

NEW APPROACHES IN EXTRACTION

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ABSTRACT

Tendencies of the development of extraction processes are presented. New ecologically friendly ideas, including those with the use of different aquatic and surfactant systems, are discussed.

Key words: extraction, green chemistry

Solvent extraction is a mature process used to recover metal ions, organic substances, pharmaceuticals and biochemicals. The process is used in great scale, i.e., to produce in one plant 160 000 ton/year cathodic copper from diluted aqueous solutions containing only 5 g/L Cu(II) [1, 2], to separate aromatic from petroleum products, to recover phenols from diluted waste aqueous streams, to separate biochemicals from fermentation broth, etc. The separation of antibodies by solvent extraction can be a new process which will reduce the price of modern drugs proposed for major diseases of an ageing society (cancer, cardiovascular diseases, metabolic diseases, e.g. diabetes and dementia).

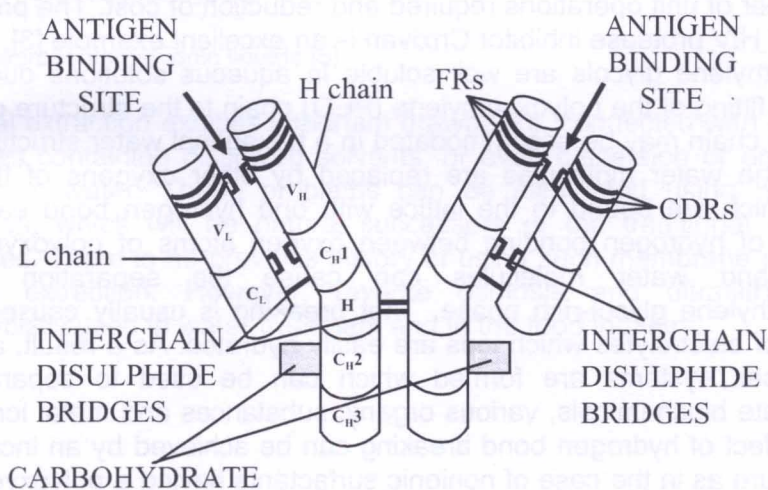


Fig. 1. Basic structure of the human IgG1 antibody.

Fundamentals of classical solvent extraction processes seems to be well recognized. However, new extraction systems which are more friendly for environment are proposed and intensively studied. The approaches take into account:

- new tailored diluents for organic synthesis and separation of components,
- polyoxyethylene glycol-water-electrolyte systems to recover and separate metal ions, organic substances and biochemicals,
- ionic liquids as solvents in extraction,
- surfactant supported separations in aqueous phase – micellar enhanced ultrafiltration to separate ions and organic substances,
- nanoparticles covered with copolymers to use instead micelles for separation in ultrafiltration,
- cloud point separations,
- reversed micelle extraction,
- phase transfer catalysis as an economical method to process waste chemicals into valuable products,
- extraction of biochemicals and pharmaceuticals in hydrophilic drug-friendly environment,
- bifunctional chelating and basic extractants which enable recovery of large amounts of neutral salts.

The use of hydrophobic octyl tetrahydrofurfuryl ether (bp =259°C) instead of tetrahydrofuran (bp=65.4°C) enable to increase the temperature and the rate of reaction, and then quench the reaction by washing with water eliminating in this way energy-intensive distillation or incineration. The solvent can be used during the entire reaction sequence and lead to significant reduction in the number of unit operations required and reduction of cost. The production of Merck HIV protease inhibitor Crixivan is an excellent example [3].

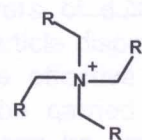
Polyoxyethylene glycols are well soluble in aqueous solutions due to the excellent fitting of the polyoxyethylene (PEO) chain to the structure of water. The PEO chain may be accommodated in a hexagonal water structure. One third of the water molecules are replaced by ether oxygens of the PEO chain, which are bound to the lattice with one hydrogen bond each. The breaking of hydrogen bonding between oxygen atoms of polyoxyethylene glycols and water molecules can cause the separation of the polyoxyethylene glycol-rich phase. That breaking is usually caused by an addition of electrolytes which ions are easily hydrated. As a result, aqueous two phases systems are formed which can be used to separate and concentrate biochemicals, various organic substances and metal ions [4]. A similar effect of hydrogen bond breaking can be achieved by an increase of temperature as in the case of nonionic surfactants having a polyoxyethylene chain. The coupling of both effects (electrolyte concentration and temperature) may cause an enormous decrease of the M_{eq} enabling the use for separation polyglycols of significantly lower molecular masses.

