

## Sheet Ion Exchangers

### I. General Aspects of Synthetic Ion Exchangers in Sheet Form

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During the development of experimental methods for beta radiography<sup>1</sup> there arose a definite need for a beta radiation source, which possessed a very uniform emissive power over an area of a few sq.cms. At that time this problem of producing an extended beta radiation source seemed to have no general solution. As most radioactive materials are supplied as inorganic ions, it was tried to obtain *ion exchanging* substances in a suitable form *e.g.* as thin *plane parallel sheets* (instead of usual grain form).

Experiments in this direction were successful in May 1949<sup>2</sup>, when it was observed, that after the immersion of plates, rods or sheets of commercial *polystyrene* in chlorosulphonic acid<sup>3</sup> at room temperature the surface layer had been converted into polystyrene sulphonic acid, which has ion exchange properties (due to the sulphonic acid group). This layer was able to sorb cations in much the same way as other ion exchangers in the usual grain form and the original need for a uniform extended beta source was met by the sorption of radioactive ions, but soon other applications were also found<sup>2</sup>. (Beischer<sup>4</sup>, faced with similar problems, has used Langmuir-Blodgett multilayers for their solution *e.g.* radioactive Ca<sup>45</sup> as calcium stearate).

It is proposed to discuss briefly aspects of nomenclature, preparation methods, properties and applications of this new type of ion exchanger. It is hoped later to publish a series of papers on special topics of this field.

#### NOMENCLATURE

The above-mentioned layer of ion exchanger (mostly 0.1–200  $\mu$  thick, corresponding to 0.05–100  $\mu\text{eq}/\text{cm}^2$ ) is lying directly on the untreated section of the original material, which in general has large dimensions. In many

cases it is easy to tear off the exchanging layer or to dissolve the untreated high polymer, getting the pure ion exchanger free for various purposes. During our later developments this technique has appeared more and more important and the term "*sheet ion exchanger*" (swedish: skiktjonbytare) seems suitable and will be used in the following discussion even when the layer is not separated from the untreated body. (Originally the term "surface ion exchanger", swedish "ytjonbytare"<sup>2</sup> was used, but is now abandoned to avoid confusion with true surface ion exchange phenomena). An ion exchanger of this sheet type is most probably identical to the usual grainy substances with regard to chemical composition and ion exchange capacity per gram of material but differ chiefly in physical form (and also in special properties *e.g.* diffusion rate for ions as well as water, mobility of sorbed ions and swelling properties). Since the new form is, however, of great experimental importance, making possible new ways of studying ion exchange phenomena and new applications (see below), it therefore seems justified to introduce a special nomenclature. The special criteria of the sheet ion exchangers (in addition to insolubility) should be:

1. Two dimensions (*e.g.* length and width for plane sheets) many times greater than the third *i.e.* the thickness (the sheets may of course be curved in one or two dimensions *e.g.* cylindrical and spherical surfaces).
2. The substance should be homogeneous in all its properties especially in composition and ion capacity calculated per area as well as per mass unit.
3. Complete coherency with no macro- or microstructure down to  $5 \mu$  or preferably to the limit of optical resolution.

More special points of view relating to experimental requirements are: (a) High ion exchange capacity per mass unit (1–11 meq/gram of dry material), (b) only functional group (*e.g.*  $-\text{SO}_3\text{H}$ ,  $-\text{COOH}$ ,  $-\text{OH}$ ,  $-\text{NH}_2$  and amino derivatives). Further the substances should preferably withstand temperatures up to  $100^\circ\text{C}$ , chemical attacks and be colorless and transparent to light. Most of the visualized applications require a thickness of about  $0.1\text{--}1\,000 \mu$ .

There exist some substances both natural and artificial, which partially fulfil our criteria *e.g.* layers of zeolites, clays, artificial mineral membranes<sup>5</sup>, feldspar surfaces, micas, glasses, organic materials such as cellulose derivatives and gelatin. Many of these are lacking either in homogeneity or coherency or they have so low a capacity per unit area (at reasonable thickness) that their use for our purposes is in most cases doubtful.

