aliphatic alcohols (47), chloroaromatic compounds (21) and aromatic amines (48).
Irrespective of the solutes and of the micellar system used, the quantitative accumulation of the analytes in the retentate can be achieved when their corresponding K_B values are higher than ca.1000 M^{-1}. This threshold limit, which is comparable to that found for quantitative cloud-point extractions, is clearly shown in Fig. 3, where the measured retention of a series of aromatic amines and phenols in HTAB micellar solution is compared.
Since the substrate binding constant largely depends on the nature of surfactant and solute and on the presence of electrostatic effects, the preliminary investigation of the partition behavior of the analytes under different experimental conditions is essential in order to predict the ultrafiltration efficiency. For example, the removal of the carboxylic herbicide 2,4,5-T (2,4,5-trichlorophenoxyacetic acid) from contaminated waters using anionic micelles (SDS) can be performed only at low pH values because the ionization of this compound ($pK_a \cong 3$) increases the hydrophilic character of the molecule and, moreover, introduces electrostatic repulsion between micelles and substrate. These two combined effects drastically lower K_B, thus reducing the R value (see Fig.4).
On the contrary, the use of HTAB cationic micelles is possible even at higher pH values since the negative effect of ionization on K_B is compensated by the electrostatic attraction and by the specific interactionsc operating between the surfactant head-groups and the aromatic ring of the pollutant.

Aromatic amines show an opposite behavior because these compounds become protonated in acid media. The variation of rejection factors of aniline with pH, in SDS and HTAB solutions, is shown in Fig. 4. The data reported in this figure and in Fig.3 were taken from refs.21,48.

The effect of surfactant concentration (above the cmc) on MEUF yield is relevant only for partitioned solutes, whereas do not alter the bound solute fraction when the substrate is highly hydrophobic. For example, %R of aniline (at pH 8) varies from ca.17 to ca.33 using SDS 0.01 M and 0.04 M, respectively, whereas %R of 2-chloro-4-bromoaniline changes from ca.95 to 100 in the same SDS concentration range (48). Of course, the added surfactant concentration must be minimized when MEUF is applied for environmental cleaning.

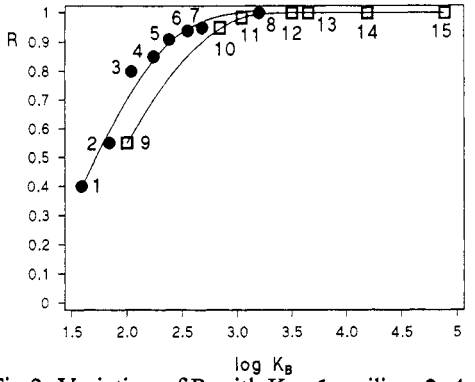


Fig.3 .Variation of R with K_B: **1**: aniline; **2**: 4-cyanoaniline;**3**: 4-ethylaniline; **4**: 4-chloroaniline; **5**: 4-bromoaniline; **6**: 2-methoxy-5-chloroaniline; **7**: 4-t-butylaniline; **8**: 2-(4-amino-2-hydroxy-phenyl)benzimidazole; **9**: phenol; **10**: 4-chloro-phenol; **11**: 3,5-dichlorophenol; **12**: 2,4,5-tri-chlorophenol; **13**: 2,3,4,5-tetrachlorophenol; **14**: 2,4-D; **15**: 2,4,5-T.

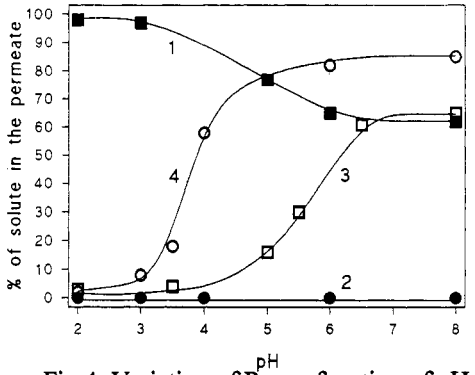


Fig.4. Variation of R as a function of pH. HTAB 0.02 M: **1**: aniline, **2**: 2,4,5-T. SDS 0.02 M: **3**: aniline; **4**: 2,4,5-T.

The effect of ionic strength is another important factor when charged substrates and ionic aggregates are present. Due to the shielding of the electrostatic solute-micelle interaction, the rejection coefficient of aniline in SDS (at pH 3) passes from ca.96% to ca. 80% after addition of 0.01 M NaCl. For 4-isopropylaniline, in the same conditions, %R slightly decreases from 100 to ca.98, indicating that the hydrophobic contribution to K_B largely predominates.

Separation and recovery of metal ions by MEUF

The removal or concentration of metal ions from aqueous dilute solutions can be accomplished exploiting two different approaches. The first one is based on the use of anionic aggregates (micelles or polyelectrolytes), which exert electrostatic attraction towards the cations (49,50). Although quite efficient for the removal of multicharged species, these systems are scarcely selective and very sensitive to the ionic strength.

The second approach, based on the use of chelating micelles able to react with a limited number of metals, has been proposed some years ago (6) and has recently confirmed its potential practical utiliy. Very efficient and selective separations can be obtained using these reactive aggregates provided that the chelating group and the ligand structure are adequately chosen.

