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Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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**To cite this Article** Pawlowski, Lucjan and Zytomirski, Stanislaw(1975) 'The Influence of Ion Exchange Capacity and Total Concentration of Solution of Ions of Different Valency on Their Chromatographic Separation', Separation Science and Technology, 10: 1, 33 — 37

**To link to this Article: DOI:** 10.1080/00372367508057066

**URL:** http://dx.doi.org/10.1080/00372367508057066

SEPARATION SCIENCE, 10(1), pp. 33–37, 1975

## NOTE

# The Influence of Ion Exchange Capacity and Total Concentration of Solution of Ions of Different Valency on Their Chromatographic Separation

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## Abstract

The influence of ion exchange capacity and total concentration of ions of different valences on the width of the working zone in a chromatographic column was analyzed by means of a theoretical investigation of the mathematical relations between the equations of the Glueckauf theory and equations of the law of mass action.

We attempted to determine by mathematical analysis the influence of ion-exchange capacity and the total concentration of solutions of ions of different valencies on their separation. In a previous publication (*1*), we solved this problem by the graphical method. In this paper we begin our discussion with the Glueckauf plate theory and the law of mass action used for the heterogeneous double exchange reaction between the ions contained in the ionite and in the solution.

According to plate theory, the two following parameters describe the effectiveness of separation processes: (a) the equivalent height of theoretical plate (EHTP), which characterizes the separation efficiency of the column, and (b) the separation factor ($K_s$), which determines the ion equilibrium between the ionite and the solution, so that it characterizes the separation ability of the ions.

Let us give the heterogenic double exchange reaction in the form

$$m\mathrm{R}_n\text{-}\mathrm{A}^n + n\mathrm{B}^m \leftrightarrows R_m\text{-}\mathrm{B}^m + m\mathrm{A}^n \tag{1}$$

The interface equilibrium state ionite–solution can be described by the law of mass action used directly to Reaction (1) only when the equilibria are simple ionic ones; when the complexing species are present in the system, the equilibria are more complicated. In this case, we can write for simple ionic equilibria:

$$K = \frac{[\mathrm{A}^n]^m[\mathrm{R}_m - \mathrm{B}^m]^n}{[\mathrm{R}_n - \mathrm{A}^n]^m[\mathrm{B}^m]^n}$$

or

$$\psi(K, C_0, q_0) = K\left(\frac{C_0}{q_0}\right)^{n-m} = \frac{[1 - y^{(n)}]^m[x^{(n)}]^m}{[y^{(n)}]^m[1 - x^{(n)}]^n} \tag{2}$$

Equation (2) will play an important role in our further discussion which concerns the material balance in the column. The balance is described by Eqs. (9)–(36) of Helfferich (*2*), presented here in a somewhat different form:

$$dl = -w\frac{d_q}{(\partial q/\partial t)} \tag{3}$$

where $\partial q/\partial t$ is the mass exchange rate, determined by particle diffusion:

$$\left(\frac{\partial q}{\partial t}\right) = \frac{D_r}{0.071r^2}(q^* - q) \tag{4a}$$

or by the film diffusion:

$$\left(\frac{\partial q}{\partial t}\right) = \frac{D_s}{-2\delta r}(c - c^*) \tag{4b}$$

From Eqs. (3) and (4a) we obtain:

$$dl = -w\frac{0.071r^2}{D_r}\frac{dx}{x - y}$$

or in the integrated form:

$$L = w\frac{0.071r^2}{D_r}\int_0^1\frac{dx}{x - y} \tag{5}$$

Glueckauf and Helfferich (*2*) have eliminated $y$ from Eq. (5) using the following definition of separation factor:

$$K_s = \frac{[\mathrm{A}^{(n)}][\mathrm{R}_m - \mathrm{B}^{(m)}]}{[\mathrm{R}_n - \mathrm{A}^{(n)}][\mathrm{B}^{(m)}]} = \frac{[1 - y][x]}{[y][1 - x]} \tag{6}$$

The relation, as it is defined above, is not adequate enough to give us any information concerning the influence of total solution concentration and capacity of ionite on the separation of the ions of different valencies.

However, if we use Eq. (2) instead of Eq. (6) for the elimination of $y$ from Eq. (5), the influence will be defined by:

$$\psi(K, C_0, q_0) = K\left(\frac{C_0}{q_0}\right)^{n-m}$$

The set of Eqs. (2) and (5) cannot be solved by analytic methods, but it is possible to obtain exact answers from using numerical methods.

In our case the discussion of limiting cases appears profitable. From Eq. (2), when $\psi(K, C_0, q_0) \to 1$, we obtain $x \to y$, but when $(x - y) \to 0$, then

$$\int_0^1 \frac{dx}{x - y} \to \infty$$

This also means that the $L \to \infty$ (Eq. 5) when $\psi(K, C_0, q_0) \to 1$. The cases are illustrated in Fig. 1.

