

APPLICATION OF ULTRAFILTRATION/DIALYSIS TO THE PREPARATION OF CLAY SUSPENSIONS

Key Words—Desalting, Dialysis, Hollow-fiber filter, Montmorillonite, Ultrafiltration.

Studies of the properties of clays in suspension generally involve pretreatment of the clay to prepare homoionic samples. Such preparations require a desalting step to remove excess ions from the solution, even for most exchange resin techniques (Bolt and Frissel, 1960). In the past, the electro dialysis and filtration techniques of Marshall and Bergman (1941) and of Faucher *et al.* (1952) were commonly used. More recently normal centrifugation (van Olphen, 1977; Jackson, 1956) or dialysis have been used almost exclusively (e.g., see Banin and Lahav, 1968; Levy and Shainberg, 1972; Allen, 1972), and it has become common to use centrifugation followed by dialysis (e.g., see Cremers and Thomas, 1966; Martin and Laudelout, 1963). Certain objections may be raised to each of these procedures. Electro dialysis has become obsolete in desalting procedures because it accelerates hydrolysis of the clay to the point of dissolution (Grim, 1968; van Olphen, 1977). Normal filtration of clay suspensions, especially those with low salt content, is inefficient due to the buildup of clay on the filter, thereby reducing its effective pore size. Dialysis is also a relatively slow process, unless the solutions on both sides of the membrane are stirred to reduce concentration polarization (stirring is very difficult in conventional dialysis). Centrifugation involves cycles of compaction followed by redispersion and requires considerable handling of the sample. The compaction step may also hinder the measurement or preservation of tactoid-size distributions.

To avoid some of these problems, a desalting procedure has been developed for clay suspensions which combines ultrafiltration with dialysis. The procedure avoids the problems of clay buildup on filtration membranes, lack of mixing in dialysis, and compaction of the clay, and involves no change in clay concentration in any of its steps. It requires a minimum of sample handling and is capable of treating large amounts of clay over a wide range of suspension concentrations.

EXPERIMENTAL

Materials

A sample of montmorillonite, API No. 27 (Ward's Natural Science Establishment) from Belle Fourche, South Dakota (Kerr *et al.*, 1950), was ground to -270 mesh, and 30-g samples were converted to the sodium form by washing three times in 500 ml volumes of 1 M NaCl. Total equilibration time was in excess of 70 hr. Preliminary desalting was accomplished by decanting and diluting until one liter of stable suspension was obtained. This suspension was allowed to stand until the >2- μ m equivalent spherical diameter fraction had settled out. If a gel formed, the suspension was filtered through a coarse polyethylene filter. The final suspension for desalting was diluted to 2.5 liters containing about 1.2 weight percent of clay and was 0.05 M in NaOH. This suspension was desalted by the ultrafiltration/dialysis procedure.

Apparatus

The experimental configuration for the ultrafiltration/dialysis procedure is illustrated in Figure 1. The system is a modified CH3 hollow-fiber ultrafiltration apparatus (Amicon Corporation, Lexington, Massachusetts) fitted with an H1P100 fiber cartridge (nominal pore size 5 nm). Other hollow-fiber ultrafiltration units, including the more elaborate DC2 model of

Amicon, can be used in the same way. The tubing pump built into the CH3 unit was replaced by a variable speed, double head tubing pump (Masterflex model 7545-00 fitted with one each of pump heads 7017 and 7014, Cole Parmer, Chicago, Illinois). The conductance cell used has a cell constant of 0.14 cm^{-1} .

