

Influence of Dilution upon Cation Exchange Equilibrium*

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Ion exchange equilibria in batch systems have been examined to see how the distribution of ions between the ion exchanger and the solution depends on the dilution of the solution. The exchanger was Amberlite IR-120. The following exchanges were studied: $K^+ - H^+$, $Mg^{++} - Ca^{++}$, $Ca^{++} - H^+$, $Ba^{++} - H^+$, $Ce^{3+} - H^+$ and $La^{3+} - H^+$. It has been found that dilution of the system causes the ion of higher affinity to pass into the resin phase. This effect is more pronounced for the exchange of ions of unequal charge than for those of the same charge.

Ion exchange is a complex process depending on many factors which have not yet been investigated in details. The distribution of ions between an exchanger and an electrolytic solution in contact with the exchanger depends not only on the kind of the exchanger and of the ions, but also on a certain number of experimental conditions such as: conditioning of the exchanger, concentration of ions on the exchanger and in the solution, kind of solvent, etc. It is as yet not possible to predict the distribution of ions knowing all experimental conditions. It is therefore necessary to have a great number of experimental results to be able to decide which factors are essential in ion exchange processes.

We have examined the influence of dilution of the liquid phase on the ion exchange equilibria. When a certain amount of an exchanger saturated with ions of one kind is brought into contact with a solution of the some other kind of ions, an equilibrium is set up after a certain time. We examined whether and how this equilibrium is affected by diluting the solution.

EXPERIMENTAL

Exchanger. The exchanger used was Amberlite IR-120, particle size 0.5–0.9 mm., obtained by dry sieving of the factory product. The metal forms of the resin were prepared in the column. A solution of nitrates of the corresponding ions was percolated through the column until the resin was completely saturated with ions of one kind. The concentration of the nitrate solution was 0.5N, except for $Ce(NO_3)_3$ and $La(NO_3)_3$ where the concentration was 0.01N. After washing the column with water the resin was air-dried on a filter paper at room temperature. Thus we obtained RK (R corresponds to the univalent resin anion), R_2Mg , R_2Ca , R_2Ba , R_3Ce , and R_3La . The moisture content of the air-dried resin was 20%, found by drying the resin in an aluminium-block at 120°C. The resin was kept in closed bottles to prevent any change in weight due to the adsorption of water.

Equilibrium measurements. 1.000 g. of the air-dried resin was equilibrated with a solution of HNO_3 , for exchanges with H^+ , and with a solution of $Ca(NO_3)_2$ for $Mg^{++} - Ca^{++}$ exchange. The concentration of the solutions varied from 0.200 to 39.96 meq.

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To attain the equilibrium, the resin remained in contact with the solution for 24 hours, with occasional shaking. After obtaining equilibrium, the concentration of the aqueous solution was analysed.

Determination of H^+ in the solution. Samples of 75 λ were titrated with standard NaOH solutions with methyl red as indicator. A micro burette of 100 λ was used for titration. The volume could be read with precision of $\pm 0.2 \lambda$.

Determination of Ca^{++} in the solution. Calcium was precipitated as calcium oxalate. The precipitate was dissolved in sulfuric acid dil., and titrated with standard solution of potassium permanganate. Precipitation, washing and dissolving of calcium oxalate was performed in centrifuge tubes.

Interpretation of results. The results are represented graphically on Figs. 1 and 2. The abscissa is a logarithmic plot of the milliequivalents of ions initially present in the solution — the hydrogen (H_o^+) and calcium (Ca_o^{++}) ions resp. On the ordinate are the equivalent percents of the same ions (H^{+eq} , Ca^{++eq}) in the solution at equilibrium.

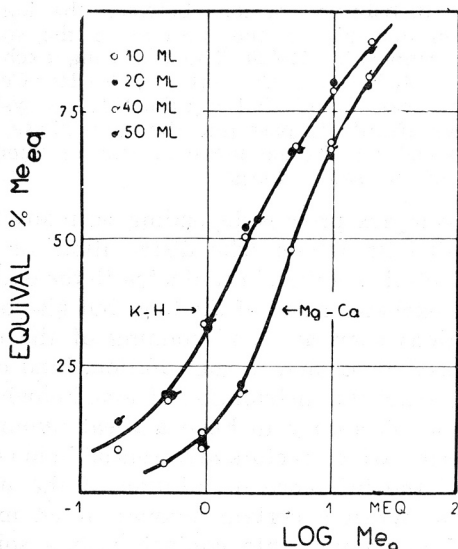


Fig. 1. Equilibrium curves for the exchange $K^+—H^+$ and $Mg^{2+}—Ca^{2+}$. Abscissa: Me_o is the amount of hydrogen and calcium ions resp. initially present in the solution, expressed in milliequivalents. Ordinate: The equivalent % of hydrogen and calcium ions resp. (Me_{eq}) in the solution at equilibrium. Volume of the batch: 10 ml., 20 ml., 40 ml., and 50 ml.

DISCUSSION

The influence of dilution upon equilibrium can be seen from the figures. When two batches differ only in the volume of the aqueous solution more ions of higher affinity will pass into the resin phase in the more diluted solution. The influence of dilution is nearly negligible for the exchange of $K^+—H^+$ and $Mg^{2+}—Ca^{2+}$, that is for the exchange of ions of equal charge. The effect of dilution is well marked for the exchange of ions of unequal charge.