The system is useful to separate various organic substances, including dyes, from aqueous waste streams. The PEG-rich phase is better compatible to the considered dyes than the nonionic surfactant-rich phase formed above the cloud point and enables total recovery of dyes, even when the less effective electrolytes, e.g. $(\text{NH}_4)_2\text{SO}_4$ are used.

Polyethylene glycol-dextrane-water system is useful to recover proteins, and may be also monoclonal antibodies. Dyes work well as affinity ligands because they change the hydrophobicity of proteins and can change the electrostatic interactions when they are important.

Ionic liquids composed of hydrophobic quaternary ammonium salts seem new solvents suitable to recover various organic substances from aqueous streams, including dyes and phenols [5]. The systems seem to be not interesting for recovery of metal ions because, due to the exchange of anions, the original form of ionic liquid must be regenerated.

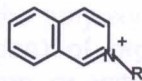
Cations:



Quaternary ammonium



N-alkylpyridinium



N-alkylisoquinolinium



1-alkyl-3-methylimidazolium

Anions: Water miscible
Water immiscible

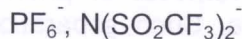
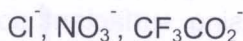


Fig. 2. Representative ionic liquids [5].

Classical extraction exhibits important drawbacks, connected with discharge of wastes containing dissolved solvents, or even dispersion or emulsion of solvents in water. These problems can be eliminated using membrane processes, which will be natural successors of the traditional extraction processes. There is no previous history of using such membrane processes for the extraction. However, reverse osmosis and ultrafiltration are commercially used in water treatment and in the food industry.

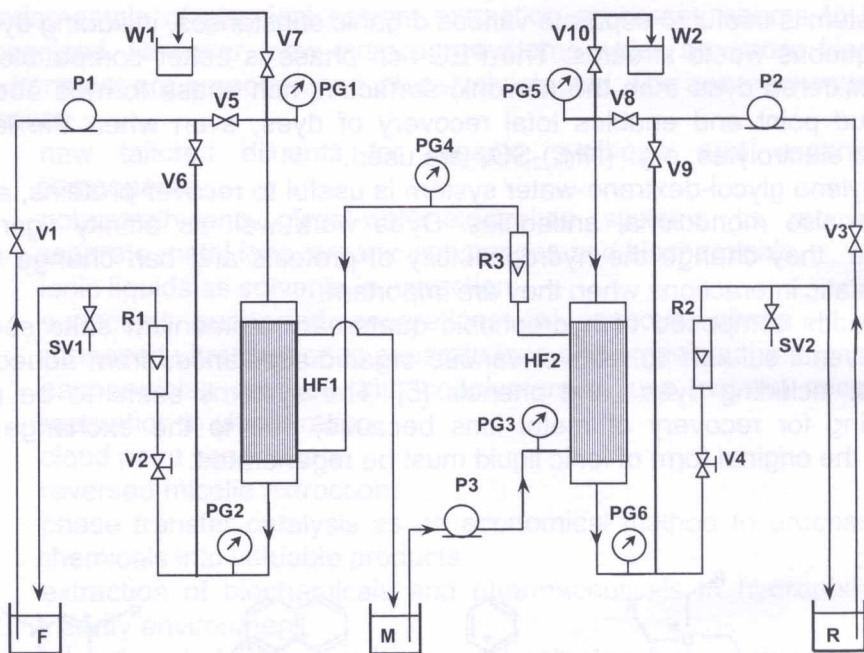


Fig 3. Hollow fiber set-up for recovery of phenols (F, M, R: feed, membrane and stripping reservoirs, each of 0.5 L volume R: flowmeter, HF: hollow fiber module, P: pump, PG: pressure gauge, SV: sampling valve, V: valve, W1, W2: reservoirs for waste aqueous phases at the first start of the process).

Direct removal of phenols by ultrafiltration of aqueous solutions is not possible. Such separation can be achieved using surfactant solutions in which organic pollutants are solubilized in surfactant micelles [6, 7]. The average molecular mass of the spherical micelles is in the range of 20-30 kDa. Hence, the micelles along with the solubilized pollutants can be separated using membranes of appropriate pore diameter or cut-off. Due to the membrane fouling, the separation is also possible on membranes with a relatively large cut-off [5, 6].

The main drawback of micellar enhanced ultrafiltration is the transfer of surfactant monomers through the membrane being in equilibrium with the micelles and the membrane fouling caused by several factors, including surfactant gelation and adsorption. Thus, the choice of surfactant type is crucial for potential applications.

