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CHAPTER 5

THE USE OF FILTRATION AND ULTRAFILTRATION FOR SIZE FRACTIONATION OF AQUATIC PARTICLES, COLLOIDS, AND MACROMOLECULES

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1. INTRODUCTION

Although a large number of techniques can be used for particle size measurements,[1-3] only a few categories of techniques can be used to separate larger from smaller size components in natural waters with minimum perturbation. They are primarily

(a) Sieving, filtration, ultrafiltration and dialysis
(b) Sedimentation and centrifugation
(c) The various types of field flow fractionation (FFF)
(d) Hydrodynamic chromatography

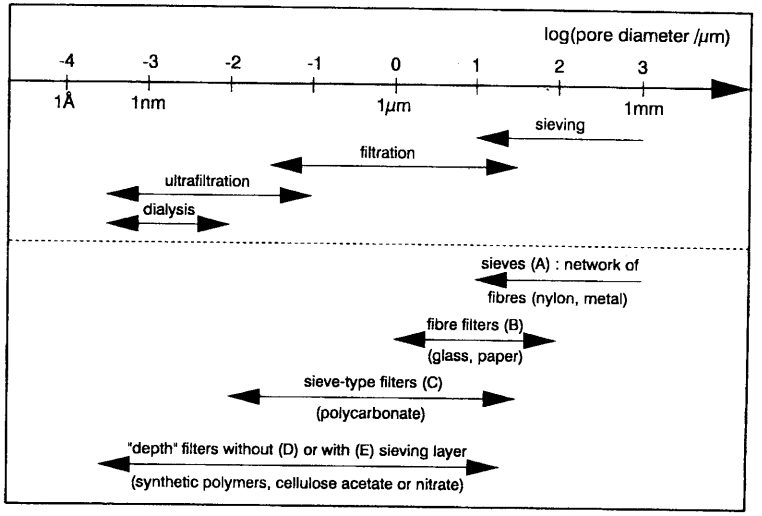

Figure 1. Size ranges for sieving, filtration, and dialysis techniques and for application of the most important filter types.

Until now, the last two categories of techniques have found limited application in natural waters. In the case of FFF, this is mostly because of experimental difficulties. Categories (b) and particularly (a), are by far the most widely used when studying natural waters, i.e., sea water, fresh water, sediment pore water, soil pore water, and ground water.

The various techniques in category (a) differ from each other by the size range of particles they can separate (see Figure 1), the nature of the filters used (Figure 1; see below) and the experimental conditions. They are discussed in detail in References 2 through 5. Sieves (A in Figure 1) are regular networks of nylon fibers or metal wires. Their use is discussed in References 2 and 3. They will not be described here. Filters may be separated into three groups (B through E in Figures 1 and 2):

(i) Filters made of a random assembly of glass or paper fiber (B)
(ii) Polycarbonate filters (C) which are made of an impermeable organic material interspersed with discrete cylindrical holes, and which act as true sieves
(iii) So-called depth filters (D) which have a spongy structure.

Filters made of organic polymeric material are usually membranes. Polysulfone membranes (Figure 2E) are intermediate between types C and D filters: their filtering surface looks like that of a polycarbonate membrane (although the pore size distribution is broader), but the inside of the membrane body is similar to that of depth filters. For polysulfone membranes, the active filter

is a thin organic "skin" (~10 μm) covering a much thicker and more porous support.

These various filters are complementary in terms of pore size ranges and distributions (Figures 1 and 2) and also in chemical nature. This is an important feature which may help to minimize sample perturbation by the filter (ad-

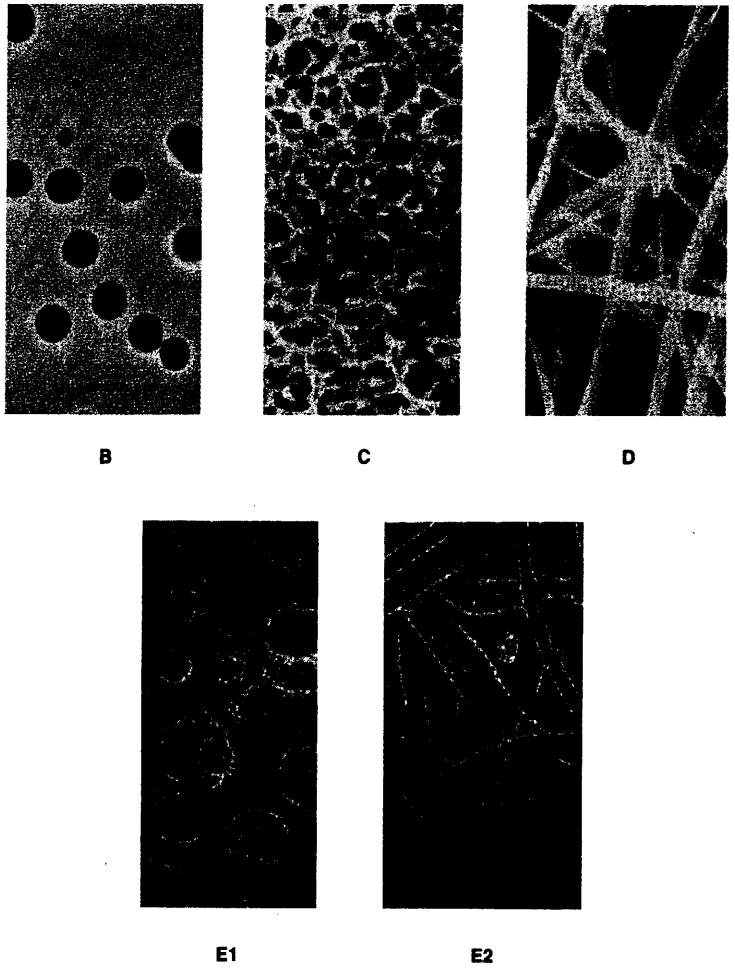

Figure 2. Electron microscopy images of the most important filter types. Letters refer to Figure 1. B: fiber filter; C: polycarbonate filter; D: depth filter; E: polysulfone filter; E1: top surface, E2: bottom surface. (From Reference 4 for B, C, and D; E from G.G. Leppard, Natl. Water Research Inst., Ontario).

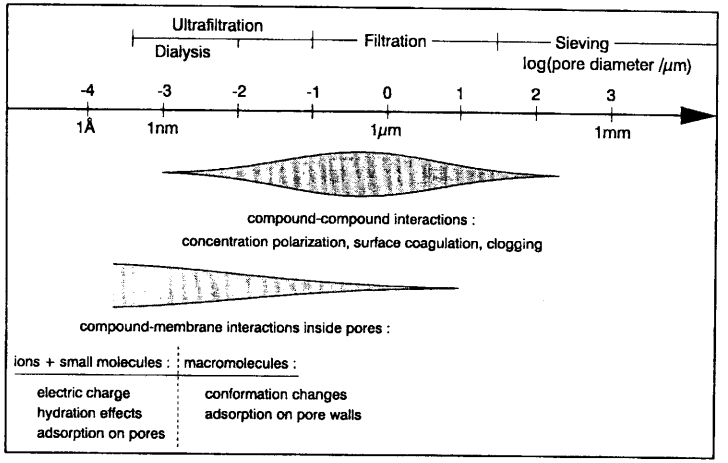

Figure 3. Schematic representation of size ranges where important filtration secondary effects are expected to play a significant role. The thickness of hatched zones reflects the relative importance of the corresponding factors. Note: the word "compound" designates any component different from water, either particulate, colloidal or dissolved (see glossary).

sorption on, contamination, or denaturation by the filters; Section 3). A large volume of literature exists on the preparation and characterization of synthetic membranes with a wide variety of properties. It is beyond the scope of this review to summarize this information, but the interested reader is referred to References 6 through 11, 90, 188, and 191 for preparation of the membranes and References 4, 12 through 23 for their characterization. Most of these synthetic membranes, however, are used for industrial purposes. Until now, almost all analytical applications to natural waters have made use of the membranes described in Figure 1.

It is also important to note the significant differences in experimental conditions between sieving, filtration, ultrafiltration, and dialysis (Figure 3). In the first two techniques, large solution flow rates can be achieved (and most often are used) thanks to the relatively large pore size of the filters, even if a rather small pressure (<1 atm) is applied on the above side of the filter. As will be discussed in details in Section 4, at such large flow rates, a so-called concentration polarization may develop at the filter surface (i.e., particle concentration is larger at the filter surface than in the bulk solution) which may induce coagulation at the surface, possibly resulting in the clogging of the filter. This effect is expected to be more important with filters than with sieves (Figure 3) because the porosity (i.e., the proportion of holes in the filter surface) decreases from loosely woven sieves to small pore size filters. Thus accumulation of compounds at the membrane surface and hence the formation of concentration polarization is favored by small pore size filters.

In ultrafiltration, the solution is pushed through the membrane using relatively large pressures (1 to 4 atm) but low flow-rates are imposed by the low porosity of the membranes. In dialysis, no pressure is applied; two different solutions are placed on opposite sides of the membrane and the small molecules diffuse through the membrane until equilibrium is reached. Therefore, the problem of surface coagulation mentioned above is much less important, or even nonexistent, both in ultrafiltration and dialysis (Figure 3). On the other hand, as pore size decreases, there is an increasing proportion of aquatic compounds whose size is similar to the filter pore size (the less porous ultrafiltration membranes have pore diameters of ~1 nm, i.e., close to the size of water molecules). Consequently, with such filters, interactions between these compounds and the inside surface of the pores may strongly affect their passage through the membrane. The most affected compounds are organic or inorganic macromolecules for the largest pore size ultrafiltration membranes, and ions and small organic molecules for the smaller pore size membranes (Figure 3).

Therefore, as a first approximation, it may be expected that the relative importance of the physicochemical factors governing particle transport will be rather different for sieving and filtration on the one hand, and ultrafiltration and dialysis on the other. Only filtration and ultrafiltration will be discussed hereafter, as they are the techniques most often used in natural water studies. This category of applications has been reviewed by Riley,[24] Grasshof,[34] de Mora et al.,[25] Hunt,[26] and Buffle.[27] Before discussing the physicochemical factors affecting filtration and ultrafiltration results (Section 4), their various modes of application to natural waters are presented in Section 2 and the various practical problems which have been reported in the literature are summarized in Section 3.

2. APPLICATION OF FILTRATION AND ULTRAFILTRATION, IN NATURAL WATER STUDIES

2.1 Discrimination between "Particulate" and "Dissolved" Material

Filtration is most widely used to separate the so-called "particulate" phase from the "dissolved" phase. Traditionally, filters with a pore size of 0.45 μm are used for this purpose, although this choice is arbitrary (see below), since size distributions of aquatic components extend in a continuous manner from tenths of nanometers to hundreds of micrometers (Figure 4). Hereafter, the term *particles* will be used for components with a size of >0.45 μm, whereas the terms "*macromolecules*" and "*colloids*" will be used for sizes between a few nanometers and 0.45 μm and "*solute*" will be used for ions and molecules in the size range of a few angstroms to a few nanometers (Figure 4). The term "*compounds in solution*" will be used to designate compounds of any size (particles, colloids, or solute). "*Permeate*" and "*retentate*" will be used hereafter to designate compounds of any size, either passing through or retained by the membrane, respectively. Figure 4 lists the most important types of aquatic particles, colloids, and macromolecules and

their probable size ranges. The characteristics of particles larger than 1 μm are relatively well known both in terms of chemical nature and size distributions,[27,28] for lakes,[29] rivers,[30,31] and the oceans.[32] These characteristics are much less well known for particles smaller than 1 μm[27,33] because of experimental difficulties in their determination and theoretical difficulties in the interpretation of results.

The distinction between "dissolved" and "particulate" material was first operationally defined by Goldberg et al.,[35] who used filters with a nominal pore size of 0.5 μm. This limit is widely adopted for arbitrarily discriminating between only two size fractions, called particulate and dissolved. It is partly justified by the following three considerations:

(i) Physically, the range of one to a few micrometers is a limit below which most natural particles (with densities between 1 to 3 g.cm^{-3}) do not settle

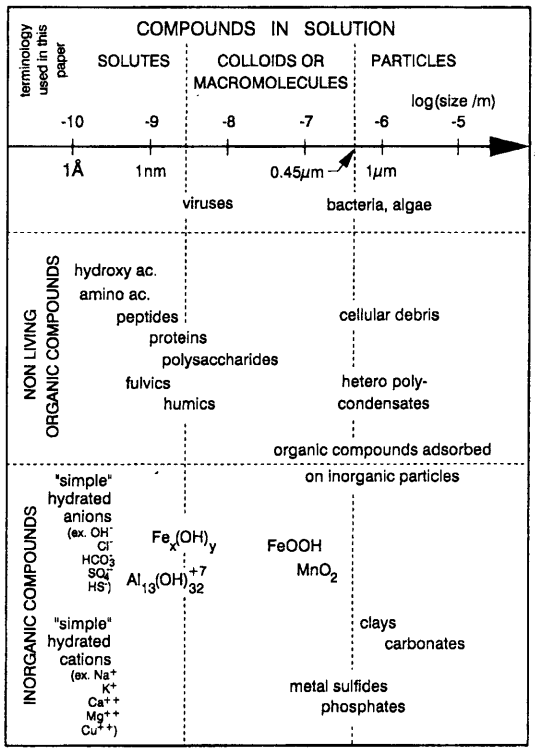

Figure 4. Schematic classification by size of important organic and inorganic aquatic components.

appreciably within a period of days.[28] It is also a limit below and above which the removal of particles from water bodies occurs by rather different processes,[36,37] irrespective of the aquatic system considered (water columns of lakes and oceans, ground waters, water treatment by filtration, water transport in pipes).

(ii) Biologically, one to a few tenths of micrometers is the minimum size range of most microorganisms (except viruses).

(iii) In practice then, the choice of a lower size limit for particles between 0.1 and 1.0 μm has the following advantages:

- The filtered sample is (at least partly) sterilized and is thus less prone to modification during any subsequent storage.
- Settling of individual particles does not occur in the filtered sample, and coagulation rate of the remaining colloids may even decrease since this process is accelerated by the presence of large particles.[36] Therefore alterations due to coagulation during storage is also minimized.
- Finally, 0.1 to 0.2 μm filters can be used by applying a rather low pressure. This is sometimes an advantage, for example, in field operations, where sophisticated apparatus cannot be used.

Despite the above arguments, it must be emphasized that the use of 0.2 to 0.5 μm filters for discriminating between "particles" and "dissolved compounds" does not imply that a well defined cut-off limit either exists in natural waters or is even achieved by such filtrations. Although most (but not all) particles larger than the filter pore size are normally retained, many smaller particles (sometimes 10 to 1000 times smaller than the pore size) may also be retained. This problem is discussed in more detail in Sections 3 to 4. Let us just mention that the main reasons for a not well-defined cut-off limit are (i) the non-negligible (sometimes broad) width of the filter pore size distribution which depends primarily on the nature of the filter (Figure 2); (ii) the coagulation properties of macromolecules and colloids in the bulk sample and at the filter surface (this latter process depends mostly on the flow rate); (iii) the interactions (in particular adsorption) of solutes, even of very small size, with the filter material; and (iv) the wide range of shapes and possible conformational changes of aquatic colloids. Effects (ii) and (iii) are often most important so that filtration and ultrafiltration cannot be viewed just as a sieving process, without physicochemical influence.

