EFFECT OF ELECTROLYTE INVASION
ON THE ION EXCHANGE RATE
OF A STRONGLY ACIDIC CATION EXCHANGER*

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The exchange rates were compared for microporous (gel-type) and macroporous strongly acidic cation exchangers for the case, where the particle diffusion is the controlling step. Under certain conditions the exchange rate of the macroporous cation exchanger was found to be higher than that of the gel-type cation exchanger with equal content of divinylbenzene. This effect depends on the solution concentration and on the charges of the counterions, which indicates that the exchange rate of a macroporous strongly acidic cation exchanger is affected by the electrolyte invasion.

In the case of a particle diffusion controlled exchange the mass transfer rate is inversely proportional to the cross-linking of the matrix. Amount of the cross-linking agent — usually divinylbenzene (DVB) — in the monomers mixture determines the size of the pores within the resin particle. If these pores exist only in the swelled resin matrix, as in the gel-type network, we speak about swelling porosity. The pore dimensions are only of that order of magnitude that do not present, for majority of the ions encountered, any spacial barrier. Owing to the action of the attractive forces of the fixed ionogenic groups the diffusion rate is retarded and becomes lower compared to that in the surrounding solution.

Polymerisation of the resin can be also conducted under the formation of the macroporous structure, which is characterised by large pores, observable even inside the dried particle (the so-called macroporous ion exchangers). The size of the macropores is large enough to cut down the influence of the charge of the fixed ionogenic groups upon the motion of the ions. The liquid phase inside the macropores can be considered a part of the surrounding solution rather than of the ion exchanger matrix. The electrolyte concentration in the liquid phase inside the macropores depends on the concentration of the external solution and also on the charges of the ions encountered[1] and finally upon the extent of macroporosity, *i.e.* on the pore sizes.

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The flow of the ions into the macropores is called invasion of the electrolyte into the matrix. This phenomenon can accelerate the supply of the ions immediately into the inside of the resin bead, thus raising the exchange rate in all cases where the particle diffusion is the controlling step.

Extremely important is the electrolyte invasion in the case of weakly basic anion exchangers[2,3]. The rate of ion diffusion through the polymeric gelular phase is very slow here, and therefore the electrolyte invasion is the phenomenon predominantly determining the overall rate of acid uptake.

For strongly acidic cation exchangers the diffusion rate is considerably higher[4], the electrolyte invasion is therefore not so significant.

The aim of this work is to investigate the conditions, under which the electrolyte invasion affects the exchange rate even in the case of strongly acidic cation exchangers. For this, we compared the exchange rates of the gel-type cation exchangers and the macroporous cation exchangers, employing different compositions and concentrations of the external electrolyte solutions.

EXPERIMENTAL

Ion Exchangers

Gel-type cation exchangers Dowex 50X8, Dowex 50X16 and macroporous cation exchanger Amberlite IR 200 with 22% DVB were used. For measurements with a fluidised resin bed, the 0·63—0·80 mm fraction was employed (screened in the swollen state in the Na form), for experiments in a column the particle size 0·3—1·2 mm was used. The cation exchangers were applied in the H form.

Kinetic Measurements

The rates of exchange H^+—Na^+ and H^+—Mg^{2+} were followed at two concentrations of the external solution. For the solution concentration 0·2N the technique of infinite bath volume with a fluidised resin bed was applied[4]: 2—3 ml of the exchanger in the H form is placed in a glass crucible with a frit SO, 20 mm i.d., connected to a water pump. The NaCl or $MgSO_4$ solution flows through at a rate of 500 ml min^{-1} thus keeping the ion exchanger in a completely fluidised bed. After some time elapsed the exchange is interrupted, the ions retained are displaced, the elution solution is analysed for Na^+ or Mg^{2+} and the estimated amount of these cations is expressed as a fraction F of the total capacity of the cation exchanger volume used.

For the determination of the exchange rate at the solution concentration 0·01N the variation of the height of the exchange zone in the fixed bed in relation to the linear filtration velocity of a solution was employed. These experiments were performed with 50 ml of the cation exchanger in a glass laboratory column 9 mm i.d. The linear filtration velocities were within the range of 15—80 m h^{-1}. The height of the exchange zone was calculated from the relation

$$h_z = \frac{tL_vL_c}{R_c + 0.4L_c},$$ (1)

where h_z the height of the exchange zone (cm), L_c the inlet concentration (val l^{-1}), R_c the break-

through capacity (val l^{-1}), L_v the linear velocity of the solution flow related to the empty cross-section of the column (cm h^{-1}), t time elapsed between the breakthrough of 3% and 97% of the inlet concentration (h).