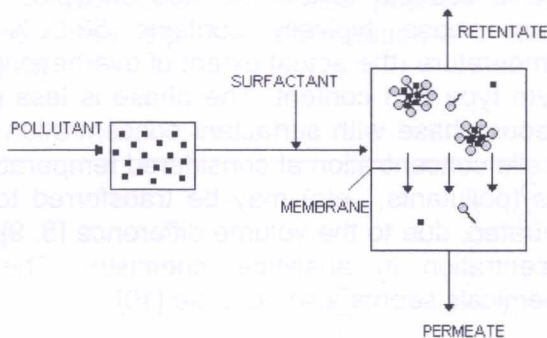


Fig. 4. Scheme of micellar enhanced ultrafiltration.

The problem of surfactant monomer transfer through the membrane can be overcome to a large extent using nanoparticles coated with various self-assembled layers of surfactant and polymers [3]. Polyoxyethylene chain stabilize the particle dispersion in water while the polyoxyethylene propylene chains enables effective sorption (solubilization) of organic solutes. The stripping can be carried out with water steam or with organic solvents. Nanoparticles can be separated in an external magnetic field giving new possibilities for design of green processes.

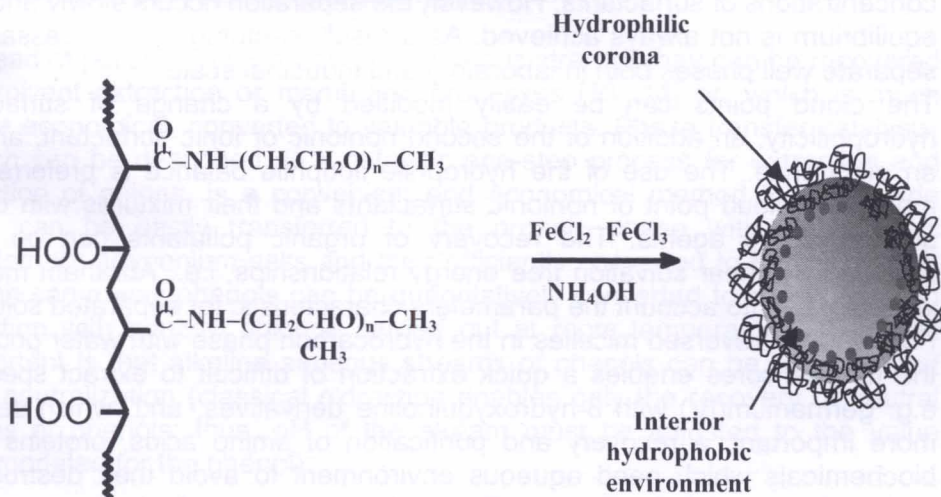


Fig. 5. Synthesis and structure of an amphiphilic magnetic nanoparticle [3].

The heating of solutions containing nonionic surfactants and cooling of solutions containing zwitterionic surfactants causes turbidity and separation of surfactants with formation of the new phase, called surfactant-

rich phase. Economic aspects favour the use of typical nonionics. The separated surfactant phase typically contains 50-90% of surfactant, depending upon temperature (the actual extent of overheating over the cloud point), the electrolyte type and content. The phase is less hydrophilic than the remaining aqueous phase with surfactant concentration assumed to be equal to critical micelle concentration at considered temperature. As a result, organic substances (pollutants, etc) may be transferred to surfactant-rich phase, and concentrated, due to the volume difference [8, 9]. The method is used for pre-concentration in analytical chemistry. The recovery and separation of biochemicals seems also possible [10].

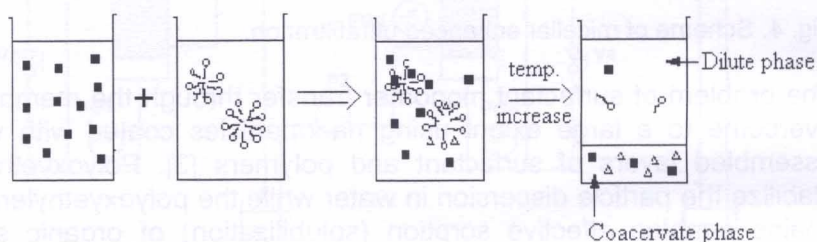


Fig. 6. Scheme of separation by cloud point technique.

In equilibrium the remaining aqueous phase should contain only low concentrations of surfactants. However, the separation occurs slowly and the equilibrium is not always achieved. As a result, centrifuging is necessary to separate well phases both in laboratory and industrial scale.