2.2 Sequential Size Fractionation

Size fractionation of aquatic components with filtering membranes of decreasing pore size is reviewed in References 25 and 27 and has been used to:

(i) Estimate the size of the various colloids and macromolecules (Figure 4)

(ii) Determine to what extent trace compounds or elements (particularly metals) are associated with these macromolecules or colloids

(iii) Separate the various categories of colloids and macromolecules from each other, for further studies

Application types (i) and (ii) have been reported, for instance, in References 30, 38 through 45, and 192 specifically in an attempt to better understand the association of trace metals with organic and inorganic colloids and macromolecules.[38,41-43] Reference 30 discusses a detailed size fractionation for particles >1 μm, whereas the others discuss fractionation of particles <0.45 μm. In most cases, sequential filtration has been used, each filtrate obtained with a particular membrane being further fractionated with a membrane of smaller pore size. Laxen et al.[43,44] however, proposed a scheme in which the initial water sample is filtered in parallel through 12 μm and 1 μm pore size filters and the filtrate of the 1 μm filter is itself filtered in parallel through filters with pore sizes in the range 1.6 nm to 0.4 μm.

Organic compounds and Fe and Mn oxyhydroxides (Figure 4) are among the most important and ubiquitous colloids in the size range 1 nm to 1 μm. Several workers have used fractionation by ultrafiltration to specifically estimate the size distribution of these compounds (e.g., References 46 through 51 for fulvic and humic compounds; References 52 and 53 for proteins; References 46 and 54 for polysaccharides; and References 55 through 58 for Fe(III) and Mn oxyhydroxides).

Type (iii) applications combine size fractionation by ultrafiltration with other methods, in order to determine more precisely the properties of the components of each size fraction, in particular the complexation capacity of organic compounds,[59,67,68] the stability of metal complexes with fulvic compounds,[60,61] the degree of lability of metal complexes,[43,62] the size distribution, morphology, and aggregation properties of fulvic molecules,[63] iron(III) oxyhydroxides,[64-66] and ground water silica,[192] and the electrophoretic mobility of iron(III) oxyhydroxides.[66]

Various fractionation procedures have been compared in Reference 51 for filtration of macromolecules with molecular weights smaller than 10^5 and in Reference 192 for the filtration of inorganic colloids of ground water. In particular one can use either washing (also called diafiltration) or concentration techniques and in each case either sequential (also called cascade) or parallel filtration (see also Reference 27). In the concentration technique, the solution to be filtered is pushed through the membrane by applying a gas (or piston) pressure. In the washing technique, a constant volume is maintained in the filtration cell by continuously compensating for the volume of filtrate by the addition of distilled water or any other "pure" solution (see Reference 27 for more details). It has been found that, although the washing technique is more time consuming, it yields more reproducible results because it avoids increasing the particulate concentration of the retentate in the cell, thus minimizing coagulation and aggregation problems. For the same reason, when the concentration technique is used, the volume reduction in the cell must be minimized as much as possible. In a sequential fractionation procedure the same solution is filtered successively through a series of membranes of decreasing pore size, the filtrate of one step being filtered on the following membrane. Part of the cell solution is withdrawn at each step for chemical

analysis. In the parallel procedure, aliquots of the same initial sample are filtered through several membranes of different pore sizes. The content of each size fraction is calculated from the difference between the contents of each filtrate. Because reproducibility of membrane filtration is not better than 5 to 10% (Sections 3 and 4), the accumulated error becomes exceedingly large in both procedures when more than ~5 filtering steps are used. However, the sequential procedure is preferred because it minimizes the coagulation and aggregation processes which occur when colloid samples are stored for more than a few hours (Sections 3.3, 5). Indeed, the rate of aggregation decreases when the colloid concentration and chemical heterogeneity decreases[36] and therefore the ultrafiltration fractions are increasingly stable with respect to coagulation with decreasing pore size of the filters.

2.3 Fractionation by Dialysis

In this technique,[25,27] the test solution (compartment 1) is separated by the dialysis membrane, from the solvent or any other pure solution (compartment 2). In this way, only the solutes of the test solution, small enough to pass through the membrane, can diffuse into compartment 2 and they are left to do so until equilibrium is reached. When the solutes are metal ions, they can be accumulated in compartment 2 by means of an ion exchange resin.[69]

Since there is no pressure applied, as in ultrafiltration, dialysis is time consuming: usually 1 to 2 days are required to reach equilibrium (this was reduced to 5 h in Reference 69). This is probably the reason why dialysis has had only limited application in laboratory studies. Dialysis has been compared to other separation techniques by Beneš[70] and it has been used to determine the trace metal complexation capacity of fulvic and humic acids,[71-73] by using membranes impermeable to fulvic and humic compounds.

Dialysis has found its most fruitful application for *in situ* sampling of sediment pore water solutes. The technique was first introduced by Beneš et al.[79] for collecting selectively the "dissolved" components of river waters. Later on, it was improved[80,81] to determine the concentration profiles of "dissolved" components in the intersticial water of sediment (see also Chapter 11 of the present book). The device (a so-called pore water peeper) consists of a plexiglass plate into which rows of small compartments (~1 to 3 ml volume and 0.5 to 1 cm high, apart in a row) are machined. The compartments are separated from the external solution (sediment pore water) by a dialysis membrane and they are initially filled with deaerated demineralized water. The peeper is inserted into the sediment and left for 1 to 2 weeks for equilibration. After its retrieval, "dissolved" components are measured in each compartment. Several membranes have been tested and compared for their biodegradability by bacteria. Cellulose membranes have been found inadequate, whereas polysulfone membranes have been found resistant and are most often used. When the purpose is to collect, as far as possible, only the dissolved compounds, the pore size is not critical:[82] even with membranes of rather large pore size (0.2 μm), colloids larger than ~10 nm do not accumulate

significantly in the compartments during a week equilibration period, because of their low diffusion coefficient. The choice of pore size is obviously much more important[72,74] when dialysis is used for complexation capacity measurements (see above) where free ions (~0.5 nm) must be discriminated from small size complexes like fulvic compounds (~1 nm).

2.4 Application of Membrane Separation to Complex Stability Measurements

In aquatic systems many complexing agents are polyelectrolytes, macromolecules, colloids, or particles[27] most of which can be retained by ultrafiltration membranes. When these agents form complexes with small molecules like metal ions, inorganic anions, or small organic compounds such as pesticides or herbicides, it is often possible to find an ultrafiltration membrane which retains the complexing agent and the complex but leaves the uncomplexed (or "free") small molecule to pass through. This provides a means to determine the free molecule concentration as a function of experimental conditions (complexant concentration, ionic strength, temperature, pH . . .) and, from these data, the corresponding equilibrium constant of the complexation reaction.[27]

Based on this principle, ultrafiltration has been applied to the determination of equilibrium constants for the distribution of organic compounds between water and synthetic micelles,[83] the binding of small compounds to macromolecules in biochemistry,[15] the complexation of trace metals by fulvic compounds,[84-86] and the complexation of atrazine, by fulvic compounds.[87-89] The role of the dissociation/association rates of the complexes has also been considered.[27] In this type of application, both the washing and concentration techniques can be applied equally well. Their advantages and limitations have been compared in References 27 and 88. Note that for this type of application it is essential to know precisely to what degree the complexing agent, the complexed species, and the free molecule can pass through the membrane[27] (since complete retention or passage are rarely achieved). This depends on factors described in Section 4 and which must be tested by a preliminary calibration of the experimental system.

3. EXPERIMENTAL FACTORS TO CONSIDER WHEN APPLYING FILTRATION AND ULTRAFILTRATION TO SIZE FRACTIONATION OF AQUATIC SAMPLES

An ideal filter, enabling us to perform particle and colloid fractionation based only on size, should satisfy a number of criteria which may be classified as follows:

(1) *Filter characteristics related to size fractionation properties* — The filter should have a well-defined average pore size and a narrow pore size distribution, and these characteristics should be reproducible from membrane to membrane. In addition, other properties which may affect the

passage of solute should also be well known and specified by the manufacturers. The properties include the pore density (number of pore/cm^2), the porosity (proportion of surface area occupied by pores), and secondary factors which may influence retention by adsorption, i.e., the chemical nature and degree of hydrophobicity, the electric charge and the physical structure of the filter (e.g., Figure 2B, C, D, or E).

(2) *Chemical composition of the sample* — The overall chemical composition of the sample should not be modified either by contamination with organic or inorganic impurities released from the filter, or by losses of dissolved trace elements or organic compounds due to their adsorption on the filter.

(3) *Physicochemical properties of the sample* — The size distribution of colloids and particles must not be modified in any way by the filtration process or the related sample handling. Important denaturation problems include changes in conformation, oxidation, or reduction of compounds followed by precipitation or degassing (e.g., $FeS \rightarrow Fe(OH)_3 + H_2S$), colloid aggregation possibly linked to clogging of the membrane filter, and biological cell rupture.

(4) *Other filter characteristics, useful for practical applications* — Other filter properties useful to consider are the following:

- Its thickness, which should be large enough so that the filter can be easily handled, but small enough to minimize solute adsorption inside the pores
- Its mechanical strength
- Its possible use as a support for electron microscopy observations
- Its amenability to drying to constant weight so that the mass of retained material could be determined gravimetrically
- Its maximum permitted flow rate (Note that high flow rates are often desired for studies on water bodies containing low particle concentrations such as sea water, but that coagulation and clogging can be avoided only by using flow rates as low as possible; Section 4.2)

Criteria of types 1 to 3 are discussed below on the basis of experimental observations reported in the literature. However, the factors related to criterion type 3 are those which most drastically affect the results of fractionation by filtration and ultrafiltration. They, therefore, will be discussed in more detail in Sections 3.3 and 4.

3.1 Filter Characteristics Related to Size Fractionation Properties

Lists of commercially available membranes, their properties and analytical applications, are given in References 4, 7, and 27 and membrane technologies and properties are described in References 5, 6, 11, 15, 90, and 188 through 191. The charge density of membranes can be deduced from measurements of membrane potential[16,18,19,91] and will not be discussed here. Pore size characterization is often more problematic. Data reported by the manufacturer, for membranes with pore size larger than 20 nm, are most often deduced from methods based on gas pressure, solvent or gas permeability, gas adsorption/desorption studies, or scanning electron microscopy measurements.[5,6,13,23] The latter is not applicable to pore sizes smaller than 0.1 μm

and, irrespective of the pore size, it is difficult to apply to fiber or depth filters (Figure 2B, D), for which pore geometry is ill defined. The other methods mentioned are indirect measurements, often difficult to relate to particle retention. The best procedures then consist in calibrating the membranes by filtration of a number of well-characterized particles or macromolecules.

3.1.1 Calibration Based on Retention Curves

For pore sizes larger than a few nanometers, calibration can be done by means of standard latex beads[12,93] which are commercially available[1,2,92] in the range 3 nm to 100 μm. These beads have a spherical shape and bear a large negative charge density which prevents them from coagulating. Plotting the percent retention as a function of the size of the standard particle gives a sigmoidal or sigmoidal-like curve (Figures 5 and 6). The size value at 50% retention corresponds to the average pore size, while the size range corresponding to the rising part of the sigmoid gives the width of the pore size distribution. Note that if the membrane is electrically charged, retention may be affected by particle charge and therefore standard particles with different charges should preferably be tested. Standard particles other than latex beads are cited in References 1, 2, and 92.

An elegant calibration method has been used by Sheldon et al.[94,95] which takes into account the possible influence of the solution composition. Indeed, adsorption of even small compounds on the filter may alter its charge and hydrophilicity and therefore its fractionation characteristics. Sheldon et al. determined the particle size distribution of a real water sample using a Coulter-Counter (in the range 0.5 to 15 μm) before and after filtration. The difference between the two curves enabled them to compute the retention curves mentioned previously. When such retention curves are determined with the same sample but different filters, they can be used to compare the efficiency of the various filters (Figure 5). In addition the curve of any particular filter can be used as a calibration curve for any water sample of the same type as that used for calibration. A similar approach has been used in References 55, 57, and 58 where electron microscopy has been used to check the size of particles retained on the filter. The efficiency of different membranes[55] or filtration modes[57,96] have thus been tested (see also Section 4.2). It has been emphasized[58] that verifying the filtration results by an independent size distribution detection method is absolutely required in determining the optimal conditions for well-controlled size fractionation by filtration.

Membranes with pore sizes smaller than about 10 to 20 nm are calibrated by determining the retentions of a number of organic compounds with different sizes and then plotting their retention as a function of their radius of gyration or, if this parameter is not available, their corresponding molecular weight[27,50,51,97,99] (Figure 6). Compounds with structures as similar as possible to those of the compounds to be tested should be used for calibration since charge or conformation may strongly affect permeation[27,90] (Figure 21). The

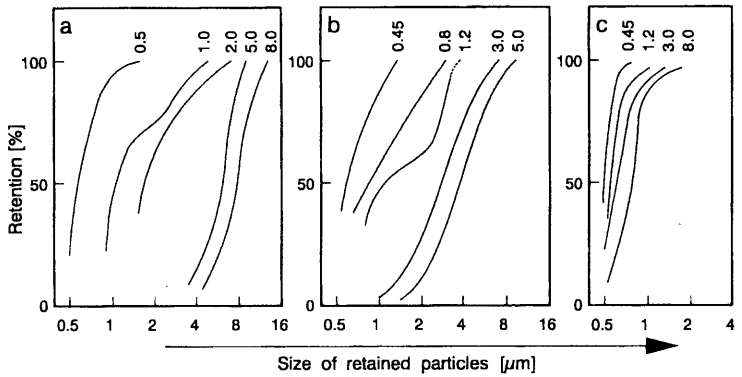

Figure 5. Retention curves for different types of membranes. Each curve is labeled with the nominal pore size (μm) indicated by the manufacturer a— Nuclepore (polycarbonate); b— Flotronic (metal membrane); c— Millipore (cellulose ester depth filters). (From Sheldon, R.W. *Limnol. Oceanogr.* 17:494–498 (1972). With permission.)

overall composition of the calibration solutions should also be as similar as possible to that of the test solutions, because, when the pore size of the membrane is similar to the size of the electrolyte ions, the nature of these ions may also affect the permeation of other solutes (Section 4.3.1).

3.1.2 Pore Size Characteristics of Different Membrane Types

In most cases, the values given by the manufacturers for the nominal pore size of membranes or their molar mass cut-off limit are the size or molecular weight values obtained from curves like those of Figures 5 or 6 (although often only a limited number of points are determined), corresponding to 90% rejection by the membrane. As these curves show, the pore size distributions of most filters are such that at least a few percent of the molecules or particles larger than the nominal pore size can pass through the filter. Comparisons between the nominal pore size, given by the manufacturers and the actual cut-off limit, have shown[55,93,94,98] that polycarbonate filters of type C give better and more reliable results than fiber (type B) or depth (D) filters (Figure 2). This is because in the latter two cases pore size is more ill defined and particles larger than pores are not only retained at the filter surface (as in type C filters), but may also be entrapped in the internal reticulum constituting the membrane. This structure is also less desirable for two additional reasons: (i) it provides a larger surface area for retention of small molecules by chemical adsorption (Section 3.2.2) and (ii) a significant amount of water may be retained in the pores; in the case of sea water this implies that a significant amount of salt is also retained by the filter,[93] which may pose problems for interpreting chemical analysis of the retained material. Because of these properties, it has often been suggested[24,25,43] that polycarbonate filters of type C

are preferable to depth filters for size fractionation, even though their flow rate is lower and they are more quickly clogged (see below). Additional advantages of polycarbonate filters are that they show the smallest change in weight on washing, making them the best choice for gravimetric purposes, and that, thanks to their flat surface, they allow the clearest observation by electron microscopy.

