

REGULARITIES OF ESTABLISHING ION-EXCHANGE EQUILIBRIUM IN SOLID-PHASE CATIONITE

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Ion exchange resin (IER) is used in filters to reduce water hardness; as part of softener filters and systems of complex water purification. Also, ion-exchange resins (cationites) are part of multicomponent mixtures for flow-through models of filters and pitcher filters. Ion exchange resin is a high-molecular synthetic compound with a three-dimensional gel and macroporous structure. A feature of IER is the ability to enter into exchange reactions with solution ions. Therefore, one of the most important characteristics of IER operation is the ion transfer number (TN).

Consider a model of an ion-exchange resin particle with a gel nonporous structure, which contains mobile counterions (Na^+)_m and fixed ions (OH^-)_f chemically bound to the matrix. This is the structure of cation exchange resin KU-2-8 in the working Na^+ form with a total exchange capacity of 1.9 mmol/g. Imagine a model of a particle in the form of a plate with a thickness of h_0 (Fig. 1a), which is in contact with a perfectly stirred NaOH solution. To simplify the analysis, we will assume that the chemical composition of the particle in the process of establishing exchange equilibrium changes over time, as shown in the figure, but at the same time, the particle itself remains homogeneous with an average concentration of C_{max} . This approximation does not affect the results of further qualitative analysis but prevents the subsequent occurrence of mathematical complications.

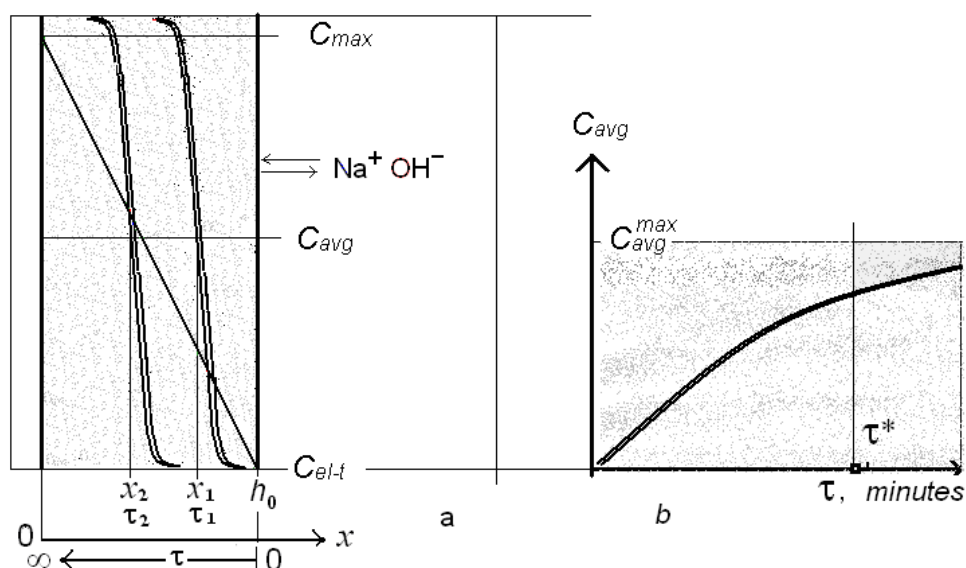


Fig. 1. Concentration profiles of ions in the ionite phase at separate consecutive moments of time (a) and the dynamics of changes in the average concentration C_{avg} .(b)

At $\tau \rightarrow \infty$, the dependence of $C_{avg}(\tau)$ asymptotically approaches the limit C_{avg}^{max} . The diagonal in Fig. 1a is the dynamics of the average concentration's temporal change in the saturation or regeneration process (non-linear time scale τ).

Pay attention to the fact that in Fig. 1b, the qualitative graph $C_{avg}(\tau)$ has a typical exponential monotonic form without characteristic points on the graph:

$$C_{cp} = C_{cp}^{max} \cdot [1 - \exp(-\tau)] \quad (1)$$

But this equation is not suitable for use because the argument of the transcendental exponent is the dimensional number τ . The equation can be made more convenient by entering into it the formal characteristic time of the process τ^* , in which the argument of the exponent will be a dimensionless number, and the value of the equation in square brackets $C_{avg}/C_{avg}^{max} = (1 - e^{-1}) = 0.631$,

$$C_{cp} = C_{cp}^{max} \cdot \left[1 - \exp\left(-\frac{\tau}{\tau^*}\right) \right] \quad (2)$$

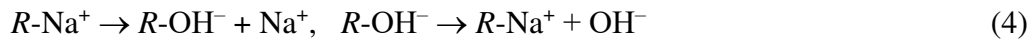
The derivative of (2) has a negative value:

$$\frac{d}{d\tau} C_{cp} = -\exp\left(-\frac{\tau}{\tau^*}\right) \quad (3)$$

This reflects an understandable regularity - in the process of ionite saturation or regeneration, the speed of the process gradually decreases due to the resistance of the medium to the diffusion flow, and the parameter τ^* precisely characterizes this speed.

It should be noted that the NaOH concentration in the saturated KU-2-8 ionite is $0.0265 \text{ mol} \cdot \text{cm}^{-3}$, while in the aqueous solution, it is 3 orders of magnitude lower, and in Fig. 1, it practically coincides with the zero value of the ordinate.