It is seen that for small $\psi(K, C_0, q_0)$, $L$ is also small. This means that the work zone is narrow, and thus the separation is sharp and the ions of higher valency are kept stronger in the ionite phase. As the value of $\psi(K, C_0, q_0)$ increases, the sharpness of the separation decreases and the range of the work zone becomes broader. However, the changes are rather small up to value of $\psi(K, C_0, q_0)$ equal to $\psi_1$. For the value $\psi_1 < \psi < 1$ the separation rapidly becomes worse, and in the vicinity of $\psi \cong 1$ it becomes practically impossible. After exceeding the value $\psi = 1$, up to $\psi_2$, it may be concluded from Eq. (5) that the width of the work zone rapidly decreases, and for $\psi > \psi_2$ the changes in the width of the work zone are negligible. The conclusions for $\psi > 1$ would be nonsense if we stuck with one and the same operation, say, $Ca^{2+}$ displacing $Na^+$; in that case the work zone concept would break down entirely since a nonsharpening boundary arises that will increase in width in proportion to the distance traveled. It would be correct only if we now reverse the operation, i.e., have $Na^+$ displace $Ca^{2+}$, so that, again, the preferred ion enters the column to displace the other ion. This reversed operation is used in regeneration in water softening to give a nonsharpening boundary at low concentration and then, above the concentration at which the Ca/Na separation factor is unity, to give a self-sharpening boundary "work zone" that becomes sharper as the concentration is further increased.

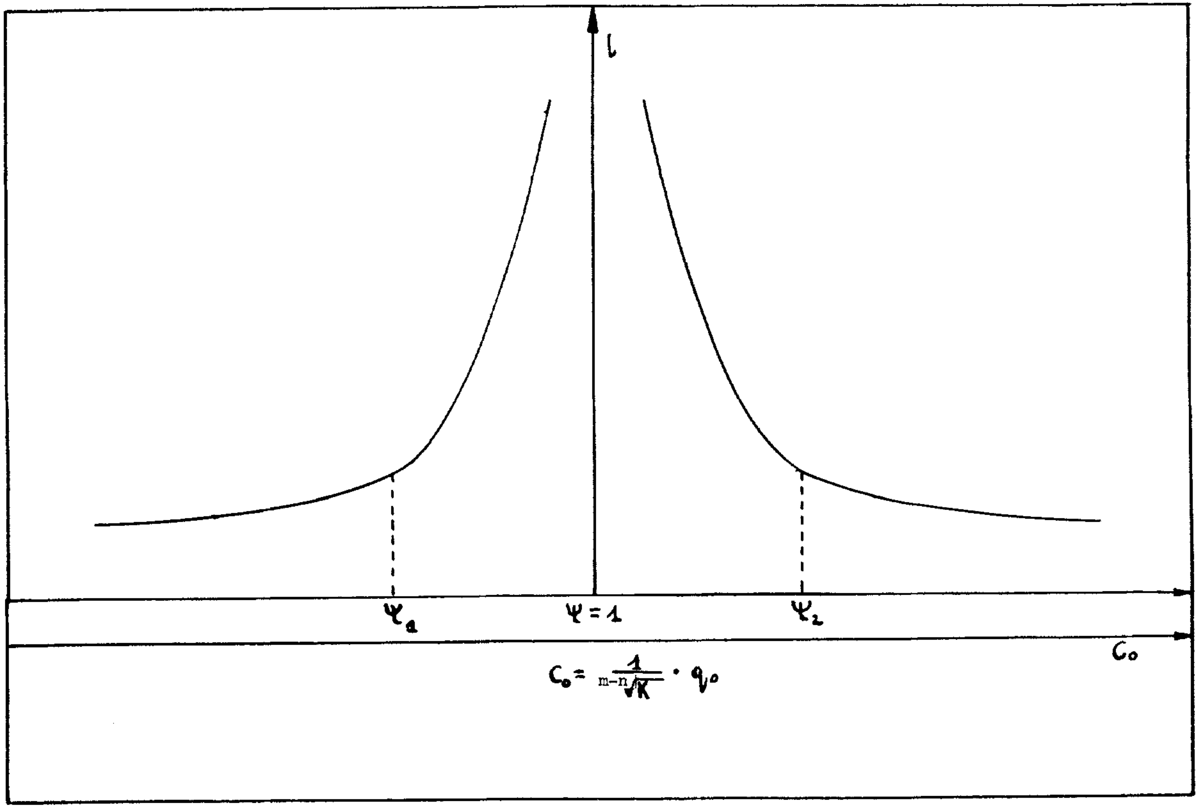

FIG. 1. Graphic representation of the mathematical relations of Eq. (5).

For

$$\psi(K, C_0, q_0) = K\left(\frac{C_0}{q_0}\right)^{n-m}$$

assuming that $K$ and $q_0$ are constant, we do not care about the influence of the concentration on $K$, and we do not take into account the activity coefficient. We can say that Fig. 1 characterizes the dependence of the work zone width on $C_0$ (see $C_0$ axis).

Concentration plays an important role for $K$ near 1. The dependence of $L$ on $C_0$ is similar to the case where the rate of ion exchange is determined by film diffusion.

## REFERENCES

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*Received by editor May 20, 1974*