3.1.3 Reproducibility of Membrane Production with Respect to Pore Size

There is little information on the reproducibility of membrane pore size distribution and porosity from one production set to another. This is partly

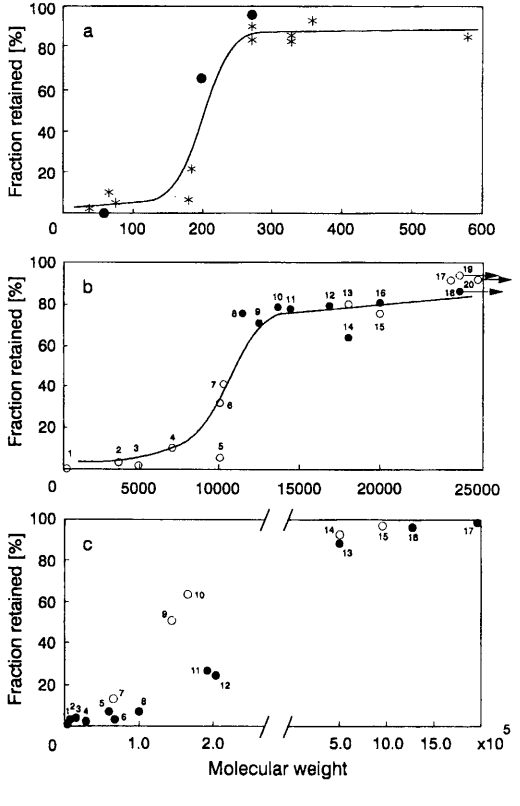

Figure 6. Calibration of ultrafiltration membranes with compounds of well-known molecular weights. Amicon membranes with nominal cut-off limits of 500 (a: UM05), 10,000 (b: PM10) and 300,000 (c: XM300). (From Reference 51 (Figure 6a) and 50 (Figures 6b,c); the compounds used for calibration are listed in the corresponding references).

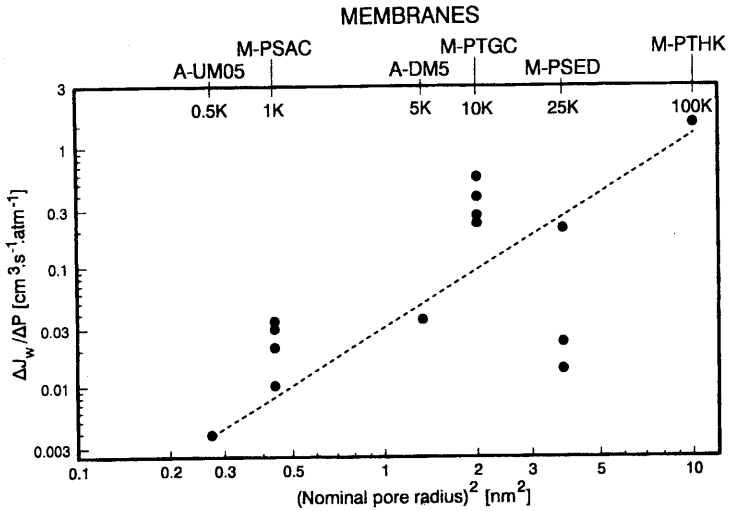

Figure 7. Relation between fluxes and pore sizes for various membranes. A = Amicon; M = Millipore. Other membrane symbols refer to the nature of the membrane. (From Macko, C. et al. *AIChE Symp. Ser.* 75:162–169 (1979). With permission.)

because a detailed check of these properties is difficult and time consuming for most filters. The easiest global test is to measure the pure water flow rate J_w (in ml.cm^{-2}.s^{-1} or m.s^{-1}), which is related to the average pore radius, r_p by:[11,21,132]

$$J_w = \frac{\epsilon r_p^2 \Delta P}{8\eta\tau l} \qquad (1)$$

where ϵ = porosity of the membrane, ΔP = imposed pressure difference, η = viscosity of water, l = thickness of the membrane, and τ = tortuosity factor. Equation 1 with $\tau = 1$ rigorously applies to ideal membranes with cylindrical pores. $\tau > 1$ is used as an empirical factor to correct for the non-ideal geometry of depth filters. Figure 7 shows that Equation 1 is roughly followed by a number of Amicon® and Millipore® depth filters.[22] The dispersion of values for different membranes may be due to different values of τ and l. The important observation here is that the various points of Figure 7 for any particular membrane type correspond to different production sets. They therefore reflect the reproducibility in the manufacture of the membranes. Note however that the dispersion may be partly due to changes in τ (less probably in l) and not only to variations in pore size.

As shown in Equation 1, the water flow rate, J_w, is an interesting global parameter for monitoring any possible change in membrane characteristics. It has been observed for depth filters,[22] that the flow rate may change (generally decrease) with sequential uses of the same membrane, even when only water or pure solutions are used. Such flux decreases are generally attributed to plugging of the pores due to crushing of the membrane. Use of the minimum pressure compatible with an acceptable flow rate is therefore recommended. Normally the largest pressure used with less porous membranes is 3 atm. Use of the minimum flow rate is also required for other reasons (Section 4.2). When using flow rate for testing membrane characteristics it is important to realize that this parameter also depends on (Section 3.3 and 4) (i) membrane and particle charge and electrolyte nature;[27,134] (ii) dissolved organic compounds which may adsorb inside the pores;[133,135,136] and (iii) retained colloids and macromolecules which may form a gel layer at the membrane surface. Therefore, intrinsic membrane parameters, such as r_p, τ, and l can only be obtained from flow-rate measurements performed with pure water or well-controlled solutions.

3.2 Sample Modification by Solute Adsorption on, or Contamination by the Filter

3.2.1 Contamination

Because of the often very low concentrations of many metals and organic compounds in aquatic samples, care must be taken to minimize possible effects of contamination by the filter or filtering device. Metal contamination by filters can be expected since most filter material contains significant metal concentrations.[43,100-102] Systematic analysis of many filters are listed in References 102, 103, and 115, in the latter reference after various treatments. Polycarbonate filters seem to have the lowest metal content.[104] However, it has also been shown[114] that the metal content of Millipore® filters may vary by a factor of 10 from one set of filters to another. Therefore all membranes need to be carefully cleaned if trace metals are of interest.[50,105] Organic membranes may also release organic compounds, sometimes initially present as preserving agents,[50,106] which may cause errors in DOC, fluorescence, or ultraviolet absorbance measurements of the filtrate.[107-109] Low molecular weight hydrocarbons may also be leached from ultrafiltration membranes.[59] Glass fiber and paper filters may release inorganic and organic fibers, respectively. Finally, it has also been observed that contaminations from NH_4^+ and NO_3^- may occur with several filters.[109,110]

It has been proposed that metal decontamination of filters be achieved by rinsing with dilute nitric acid,[111] but Mart[112] found that to avoid contamination of sea water, which contains very low metal concentrations, membranes must be stored for at least a week in acid, followed by repeated washing with distilled water. It has even been suggested to avoid filtration of open sea water because the heavy metal content of particulate matter collected on filters is usually lower than the filter blank.[112] A simpler cleaning procedure proposed for trace metals, which also eliminates organic compounds, consists of filtering at least 50 ml·cm^{-2} of 0.01 *M* HCl through the desired membrane, followed by distilled water.[50,107,109] To find the best cleaning conditions, the

decrease of contaminant concentration in the filtration should be traced, as a function of the filtrate volume. In dialysis experiments metal contamination may also be a problem but membranes can be cleaned by soaking in mineral acids.[72,79,113] The filtration apparatus must also be cleaned with acid as carefully as the storage bottles. Polycarbonate filter assemblies are easier to decontaminate than glass assemblies.[104]

3.2.2 Losses by Adsorption on the Filter and Filter Unit

Losses of solutes may occur during filtration due to adsorption onto the filter, the porous filter support, and the filtration vessel.[79,121-124] The latter problem is the same as losses by adsorption on any container (e.g., References 101 and 112) and will not be discussed here. An additional problem is the retention of small molecules, which should pass through the membrane, by adsorption on the material already deposited on the membrane. This is related to clogging problems and will be discussed in Section 3.3.

It is presently difficult to generalize the results reported for adsorption losses on filters and filter supports. Tests are often done with either synthetic solutions or real samples spiked or pretreated in order to characterize them as well as possible. However, adsorption reactions are highly dependent on the chemical nature and physical structure of the adsorbed species. Therefore, synthetic or spiked solutions may give unrealistic results. On the other hand it is difficult to generalize observations made with unspiked real samples because the results are specific to the nature of the adsorbed species which are often too difficult to characterize.[25,43] As a result, contradictory results have been reported. Florence,[104] for instance, states that serious adsorption losses have indeed been observed from synthetic solutions,[116,117] but not from natural waters,[112,116] and that all-glass filtration apparatus are therefore suitable for trace metal analysis. There are, however, reports of adsorption on glass apparatus from sea water[118,119] and tap water,[120] so that a polycarbonate filtration apparatus seems to be by far preferable.[26,105,127]

Despite the difficulty of making generalizations, the few following features are worth noting:

- Alkaline and alkaline-earth metal cations reduce adsorptive losses of trace metals on filters and filter units.[116,117] Based on this property, efficient preconditioning of filters and apparatus, to minimize adsorption of metals, can be accomplished with 0.1 *M* $Ca(NO_3)_2$.[43]
- In many cases, an important source of metal adsorption seems to be the filter support,[105,125] particularly glass frits. Adsorption of NH_4^+ on glass frits has also been reported.[126] Glass parts should be avoided for the filter apparatus, polycarbonate being by far preferable in particular for the frit.[26,105,127]
- The choice of membrane nature, with respect to adsorption problems, is more difficult to generalize. There seems to be an agreement that metal adsorption on polycarbonate membranes (Figure 2C) is low.[34,43,72,105,127] Cellulose-based depth filters apparently have significantly stronger adsorption properties,[24,105,127] adsorptive effects being pH dependent and losses being very large at pH >9. Most of these observations are based on filtration with Millipore® filters. Adsorption of trace metals on Amicon® PM10 ultrafilters, which are made of similar material, is more controversial: negligible adsorption of trace metals is reported in References 128 through 130, whereas more than 60% adsorption was observed for Fe, Al, and Sc.[79] Hydrolysis properties of these metals might be an explanation of this behavior. Finally, trace metal adsorption was found to be strong on glass fiber filters.[72]
- Adsorption of organic compounds on filters has been much less studied. Fatty acids and lipids seem to adsorb strongly on Millipore® depth filters, but apparently not on paper filters.[131] Humic acids might adsorb on polycarbonate filters.[93]

3.3 Physico-Chemical Artifacts Produced by the Filtration Process

A number of artifacts may result directly or indirectly from the filtration process and must be considered in choosing the best filtration conditions.

3.3.1 Perturbations in the Bulk of the Sample: Field vs. Laboratory Filtration

In addition to the classical problems of contamination and loss by adsorption during water sampling and sample handling, a number of other perturbations may occur, where chemical compounds are not lost but undergo physico-chemical transformations (e.g., dissolution, formation of gas or solid, coagulation, or conformation changes of macromolecules[27]). Such problems are particularly important when studying anoxic waters where a number of compounds (Fe^{II}, Mn^{II}, $S^{(-II)}$) are easily oxidized by O_2 contamination resulting in concomitant precipitation reactions, pH changes, and speciation modifications. With natural samples containing colloids or particles, changes in the physical and structural characteristics occur *in most cases* even when the system is chemically stable, and stored in a fully closed container at its initial pressure.

For suspensions of hydrophobic colloids and particles (e.g., for most inorganic colloids) this is because they are inherently unstable systems which always tend to coagulate[137,138] (see also Chapter 10 in the present book). This is the more so for aquatic samples in which colloids and particles are highly polydisperse and chemically heterogeneous.[36] It has been shown theoretically that even for homodisperse synthetic systems the average particle radius of colloids increases due to aggregation, by a factor of 100 over 1 to 8 h (depending on the rate-limiting factor),[138] and it may be estimated that for the particle concentrations typically found in fresh waters (10^5 to 10^8 particles.cm^{-3}) coagulation of half of the particles occurs over a period of hours to days, depending on the chemical conditions. In the few cases where analytical techniques allowed the size distribution of particles in water samples to be followed as a function of time, it has indeed been observed that sig-

nificant changes occur after a few hours in sea[75] and even in fresh waters[55,56,139] (see also Section 4.2). Another observation supports the importance of aggregation process, even with samples containing the rather small hydrophilic fulvic molecules which form most of the aquatic organic matter: in size fractionation of fulvics by ultrafiltration, the proportions of their lowest molecular weight fraction were found to be inversely related to the total organic matter concentration in the sample[51,63] and this could be related to the formation of aggregates by complementary measurements of electron microscopy, fluorescence, and surface tension.[63] These findings confirm that the tendency to aggregate is general, for most macromolecules, colloids, or particles, irrespective of their nature, even though the nature of the aggregation process may change from one type of colloid to another. Aggregation has been largely underestimated in the last decades by people using filtration, in spite of the fact that the main purpose of filtration was, and remains, to get realistic size fractionation.

On the basis of these considerations it is highly recommended, in order to obtain a size fractionation representative of the sample under study,[39,55-58] that filtration be performed in the field immediately after sampling with no or minimum preconcentration, and under well-controlled conditions. For anoxic waters or other samples which are easily denatured, it has even been shown that the sampling step itself must be avoided and that at-depth filtration[57] is required. An at-depth cascade filtration unit, controlled from the surface and allowing filtration of water through up to five filters, has been described in Reference 192.

3.3.2 Surface Coagulation and Clogging of the Membrane

A basic problem in filtration is the clogging of the membrane by the retained particles or colloids,[25,39,55,140,141] when the filter load is too large. During their accumulation at the membrane surface, particles gradually form a gel layer, less porous than the filter. The effective pore size then becomes smaller, and, consequently, at constant pressure, the water flow rate and the overall concentration of compounds passing through the filter (permeate) are reduced (Equation 1). Membrane clogging, therefore, can be detected by following the flow rate or the permeate concentration in the filtrate, as a function of filter load, at constant pressure[140,141] (Figure 8). This process is well known in industrial applications (Section 4.2.2) where high concentrations of colloids are filtered.

As mentioned above, gel formation results in a gradual decrease of the effective pore size, i.e., the basic characteristic of the filter is no longer maintained. In addition, most aquatic particulate matter has strong adsorption properties. Consequently, this gel layer retains, by both filtration and adsorption, ions or molecules which should pass through the filter. Gel formation can therefore be seen in two different ways:

- If total retention of particles, colloids, and even dissolved compounds is desired, gel formation should be favored.

