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Interrelation of Swelling and Selectivity of Ion-Exchange Resins. II. Relation between Swelling and Exchange Isotherms of a Sulfonic Resin: Alkaline and Alkaline-Earth Counterions

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Abstract

The swelling of a sulfonic ion exchange resin (ES 28; 8% divinylbenzene) was measured for hydrogen, alkaline, and alkaline-earth counterions in water, or in equilibrium with solutions of the corresponding chloride, and also for mixed forms. Compared with the (1 M) isotherms, the monomonovalent biionic mixed forms show linear variations of swelling with composition and verify the Rice and Harris model. For monobivalent biionic forms, the equal swelling-equal affinity relationship is only verified at high solution concentrations.

INTRODUCTION

It is an experimental fact that the swelling of an ion-exchange resin decreases when the affinity (or selectivity) of the counterions increases. This is necessarily reflected in all theoretical models of ion exchangers; for example, in the Rice and Harris model (*1*). However, only a very limited number of quantitative experimental confrontations of these two properties are reported in the literature. Quantitative predictions of selectivity constitute powerful tools for the creation of analytical techniques.

We have selected beads of a sulfonic ion exchanger (ES 28, experimental resin Duolite-Diaprosim, France, 8% divinylbenzene, prepared by low-temperature chlorosulfonation. As previously described (*2*), when it is double-sieved (limiting diameters, 0.68 and 0.8 mm) it shows isotropic swelling variations, and an acceptable constancy of the column packing coefficient β when the resin is converted from one form to another. Thus for these beads the volume variations are determined with good agreement and reproducibility by measuring the variations of the height of a resin bed in a calibrated column with a cathetometer.

In order to test the selectivity-volume interrelation, we now report on the swelling with monocounterionic or biionic forms at different concentrations of the equilibrium solution and also on the exchange isotherms reflecting the selectivity.

EXPERIMENTAL

Swelling Variations

We have systematically used the column technique previously described (*2*) (measurements of bed height h).

Exchange Isotherms

M^+/H^+ Isotherms. We have used the general method to draw the isotherms. An influent solution of known composition (MCl + HCl mixture) passes through a resin bed initially in the hydrogen form (the value h is recorded). The resin column is quickly washed with water [this washing has little effect on the ionic composition of the resin because an exchange of monovalent ions is characterized by a single isotherm (*3*)]. After the resin has been washed, a KCl solution is passed through it to eluate the H^+ ions which will be measured by volumetric means. Since the exchange capacity of the column is known, $\bar{X}_M$ can be calculated.

M^{2+}/M^+ Isotherms. For any ion-couple there are as many curves as there are total ionic concentrations (*3*). For a given value of $X_{M^{2+}}$, $\bar{X}_{M^{2+}}$ increases when the external concentration decreases. Since washing the resin column causes the external concentration to decrease progressively, the value found for $\bar{X}_{M^{2+}}$ (if we proceed in the same way) will be too high. Therefore the column must be washed very quickly so as to modify the ionic composition of the resin as little as possible. The M^{2+} ions are eluated by a solution of MCl and measured volumetrically.

RESULTS AND DISCUSSION

The results are represented in Figs. 1, 2 and 3.

Swelling of the ES 28 Resin in Different Monoionic Forms in Contact with Pure Water or in the Presence of Added Salts at Different Concentrations

The results given in Fig. 1 indicate that the swelling decreases according to the sequence generally observed (*4*) for sulfonic-type ion exchangers and for the monovalent counterions H ~ Li → Na → K and for the divalent ones Mg → Ca → Sr.

The swelling decreases with an increase of the external concentration in good agreement with known previous results and is a consequence of the penetration of salt into the resin by Donnan diffusion. The penetrating salt diminishes the electrostatic repulsions between the fixed groups by charge-screening, and there is also a decrease in the internal-external osmotic pressure difference. Fig. 1 shows that this decrease in the swelling for the ES 28 resin is greater for monovalent than for bivalent counterions. Thus the curves representing the swelling of monovalent ionic forms intersect with that of bivalent ionic forms for an equivalent-ionic concentration C_i.

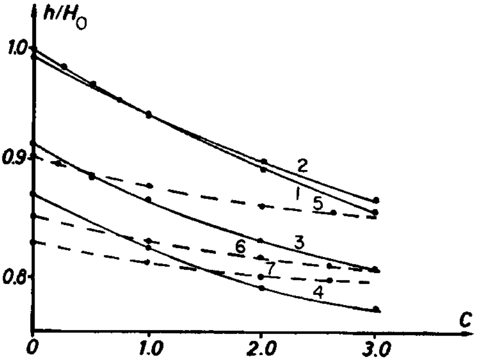

FIG. 1. Relative variations of the bed-height (h/H_0) of the ES 28 resin with the equivalent-ionic concentration of the equilibrium solution (C) for different mono- or bivalent counterions. (1) H^+; (2) Li^+; (3) Na^+; (4) K^+; (5) Mg^{2+}; (6) Ca^{2+}; (7) Sr^{2+}. Co-ion: Cl^-; $H_0 = 153$ mm (bed-height in H^+ form in water); $S = 3.12$ cm^2 (cross-section of the column).

