Translated from *Uspkekhi Khimii* **60** 2463–2468 (1991) U.D.C. 66.066–278:532.711

Micellarly enhanced (reagent) ultrafiltration

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ABSTRACT. The few data available in the scientific and technical literature on a new method for membrane separation—micellarly enhanced or reagent ultrafiltration (RUF)—are presented. Three versions of reagent ultrafiltration are considered in which sols are separated on a membrane. Data are presented concerning the influence of the characteristics of the disperse phase on the ultrafiltration process.

The bibliography includes 17 references.

Membrane separation and the usual filtration are frequently regarded as identical technological processes. The series of procedures filtration, microfiltration, ultrafiltration, and reverse osmosis are outwardly similar because of the presence of a partition and a common driving force—the pressure gradient. However, in this series the size of the retained particles diminishes (from micrometres to angstroms), the pressure gradient increases, and the specific productivity of the partition falls rapidly. Furthermore with increase in dispersity, for example, in the sequence coarse suspensions/emulsions–sols/microemulsions–lyophilic colloid systems (polymer and surfactant solutions), the influence of the sieve effect diminishes and the role of the aggregative behaviour of the disperse phase in the solution (its interaction with the surface of the membrane) increases appreciably.

The objects to be separated, for example industrial waste waters, very often consist of inhomogeneous mixtures containing a vast amount of an indifferent inorganic electrolyte and the contaminant proper, the amount of which can be very low but is nevertheless much greater than the limiting permissible amount. In particular, liquid radioactive waste consists of aqueous solutions of salts with an overall ionic concentration amounting to hundreds of milligrams per litre. Under these conditions, the contaminating components (radionuclides) cannot be determined in terms of weight concentrations and only the radioactivity is measured. Such systems can be conveniently separated by micellarly enhanced or reagent ultrafiltration (RUF). This membrane separation method, which can combine a high productivity with a low working pressure and the ability to eliminate ionic components from water with selective separation of the components, is based on the conversion of dissolved low-molecular-weight components into a new associated molecular or colloid state with subsequent separation on a macroporous membrane of the associated species produced.

Reagent ultrafiltration can be applied in several versions.[1]

1. The addition to the solution of a water-insoluble organic compound which interacts with the required component according to the extraction mechanism. The resulting emulsion is separated on a porous membrane subject to appropriate requirements.

2. The addition to the solution of surfactants which lead to additional purification at a concentration above the critical concentration for micelle formation (CCM) as a consequence of the physical adsorption of the contaminant on the surfactant micelles.

3. The addition to the solution of water-soluble polyelectrolytes with functional groups which are able to combine with the required components via an ion-exchange complex formation, etc. mechanism. The solution remains homogeneous and its separation is achieved in accordance with the laws governing the ultrafiltration of solutions of high-molecular-weight compounds.

4. The addition to the solution of a freshly prepared sol on the particles of which the required component is bound as a result of physical adsorption.

5. The conversion of the dissolved ionic species of the components into a molecular and subsequently a colloid phase in the course of the hydrolysis as a result of the addition of alkali to the solution. The electromembrane method of hydrolysis is a variety of this version.

6. The addition to the solution of chemical reagents whose interaction with the reqired component converts the latter into an insoluble form. The formation of a deposit should be stopped at the colloid phase formation stage.

We should like to emphasise that there may not in fact be a distinct boundary between the above versions, i. e. the solution of the given problem may require different versions to supplement one another.

At the present time, certain versions of the RUF have already undergone a far reaching theoretical development and have even found industrial application, whereas others are only being investigated.

This review deals with the application of the last three versions, where sols are subjected to membrane separation and it is therefore necessary to take into account the stability of the system and the size of the colloid particles in the concentration process.

It is known[2,3] that a deposit begins to be formed on supersaturation of the system and that the process can be divided arbitrarily into three stages: (1) the formation of nuclei of critical size; (2) the growth of particles (the particles are aggregates of the nuclei); (3) precipitation and ageing of the deposit.