- If size fractionation of particles representative of the real sample is desired, then gel formation must be avoided by fair means.

The factors affecting gel formation and clogging will be discussed in detail in Section 4.2. Surface coagulation is the key process leading to gel formation and may be minimized by using very low flow rates. This coincides with earlier empirical findings stating that correct size fractionations are obtained only (i) at low filter load,[140] (ii) at low particle concentration[94] (coagulation increases with particle concentration: Section 4.2.2), and (iii) at low pressure difference across the membrane[94] (this favors a low flow rate: Equation 1). Furthermore, filtration should be stopped well before noticing a decrease in flow rate (at constant pressure), or an increase in pressure (at constant flow rate).[55]

The evolution of the clogging process depends on the nature of the filter. Figure 8 shows typical examples for the filtration of iron(III) hydroxide particles. Nuclepore® membranes are often reported to clogg at lower loadings than other membranes. However, it can be seen in Figure 8 that filtration with this membrane is little affected by the process of gel formation before clogging. Millipore® and glass fiber filters have retention properties which change much more gradually and are therefore expected to give less reliable results. To check these properties, means for directly observing the behavior of the particles of interest must be used in addition to flowrate measurements.

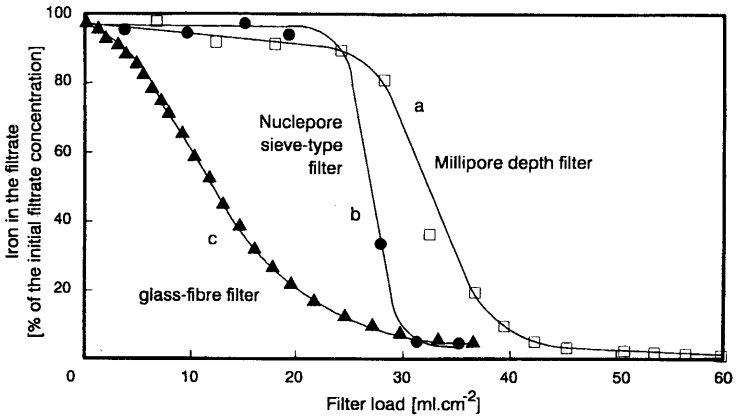

Figure 8. Effect of filter load on the retention of iron based colloids: a— Millipore HAWP depth filter (0.45 μm); b— Nuclepore polycarbonate filter (0.40 μm); c— Spectrograde glass fiber filter (0.7 μm). Because pore sizes are similar but not equal, the position of the curves on the horizontal axis is not relevant. Only the shapes of curves are comparable.

3.3.3 Biological Cell Rupture at the Membrane Surface

An additional filtration artefact is the possible rupture of biological cells when the pressure is too large.[24,25] Even if microorganisms are not the object of the measurements, ruptured cells will contribute to an increase in soluble organic matter, nutrients, and trace metals[142] in the test sample (concentration factors of 10^3 to 10^4 have been reported for many metals in plankton compared to sea water[143]), which may in turn significantly affect speciation studies. Furthermore, ruptured cells may liberate enzymes able to degrade organic compounds present in the sample. This has been shown to occur, for instance, during the determination of ATP in water.[144] Much less ATP was observed after filtration than without filtration, due to cell rupture and the subsequent release of enzymes.

To avoid cell rupture of phytoplankton, pressures less than 25 kPa must be used.[142] This is high enough for filtration with a pore size larger than 0.1 μm, on which all biological cells are retained, provided a high flow rate is not required. At any rate, maintaining a low flow rate is also preferable to minimize clogging.

4. PHYSICO-CHEMICAL FACTORS INFLUENCING RETENTION BY FILTERS: THEIR SPECIFIC NATURE AND QUANTITATIVE INFLUENCE

Many often sophisticated models have been developed in order to interpret quantitatively the effects on retention efficiency of the physicochemical factors pertaining either to the compounds to be fractionated or to the solution properties or composition. All of these models, however, have been developed for industrial applications, in particular food chemistry. Their application to water analysis is somewhat limited because in this case colloid and particle concentrations are much lower and their chemical diversity is much larger. Another important difference is that the goal in industrial application is generally the total retention of particles and not their size fractionation. Because of these different conditions, the relative importance of the various factors affecting filtration is different. Therefore, even though the models mentioned above are useful in understanding the specific role of each factor, they are most often difficult to transfer directly to natural water studies. Since no rigorous model has been developed for water analysis, the effects of the various factors will be discussed hereafter on the basis of a quantitative treatment which is only approximate, but which is specifically adapted to water analysis.

Before discussing the role of physicochemical factors related to solution composition (Sections 4.2 and 4.3), the relationship between the fluxes of water and the compound of interest must be established (Section 4.1) in the ideal case, i.e., without any influence of the solution properties or composition.

4.1 Flux and Retention Coefficients of Non-Reactive Compounds in Solution

Detailed thermodynamic and mechanistic theories explaining the separation of particles from solution with a polymeric membrane are given in References 5, 11, and 145. A recent comparison of the existing theories for the transport of water and compounds in solution through membranes is given in Reference 146. These theories differ in the assumptions made concerning the nature of the physicochemical process controlling transport through the membrane. For an uncharged compound and membrane, the two most important forces are often diffusion and convection due to the water flux, J_w (Equation 1). For such conditions the flux of solute X, J_x (in $mol.m^{-2}.s^{-1}$) through the membrane can be expressed by Equation 2:[146]

$$J_X = (1 - \sigma_X)\, J_w [X]_c + D_{m,X} \cdot \frac{d[X]_m}{d\chi} \qquad (2)$$

where the first term expresses the transport of solute X by the solvent (convection) and the second term its transport by diffusion in response to the concentration gradient existing within the membrane. (Note that Equation 2 is a simplified one. For more details see References 5, 11, and 146). $[X]_c$ and $[X]_m$ are the concentrations of X in the filtration cell and inside the membrane, respectively (expressed in $mol.m^{-3}$), $D_{m,X}$ ($m^2.s^{-1}$) is the diffusion coefficient of X through the membrane and $d[X]_m/d\chi$ is the concentration gradient of X in the membrane, which is assumed to be time-independent. $(1-\sigma_X)J_w$ represents the fraction of the total flux (J_w) that flows through the pores large enough for the passage of X: therefore $0 \leq \sigma_X \leq 1$: $\sigma_X = 0$ if X can pass through all pores indiscriminately and $\sigma_X = 1$ if X is completely retained. Although a rigorous calculation of the flux of X[11,148,19] is somewhat complicated because the diffusion process of X in the membrane must be solved, a good approximation may easily be obtained.[27] In most cases, however, convective flux is reported to be the predominant mechanism,[132] possibly with the exception of ultrafiltration membranes with the smallest pore size where diffusion might be non-negligible. J_X is then given by:

$$J_X = (1 - \sigma_X) \cdot J_w [X]_c \qquad (3)$$

which shows the dependency of J_X on pore and particle sizes: J_w depends on the effective pore size only, whereas σ_X is the so-called retention coefficient, which depends on the ratio of the effective sizes of pores to particles. Note that J_X may also be expressed as:

$$J_X = [X]_f \cdot J_w \qquad (4)$$

where $[X]_f$ = filtrate concentration of X. Equation 4 also follows from Equation 3 and the definition of σ_x:

$$\sigma_X = 1 - [X]_f/[X]_c \quad (5)$$

The term *effective* size of pores (r_p) and particles (r) refers to the fact that size values which effectively control σ_X and J_w depend not only on the true values of r_p and r, but also on filtration conditions and more precisely on interactions between compounds in solution and between these compounds and the membrane. Essentially three types of such interactions may occur and are discussed below:

- Aggregation of particles and colloids at the membrane surface, possibly resulting in gel formation
- Adsorption of compounds of any size onto the membrane and pore walls
- Interactions due to electrostatic and hydration properties of small molecules and membrane pores

All these factors may influence the effective pore size and therefore the value of J_w. As mentioned in Section 3.1, monitoring changes in J_w is then a possible means of detecting the above interactions. However, for particle fractionation purposes, it is better to follow J_X (or preferably, both J_X and J_w) since the above effects may alter σ_X without greatly affecting J_w. A fractionation process can be considered as reproducible and well controlled only if J_X is constant during the filtration process (when performed by the concentration techniques) and independent of filtration conditions (in particular of colloid concentration and flow rate).

4.2 Concentration Polarization, Gel Formation, and Clogging: Compound-Compound Interactions at the Membrane Surface

4.2.1 Concentration Polarization Principle

Deposition of particles and gel formation at the membrane surface are well-known processes, particularly in concentrated solutions such as those used in industrial applications (solutions of several grams per liter organic macromolecules, or suspensions of a few percent by weight of colloidal particles). In such cases a gradual decrease of J_w with increasing macromolecule concentration is observed.[5,11] These observations are parallel to the decrease in J_w with increasing filter load which is sometimes observed in natural water studies. Such changes in water flux during the course of filtration have been modeled and it has been shown[141,150,151] by monitoring J_w as a function of filtration time and volume of filtrate, that two steps in the development of clogging and the formation of gel can be discriminated.

Such relationships, however, are not very useful for the application of filtration to well-controlled size fractionation, since such a fractionation is obtained only in the complete absence of clogging, i.e., when J_w is constant.

Understanding of the processes leading to clogging is therefore preferable in order to minimize it. Two main processes have been proposed and modeled:

- Specific interaction of particles with the membrane surface (adsorption)[155,156,159,160,168]
- Coagulation at the membrane surface due to the existence of a concentration polarization[21,152-154,157-159]

The first process should be rather specific to the nature of both the particle and membrane compositions, whereas this is not the case for aggregation processes.[138] The fact that clogging has been reported in many water analyses with almost all type of filters, despite of the broad diversity of particle and colloid nature in various water samples (Figure 4), then suggest that aggregation is the predominant process. This observation seems to be corroborated by all of the data reported specifically on these processes in the literature (e.g., References 154 through 159; see also discussion of Figure 15, Section 4.2.3). These references suggest that adsorption might play a role, but as a secondary factor affecting the strength of binding between the membrane and the gel formed by coagulation. As we are mostly interested in the factors affecting the initial steps of gel formation, adsorption of particles and colloids will not be considered here.

Concentration polarization is a fundamental effect of filtration: because of the partial ($0 < \sigma_x < 1$) or complete ($\sigma_x = 1$) rejection of the compound X by the membrane, its surface concentration, $[X]_{c,0}$, tends to increase relative to that in the bulk solution (Figure 9). This increase can be estimated by Equation 7.[76,77] At any distance, χ from the membrane, the flux of X carried along by the solvent is $J_w[X]_{c,x}$. Since $[X]_{c,0} > [X]_c$, a flux of back-diffusion is created: $D_X d[X]_{c,x}/dx$. After some transitory period a steady state is established at any χ such that:

$$J_w[X]_{c,x} = D_X \cdot \frac{d[X]_{c,x}}{dx} \quad (6)$$

This equation can be integrated with the following boundary conditions: (i) a gradient of [X] exists only inside the diffusion layer, of thickness δ, i.e., $[X]_{c,x} = [X]_c$ for $\chi > \delta$ ($[X]_c$ = concentration of X in the filtration cell); (ii) at $\chi = o$, the flux of back-diffusion is equal (but of opposite sign) to the flux of the retained fraction of X carried along by the solvent, i.e.:

$$J_w\sigma_X[X]_{c,0} = D_X \left(\frac{d[X]_{c,x}}{dX}\right)_{X=0}$$

On integrating Equation 6 with these conditions, one gets:

$$\frac{[X]_c}{[X]_{c,0}} = (1 - \sigma_X) + \sigma_X \cdot \exp\left[-\frac{J_w}{D_X/\delta}\right] \quad (7)$$

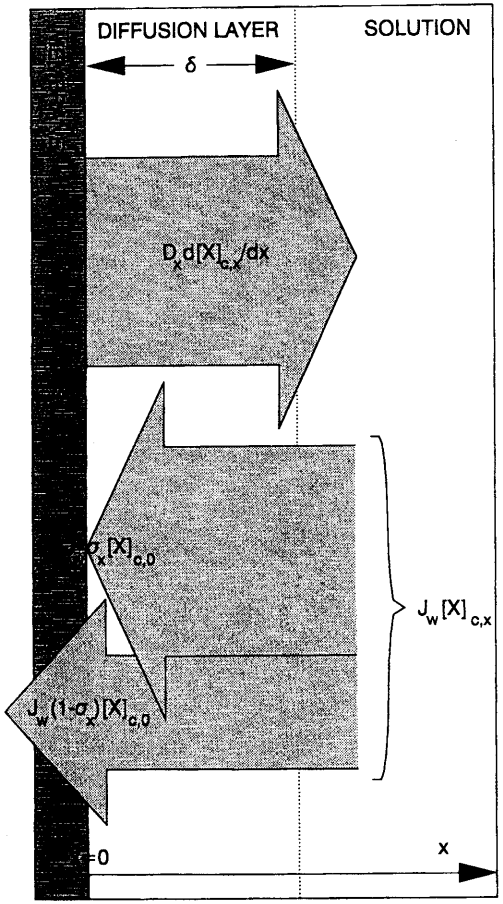

Figure 9. Schematic drawing of the fluxes of a compound, X, strongly rejected at the surface of a membrane causing concentration polarization. δ = diffusion layer thickness; $J_w(1-\sigma_X)[X]_{c,0}$ = flux of X passing through the membrane; $J_w\sigma_X[X]_{c,0}$ = flux of X not allowed to pass the membrane; $D_X.d[X]_{c,x}/d_X$ = flux of X diffusing back in the solution. (From Buffle, J. *Complexation Reactions in Aquatic Systems: An Analytical Approach.* (Chichester: Horwood, 1988). With permission.)

where δ, the diffusion layer thickness, is constant if the filtration cell is stirred. Note that Equation 7 is approximate because its derivation implies a discontinuity at $\chi = \delta$. Nevertheless it is a good approximation for estimating $[X]_{c,0}$ values and it allows an easy discussion of the factors affecting $[X]_{c,0}$. Table 1 gives values of $J_w\delta/D_X$, for various particle sizes. The flow rate used

to compute these values, 0.01 $cm.s^{-1}$, is typical of that obtained with the least porous membranes.[27] It is therefore a common flow rate for separating particles of 1 to a few tens of nanometers, but it is 100 times lower than usual for separation of particles larger than 0.1 μm by syringe filtration. Despite this very low flow rate, Table 1 shows that the term $J_w\delta/D_X$ is always very large. Therefore the exponential term of Equation 7 is most often negligible, except when $\sigma_X = 1$, i.e., for completely retained particles. For partly retained particles: $[X]_{c,0}$ is larger than $[X]_c$ but not dramatically: $[X]_{c,0}/[X]_c \sim 1/(1 - \sigma_x)$. However, for completely retained particles, ($\sigma_x = 1$), one gets, irrespective of the filter pore size:

$$[X]_{c,0}/[X]_c = \exp\left[+\frac{J_w\delta}{D_X}\right] \qquad (7')$$

Table 1 shows that, in such a case huge concentration factors may be reached for particles larger than a few tens of nanometers. The numbers computed in Table 1 for particles of 100 and 1000 nm are obviously not reached in practice for two reasons. First, for particles larger than a few tenths of microns, processes other than molecular diffusion, such as shear-enhanced diffusivity,[153,154] may reduce the concentration factor. Above all, when particle concentration becomes exceedingly large, coagulation occurs almost instantaneously.[137] The purpose of Table 1, however, is to suggest that for the fully retained particles extremely large concentration factors are reached during filtration, because of the concentration polarization effect, and that this is likely to affect the behavior of compounds at the membrane surface (Section 4.2.2).