During the development of the sheet ion exchangers (since 1949) some papers have been published which contain similar trends to our works: Wyllie<sup>6</sup>, Juda<sup>7</sup> and Kressman<sup>8</sup> have taken the logical step from Marshalls artificial mineral membranes<sup>5</sup> made for membrane potential studies, to make membranes

containing synthetic organic ion exchangers for the same purposes. From Wyllie's paper it is clear that plastic binders (30–80 %) are used and that a mosaic structure is present and thus these membranes are supposed not to be homogeneous in structure and properties. Juda's paper<sup>7</sup> states that the membranes are "coherent" and of "high conductivity" but does not give enough details to permit a discussion of them from our point of view. Kressman's membranes seem to have very interesting properties, but before the preparation procedures have been published their relations to the present sheets cannot be discussed. — It is felt that all membranes made for potential studies, including both inorganic and organic ones, are of a thickness (mostly 1–5 mm) which is too great for our visualized applications, but it is possible that they will in future prove to be of great interest even outside the potential studies.

#### PREPARATIONS

Many high-polymers can be treated to yield sheet ion exchangers. Of special importance are those, which yield colorless, transparent products *e.g.* polystyrene and polyacrylates and their derivatives.

On sulphonation, polystyrene plates, rods or sheets from commercial sources give satisfactory sheet cation exchangers. Sheets of polystyrene gave, for instance, after 1 minute's immersion in chlorosulphonic acid at 20°, 15  $\mu$  thick layers on each side of an unsulphonated section, the three layers being easily separable after immersion first in benzene for some minutes and then in water. The thickness is varied by altering the time of contact and the temperature. The sulphonation is also easily made with fuming sulphuric acid at room temperature.

The mechanical stability of the sheets affords the greatest problem. Due to swelling (especially in distilled water) the sulphonated layer flakes off, when it is too thick probably due to the very small cross-linkage of the high polymer used (commercial thermoplastic material). Still it is possible with some care, to get large sheets of up to 30–40  $\mu$  thickness (10  $\times$  10 cms are easily made). After preliminary experiments, copolymerized products of styrene-divinylbenzene *i.e.* with a small but definite degree of cross-linkage yield much better results.

After partial sulphonation the boundaries can be easily detected, because the treated part is highly hydrophilic and thus wetted, whereas the untreated part is hydrophobic and not wetted. A valuable test method is to measure the electrical resistance between two points, say 5 mm apart. The untreated surface has a resistance much higher than 10<sup>10</sup> ohm whereas the sulphonated surface only 10<sup>5</sup>–10<sup>6</sup> ohm. Another method is to sorb nickel ions, rinse with distilled

water and develop with dimethylglyoxime when the red colour immediately indicates where the surface has developed ion exchange properties. The separated product showed a capacity (within the experimental error) similar to that of polystyrene monosulphonic acid (5.4 meq/gram).

"Surface hydrolysis" of polyacrylate plates (Lucite, Perspex *etc.*) with alcoholic alkalis yield a hydrophilic layer of polyacrylic acid (or derivatives). For example, boiling a Lucite plate in a 30 % solution of KOH in 96 % alcohol yielded after 5 hours a layer of ion exchanger of 1.5 mg/cm<sup>2</sup> in dry state. Because of the weak acidity of the carboxyl group it is very sensitive to acid solutions where the surface becomes hydrophobic at once (and shows a very much higher surface resistance). The layer is rather slimy, due probably to a very low degree of cross-linkage of the high polymer.

Other polymers *e.g.* bakelite and other plastics of aromatic type can be given on exchange properties after immersing in chlorosulphonic acid.

Only one way of preparing anion exchanger of the sheet type has been studied: Polystyrene plates were dipped into fuming nitric acid for about 10 seconds (with the probable formation of a polynitrostyrene) and subsequently reduced by TiCl<sub>3</sub> or SnCl<sub>2</sub> solutions in HCl. An anion capacity of the order 0.1  $\mu$ eq/cm<sup>2</sup> was observed (probably due to a polyaminostyrene). The determination of the capacity was made by means of a radioactive tracer method using P<sup>32</sup> as H<sub>3</sub>PO<sub>4</sub>.