The cloud points can be easily modified by a change of surfactant hydrophilicity, an addition of the second nonionic or ionic surfactant, and/or an electrolyte. The use of the hydrophile lipophile balance is preferred to model the cloud point of nonionic surfactants and their mixtures with other surface active agents. The recovery of organic pollutants can be well modeled by linear solvation free energy relationships, i.e., Abraham model, which takes into account the parameters characteristic for separated solutes. Formation of reversed micelles in the hydrocarbon phase with water pools in the micelle cores enables a quick extraction of difficult to extract species, e.g. germanium(IV) with 8-hydroxyquinoline derivatives, and, which seems more important, a recovery and purification of amino acids, proteins and biochemicals which need aqueous environment to avoid their destruction and/or change of their structure. Due to limited volume of micelle cores, the recovery is limited to substances having the molecular mass below 50 kDa.

Aqueous solutions of surfactants are useful for remediation of soil deeply contaminated (up to 50 m) with hydrocarbons and chloroderivatives [11]. Depending upon surfactant composition only solubilization of pollutants in the micelle cores (Winsor I) or rapid formation of microemulsion (Winsor III) can be exploited to achieve successful remediation in short periods when the

classical bioremediation failed. It is also possible to carry out important technological processes, e.g., hydroformylation of olefins (oxo process) in microemulsion [12].

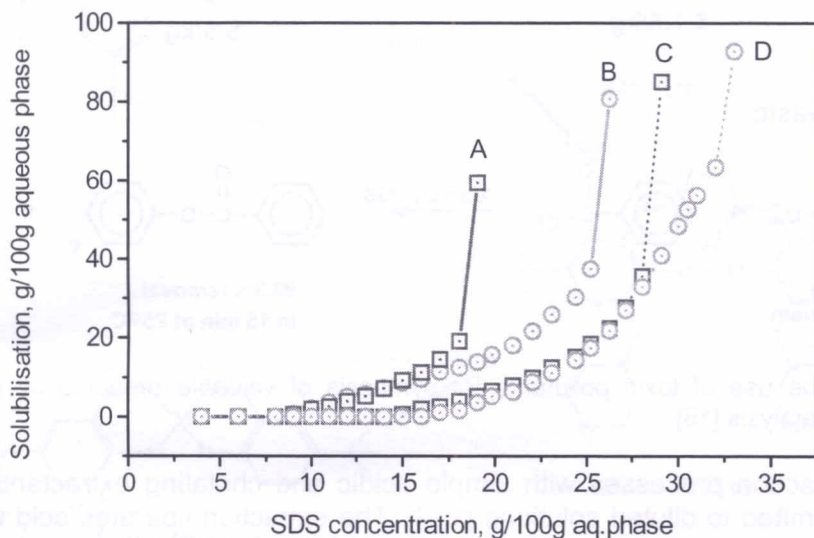
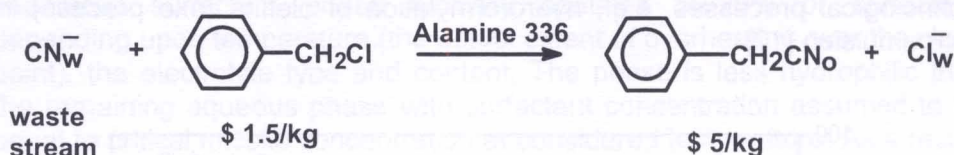


Fig. 7. Solubilisation of various components in sodium dodecylsulfate-butanol (43%)-water system at 19°C (A, hexene; B, hexene and 3% Na-TPPTS; C, heptanal; D, heptanal and 3% sodium tri(m-sulfophenyl)phosphine) [12].

Instead of pollutant neutralization in aqueous streams they can be recovered by solvent extraction or membrane processes [13, 14] or, which is much more economical, converted to valuable products. Phase transfer catalysis, which can be described as a catalytic one-step process for extraction and reaction of anions, is a convenient and economical method [15]. Cyanide ions can be easily transferred to the organic phase with hydrophobic quaternary ammonium salts and their efficiently converted to benzyl nitriles. In the same way phenols can be quantitatively converted to esters, e.g., in reaction with benzoyl chloride carried out at room temperature. The most important is that alkaline aqueous streams of phenols can be used without any neutralization (classical extraction enables only the recovery of neutral forms of phenols; thus, pH of the stream must be adjusted to the value appropriated for the phenol).