4.2.2 Consequences of Concentration Polarization

The gel layer model — Considering Table 1, it is easily understandable that, for a given solution, when J_w is increased by increasing the applied pressure, $[X]_{c,0}$ may reach a concentration $[X]_g$ where the solution at the membrane surface is no longer fluid. A gel layer is thus formed, which has a hydraulic resistance opposing any further increase in J_w, and in which $[X]_g$

Table 1. Value of $[X]_{c,0}/[X]_c$ Computed From Equation 7, for Typical Values of Particle Size (r) and Flow Rates (J_w). $\sigma_X = 1$; δ = 10 μm; J_w = 0.01 cm/s (=2.4 ml.min^{-1} for a Membrane of 4 cm²)

r (nm)	D_X ($cm^2.s^{-1}$)	$J_w.\delta/D_X$	$[X]_{vc,0}/[X]_c$
1	$3.2\ 10^{-6}$	3.13	1.37
10	$3.2\ 10^{-7}$	31.3	23.0
100	$3.2\ 10^{-8}$	313.0	$3.7\ 10^{13}$
1000	$3.2\ 10^{-9}$	3130.0	$5.0\ 10^{135}$

is nearly constant.[158] Consequently, J_w approaches a limiting value J_{lim} obtained from Equation 7′:

$$J_{lim} = \frac{D_X}{\delta} \cdot \ln \frac{[X]_g}{[X]_c} \quad (8)$$

$[X]_g$ being constant, linear plots of J_{lim} vs. $\ln[X]_c$ are predicted by Equation 8, which is indeed observed in practice (e.g., References 164, 165, 167, and 169) for large values of $[X]_c$ (larger than fractions of $g \cdot dm^{-3}$).

The osmotic pressure model (case of ultrafiltration of small compounds) — Although the merit of the gel model is to give a simple qualitative representation of the hydraulic resistance, it has been shown not to be reliable or realistic in terms of gel properties.[158] For the retention of small compounds, by ultrafiltration membranes in particular, this resistance is better explained by the development of a high osmotic pressure, $\Delta\Pi$, inside the concentration polarization layer.[157,158,166] $\Delta\Pi$ constitutes a back-pressure opposing the applied pressure, ΔP, so that J_w = constant.$(\Delta P - \Delta\Pi)$ (compare to Equation 1). When ΔP is increased, $[X]_{c,0}$ increases and so does $\Delta\Pi$. For small compounds $\Delta\Pi$ may become large enough to compensate ΔP completely; then J_w approaches 0. For large macromolecules $\Delta\Pi$ is small and the effect is negligible. It is therefore expected to occur mostly for separation of rather small macromolecules with smaller pore size ultrafiltration membranes. (Note, however, that this generalization must be taken with caution, because solute coupling may sometimes occur between small compounds and macromolecules.[166])

When the compound in solution is only partly rejected and penetrates the membrane (in particular in depth filters), the $\Delta\Pi$ thus produced inside the membrane may change the pore size. This might be the origin of the increased permeate concentration observed in the ultrafiltrate of natural waters when the retentate concentration in the cell becomes too large.[22,46,51] For this reason, it has been recommended not to ultrafiltrate more than 80% of the initial volume.[51]

Surface coagulation (case of filtration of colloids and particles) — Aggregation and coagulation of colloids and particles in well-mixed conditions are second order reactions,[36,137] whose rates increase strongly with particle concentration. Since very high concentrations are predicted for large particles at the membrane surface by Equation 7′ (Table 1), coagulation is likely to occur at the membrane surface unless specific precautions are taken. Until now, no rigorous theory has been developed to quantitate the correct conditions for minimizing surface coagulation. Such a theory should consider:

- The concentration polarization effect (Section 4.2.1)
- The perikinetic coagulation process, i.e., coagulation resulting from collisions due to Brownian motion of particles. This process is controlled by temperature, T, viscosity of the solution, η, and the corresponding collision efficiency factor, α_p, which depends on the chemical composition of the particles and of the solution.

- The orthokinetic coagulation process, i.e., coagulation due to movement of the solution. This process depends on the velocity gradient G, the radius of particles, r, and the corresponding collision efficiency, α_o.
- The fact that particles in real samples have broad size distributions. This dramatically complicates computation, since (i) the concentration gradient in the diffusion layer depends on particle size (through the term J_w/D_x), (ii) all the concentration gradients are influenced by each other through the coagulation process, and (iii) coagulation of heterodispersed particles is much more complicated than that of a homodispersed system.[36]
- The fact that for particles larger than a fraction of micron, their size is comparable to that of the diffusion layer thickness itself. For such particles (which are the most important for filtration on 0.1 μm membranes), the concept of concentration gradient in the diffusion layer is no longer valid. In addition, their elimination from the diffusion layer is not only due to diffusion but also to the shear produced by stirring at the limit between the bulk solution and the diffusion layer.[154]

In the absence of a rigorous theory an order of magnitude estimate of the maximum flux, leading to the maximum concentration factor tolerable at the membrane surface in order to avoid coagulation, can be estimated by Equation 9 (Appendix 1):

$$J_w \leq \frac{D_X}{\delta} \cdot \ln \left(\frac{C_o}{f^2 \cdot [X]_c} \right) \quad (9)$$

with $C_o = 3D_X/4.\delta^2.\alpha.[4Gr^3 + kT/\eta]$ (with $\alpha = \alpha_p = \alpha_o$). The most important assumption of Equation 9 is that of homodispersed particles. Since it is known that coagulation is faster in heterodispersed systems than in homodispersed ones,[36,37] the values computed from Equation 9 must be considered as upper limits of J_w. Furthermore, as stated above, for large colloids or particles it is not correct to estimate the values of $[X]_{c,0}$ by introducing in Equation 7 the value of the diffusion coefficient valid in quiescent solution, since shear-enhanced diffusion must be considered. In other words, effective D values, larger than those valid for diffusion in quiescent solutions, must be used. The particle size corresponding to the limit between the application of true diffusion coefficients and shear-enhanced diffusion coefficients in Equation 7 seems to be between r ~0.1 to 1.0 μm. Figure 10, for instance, shows the change in water flux obtained by filtering suspensions of different particle sizes.[153] For sizes lower than 0.1 μm the water flux decreases as particle size increases due to the increased concentration polarization resulting from the decrease in the diffusion coefficient value introduced in Equation 7. For larger sizes, the water flux increases as particle size increases. This is attributed to a decreased concentration polarization due to the shear-enhanced diffusion of these larger particles; the shear enhanced diffusion coefficient indeed increases with the square of particle radius.[154]

With the above restrictions in mind, Equation 9 is useful to discuss the

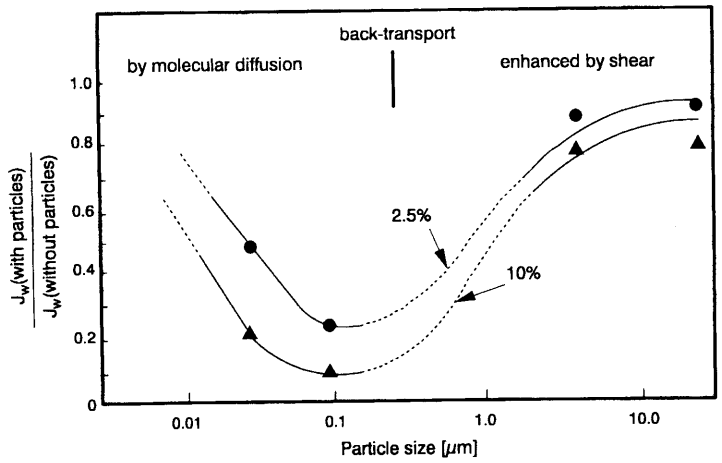

Figure 10. Change in water flux through a PM30 membrane, as a function of the size of retained particles from the filtered suspension. J_w (with particles) and J_w (without particles) = water fluxes in presence and absence of suspended particles, respectively. (From Fane, A.G. *J. Memb. Sci.* 20:249–259 (1984). With permission.)

maximum tolerable value of J_w, and the relative importance of the various filtration conditions. Values of Figure 11 are computed for various diffusion layer thicknesses (δ) and particle concentrations in the filtration cell, $[X]_c$, in the most restrictive condition, i.e., that corresponding to particles having the lowest diffusion coefficient, D_X. From Figure 10 it may be expected that this corresponds to particles having radii of a few tenths of microns, which corresponds to a shear-enhanced diffusion coefficient of $D_X \sim 3\ 10^{-8}$ cm^2.s^{-1}. The values of the velocity gradient, $G = 100$ s^{-1}, and of the coagulation collision efficiency factor,[137] $\alpha = 2.5\ 10^{-3}$, have been used. The former is typical for well-stirred solutions and the second is a minimum value found for lakes.[161] Interestingly, Figure 11 shows that particle concentration does not have an important effect on the maximum usable value of J_w. This is due to the fact that $[X]_c$ is inside the logarithm of Equation 9. Similarly, α, G, and the thickness of the surface layer in which coagulation effectively occurs (see discussion in the appendix) will not have an important influence on the maximum tolerable value of J_w. On the other hand, D_X and δ are the two most important parameters. D_X primarily depends on the particle size, but δ may be controlled by experimental conditions. In order to allow the use of larger J_w values, δ must be minimized, for instance by means of efficient stirring. The exact role of stirring is, however, controversial since strong stirring will simultaneously increase the coagulation rate of particles in the bulk solution inside the filtration cell.[137]

At any rate, Figure 11 shows that for classical filtration cells, where δ is larger than a few microns, J_w must not exceed 10^{-4} to 10^{-3} cm.s^{-1}. This value (corresponding to 0.03 to 0.3 ml.min^{-1} for a 4 cm^2 membrane surface area) is orders of magnitude smaller than that classically used, at least for filters with pore size ≥ 0.1 μm. The fact that membrane clogging is often observed in these conditions is therefore not surprising. Furthermore, it is unlikely that δ might be decreased much below 1 μm, even with sophisticated filtration techniques (pulsed filtration, tangential flow filtration . . .). Therefore, even with these techniques, low J_w values must be used.

It may also be inferred from the above estimation and from Table 1 that surface coagulation will not be an important problem for fractionation of colloids less than a few tens of nanometers in size by ultrafiltration, *provided larger particles have previously been eliminated.* Thus it is always preferable to perform size fractionation by sequential cascade filtration, rather than by parallel sets of filtration.

4.2.3 Experimental Evidence of Surface Coagulation

Systematic tests have been performed to check the above considerations on the occurrence of surface coagulation induced by concentration polarization.[57,96,162,163] These tests have been performed by filtering under various conditions iron oxyhydroxophosphate particles formed at the oxic-anoxic boundary in a eutrophic lake[57,58,96] (see also Chapter 8 of the present book).

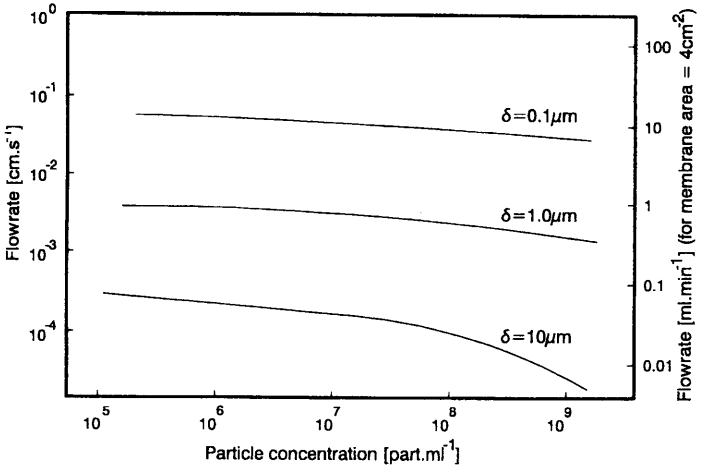

Figure 11. Theoretical maximum tolerable value of the flow rate, J_w, as a function of particle concentration in the filtration cell, in order to avoid surface coagulation at the membrane surface. Computed from Equation 9, with $\alpha = 2.5 \cdot 10^{-3}$ and f = 10 (i.e., 90% of particles are coagulated: see Appendix). $D_x = 3 \cdot 10^{-8}$ cm^2.s^{-1}. For other parameter values: see text.

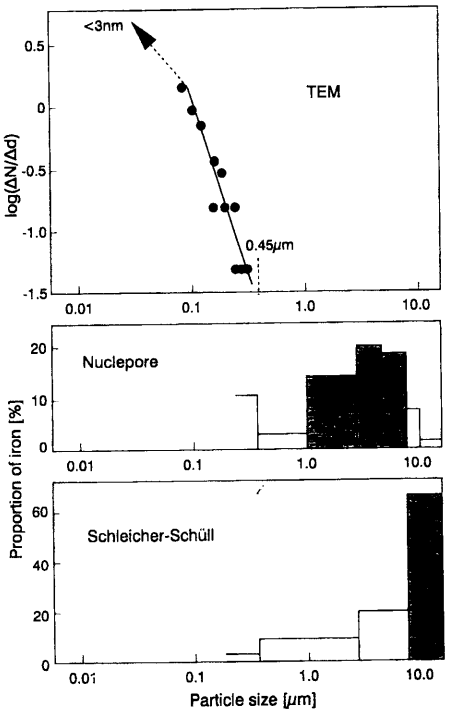

Figure 12. Size distributions of iron oxyhydroxophosphate particles obtained by transmission electron microscopy (true distribution), syringe filtration on Nuclepore polycarbonate filters, and Schleicher and Schuell cellulose ester depth filters. Iron particles formed at the oxic/anoxic interface of eutrophic Lake Bret (Switzerland). (From R.R. De Vitre, D. Perret, and J. Buffle. Unpublished results).

These natural iron particles have been well characterized chemically and physically.[64,65,163] In particular, their study by transmission electron microscopy (TEM), on a particle by particle basis, has shown that their shape is always nearly spherical and their size distribution extends from a few nanometers to a maximum size of ~0.3 μm (Figure 12). Figure 12, however, also shows that by classical syringe filtration (flow rate ~20 $ml.cm^{-2}.min^{-1}$ = 0.3 $cm.s^{-1}$), they are retained on filters with pores much larger than 0.3 μm, emphasizing the important role of the clogging effect. Furthermore, Figure 12 shows that even though the size distribution obtained with polycarbonate filters is less erroneous than that obtained with depth filters (as pointed out in Reference 53), both size distributions depart from reality by more than an order of magnitude.