All measurements were performed at 20°C.

Analytical Methods

The course of the sorption on the fixed bed was followed by an alkalimetric titration of the acid in the effluent. The course of exchange in the fluidised bed was followed by the elution solution analysis: Mg^{2+} was determined by titration with EDTA using eriochrom black T as the indicator, the H^+—Na^+ exchange was followed by alkalimetric titration of the acid (after regeneration by 1M-NaCl solution).

RESULTS AND DISCUSSION

The experimental conditions chosen (the high solution concentration or the high linear filtration velocity of the solution) ensure the exchange rate to be controlled predominantly by the particle diffusion in all the cases studied.

From the course of the H^+—Na^+ and H^+—Mg^{2+} exchanges at the solution concentration 0·2N the exchange halflives were determined as given in Table I.

As mentioned above, the particle diffusion rate is determined by the content of the cross-linking agent (DVB) in the matrix. Despite this we find (Table I) the overall exchange rate to be the lowest for the gel-type cation exchanger with 16% DVB, whereas the exchange rate of the macroporous exchanger with 22% DVB can be compared to the gel type exchanger containing only about 14% DVB (ref.)[4]. This
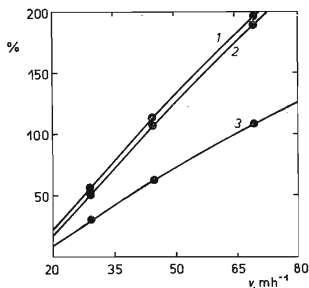

Fig. 1

Relative Increase in the Height of the Exchange Zone for the H^+—Na^+ Exchange

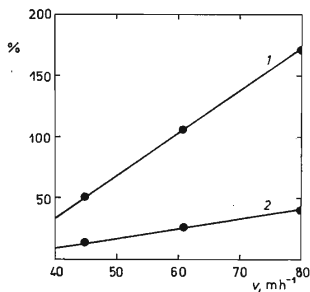c 00·1N; 15 m h^{-1} = 0%. *1* Dowex 50X16, *2* Amberlite IR 200, *3* Dowex 50X8.

Fig. 2

Relative Increase in the Height of the Exchange Zone for the H^+—Mg^{2+} Exchange

c 0·01N; 30 m h^{-1} = 0%. *1* Amberlite IR 200, *2* Dowex 50X16.

TABLE I

H$^+$—Na$^+$ and H$^+$—Mg^{2+} Exchange Rates for the Solution Concentration 0·2N

Cation exchanger	% DVB	Exchange halflife, s	
		H$^+$—Na$^+$	H$^+$—Mg^{2+}
Dowex 50	8	27	29
Dowex 50	16	50	125
Amberlite IR 200	22	35	90

enhanced exchange rate occurs for the H$^+$—Na$^+$ as well as H$^+$—Mg^{2+} reactions and is accounted for by the invasion of the electrolyte into the macroporous matrix.

For the lower concentration of the solution 0·01N, the exchange rate was expressed by the relative change in the height of the exchange zone with the linear filtration velocity of the solution (Fig. 1 and Fig. 2).

For the H$^+$—Na$^+$ exchange (Fig. 1) the same order of exchange rates of the various exchangers was observed as at the concentration 0·2N: the increase in the height of the exchange zone is the highest (and hence the reaction rate the lowest) for the gelular cation exchanger with 16% DVB. The exchange rate of the macroporous exchanger is, however, only slightly higher. Obviously the invasion of NaCl into the macroporous matrix proceeds at the concentration 0·01N still at a sufficient velocity, but to a lower extent than if higher concentrations are applied.

For the H$^+$—Mg^{2+} exchange (Fig. 2), however, the order of the exchange rates is reversed: the increase in the height of the exchange zone is the greatest for the macroporous cation exchanger, which indicates that during the exchange of bivalent cations the velocity of MgSO$_4$ invasion is markedly suppressed even in the macroporous matrix and therefore the overall exchange rate is controlled by the diffusion of the ions through the gelular phase of the resin matrix only.

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