The precipitation reaction in the colloid range of dispersity can be stopped in different ways: by introducing into the reaction mixture various stabilisers (surfactants, polymers), which on being sorbed on the surfaces of colloid particles prevent their further aggregation, by altering the temperature, pH of the reaction medium, etc. The choice of specific conditions and additives for controlling the dispersity of the colloid system is determined by the nature of the disperse phase and the solvent.

The ultrafiltration process is greatly influenced by the particle size, which depends on its turn on the mechanism and kinetics of the process leading to the formation of the new phase. The formation of the new phase begins either as a result of the fluctuation generation of a nucleus of critical size (homogeneous fluctuation of crystallisation centres) or following the introduction into the system of ready made nuclei from outside (heterogeneous formation of crystallisation centres).

According to the Gibbs–Thomson equation, we have for a critical nucleus of spherical shape

$$r_{cr} = \frac{2\sigma V}{RT \ln \gamma},$$

where r_{cr} is the critical radius of the nucleus, σ the interfacial tension, V the molar volume of the new phase, R the gas constant, T the temperature, and γ the critical degree of supersaturation. For non-electrolytes, $\gamma = c/c_0$, c is the concentration of the test substance in the supersaturated solution, and c_0 the equilibrium solubility of the macrocrystals. For strong electrolytes, $\gamma = ab/L$, where a and b are the activities of the cations and anions and L is the solubility product. It follows from this equation that the lower the degree of supersaturation, the higher the values of r_{cr} and the appearance of the critical nucleus therefore becomes increasingly more difficult with decrease in the degree of supersaturation of the system.

Depending on the conditions, there is a possibility of both homogeneous and heterogeneous formation of nuclei.[2,4,5] Furthermore, depending on the degree of supersaturation, the process can proceed in the same system via both the nucleus formation mechanisms. This has been demonstrated by Mikhnevich.[3] When the degree of supersaturation in the system diminishes, crystallisation becomes possible only on increasingly larger particles. Finally, if r_{cr}, defined by the Gibbs–Thomson equation, becomes greater than the size of the impurity particles, "spontaneous" formation of nuclei on the latter begins. The energy necessary for such a heterogeneous process is then found to be lower than the energy of the homogeneous formation of nuclei of the same size.

The next stage of crystal growth is determined by two processes:[6] the supply of the substance from the bulk of the solution to the surface of the crystal (diffusion) and incorporation of molecules in the crystal lattice (surface reaction). The growth rate is determined by the rate of the slower of the two processes. Crystal growth processes controlled by either diffusion or the surface reaction are therefore distinguished. The rate of the surface reaction is independent of the hydrodynamic conditions and is determined by the state of the surface of the growing crystal. Experiments have shown that, when small amounts of other substances, capable of being sorbed on the surface, are added, they may influence significantly the rate of growth and shape of the crystals. As regards the rate of supply of the substance, one may claim that it depends on the stirring. As the stirring becomes more intense, the rate of crystallisation increases but only up to a certain limit, at which the rate-limiting factor is the surface reaction.

Between the establishment of supersaturation in the system and the appearance of the first traces of the new phase which can be distinguished in one way or another, there is a definite time interval called the induction period. During this period, crystallisation centres are formed vigorously. The duration of the induction period τ_i varies markedly depending on the nature of the deposit and for a given deposit is a function of the initial degree of supersaturation.[7] Thus, for $BaSO_4$ and AgCl deposits having approximately the same molar solubilities, we have, for equal initial concentrations,

$$\tau_i(BaSO_4) \gg \tau_i(AgCl).$$

According to Nielsen's studies,[8] where the crystallisation of $BaSO_4$ was investigated, the induction period τ_i, the total number of grown crystals N, and the average rate of formation of nuclei N/τ_i were determined, the number of crystals N remains approximately constant up to a concentration $c \simeq 0.01$ M and then increases sharply: N/τ_i increases in proportion to the concentration raised to the power 18. Evidently in this case there is a change from the heterogeneous to the homogeneous mechanism of the formation nuclei. The size of the nucleus (18 ions or 9 molecules), the critical degree of supersaturation ($\gamma_{cr} = 630$), and the interfacial tension ($\sigma = 90$ erg cm^{-2}) were calculated from the data presented.[9]