In the following, F_m is defined as the proportion of iron (in percent of total iron in the sample) "stuck" on the membrane surface, irrespective of the

nature of the "sticking process" (surface coagulation or chemical adsorption). Hereafter, F_m will be termed "adsorbed" iron to discriminate it from the proportion of the whole of retained particles which include "adsorbed" particles plus those remaining in solution in the filtration cell. Optimum conditions are those for which $F_m = 0$. F_m has been measured as a function of experimental parameters. Figure 13 shows F_m values for filtration on 0.2 μm membranes. As expected from TEM size distributions, F_m is low at low flow rates (~$4 \cdot 10^{-4}$ $cm.s^{-1}$) but increases drastically at a larger flow rate ($7.4 \cdot 10^{-3}$ $cm.s^{-1}$) even though this latter is still 100 times lower than that normally used with this type of filter. Figure 13 also shows that this effect occurs with all the membranes tested. Although Figure 13 seems to suggest that F_m depends on the nature of the membrane this is misleading because the opposite relationship between F_m and the membrane nature was observed for the same sample with membranes of higher porosity (3 μm). In other words, after cascade filtration through 3 and 0.2 μm membranes, 81 ± 6% of total iron is adsorbed on the two membranes, irrespective of the nature of these membranes. This has been found for 11 different conditions (six types of membrane, with and without stirring, at $7.4 \cdot 10^{-3}$ $cm.s^{-1}$).

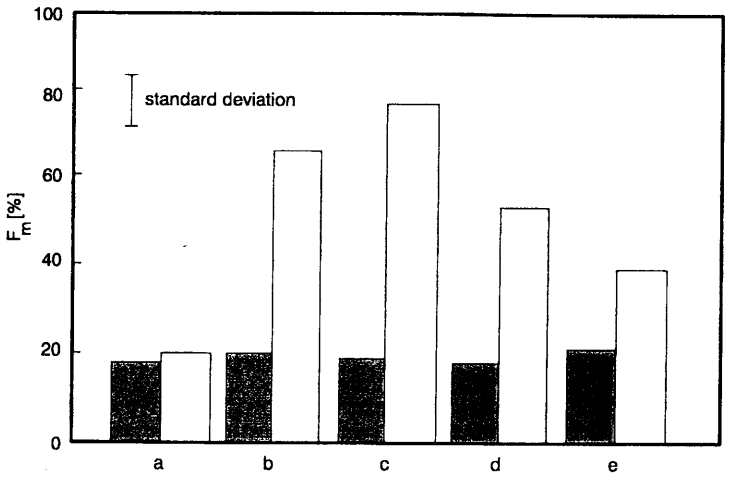

Figure 13. Fraction of iron particles (same as Figure 12) "adsorbed" on various 0.2 μm pore size filters. All solutions were initially filtered through 3.0 μm filters of the same nature. All filter surface areas were 4.5 cm^2. Fluxes: dashed bars = $3.7\ 10^{-4}$ $cm.s^{-1}$ (=0.1 $ml.min^{-1}$); white bars = $7.4\ 10^{-3}$ $cm.s^{-1}$ (=2.0 $ml.min^{-1}$). a— Gelman acrylic copolymer; b— Schleicher and Schuell mixed cellulose esters; c— Nuclepore polycarbonate; d— Schleicher and Schuell cellulose nitrate; e— Rhône-Poulenc polyvinyliden fluoride. (From References 96 and 162, see also Reference 57.)

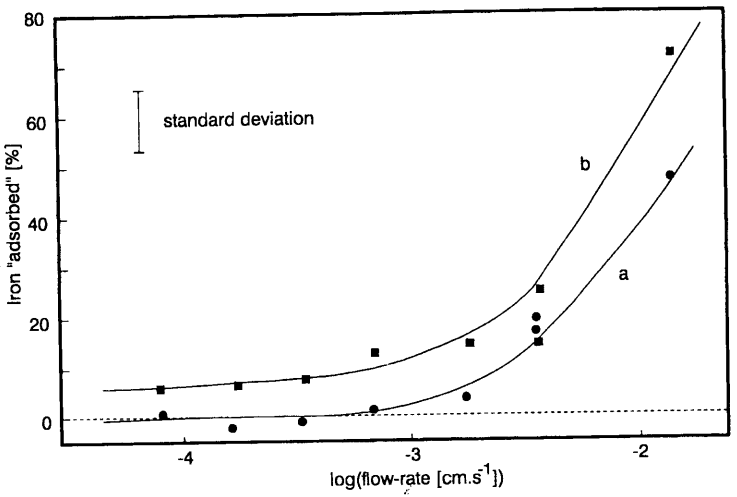

Figure 14. Fraction of iron particles (same as Figure 12) "adsorbed" on 3.0 μm membranes as a function of flow rate. a— Nucleopore polycarbonate; b— Schleicher and Schuell cellulose nitrate. In the absence of coagulation or adsorption no particles should be retained. (From Perret, D. Ph.D. thesis No. 2395, University of Geneva (1989). With permission.)

Figure 14 shows the effect of flow rate on the value of F_m for filtration on a 3 μm pore size membrane. Note that this pore size is 10 times larger than the maximum particle size. Despite this, F_m departs significantly from zero for $J_w > 1{\cdot}10^{-3}$ cm.s^{-1} with polycarbonate filters, due to surface coagulation. For the depth filter tested, a sharp increase of F_m is also observed for $J_w \geq 10^{-3}$ cm.s^{-1}, but, for lower values F_m is not zero. This might correspond to the adsorption of the particles on (or their entrapment in) the depth filter; but clearly for $J_w > 2{\cdot}10^{-3}$ cm.s^{-1}, this effect is negligible compared to retention by surface coagulation.

The result represented in Figure 14 and the fact that F_m is only slightly dependent on the nature of the membrane (see above) confirms that, although specific chemical adsorption effects might play a role, the predominant cause of particle retention by the membrane surface is surface coagulation induced by concentration polarization. This is clearly demonstrated in Figures 15 and 16. Figure 15 includes scanning electron microscopy (SEM) images, showing top views of the surface of polycarbonate membranes (0.2 μm) before and after filtration at different flow rates. Clearly particle retention decreases with flow rate, retention being very low at 50 μl/min (i.e., $1.9{\cdot}10^{-4}$ cm.s^{-1}). Interestingly, at large flow rates, a non-negligible proportion of particles have a size larger than 3 μm despite the fact that the sample was initially filtered on a 3.0 μm pore size polycarbonate filter. This results from the fact that only "apparent particles" which are in reality aggregates are seen in Figure

15 due to the low resolution of SEM. This can be seen in Figure 16 which shows a TEM image of a microtomic section of one of the above "apparent particles", cut perpendicularly to the membrane surface. Clearly it is a heterogeneous aggregate. Observations of large numbers of filters have always confirmed these observations. In most cases, aggregates are formed on the membrane surface and do not penetrate inside the pores, even with the so-called "depth filters" (only a few exceptions have been noticed). Chemical analysis by TEM-EDS of individual aggregates formed on the filter, has shown that in addition to Fe particles (which include P), the aggregates are composed mostly of Si, Al, and Ca, suggesting that they are composed of clays, silica, and some calcium carbonate. Organic carbon is probably an important additional constituent, but could not be determined. For a large number of aggregates, no correlation could be found between their Fe content and their Si, Al, or Ca content.[162] Once again this suggests that particle retention by

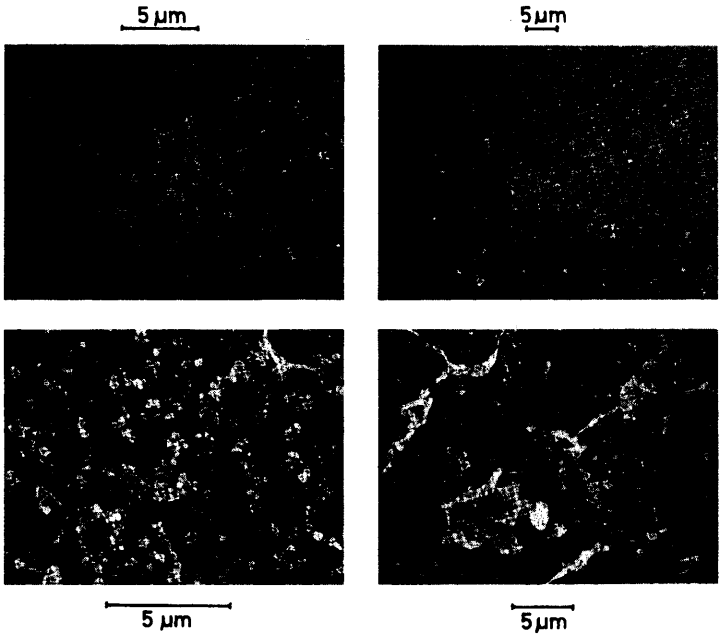

Figure 15. Scanning electron microscopy images of the surface of 0.1 μm Nuclepore polycarbonate membranes used to filter iron particles (same as in Figure 12) at different flow-rates. All bars represent 5 μm. a— membrane which was not used; b— $J_w = 2.1 \times 10^{-4}$ cm.s^{-1}; c— $J_w = 4.2 \times 10^{-3}$ cm.s^{-1}; d— $J_w = 4.2 \times 10^{-2}$ cm.s^{-1}. All solutions were previously filtered on 3.0 μm polycarbonate membranes with the same flow rate. (From Perret, D. Ph.D. thesis, University of Geneva (1989). With permission.)

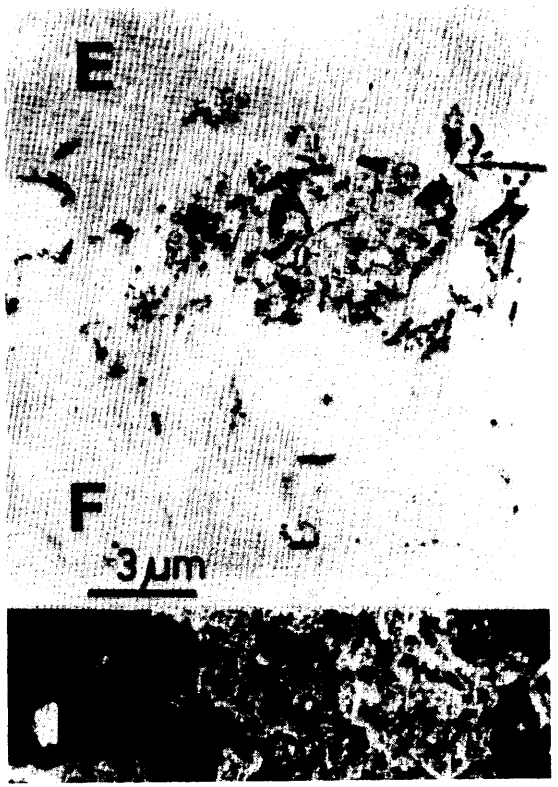

Figure 16. Transmission electron microscopy image of particles retained by filters as in Figure 15, but with a Schleicher and Schuell cellulose nitrate depth filter. Deposit and membrane were cut transversally. E = external solution on the top part of the membrane, F = filter material. Note that by SEM (bottom picture) this agglomerate is seen as only one single particle. (From References 96, 162 and 163.).

the membrane results from coagulation due to nonspecific particle interactions, which is expected at very high particle concentrations.

Figure 17 shows the evolution of the Fe content in the filtrate, during filtration on a 3.0 µm membrane at a flow rate ($3.4 \cdot 10^{-3}$ cm.s^{-1}) for which surface coagulation occurs. Without coagulation, the Fe concentration in the filtrate should be the same as the initial Fe concentration of the sample (7.5 µmol.dm^{-3}). Figure 17 clearly shows that for a polycarbonate membrane, surface aggregates gradually form an additional filter of increasing efficiency, which retains all Fe particles after a sufficient loading has been reached. For the cellulose nitrate depth filter clogging occurs even more easily, as is also seen in Figure 14.

The effect of solution stirring (i.e., decreasing δ; Equation 7) during filtration is shown on Figure 18 for various membranes. There is a systematic, though only slight, decrease in F_m. The weak influence of stirring has already been noted by Laxen et al.[55] The weakness of this effect may be partly due to the inefficiency of stirring, but it might also be due to the fact that a relatively large flow rate ($6.6 \cdot 10^{-3}$ cm.s^{-1}) was used in this experiment and that even a decrease of δ by a factor of 2 or 3 was not enough to decrease the surface concentration to a value low enough to avoid coagulation.

4.3 Solute-Membrane Interactions Inside Pores

When small pore size membranes are used for fractionation, rather small macromolecules are separated from each other. These small macromolecules are hereafter referred to as solutes (Figure 4). In such cases, fluxes of water and solutes are influenced by solute membrane interactions (Figure 3). The main types of interactions result from (i) electric and hydration properties of the solute and membrane; (ii) conformational changes of the solute in the membrane, and (iii) modifications of the membrane surface by adsorption of solute. The first two types of interactions are particularly important for solutes whose size is similar to the pore size.

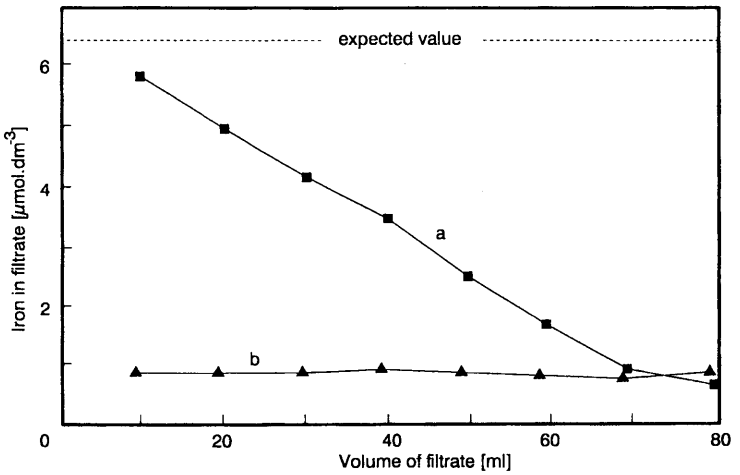

Figure 17. Fraction of iron particles, (same as in Figure 12), passing in the filtrates of a 3.0 µm Nuclepore polycarbonate filter (a) and Schleicher and Schuell cellulose nitrate filter (b). Note that iron particle size is much smaller than 3.0 µm. One therefore expects a constant Fe concentration as shown in the figure. Initial volume in the cell = 200 ml. Flow rate = J_w = 0.0037 cm.s^{-1}. (From Perret, D. Ph.D. thesis, University of Geneva (1989). With permission.)

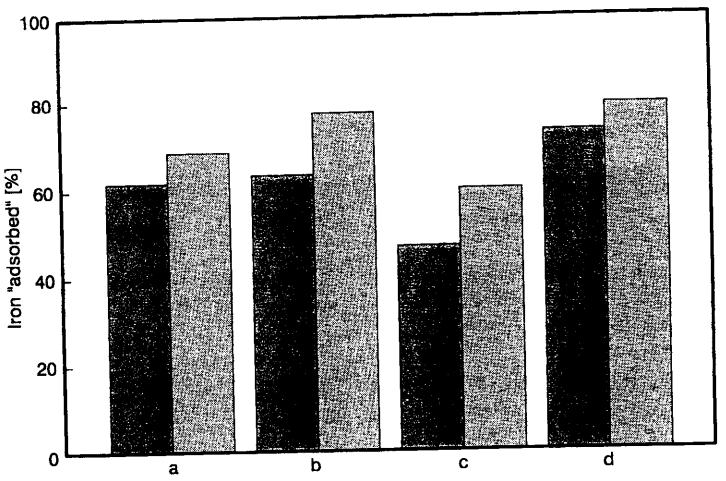

Figure 18. Effect of stirring on the fraction of iron particles (same as in Figure 12) "adsorbed" on various 3 μm pore size membranes during filtration at J_w = $7.4 \cdot 10^{-3}$ cm.s^{-1}. Letters a to d refer to the same membranes as in Figure 13. Dark gray bars: solution strongly stirred by a magnetic bar close to the membrane; light gray bars: non-stirred solutions. (From Perret, D. Ph.D. thesis, University of Geneva (1989). With permission.)