In the mode of establishing ion-exchange equilibrium, two flows of ions of the same charge with opposite signs move in the resin phase: Na^+ and OH^- ions. Both ion streams move at the same speed in parallel in the same direction, because in the act of ion exchange, one ion is absorbed, while an ion of the opposite sign appears:



In this equation, the symbol $R\text{-Na}^+$ means one element of resin R ($\text{C}_8\text{H}_8 + \text{C}_{10}\text{H}_{10}$, $M = 104.15 \cdot 0.5 + 130.20 \cdot 0.5 \text{ g/mol}$) chemically bound with the Na^+ ion. The arrows indicate the directions of transformation in the processes of absorption or regeneration.

In the solid phase of the resin, some ions are absorbed due to the action of ion exchange mechanisms in the movement process along the x coordinate, and therefore, their concentration gradually decreases to the minimum value at the outlet. Similarly, ions of the opposite sign pass into the solution in the same amount, and their concentration in the resin also decreases.

Inside the solid phase, there is no convection, therefore, in the process of exchange, certain concentration profiles of $C(x)$ and corresponding concentration gradients of both ions are established there. At the same time, both gradients, $(dC/dx)^{\text{Na}}$ and $(dC/dx)^{\text{Cl}}$, also change in the same way, in the same direction.

The described phenomena of ion exchange in dynamics are the result of theoretical considerations. In a physical experiment, the initial and final state of the resin can be

determined by measuring the change in the concentration of the solution. The duration of the experiment τ_{EX} with constant stirring is several hours.

Over time, the resin is depleted, that is, the concentration profiles in Fig. 1 are not stationary and must change over time. However, in a relatively short experiment, the change in the state of the ion exchange resin is insignificant compared to long-term saturation-regeneration cycles. Therefore, as shown in Fig. 1, the ion concentration profiles can be considered practically stationary, and the conclusions obtained during their analysis - correct.

In the solution in the diffusion layer Δ of great thickness, which is orders of magnitude greater than the thickness δ of the diffuse part of the electric double layer ($\Delta \gg \delta$), some effective value of the diffusion coefficient D_{\pm} and the same speeds and directions of ion movement are established, $g^{OH} = g^{Na}$,

$$D_{\pm} = \frac{2D^{Na} \cdot D^{OH}}{D^{Na} + D^{OH}}, \quad (5)$$

$$g^{OH} = -D_{\pm} \cdot \frac{dC^{OH}}{\Delta}, \quad (6)$$

$$g^{Na} = -D_{\pm} \cdot \frac{dC^{Na}}{\Delta} \quad (7)$$

The diffusion potential arises in the medium where there is an electrolyte concentration gradient, and the ion mobilities are not the same. A gradient also occurs at the interface of the phases, that is, on the surface of the ionite. By the Planck-Henderson equation, a corresponding value of the diffusion potential is established at the interface, which in the first approximation (under the condition that transfer numbers are independent of the concentration of the electrolyte) is a linear function of the difference in ion transfer numbers:

$$E_{DIF} = \frac{D^{Na} - D^{OH}}{D^{Na} + D^{OH}} \cdot \frac{RT}{F} \ln \left(\frac{C_2}{C_1} \right) = (n^{Na} - n^{OH}) \cdot \frac{RT}{F} \ln \left(\frac{C_2}{C_1} \right), \quad (8)$$

where C_2 and C_1 are the concentrations in the contacting phases.

The equality of the flows of both ions through the solution-ion exchanger interface is ensured by the electric fields arising in both phases at the boundary of their interface and automatically maintain the necessary concentration profiles $C^{OH}(x) = C^{Na}(x)$ in both phases.

If you calculate the speed of each of the ions using the Nernst-Einstein formula:

$$D = v^0 \cdot \left(\frac{RT}{zF} \right) \quad (9)$$

where v^0 is the mobility of the ion (at $C \rightarrow 0$), for a simple one-component electrolyte under the condition $v_+ = v_-$, which operates in the presence of a diffusion potential, we obtain equations for individual ion flows:

$$g^{OH} = -v_+^0 \cdot \frac{RT}{z_+ F} \cdot \frac{1}{C_+} \cdot \frac{dC_+}{dx} - v_+^0 \cdot \frac{dE}{dx} \quad (10)$$

$$g^{Na} = -v_-^0 \cdot \frac{RT}{z_- F} \cdot \frac{1}{C_-} \cdot \frac{dC_-}{dx} + v_-^0 \cdot \frac{dE}{dx} \quad (11)$$

According to the law of electroneutrality, these flows have the same numerical values. Under equilibrium conditions, the concentration gradients of both ions will also be the same.

By integrating the system of equations (10, 11), we find the value of the effective diffusion coefficient D_{\pm} according to (5) and the diffusion potential $E_{DIF} = dE/dx$ according to (8).

A feature of the system of Planck-Henderson equations (10, 11) is that the diffusion potential assumes such a value when the oppositely directed diffusion and migration components (the first and second terms in each equation) are equal to each other.

In the solution of equations (10, 11) along the coordinate x in Fig. 1a, the transfer numbers of both ions change. On the right boundary (electrolyte), the transfer numbers are the same as in the free NaOH solution: $n^{Na^+} = 0.38$, $n^{OH^-} = 0.62$. In the solid phase of the ionite in the direction of the boundary $x=0$, they change: for a mobile ion, n^{Na^+} increases, and for a fixed n^{OH^-} decreases. Ideally, at $\tau \rightarrow \infty$, the concentration profile should become linear, and the transfer numbers at $x=0$ should equal $n^{Na} = 1$, $n^{OH} = 0$. In reality, the duration of establishing exchange equilibrium in experiments is relatively small, and to a first approximation, the profiles can be considered stationary. Their use for the analysis of equations (9-11) is permissible.