Thus, on the basis of the foregoing, one may postulate that, by altering the degree of supersaturation of the system, the rate of supply of the test substance, and the rate of the surface reaction, it is possible to achieve control of the induction period and the dispersity of the colloidal phase and hence also of the particle size. Then, having stabilised the system obtained, the ultrafiltration process can be carried out. The barium chromate colloid system has been obtained by this method. It is important to note that sometimes, when the precipitation process is carried out without satisfying the technological requirements, colloid systems are formed in settling tanks.[10] In this respect, a result which is undesirable for a given process may prove positive for reagent ultrafiltration.

It has been suggested[11] that sodium sulphide, forming disperse systems with contaminants, be used as the reagent for the isolation of mercury, lead, and cadmium ions. As a result of the formation of colloid systems, it became possible to remove them by means of ultrafiltration.

When the fourth version of reagent ultrafiltration is carried out, satisfactory results are achieved at low concentrations of the contaminant, which is sorbed on the colloid particles. This can naturally limit the application of the given method. However, it proved effective for the elimination of caesium-137 from liquid radioactive waste from atomic power stations.[12] Copper ions Cu^{2+} and the $[Fe(CN)_6]^{4-}$ ions were introduced into the caesium-containing liquid waste. The reaction resulted in the formation of a colloid system in which caesium was sorbed on the colloid particles retained by subsequent ultrafiltration. The degree of extraction of caesium-137 was 99% and the consumption of the reagents was 2% of the amount required for the precipitation.

The fifth version of reagent ultrafiltration, where the colloid particles are obtained by hydrolysis, can find extensive application if it proves possible to shorten the hydrolysis time, i.e. to increase the rate of reaction. It is known that, at a concentration of the component isolated in excess of 10^{-3} M, the hydrolysis proceeds with formation of polynuclear complexes in several stages, including the formation of monomers and dimers, their polymerisation, the appearance of amorphous colloid particles, and their subsequent transformation into a crystalline form. Any of the atoms forming part of the polymer chain can be hydrolysed twice and three times, which leads to the branching of the chain. The identification of the species formed is exceptionally difficult, but for practical applications only one parameter is important—their size, which after the addition of alkali has ceased may increase owing to coagulation and may lead to the loss of resistance to aggregation by the colloid system. There are several methods for preventing this phenomenon: the addition of surfactants and a change of temperature.[13]

The results achieved in the removal of iron and chromium from solutions are presented in Figs. 1 and 2 and the influence of surfactants on this process is illustrated in Fig. 3.

Hydrolysis with the aid of electroadjustment of the pH of the solution, i.e. the gradient-free micellarly enhanced ultrafiltration method, is a variety of the fifth version. In this procedure, the question of the resistance of the system to aggregation is even more

acute, but at the present time the method has not yet been investigated.

Membrane separation is evidently determined in many respects by the stability of sols as regards an increase in concentration, by the size and charge of their particles, and by the hydrodynamic conditions in the apparatus. The creation of optimum hydrodynamic conditions is especially important for diminishing the phenomenon of concentration polarisation.

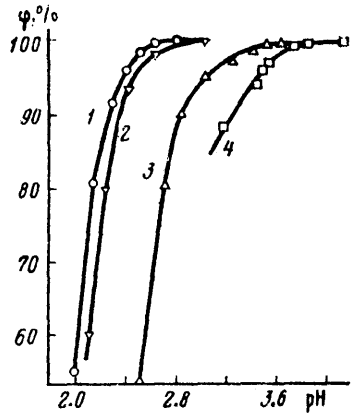


Figure 1. Dependence of the selectivity of the purification (φ) on the pH of the medium for an iron solution; [Fe] (mg litre^{-1}) in the initial solution:[1] *1*, 1000; *2*, 300; *3*, 60; *4*, 25.