4.3.1 Interactions Based on Electric and Hydration Properties: Role of the Electrolyte

The role of solute and membrane electric charges on solute retention has been demonstrated by several authors (e.g., References 22 and 97) and is discussed in Reference 27. Figures 19 through 21 show that this effect may be very important for retention of solutes, sometimes even more than the solute/pore size ratio. It has been observed for inorganic ions[97] (Figure 20) as well as for small organic molecules[97] (Figures 19 and 21) and macromolecules.[170] Theoretical interpretation of electrical phenomena have been well studied.[5,11,19,91,134,171,175] The observed effects have several causes which, in practice, result in a complex but important influence of the solution electrolyte:

(a) *Electrostatic repulsion or attraction* between membrane and solute when both are charged. This effect can be seen in Figure 19 by comparing Amicon® (negative) and Nuclepore® (neutral) membranes.

(b) *Hydration* of membrane pores (Figure 22) and solute:[90,172] in hydrophilic membranes, the pore surface is covered by a layer of highly ordered hydration water of low mobility, which diminishes the effective pore radius ($r_p^{eff} < r_p$). Solutes also have hydration layers which increase in thickness with charge density.[173] These two effects together explain (Figure 22) the following phenomena:

- Compounds or inorganic ions of size $r < r_p$ may be retained. For membranes for which r_p is slightly larger than r, there is a good

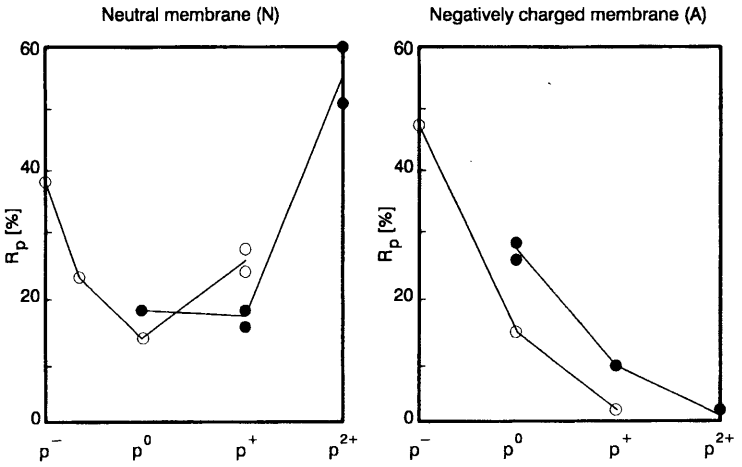

Figure 19. Role of membrane and solute electric charges on solute retention, R_p. Membrane A = Amicon UMO5 and N = Nuclepore MW500. Both are filters of type E (see Figure 2) with a nominal molecular weight cut-off limit given as 500 (but see also Figures 6a and 21). A = negatively charged membrane, N = neutral membrane (no net charge). ●: p = pyridoxamine; ○: p = pyridoxol. In both cases molecular size is the same and shape is similar. Charges on p are changed by varying pH. (From Staub, C. et al. *Anal. Chem.* 56:2843–2849 (1984). With permission.)

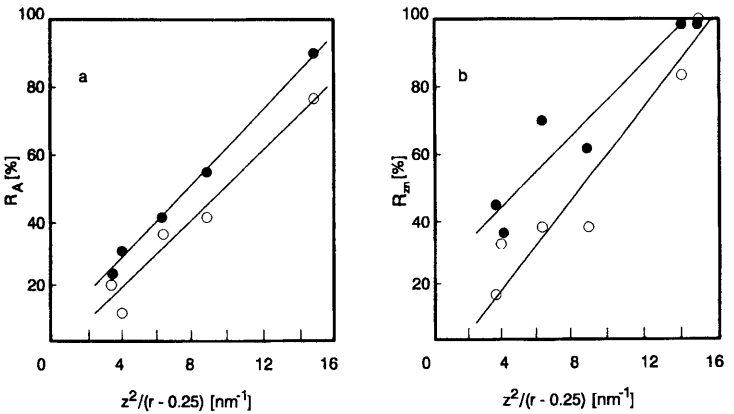

Figure 20. Role of ion hydration energy (abcissa) on retention coefficients of inorganic ions by the two membranes of Figure 19 (● = Amicon UMO5; ○ = Nuclepore MW500). (a) Retention R_A of the electrolyte anions A: Cl^-, NO_3^-, ClO_4^-, F^-, SeO_4^{2-}, SO_4^{-2} (in all cases cation = Na^+). (b) Retention of the minor ion Zn^{+2} R_{Zn}, in presence of the above electrolytes, as a function of the hydration energy of the electrolyte anion z, r = charge and radius of A, respectively. Ionic strength = 3.10^{-3} mol.dm^{-3}. (From Staub, C. et al. *Anal. Chem.* 56:2843–2849 (1984). With permission.)

correlation (see Figure 20a) between the degree of ionic hydration and the retention coefficient[97]). Increasing retention as a function of the degree of hydration has also been observed for polymers.[174]

- Retention of the solute on neutral membranes increases with its electric charge (Figure 21), whatever its sign. For cations and anions, solute hydration increases with the absolute charge value.
- When r_p is only slightly larger than r, the diffusion coefficient value for a solute X in the membrane, $D_{m,X}$, decreases strongly with r_p, relative to its value in solution, D_X. Indeed being highly ordered, the pore hydration layer is also highly viscous (10 to 100 times more than in solution; Reference 90). So it exerts a significant frictional drag on the solute hydration layer (Figure 22). Low values of $D_{m,X}$ may influence J_X values (Equation 2) for membranes of small pore size, for which J_w is also small.

(c) *Electrokinetic effects.*[11,22] They occur when an ion is moving in the electric field of a pore with a charged surface.

These effects explain the stronger ion adsorption on charged membranes,[97] and above all explain the important role played by the *major electrolyte* on the retention of minor solutes by small pore ultrafiltration membranes:[27,86,97,176-178]

- It masks the surface charge inside the pores. The importance of electrokinetic processes therefore decreases with increasing electrolyte concentration.[22]

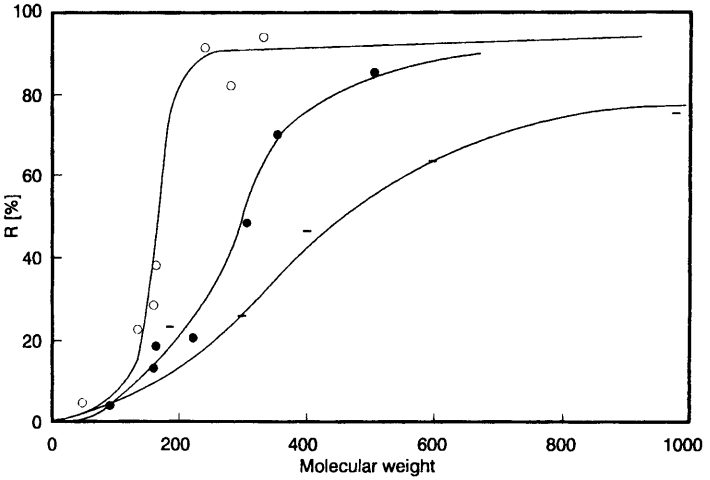

Figure 21. Retention of small organic molecules of different shapes on the neutral polycarbonate Nuclepore membrane MW500. ● = neutral molecules having rigid skeleton; ○ = negative compounds; — = neutral flexible linear polyethyleneglycols. Compounds are listed in Reference 97.

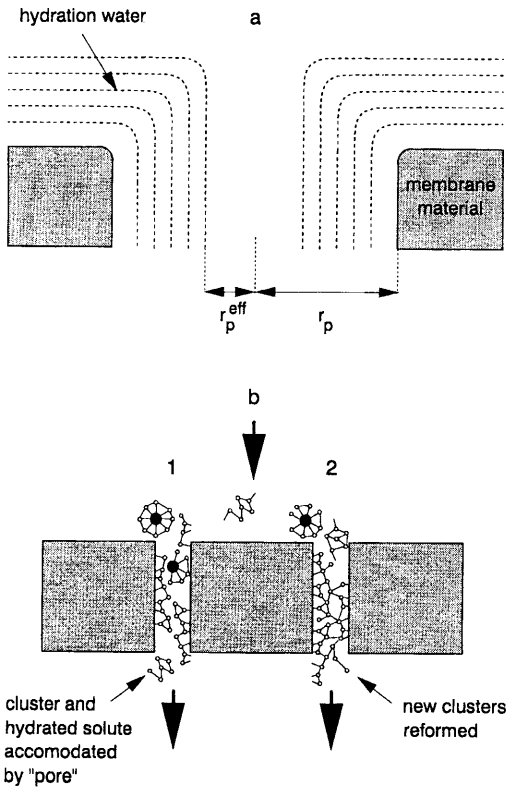

Figure 22. Schematic representation of (a) the water hydration layer in the membrane pores and (b) the effect of pore and solute hydration on solute retention. In pores No 2, pores are blocked by their hydration water and that of the solute. In order to permit the latter to pass, their hydration layers must be broken. (From Buffle, J. "Complexation Reactions in Aquatic Systems: An Analytical Approach." (Chichester: Horwood. 1989). With permission.)

- In the case of minor cation loss by adsorption (particularly on net negative membranes), the electrolyte cation can act simultaneously through masking and by competing for adsorption sites.[97] In general, therefore, adsorption decreases as the electrolyte concentration and the charge of the electrolyte cation increase. These results suggest that adsorption losses during filtration should be lower for hard waters or sea waters than for soft waters. This is indeed observed in practice and pretreatment with Ca^{2+} to minimize these losses (Section 3.2.2) is based on the same property.
- The electrolyte can also mask the charge of organic polyelectrolytic compounds in the solution and thereby facilitate their folding. An increase in electrolyte concentration leads, in this case, to a decreased retention of

these compounds. This has been observed for biochemical[170] and synthetic compounds.[174]

- The retention of the major electrolyte ions can increase that of a minor ion under study.[97] For example, in Figure 20a and b, the passage of Zn^{2+} cation through the membrane must be accompanied by anions for solution electroneutrality to be maintained. As the most probable accompanying anion is that of the electrolyte, any retention of this anion (Figure 20a) is reflected by a corresponding retention of Zn^{2+} (Figure 20b). Major cations may also play an indirect role in retention of minor cations.[97]

4.3.2 Role of Steric Conformation of Solute

There have been very few studies[22,97] on the role of the conformation of organic molecules on their retention by membranes. There is, however, no doubt that this plays an important role, as is shown by Figure 21 (Reference 27): clearly retention depends on molecular shape and increases with rigidity of the molecule. Similar results have been obtained for proteins and polyethyleneglycol macromolecules. The quantitative role of flexibility has been theoretically and experimentally studied in References 169, 174, and 179 for polyethyleneglycols, dextran, poly(L-glutamic acid), and polyvinylpyrrolidone. It has been shown that the nature of the solvent, the nature and concentration of electrolytes or complexable ions, as well as the increased concentration of polymer at the membrane surface due to concentration polarization, may modify the conformation of the polymer and therefore its retention coefficient. Such behavior has also been observed for biochemical compounds.[170]

4.3.3 Modification of Pore Properties by Adsorption of Solutes

Little is known on the exact role played by adsorbable compounds when they adsorb on pore walls and thus modify the pore properties. Modification of pore size, charge, and/or hydration properties may, however, be expected and has been used to explain the increased rejection of proteins with time.[135] Another interesting effect results from the adsorption of (even small) amphiphile molecules onto the surface of (even large pore size) membranes.[133,136] The magnitude of the water flux may be changed by factors as large as 10 even with low concentrations ($\sim 10^{-4}\,M$) of adsorbable compounds. The water flux is increased when adsorption occurs on the low pressure side of the membrane and decreased in the opposite case.

5. CONCLUSIONS

Based on the previous results and discussion, it is possible to propose a number of optimum conditions for filtration as well as a few tests of the reliability of the results.

5.1 Optimum Operating Conditions

5.1.1 Choice of Membranes

For *size fractionation,* all the results reported in the literature suggest that polycarbonate sieve-type filters are preferable to depth filters, but this choice

is by no means sufficient to get reliable results; the conditions listed below, particularly concerning low flow rate, should also be obeyed.

For *total retention* of particles and colloids, depth filters seem preferable as surface coagulation occurs at an earlier stage of filtration. But this choice must be combined with high concentration polarization conditions, in particular, high flow rate. For gravimetric purposes, however, polycarbonate filters are preferable because of their lower and more reproducible blank values.

New membranes should preferably be used for each new filtration experiment as (i) adsorption may modify membrane properties and no reliable membrane cleaning process has been reported up to now and (ii) change of porosity with time, due to slow plugging of the membrane by the applied pressure, may occur with some membranes.

Membrane dimension is a parameter to consider since pore size distribution is never infinitely narrow and may not be uniform over the same membrane. For this reason, membranes with small surface areas are preferable; but when low flow rate must be used (see Section 5.1.3), large surface areas may be necessary. For analytical purposes, areas ranging between 1 and 100 cm^2 are normally used.

5.1.2 Minimizing Adsorption and Contamination

This problem is most important for the analysis of trace compounds, either organic or inorganic.

- *Contamination* by the membrane may be minimized by washing, by filtering through it a sufficient volume (to be tested; at least 20 $ml.cm^{-2}$) of 10^{-2} $mol.dm^{-3}$ HCl (for metal decontamination) followed by distilled water, or preferably by the water sample prefiltered on a less porous membrane. This last step may then also serve as a preconditioning step to minimize adsorption losses.
- *Adsorption losses* can be minimized by preconditioning the filter by passing through it 10^{-2} $mol.dm^{-3}$ Ca^{2+} solution (for trace metal adsorption), or preferably the water sample prefiltered on a less porous membrane.

5.1.3 Minimizing Concentration Polarization and the Related Artifacts (Coagulation, Gel Layer Formation . . .)

The various factors which may be used to minimize concentration polarization are summarized below. Note that this is valid for size fractionation purposes. For total retention of particles, a concentration polarization as large as possible is desirable, and therefore the opposite conditions should preferably be applied.