A certain number of hydrophobic ligands, generally obtained by introduction of suitable alkyl chains in common chelating molecules, have been used. After formation of large mixed aggregates with unreactive surfactants, the solution is ultrafiltered through cellulosic hydrophilic membranes having a molecular weight cutoff in the range 5,000-20,000 Dalton.

Several examples of selective and efficient metal separations, recently reported in literature, are given in Table 3. In some cases, as for the removal of U(VI) from waste water, the structure of the bulky complexes does not allow their strong binding to the aggregates. The introduction of an auxiliary ligand (TOPO: trioctylphosphine oxide) improves in this case the retention because a ternary complex is formed, which is more strongly bound to the HTAB micelle through the TOPO alkyl chains (52).

TABLE 3. Removal and separation of metal ions from aqueous media by MEUF using ligand micelles.

Metal	Ligand	Host micelles	pH	%R	Ref
Fe(III)	Y-PAS-C_4	$C_{12}E_8$ 0.01 M	4.0	89.5	51
Fe(III)	Y-PAS-C_8	$C_{12}E_8$ 0.01 M	3.5	>99.9	
Fe(III)	PAS-C_8	$C_{12}E_8$ 0.01 M	3.5	70.0	
UO_2^{2+}	Phe-2-O	HTAB 0.04 M	8.0	76.0	52
UO_2^{2+}	Phe-2-O/ TOPO	HTAB 0.04 M	8.0	99.0	
Al(III)	Lumogallion	HTAB 0.02 M	5.9	>99.9	53
Mn(II)	PAN-C_4	TX100 0.02 M	7.5	97.0	54
Co(II)	PAN-C_4	TX100 0.02 M	3.0	>99.9	
Ni(II)	PAN-C_4	TX100 0.02 M	5.0	>99.9	
Zn(II)	PAN-C_4	TX100 0.02 M	6.0	98.0	
Cu(II)	NIDA	HPC 0.157 M	7.0	95.0	55
Cu(II)	C_{16}NHMePyr	$C_{12}E_6$ 0.02 M	5.7	>99.0	56

TX 100: Triton X-100; Phe-2-O: dicarboxylic ligand formed by two (S)-phenylalanine residues joined by an ethylenedioxide bridge; PAN-C_4: 4-n-butyl PAN; NIDA:N-n-dodecyliminodiacetic acid; C_{16}NHMePyr: 6-[(hexadecylamino)methyl]-2-(hydroxymethyl)pyridine.

The R vs. pH curves are very similar to the classic liquid-liquid extraction profiles and, by properly chosen the pH, the selective enrichment of a given component can be performed using simple or multistage MEUF. Working with PAN-C_4 $1x10^{-4}$ M in Triton X-100 $6.6x10^{-3}$ M at pH 3, the initial Co(II)/Zn(II) ratio in water (0.5 mg/L of each metal) varies until 0.5/0.01 mg/L (in the retentate) after three repeated ultrafiltrations. The corresponding R values at this pH are ca.1 for Co(II) and ca.0.3 for Zn(II) (54).

Attention must also be paid to the changes in stoichiometry of the complexes occurring when the ligand hydrophobicity varies.
For example, the ligand PAN reacts with Ni(II) in homogeneous solutions (water-dioxane) and in Triton X-100 micellar solutions forming mainly a 1:2 metal-ligand chelate, whereas PAN-C_4 tends to form 1:1 complexes in the same micellar system (see the shift of the corresponding Job plots in Fig.5).

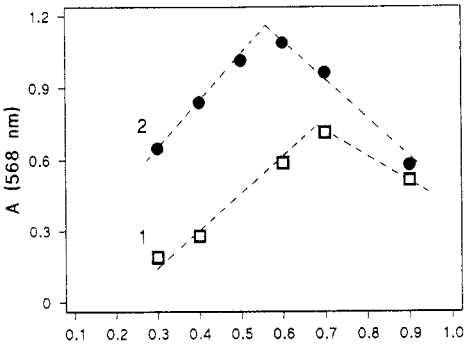


Fig.5. Job plots of Ni(II)-PAN (**1**) and Ni(II)-PAN-C4 (**2**) in Triton X-100 0.02 M, at pH 7.

Due to the steric constraints operating at the micelle-water interface is probably difficult to form higher complexes, whereas for the less hydrophobic members of the homologous series, the chelate formation takes presumably place in the bulk aqueous phase.
Among the advantages of MEUF in metal separations, the addition of moderate quantities of surfactants (5-10 g/L) and ligands (less than 1 g/L) to the aqueous phases can be mentioneded. Nearly the same concentration performances obtained in extractions using larger amounts (100-150 mL) of more toxic and expensive organic solvents can be achieved. Moreover, the concentration factors can be increased by selecting amphiphiles with low cmc values and MEUF can be conveniently coupled with micelle-based determination methods without changing the matrix composition.
The main disadvantage of MEUF arises from the modest solubilization power of the micellar phase, which represents a very low volume fraction of the solution. This imposes a limit on the

amount of ligand excess present in the system. Another problem is that the recovery and purification of the metals in the surfactant-rich retentate may be more difficult.
The development of mild demetallation treatments appears at the moment one of the more promising environmental applications.

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