Electroplating waste



Phenol waste

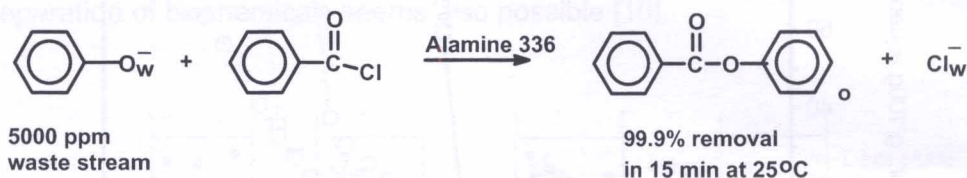
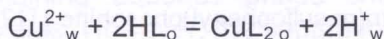
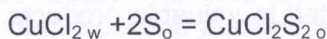


Fig. 8. The use of toxic pollutants for synthesis of valuable products by phase transfer catalysis [15].

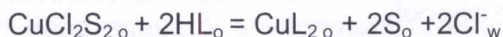
The extraction processes with simple acidic and chelating extractants are usually limited to diluted solutions [1, 2]. The extraction liberates acid which increased concentration shifts the extraction equilibrium towards free extractants, i.e., disturbs extraction and facilitates stripping.



The problem can be overcome when solvating reagents are used [16-18].



However, it means the change of the sulfate system into the chloride one which usually is not acceptable in industry due to corrosion problems and unconventional electrowinning. The problem can be overcome using a mixture of basic or solvating reagent S and chelating reagent HL, and the transfer of metal from a weak complex to the chelate by washing out chloride ions [16]. As a result, stripping can be carried with sulfuric acid and traditional electrolyzer can be used for electrowinning.



The use of bi-functional extractants which contain two different fragments enable to form chelates with metal cations, bond liberated protons and form ions pairs with remaining anions. Such reagents are suitable to extract large amounts of salts with any regulation of acidity [18].

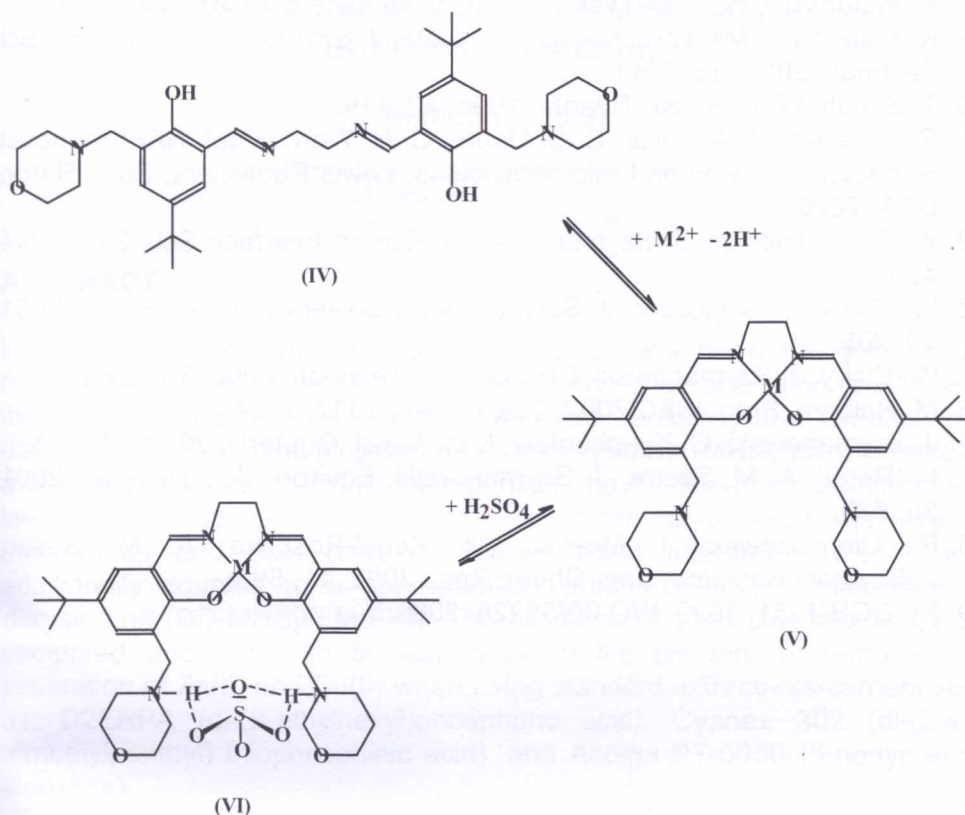


Fig. 9. Bi-functional reagents for extraction of metal sulfates [19].

ACKNOWLEDGEMENT

The work was supported by DS 32/044/2003.

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