Optimal condition	Possible approaches
• Low concentration at the membrane surface	a— Low J_w value obtained by means of: → low pressure for larger pore size membranes or independent control of J_w → naturally low J_w for smaller pore size membranes b— Low δ value obtained by a high stirring rate

- Low concentration in the filtration cell

c— Low concentration factor during filtration
d— Low concentration in the initial sample

5.1.3.1 Flow Rate. From Figure 11 and the results reported in Section 4.2.3, an approximate maximum limit for J_w can be set at $J_w \sim 3 \cdot 10^{-4}$ cm.s^{-1} (corresponding to 0.02 ml.cm^{-2}.min^{-1}) (Figure 23). This rather low value has two practical consequences:

- Only relatively small sample volumes can be size fractionated in a reliable manner (at this flow rate, 1 h is required to filter 100 ml on a 100 cm^2 membrane). This implies that sensitive detection techniques must be used to study the fractionated material, when its concentration is very low in the initial sample, as is the case for sea water or ground water.
- When fractionation time becomes larger than ~1 h, aggregation and coagulation in solution within the filtration cell becomes an important factor to consider (Section 3.3.1). This is shown in Figure 24 where Fe and Mn oxyhydroxide particles formed at the oxic/anoxic boundary layer of an anoxic lake have been filtered at different flow rates, all smaller than $3 \cdot 10^{-4}$ cm.s^{-1}. By comparing particle size with the pore size of the polycarbonate membrane used (0.2 μm), it is expected that only 10% of Fe and less than 10% of Mn particles should be retained. Clearly, retention increases with the duration of filtration plus storage, irrespective of the flow rate used for

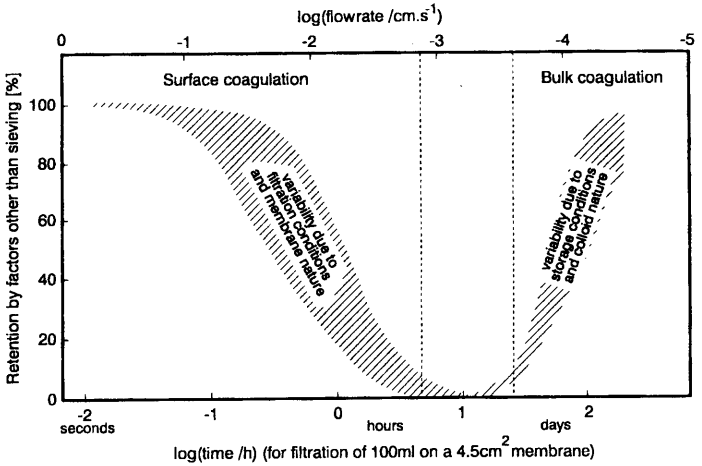

Figure 23. Semi-quantitative representation of the change in retention with flow rate due to concentration polarization (high flow-rate domain) and aggregation in the filtration cell (low flow-rate domain). Only an intermediate flow rate window is usable for size fractionation without artifact. (This figure is based on Figures 11, 14, 24 and additional data.)

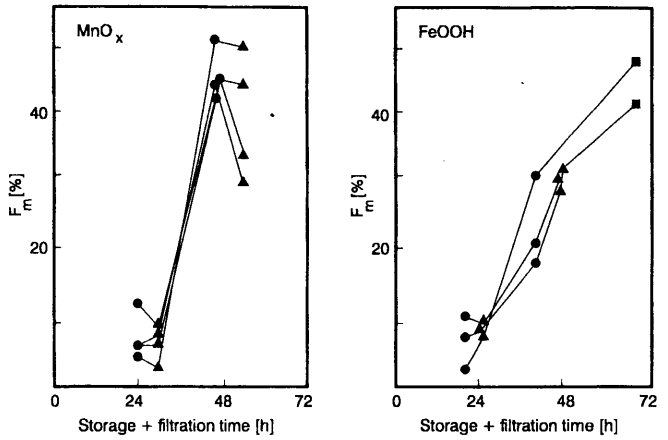

Figure 24. Effect of storage plus filtration time on the "adsorption" of iron particles (same as in Figure 12) and MnO_2 particles formed in the same lake (with size ≤0.2 μm) on 0.2 μm membranes. The various lines refer to five different membranes (Gelman acrylic copolymer, Nuclepore polycarbonate, Schleicher and Schuell cellulose nitrate and mixed esters, and DDS polysulfone filters). The various symbols refer to: ■ $J_w = 3.3 \times 10^{-4}$ cm.s^{-1}. ● 1.6×10^{-4} cm.s^{-1} and ▲ 0.3×10^{-4} cm.s^{-1}, respectively. Clearly at these low flow rates, membrane nature and flow rate values are unimportant. Considering the true particle size (<0.3 μm for iron particles; <0.2 μm for MnO_2) one expects not more than 10% of Fe and a few percent of Mn to be retained on the membrane in the absence of secondary factors. All solutions were previously filtered on 3 μm membranes and stored at 4°C in the dark.

filtration. This is due to aggregation in solution which, in this case, becomes significant after ~24 h. As a consequence

(i) Too low values of J_w should be avoided (Figure 23), so that only a certain window of J_w is accessible for size fractionation. The lower limit depends on the volume to be filtered and the surface area of the membrane.
(ii) Filtration must be done as soon as possible after sampling (see below)
(iii) Laboratory dialysis should preferably be avoided for size fractionation because of the very long equilibration time required.

5.1.3.2 Minimization of δ (Stirring). In principle, a high stirring rate is preferable to minimize δ and therefore concentration polarization. However, this may also have an adverse effect by favoring coagulation within the filtration cell, in particular when long filtration time (low flow rates) are used. Although stirring seems to slightly improve the results, more detailed studies are required in order to draw definite conclusions.

Ultrasonic stirring has been proposed, but it may damage the membrane. Filtration modes other than in stirred batch cells have also been proposed, such as cross-flow filtration,[154,185] pulsed filtration,[186,187] filtration on rotatory

cylinders or discs,[181,184] and hollow fiber filtration.[182,183] However, these methods have mostly been applied to industrial purposes and they generally require a very large volume of sample, as recirculation is often necessary. At any rate, it must be realized that decreasing δ below 1 μm will probably be very difficult so that, even with these techniques, flow rates larger than 10^{-2} cm.s^{-1} should not be used (Figure 11).

5.1.3.3 Concentration Factor. The washing technique (diafiltration) is preferable to the concentration technique (Section 2.2) because in the former the concentration of the retained compound does not increase during filtration. Unfortunately the washing technique is quite long since it requires passing about five times the volume of sample through the membrane, in order to completely separate the colloids smaller than the pore size from larger ones.[51] At very low flow rate, this may require an exceedingly long time. When the concentration technique is used, filtering less than 80% of the initial sample volume is recommended in order not to reach too large concentration factors inside the filtration cell. For complete purification of the retained particles, the washing technique may be applied to the remaining solution.

5.1.3.4 Cascade Filtration. In order to minimize coagulation in the cell as well as at the membrane surface, sequential or cascade filtration is highly recommended, since aggregation rate is generally much larger in physically and chemically heterodisperse colloid suspensions (like those of natural waters) than in a homodisperse suspension. Filtration through more than four to five membranes is not useful because the reproducibility of filtration on a single membrane is not better than 5 to 10% and accumulation of experimental uncertainties may lead to unreliable results.

5.1.4 Minimization of Sample Perturbation

Several aspects of this problem are not specific to filtration.[24,27,57,112] The relevant point here is to ensure that size fractionation by filtration gives results which are realistic of the initial composition of the sample. For this purpose filtration must be done as soon as possible after sample collection (Section 5.1.3.1) without modification of temperature, pH, or electrolyte concentration in order to minimize artifacts such as aggregation processes. Therefore, filtration must be done in the field immediately after sampling and under thermostated conditions if filtration time is long. In very easily perturbed samples, cascade filtration must be done directly at depth.[57]

5.2 Checking the Validity of Results

A number of tests may be used to check the reliability of results. Several of them are easy to apply. They are listed below. A rule of thumb for discriminating between correct and incorrect retention when different conditions are applied to unknown samples, is based on the fact that many artifacts result in an increase of the retention of the test compound. Therefore, in many

cases, conditions favoring passage through the membrane should be considered as giving more realistic results (this rule obviously must be used with caution by considering in particular all the effects mentioned in Section 4).

- *Flow-rate* may be varied at constant pressure by using a valve at the output of the cell. Retention must be independent of flow rate.
- *Stirring*: retention must be independent of stirring rate.
- *Filtrate concentration*: in the absence of secondary effects, (i.e., in the absence of a change of σ_x), filtrate concentration $[X]_f$ is given by:[27,22]

$$[X]_f = (1 - \sigma_x) \cdot [X]_c$$

  Therefore $[X]_f$ should be constant during filtration and lower or equal to $[X]_c$ ($0 \leq \sigma_x \leq 1$). This has been observed for instance in Reference 22. In particular, a decrease of $[X]_f$ with filtration time is a much more sensitive indication of membrane clogging than the decrease in J_w, which is normally detectable only after a thick gel layer has already formed.

- *Scanning and trasmission electron microscopy* (SEM and TEM) are very powerful tools[96] for checking whether or not particles are retained on the membrane, what are their sizes and whether or not they are the result of aggregation process (Figures 15 and 16). Note, however, that SEM may be highly misleading. Because of SEM's low resolution, aggregates are often "seen" as single particles (Chapter 6 of the present book). As a consequence, size distribution should never be inferred from SEM observations of particles collected on filters, unless the absence of induced coagulation by concentration polarization has been proven. TEM is much preferable. Other techniques for characterizing particles on filters are described in Chapter 3 of the present book.
- *Electrolyte nature and concentration* may have important influences on diverse processes relevant in filtration and, consequently, on separation results. As a consequence generalization of this effect is difficult and its influence should be tested in each particular case.
  - — Coagulation of colloids and particles
  - — Change of conformation, size, and hydration of macromolecules
  - — Adsorption of ions and molecules on filters
  - — Retention of ions and small molecules on the least porous membranes, by flux coupling between these compounds and the ions of the electrolyte

APPENDIX

The maximum tolerable flux to avoid surface coagulation may be estimated as follows, by considering a homodispersed suspension of fully retained particles X ($\sigma_X = 1$). The limitation due to heterodispersion of real samples is discussed in the text. Due to the concentration polarization effect, a diffusion layer, in which the concentration of X is larger than in the bulk solution, is formed close to the membrane. X may then undergo two processes: back-

diffusion into solution, and possibly, coagulation. Coagulation will be negligible, provided the corresponding elimination flux is much smaller than the elimination flux by back-diffusion:

$$\left(\frac{dN_X}{dt}\right)_{coag} \leq \frac{1}{f} \cdot \left(\frac{dN_X}{dt}\right)_{diff} \qquad (A1)$$

where f is any arbitrary value larger than 1 (f = 10 is used in Figure 11).

The following treatment only deals with coagulation at the membrane surface. Since, however, the concentration of X is maximum at the membrane surface, and the coagulation rate of X depends on the square of its concentration (see below), this rate will also be maximum at the membrane surface. Conditions which minimize coagulation at the membrane surface will therefore also be applicable to the rest of the diffusion layer.

When concentration polarization occurs, the concentration of the fully retained particles X at the membrane surface, $[X]_{c,0}$, compared to that in the filtration cell, $[X]_c$, is given by Equation 7′:

$$\frac{[X]_{c,0}}{[X]_c} = \exp(J_w \cdot \delta/D_X) \qquad (7')$$

The back-diffusion flux at the membrane surface is given by Fick's first law which may be simplified as:

$$\left(\frac{dN_X}{dt}\right)_{diff} = -A \cdot D_X \cdot \frac{[X]_{c,0} - [X]_c}{\delta} \qquad (A2)$$

where the diffusion layer thickness, δ, is assumed to be constant, since the solution in the filtration cell is stirred. A is the membrane surface area.

Particles may also be eliminated from the diffusion layer by coagulation, either perikinetic (first term in Equation A3) or orthokinetic (second term in Equation A3). At the membrane surface, where concentration of X is $[X]_{c,o}$, the overall rate of concentration decrease is given by:[137]

$$\left(\frac{d[X]_{c,0}}{dt}\right)_{coag} = -\left(\alpha_p \cdot \frac{4kT}{3\eta} + \frac{16}{3} \cdot \alpha_o \cdot G \cdot r^3\right) \cdot [X]_{c,0}^2 \qquad (A3)$$

The parameters are defined in the text (see Section 4.2.2). The corresponding flux of particles eliminated by coagulation is given by:

$$\left(\frac{dN_X}{dt}\right)_{coag} = \left(\frac{d[X]_{c,0}}{dt}\right)_{coag} \cdot A \cdot \mu \qquad (A4)$$

where μ is the reaction layer thickness in which coagulation occurs. It is related to D_X and the mean life-time, τ_X, of X inside the reaction layer.[78] For a monomolecular reaction τ_X is itself equal to the reciprocal of the rate constant, k, of the reaction that inactivates X, i.e., the coagulation reaction:

$$\mu = \sqrt{D_X \cdot \tau_X} = \sqrt{D_X/k} \qquad (A5)$$

Coagulation is a bimolecular reaction (see Equation A3). However, after a short transition period of filtration, the concentration polarization effect is assumed to produce a stationary state in the diffusion layer (Section 4.2.1), and Equation 7′ is only valid in this condition. $[X]_{c,0}$ being constant, Equation A3 may be written in the form of a pseudo first-order reaction:[137]

$$\left(\frac{d[X]_{c,0}}{dt}\right)_{coag} = -k \cdot [X]_{c,0} \qquad (A6)$$

with:

$$k = \frac{4\alpha}{3} \cdot (kT/\eta + 4Gr^3) \cdot [X]_{c,0} \qquad (A7)$$

where α_p and α_o are assumed to be equal ($\alpha = \alpha_p = \alpha_o$).

By combining Equations A1, A2, A4, A5, and A7 with the condition of a large concentration polarization (i.e., $[X]_{c,0} \gg [X]_c$), one gets the following expression for the maximum limiting value, $[X]_{c,0}^{max}$, of $[X]_{c,0}$, for which no coagulation occurs:

$$[X]_{c,0}^{max} \leq \frac{3 \cdot D_X/\delta^2}{4f^2 \cdot \alpha \cdot (4Gr^3 + kT/\eta)} = \frac{C_o}{f^2} \qquad (A8)$$

where C_o is the value of $[X]_{c,0}$ for which the fluxes of back-diffusion and coagulation are equal at the membrane surface.

Combining Equation A8 with Equation 7′ gives the maximum tolerable flux for filtration:

$$J_w \leq \frac{D_X}{\delta} \cdot \ln\left(\frac{C_o}{f^2 \cdot [X]_c}\right) \qquad (A9)$$

GLOSSARY

In this chapter, the following definitions are used:

- *Particle*: any compound with size larger than 0.45 μm
- *Colloid*: any compound with size larger than a few nanometers and smaller than 0.45 μm

- *Macromolecule*: synonymous to colloid
- *Solute*: any compound or inorganic ion with size smaller than a few nanometers
- *Compound in solution*: any compound or inorganic ion, irrespective of its size (compounds in solution include particles, macromolecules, or colloids and solutes)
- *Permeate*: a compound or ion of any size passing through the membrane of interest
- *Retentate*: a compound or ion of any size retained by the test membrane, irrespective of the retention mechanism
- *Concentration polarization*: formation of a concentration gradient compounds, at the membrane surface, due to their retention by the membrane and their non-infinite rate of back-diffusion in solution

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