Our results can be compared with some from the literature. Eaton and Sokoloff¹ examined $Na^+—Ca^{2+}$ exchange and found that after dilution there are more Na^+ in the aqueous phase. Ivanov and Gapon² state that dilution of the aqueous phase increases the adsorption of the ions of greater valence, whilst the amount of adsorbed ions is independent of dilution when the

exchanging ions have the same valence. The latter is confirmed by Kressman and Kitchener³. Marshall and Gupta⁴ give data for the $Tl^+—H^+$ exchange, where equilibrium varies with dilution. Saldadze and Boževoljnov⁵ studied $Ba^{2+}—H^+$, $H^+—Ba^{2+}$, $Mg^{2+}—Ba^{2+}$, $K^+—Ba^{2+}$, $Ba^{2+}—K^+$, and $K^+—H^+$ exchanges and found that dilution effects equilibrium according to Nikolsky's equation⁵ when ions of different charge are exchanged. $NH_4^+—H^+$ exchange, studied by Wiklander⁶, was independent of dilution, while $NH_4^+—Ca^{2+}$ equilibrium changed with dilution as predicted by the Donnan theory.

All the above mentioned authors found the influence of dilution when

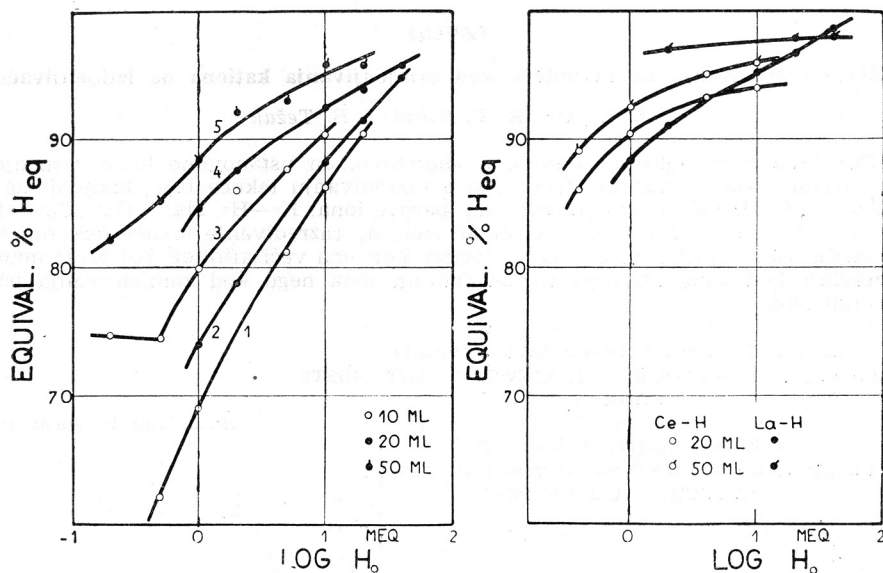


Fig. 2a. Equilibrium curves for the exchanges: $Ca^{2+}—H^+$, (curves 1 and 2) and $Ba^{2+}—H^+$ (curves 3, 4, and 5). Abscissa: H_0 is the amount of hydrogen ions initially present in the solution, expressed in milliequivalents. Ordinate: Equivalent % of hydrogen ions, (H_{eq}) in the solution at equilibrium. Volume of the batch: 10 ml., 20 ml., and 50 ml.

Fig. 2b. Equilibrium curves for the exchange: $Ce^{3+}—H^+$ and $La^{3+}—H^+$. Abscissa and ordinate are the same as in Fig. 2a. Volume of the batch: 20 ml. and 50 ml.

exchanging ions of dissimilar charge. The results do not agree when univalent ions are exchanged.

There are several theories which deal with the effect of dilution on ion exchange equilibria. Our results are in qualitative agreement with Jenny-Davis's theory⁷ regarding the influence of dilution on equilibrium. Jenny presumes a negligible influence of dilution upon equilibrium for the exchange of univalent ions, while Davis, applying Jenny's oscillating theory to the exchange of ions of unequal charge, predicts that ion exchange equilibrium will depend on the concentration of the exchanging ions. Our results are also in qualitative agreement with the Donnan theory. According to this theory the dilution of the external solution causes a shift in the equilibrium only when ions of unequal valence are used.

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IZVOD

Utjecaj razređivanja na ravnotežu kod zamjenjivanja kationa na izmjenjivaču*E. Reiner, K. F. Schulz i B. Težak*

Proučavali smo ionsku zamjenu u »batch«-u, da ustanovimo kako raspodjela iona između tekuće i rezinske faze ovisi o razređivanju tekuće faze. Izmjenjivač je bio Amberlite IR-120, a zamjenjivali smo parove iona: $K^+—H^+$, $Mg^{++}—Ca^{++}$, $Ca^{++}—H^+$, $Ba^{++}—H^+$, $Ce^{3+}—H^+$ i $La^{3+}—H^+$. Ustanovili smo, da razređivanje tekuće faze mijenja raspodjelu iona u korist onog iona na rezinu, koji ima veći afinitet. Taj efekt mnogo je izrazitiji kod zamjenjivanja raznovalentnih iona nego kod zamjenjivanja istovalentnih iona.

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