Procedure

The hollow fiber system was flushed until the filtrate conductance reached that of the deionized water being pumped in. The system was set up as shown in Figure 1 with the 2.5 liter suspension described above. The clay suspension was pumped through the hollow fibers of the hollow-fiber ultrafiltration apparatus and back into its reservoir while deionized water was pumped countercurrent around the fibers and out to a "flow-through" conductance cell where it was drained. A fairly high flow rate (~4 ml/sec) was necessary through the fibers to prevent concentration polarization and settling of the clay. Similarly, deionized water was pumped on the filtrate side of the fibers at a rate sufficient to minimize concentration polarization here as well. The filtrate/deionized water was pumped at a flow rate somewhat less than that of the suspension. In this way it was possible to achieve a relatively high flow rate for the suspension while maintaining a transmembrane pressure low enough to prevent the formation of filter cakes inside the fibers (as happens during stirred-cell ultrafiltration) yet high enough for ultrafiltration to occur. The large surface area of the filter membrane (740 cm^2 for the H1P100 unit) and the suppression of concentration polarization on both sides of the membrane maximized the concentration gradient across the fiber membrane, thereby removing excess ions from the clay suspension. Because of the ultrafiltration effect relatively rapid concentration of the suspension occurred, requiring a reservoir of deionized water (shown to the left in Figure 1) to maintain the concentration of the bulk suspension. The desalting was continued until a steady dialysate/filtrate conductance value of about 1.5 $\mu\text{mho/cm}$ was obtained.

By disconnecting the reservoir shown to the left in Figure 1, the desalted suspension was concentrated due to the ultrafiltration effect. In a typical preparation 2.5 liters of 1 weight percent suspension was concentrated to a 3% suspension in 3-4 hr. The concentrated Na-form suspension was either subjected to further ion-exchange as described below or freeze-dried as desired. In the latter case preconcentration of the dilute suspension resulted in appreciable time savings.

To prepare other ionic forms from the stock sodium-form clay, the concentrated suspension was made up to 2.5 liters by the addition of the appropriate 1 M salt and was further treated by pumping a solution of the same salt around the fibers in place of deionized water while maintaining sufficient pressure (on the outside solution) to minimize ultrafiltration. Once the exchange was completed the suspension was desalted by switching back to deionized water (with no handling of the suspension). Such a procedure could be advantageous where the size of tactoids can vary with counterion composition. An alternate method used in this laboratory is to replace the ultrafiltration compensating solution with salt solution so that the new ions are added to the clay directly.

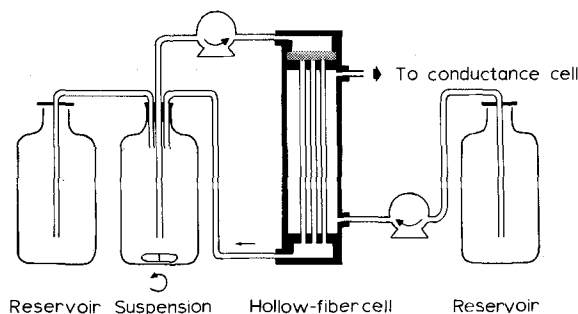


Figure 1. Schematic diagram of the hollow-fiber cell and flow systems. (Not drawn to scale.)

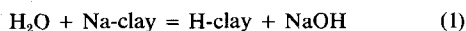
Cation exchange capacities (CEC) were measured following the procedure of Rollins and Pool (1968) except that for maximum Ca-CEC values, it was necessary to use alcohol-soluble calcium nitrate rather than calcium acetate in order to remove all of the excess salt from the clay. Cation-exchange capacities are reported on a freeze-dried weight basis. Analyses for sodium and calcium were carried out by atomic emission and absorption spectroscopy, respectively.

RESULTS AND DISCUSSION

There is a practical limit to the speed with which the suspension may be pumped through the prefilter in the hollow fiber unit due to clogging. At the flow rates used (4 ml/sec), the initial specific conductance of the dialysate/filtrate was generally about 1500 $\mu\text{mho/cm}$, and an ultrafiltration rate of about 4 ml/min was obtained. Increasing the flow rates (at a constant flow-rate ratio) increased the ultrafiltration rate only marginally. An analysis of the conductance data of a typical run (Figure 2) indicates that under these conditions dialysis and ultrafiltration each contribute about equally to the process of desalting. Under these experimental conditions, the entire process took about 70 hr, as illustrated in Figure 2, and required about 100 liters of deionized water. Time and wash-water volume could be reduced proportionally if smaller initial volumes of clay suspension were treated, if the initial salt concentration was lower, or if it was desirable to adjust the salt concentration to a finite final value in order to prevent the possible hydrolysis of the clay as described below.