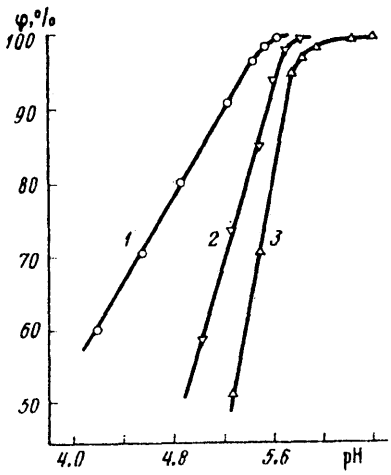


Figure 2. Dependence of the selectivity of the purification on the pH of the medium for chromium solutions; [Cr] in the initial solution (mg litre^{-1}):[1] *1*, 500; *2*, 350; *3*, 100.

The change in the properties of hydrosols during their concentration from 3.5 to 43% has been investigated[14] by the ultrafiltration method. It was noted that during concentration there is an increase in the viscosity of the sol, which exerts an appreciable influence on the rate of ultrafiltration, especially on increasing the concentration above 35%. This is explained by the fact that, for a given size of the particles and taking into account their hydration shells, the closest packing is attained under these conditions. The shells of the stabilising counterions begin to overlap, so that a slight increase in the concentration of the sol entails an appreciable increase in viscosity. Ultimately this leads to a lower stability of silica sols in relation to gel formation.

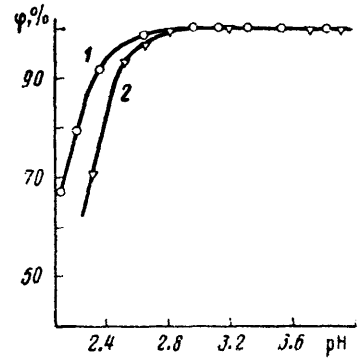


Figure 3. Dependence of the selectivity of the purification on the pH of the medium for the iron–surfactant system; [Fe] in the initial solution (mg litre^{-1}):[1] *1*, 1000; *2*, 100; the surfactant concentration was 100 mg litre^{-1} in both cases.

Studies[15] of the influence of hydrodynamic conditions and of the diameter of the SiO_2 sol particle on the rate of ultrafiltration showed that, on vigorous stirring of the disperesions, whereupon a gel layer made up of the sol particles is not formed on the surface of the membrane, the rate of filtration is constant and independent of the particle diameter. A highly concentrated sol (106 kg m^{-3}) is an exception. In the absence of stirring, the rate of filtration increases with increase in the particle diameter, which can be explained by the increase in the porosity of the gel layer. An increase in pH diminishes the resistance of the gel layer as a consequence of the increase in the repulsion between the sol particles. In these experiments, the size of the colloid particles was less than the size of the membrane pores. However, in practice one may encounter opposite cases where the colloid particles, penetrating into the pores, irreversibly contaminate the membrane. In order to solve this problem, it has been suggested[16] that the particles capable of penetrating into the membrane pores be aggregated until particles which are retained on the surface of the membrane are obtained. An increase in the size of the particles and the presence of a charge on their surface have positive influence on the rate of filtration.

Certain aspects of the ultrafiltration of colloid systems have been described by Bryk and Tsapyuk.[17]

Studies in the field of the ultrafiltration of colloid systems are just being activated, but it is already possible to formulate preliminary results: (1) the irreversible contamination of the membrane is caused by particles whose size is smaller than the pore size; (2) the charge on the colloid particles, by virtue of which there is a possibility of

their electrostatic repulsion from the membrane, is very important; (3) by controlling the conditions in the formation of the colloid system, it is possible to achieve the best ultrafiltration conditions by an appropriate combination of the size and charge of the particle; (4) it is important to set up the optimum hydrodynamic situation over the membrane, the elimination of stagnant zones being of primary importance.

Reagent ultrafiltration increases markedly the applications of the membrane separation methods. It becomes possible to use highly productive processes for the purification of liquid industrial waste, which could be achieved previously only by reverse osmosis, and to eliminate selectively contaminating components from the waste without involving the salt ballast, which is especially important in the handling of radioactive and electroplating waste. A new method has arisen for the fractionation of components of liquid mixtures which may become analytical after appropriate further developments. Finally, new approaches to the utilisation and processing of toxic concentrates are appearing.

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