#### APPLICATIONS

It has already been mentioned that a very uniform sorption of ions on the sheet ion exchanger takes place. This is of interest for the preparation of many kinds of radioactive sources. The capacities of the cation exchangers made are of the order 0.1–100  $\mu$ eq/cm<sup>2</sup> and thus the method is of certain value when a high specific activity is present, which is the case for the uranium fission products, nuclides made by the Szilard-Chalmers reaction, many daughter products in the radioactive series, products from (n,p) and (n, $\alpha$ ) reactions *etc.* For example the method has hitherto been used for the nuclides Sr<sup>90</sup> + Y<sup>90</sup>, RaD + E, ThB + C, Ca<sup>45</sup>, UX<sub>1</sub> *etc.* Because the exchange reaction is not complete, quantitative preparations can not be made using the usual single stage technique. However the method should be of value for those cases where losses can be tolerated *e.g.* the preparation of radiation sources for beta radiography, beta thickness gauges, the calibration of photographic emulsions and also as standard preparations all of which have been preliminarily studied. Also other similar fields are suggested: for use in medical applicators, sources for beta spectroscopy (where the uniform and low self-absorption is the most important feature), preparation of static eliminators, phosphors *etc.* Because

of the hygroscopic nature of the layers they should be carefully sealed when high precision is required in radiation studies *e.g.* when working with standards.

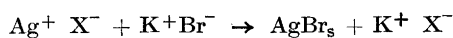
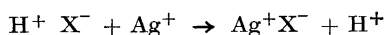
It is also possible to carry out separations of different ion species on treated plates or strips, both as one- and two-dimensional chromatography. Only a few trial experiments have been made. The supposition that the submicroscopical "grain size" would give very sharp fronts was supported by experimental observations. On the other hand, the relatively closedpacked structure gives a rather low transport velocity and thus a long experimental time. The plates or strips are easily developed by spraying with colour-developing solutions using techniques usual in paper chromatography. Working with radioactive substances the chromatogram is easily studied by means of a radiation detector provided with a narrow slit. The detection of soft beta rays and alpha rays, difficult to realise in the usual column apparatus, is rather easy in this case due to the low self absorption. Autoradiography gives a complete picture of the result. More work has to be done before practical methods for sheet ion exchange chromatography can be recommended. Such works are in progress.

The ions in the sheet ion exchangers possess a certain mobility in electric fields, which, when the layer is wet, is of the order of 1–10 % of the known mobility for aqueous solutions. These properties have been used to study the migration of inorganic ions and experiments are now being directed towards the separation of ions and radiocolloids (in collaboration with Mr L. W. Holm).

SIE loaded with different ions are useful as ionic absorbers *e.g.* for beta rays and neutrons. This method is now being applied in an extended study of the effect of chemical state on the absorption of beta rays.

Sheet ion exchangers can also be used as filters rendering other applications possible *e.g.* "pile chromatography", test methods for radiocolloids, indicator "papers", semipermeable membranes, ultrafilters.

One modification of the technique is to make solid precipitates in the layer itself after having loaded it with certain ions. Silver bromide photographic emulsions can be made using the steps:



rinsing with distilled water after each reaction ( $\text{X}^-$  represents the negative group of the ion exchanger). From the above equations it can be seen that such a process yields a AgBr content of 50 %, but the process can be repeated again giving theoretically 75 %. Thus it is possible to obtain light sensitive layers with similar AgBr content to those of ordinary photography as well as to the

socalled nuclear emulsions. The ion exchanging high-polymer gel takes the role of gelatin as protection colloid for the silver bromide.

The same technique has been used to produce layers containing  $\text{BaSO}_4$ ,  $\text{Cu}_2\text{Fe}(\text{CN})_6$ ,  $\text{ZnS}$ ,  $\text{PbS}$ ,  $\text{Ag}_2\text{S}$  etc.

The sheet ion exchangers possess promising features for the study of the ion exchangers themselves and the ion exchange process *e.g.* rendering possible electronmicroscopic preparations, studies of diffusion and ion mobility, water sorption properties and swelling, optical and mechanical properties *etc.*

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