Hydrolysis

Sodium-exchanged montmorillonite is particularly susceptible to hydrolysis in suspensions where the salt content is below 10^{-3} M (Kamil and Shainberg, 1968; Brown and Miller, 1971; Bar-On and Shainberg, 1970). The mechanism proposed by Shainberg (1973) consists of a rapid exchange reaction between solution hydrogen ions and exchangeable sodium ions:



The NaOH reacts to form NaHCO_3 so that large pH increases are not observed. Reaction (1) is followed by the slow diffusion of the adsorbed H^+ ions into the lattice where octahedral Al or Mg are displaced:



The second reaction determines the rate of the hydrolysis even though initially a rapid release of some Na is expected until quasi-equilibrium is established with the bulk solution. The amount of Na released under these conditions may be estimated from the Gouy theory predictions of Kamil and Shain-

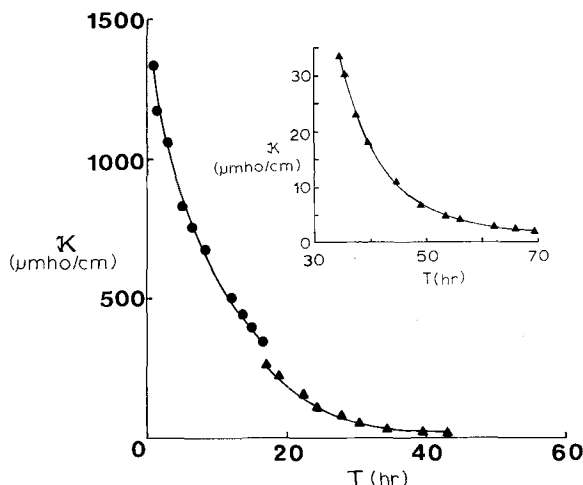


Figure 2. Variation of specific conductance (κ) with time (T). Circles represent data for a suspension flow rate of 2.3 ml/sec and the triangles for 3.6 ml/sec. These correspond to filtration rates of 3.8 and 4.0 ml/min, respectively.

berg (1968) and Bar-On and Shainberg (1970) at about 10% for equilibrium with distilled water according to reaction (1).

During the sodium-clay desalting procedure described here, where CO_2 has been largely excluded from the system, suspension pH values of 8.5–9 were observed in agreement with the data of Kamil and Shainberg (1968) for equilibrium according to reaction (1). About 10% of the sodium initially associated with the clay went into solution by the end of the procedure but no evidence was found for a reduction of the charge density in the clay. The maximum CEC for this clay whether determined as sodium or as calcium, is 93 meq/100 g (16 determinations, ± 3 meq/100 g) following the method of Rollins and Pool (1968) which minimizes the possibility of hydrolysis interference. Samples of desalted, freeze-dried Na-montmorillonite had an exchangeable sodium content of 80 meq/100 g. After re-saturation, the exchangeable sodium content was determined to be 93 meq/100 g. Samples of desalted, freeze-dried Ca-montmorillonite were found to have an exchangeable calcium content of 93 meq/100 g; resaturating with calcium resulted in no change. These results indicate that hydrolysis of Ca-montmorillonite did not occur during the desalting procedure and that some of the Na-montmorillonite hydrolyzed, but to a predictable extent and reversibly, with no apparent change in the charge density of the clay. It is of interest to note that in the study of Bar-On and Shainberg (1970), where all of the exchangeable sodium was released after long-term exhaustive leaching (15 liters over five months), the concentration of sodium in the equilibrium solution reached a constant value fairly quickly and persisted until the exchange capacity was exhausted. The onset of such constant sodium release may correspond to the constant ionic-strength level of the filtrate which was observed at the end of the desalting procedure (cf. Figure 2 in Bar-On and Shainberg, 1970) and which may in the present work signal the beginning of hydrolysis of the clay. Apparently the results of reaction (2) are significant only if washing is continued over a much longer period of time. Investigation of these questions is continuing.

The procedure presented here has several advantages which distinguish it from other techniques in common use and offers a useful option to the colloid chemist. Because the clay is kept in suspension at all times, the method is especially suited when clays necessary for studies in dilute suspension have to be

prepared. However, in such cases care should be taken to minimize the time of ultrafiltration to avoid possible hydrolysis. In any case, the ionic content and CEC of the final clay preparation should be determined and compared with the same determinations on the clay before the treatment, as for any experiment in very dilute suspensions. Finally, when very concentrated suspensions have to be prepared, freeze drying or centrifugation steps are still necessary.

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