Mixed Monovalent Biionic Forms of the Resin

The swelling has been determined at a total ionic concentration of the solution equal to 1, which is a function of the composition of the solution and resin phase for different couples of monovalent counterions. Two major remarks can be made concerning the results of Fig. 2: (a) The swelling of the ES 28 resin varies linearly with the ionic composition of the resin. This result should be considered as an indication that the ion pairs do not interfere with each other. (b) As the swelling is nearly the same for the Li^+ form and the H^+ form, there is no variation in the swelling during the progressive exchange of these two ions. There is also no selectivity (the isotherm is superimposed with the diagonal of the graph). The confrontation of these two facts is in agreement with the idea that with the model selected, the ion-pairs have the same stability and give the same swelling.

Mixed Monovalent-Bivalent Biionic Forms

Figure 1 shows the crossing-over of the curves representing the swollen volumes of the pure monovalent or bivalent forms of the resin for an equivalent ionic concentration C_i. For all the couples M^{2+}–M^+ at this concentration C_i, we first notice a constancy in the swelling for mixed mono bivalent forms. If swelling and selectivity were as well interconnected here as in the case of monomonovalent ion exchange, we should observe no preferential selectivity for this equivalent ionic concentration. This evidently should be valid in a first approximation by neglecting the changes of the activity coefficients with pure solutions (and mixtures) and pure forms (and mixed forms).

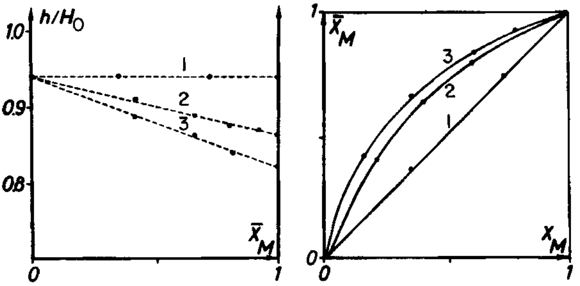

Fig. 2. Relative variations of the bed-height (h/H_0) and exchange isotherms of the ES 28 resin with monovalent alkaline and hydrogen counterions. (1) Li^+/H^+; (2) Na^+/H^+; (3) K^+/H^+. Co-ion: Cl^-; $C = 1\ M$; $H_0 = 153$ mm; X_M is the equivalent-ionic fraction of the alkaline ion M^+ in the resin phase; X_M is the equivalent ionic fraction of the same ion in the solution.

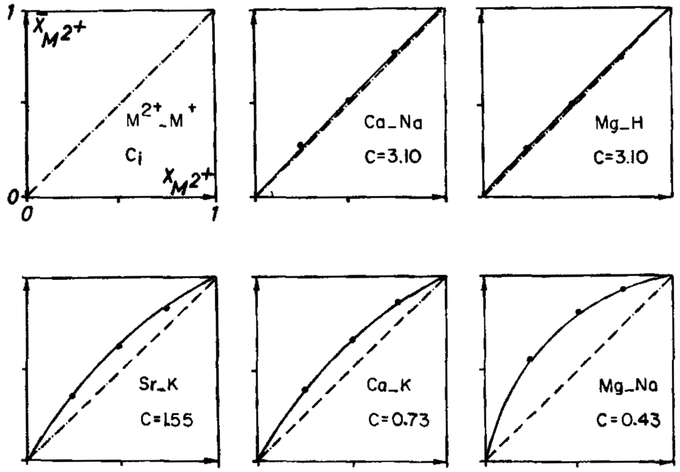

FIG. 3. M^{2+}–M^{+} exchange isotherms of the ES 28 resin for the equivalent ionic concentration C_i for which the pure monoionic forms have the same swelling (no change in swelling was found between pure and mixed forms in any of these isotherms). Co-ion: Cl^-.

To test this hypothesis, isotherms have been determined for these concentrations (Fig. 3). Two types of results have thus been obtained: (a) When the equality of the swollen volume for the pure forms is obtained at a high external concentration (Ca–Na, Mg–H), the volume remains constant for the mixed forms and the isotherms indicate equal affinity for the monovalent and bivalent ions. (b) When the crossing-over concentration is lower, the isotherms indicate a higher selectivity for the bivalent than for the monovalent ion, but without any significant modification of the volume along the isotherm.

Thus the above assumptions seem to be correct only when the external concentration is high. More detailed experimental and theoretical analysis is necessary for the other cases.

CONCLUSION

Measurement of swelling has enabled us to test the Rice and Harris model for alkaline and alkaline-earth ions. The model has been verified for alkaline ion exchanges, but for the M^{2+}–M^{+} ion exchanges studied it has only been verified for high external ionic concentrations.

Other determinations made on carboxylic resins in the presence of alkaline ions by this method also give results in agreement with the Rice and Harris model (*5*).

However, the Donnan exclusion of salts plays a smaller role at higher solution concentrations than at lower ones, and this exclusion is more efficient for salts of monovalent than of bivalent counterions (for the same net-charge density in the resin). This can play a role in the observed differences with different monobivalent exchange isotherms.

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