Sorption Isotherms on Ion Exchangers by emf Titrations

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For the experimental study of ion exchange equilibria the batch equilibrium method has been the one most frequently used. Very recently two methods that permit the calculation of sorption isotherms from leaking curve data have been developed. Duncan and Lister [1] have shown how points on the isotherm can be obtained from sorption curves, the so-called break-through method. Glueckauf [2] and Sillén [3] have given equations that permit calculation of the isotherms from desorption curve data.

Of the above-mentioned methods, the batch equilibrium method is simple but time-consuming. The break-through method gives only one point on the isotherm for every sorption curve measured and is thus rather laborious. The third method mentioned allows the whole isotherm to be calculated from a single desorption curve, but large errors may be introduced if the values of the equilibrium quotient at the ends of the diagram are unknown (*cf.* below.)

By modifying the batch equilibrium method to a titrimetric one, time is saved and the calculations are still very simple.

This method has been applied to the $Ag^+ - H^+$ exchange on Wofatit KS. 1.00 g H^+ saturated resin, 0.5—1.0 mm in diameter, and 200.0 ml 100.0 mC HNO_3 have been titrated with 100.0 mC $AgNO_3$ or 10.00 mC $AgNO_3$—90.00 mC HNO_3 mixture. The whole apparatus was kept in a thermostated room at 25.0 ± 0.3° C. The Ag^+ concentration was measured with the Forsling-Sillén apparatus, as described in an earlier paper [4]. Equilibrium was, in most cases, attained within 30 minutes with the stirring speed used in the experiments.

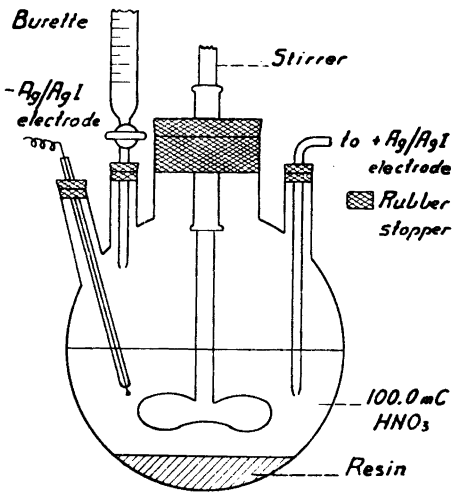

Fig. 1. Schematic figure of the titration apparatus. When the emf was measured the stirrer was stopped.

After the titration the sorption capacity (s_0) of the resin was determined by saturation with H^+, expelling the H^+ with KNO_3 and titration with NaOH. From the assumption of the equivalent exchange and a knowledge of s_0, $[Ag^+]$, $[Ag^+]_{tot}$ and the added amount of HNO_3, the equilibrium quotient ($\varkappa$) was calculated for the reaction:

$$Ag^+ + HR \rightleftharpoons H^+ + AgR \qquad (1)$$

In Fig. 1 is given a picture of the apparatus and Fig. 2 gives a comparison between $\varkappa$ values obtained by titration and by the batch method. $\varkappa$ is plotted against the mole fraction of silver in the resin (β). The batch equilibrium values are taken from Table 7a in ref. 4. The agreement is quite good. The spread of the values obtained by titrations is not larger than for that of the values obtained by

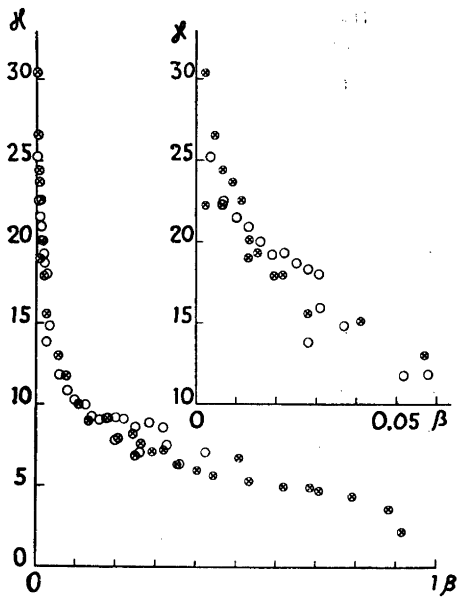

Fig. 2. $\varkappa$ is plotted against β. ⊙ denotes values obtained by titrations. (⊗) denotes values obtained by the batch method.

the batch method. The titration method has proved to be much simpler and faster than the batch equilibrium method.

It may be noted that only about half the β interval has, in this case, been covered by the titration method. By starting from Ag^+ saturated resin and $AgNO_3$ it is possible to cover the whole interval by titrations. However, the amount of H^+ in the solution is, in this case, very uncertain as it is determined as a difference. In this case it would be better to use a H^+ sensitive electrode *e.g.* a glass electrode and change to a Ag/AgI electrode for $\beta \approx 0.5$.

As electrodes sensitive to a number of ions are available, many ion exchange equilibrium studies can be carried out as emf titrations. For instance the $Cu^{2+}-H^+$ exchange can be studied with both a copper amalgam and a glass electrode. The diffusion potentials must be known for the ion pair and the ionic strength in question. They can according to Ekedahl [5-6] be determined rapidly by titrations without resin.

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Received February 20, 1952.

Preparation of D-Valine by Asymmetric, Enzymatic Hydrolysis of the Isobutyl Ester of DL-Valine

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DL-valine has earlier been resolved by fractional crystallization of the brucine salt of its formyl derivative [1] or of its menthoxyacetyl derivative [2]. Duschinsky and Jeannerat [3] prepared the L-isomer of valine by oxidation of the D-isomer in the racemic form of valine with D-amino acid oxidase from hog kidneys. Because the enzymes in yeast destroy the L-valine and leave the D-form intact, it is possible with this procedure to obtain the latter free from the L-isomer [4]. Price, Gilbert and Greenstein [5] produced the valine isomers by means of asymmetric hydrolysis of chloroacetyl-DL-valine.

A simple method for producing D-valine is described in the present paper. It is based on the asymmetric hydrolysis of the isobutyl ester of DL-valine with an enzyme preparation obtained from pancreas. Complete digestion of the ester results in free L-valine and the isobutyl ester of D-valine.