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## Discussion

# Comments on a general theory of ion-exchange chromatographic separation processes

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### Abstract

In this paper, a theory presented by Kakihana and Oi is discussed and the mistakes made in their theoretical development are pointed out. From the discussion, it is concluded that application of this theory to experiments will need further consideration.

*Keywords:* Ion-exchange chromatography, theory

### 1. Introduction

As an important separation technology, ion-exchange chromatography has been widely applied to the separation of various kinds of mixtures. Theoretical treatment of chromatographic processes is an old and a complex problem. There are a large number of theories that differ from each other in their assumptions and their degree of complexity [1,2]. In a series of papers [3–8], Kakihana and Oi presented a theory for chromatographic separation processes and applied it to experiments.

In deriving their equation, Kakihana and Oi divided the causes that make the concentration of species  $i$  in a volume element  $\Delta V$  change into two parts: the first part originates from the movement of the species  $i$  caused by the convective transport; the

second part originates from the movement of species  $i$  caused by dispersive transport. Then their equation was given as

$$\frac{\partial C'_i}{\partial t} = D'_i(x, t) \frac{\partial^2 C'_i(x, t)}{\partial x^2} - v'_i \frac{\partial C'_i}{\partial x} \quad (1)$$

where, in their definition,  $v'_i(x, t)$  is the velocity of species  $i$  caused by the external force acting along the  $x$ -axis.  $D'_i(x, t)$  denotes a kind of mathematical index representing all mass transfer effects caused by a concentration gradient in and between those phases along the  $x$ -axis,  $C'_i(x, t)$  is the concentration of species  $i$  at  $x$ . The first and second terms on the right-hand side of Eq. (1) originate from internal concentration gradients and the external force, respectively, in their theory.

In chromatography, it is well known [1,2,14] that the generally used equation describing chromatographic separation processes is

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$$\frac{\partial C_i}{\partial t} + v_0 \frac{\partial C_i}{\partial x} = \frac{\partial}{\partial x} D_i \frac{\partial C_i}{\partial x} - F \frac{\partial q_i}{\partial t} \quad (2)$$

where  $v_0$  is the linear velocity of mobile fluid along the  $x$ -axis,  $C_i(x, t)$  is the concentration of species  $i$  in the mobile phase and  $D_i$  is the dispersion coefficient.  $F$  is the phase ratio,  $(1-\alpha)/\alpha$ , and  $\alpha$  is the porosity of the column;  $\partial q_i/\partial t$  represents the rate of accumulation of species  $i$  in stationary phase.

Eq. (2) has been widely applied in the study of column chromatography [1,2].

Generally speaking,  $q_i$  has a very complex relation with  $C_i$ .

For a mixture of two different species A and B, in an attempt to work with mobile phase concentrations and to get rid of the  $q$ 's, one has to divide out a factor  $(1+f')$ , where  $f'$  is the derivative of the isotherm,  $\partial q_i/\partial C_i$ . Thus, their  $v_A$  and  $v_B$  are in fact values of

$$v_0/(1 + Fdq_A/dC_A)$$

and

$$v_0/(1 + Fdq_B/dC_B)$$

It should be pointed out that this is only applicable for either a one-component case, or a linear multi-component case. In fact in a two-component non-linear case the term with the time derivatives of  $\partial q_i/\partial C_i$  in Eq. (2) (for A) results in:

$$\frac{\partial q_A}{\partial t} = \frac{\partial q_A}{\partial C_A} \frac{\partial C_A}{\partial t} + \frac{\partial q_A}{\partial C_B} \frac{\partial C_B}{\partial t} \quad (3)$$

which leads to a set of coupled differential equations. It is not possible to divide out a factor, in an attempt to work with the mobile phase concentrations  $C_A$ ,  $C_B$ , as  $C_B$  also occurs.

Although one can transform Eq. (2) into Eq. (1) in the way Kakihana and Oi did [3], after the transformation the physical meanings of the parameters  $D'_i$ ,  $v'_i$  in Eq. (1) are very ambiguous. And it is inappropriate to say that "a fundamental equation for chromatography can be derived starting from a very simple concept that the chromatographic movement of species can be expressed as a sum of the movement caused by the external force [the second term on the right-hand side of Eq. (1)] and the movement caused by the internal concentration gradients [the first term on the right-hand side of Eq. (1)]" [3–8],

especially for a multi-component, nonlinear case. Another problem that will arise is how to apply Eq. (1) to actual separation processes such as displacement ion-exchange chromatography.

When Kakihana and Oi applied Eq. (1) to a nonlinear chromatographic separation system (displacement ion-exchange chromatography) in which the sum of the concentrations of all the species is kept constant during chromatographic processes, for a mixture of two different species A and B, they obtained the following equations from Eq. (1) [3–8]:

$$\frac{\partial C'_A}{\partial t} = D'_A \frac{\partial^2 C'_A(x, t)}{\partial x^2} - v'_A \frac{\partial C'_A}{\partial x} \quad (4)$$

$$\frac{\partial C'_B}{\partial t} = D'_B \frac{\partial^2 C'_B(x, t)}{\partial x^2} - v'_B \frac{\partial C'_B}{\partial x} \quad (5)$$

where they made the assumptions that  $D'_i$ ,  $v'_i$  were constants.

By solving Eq. (4) and Eq. (5), they got the following solutions for  $C'_A$  [3]

$$C'_A = -k_0 + C \exp(kKt) \exp(kx) \quad (6)$$

where

$$k = \frac{v_A - v_B}{D_A - D_B}; \quad K = v_B \left[ \frac{D_B(v_A - v_B)}{v_B(D_A - D_B)} - 1 \right] \quad (7)$$

From Eqs. (4,5), it is clear to see that Eqs. (4,5) are linearly independent. They are only suitable to linear chromatography. In ion-exchange displacement chromatography, the movements of different species are coupled with one another and the mathematical equations that describe the separation processes must also be coupled ones. It is impossible to describe such a chromatographic process by Eqs. (4,5). The correctness of Eq. (6) is doubtful.

In order to see this more clearly, one can rewrite Eq. (6) as

$$C'_A = -k_0 + C \exp[k(Kt + x)] \quad (8)$$

It is obvious that Eq. (7) represents a propagating wave which travels with velocity  $-K$  in the direction of  $x$ . If one observes the experiment in the framework that is moving with the velocity  $-K$ , one will get a constant profile that does not change with time. This is not true, otherwise, how can one get the species separated? So we can say that Kakihana and

Oi's theoretical treatment here is incorrect and it cannot be applied to experiments.

In conclusion, we would like to point out that:

(1) More consideration should be taken into account when applying the theory of Kakihana and Oi to actual separation processes, especially for multi-component, non-linear chromatography.

(2) The theoretical result (Eq. (5)) obtained by them from Eq. (1) is not valid and is inapplicable to experiments.

There is in practice a great demand for chromatography column theories. At present, two basic theories are commonly used to study the processes that occur in a chromatographic column, the local theory and the rate theory. Both are essential to understanding the function of the column and column design, and they were developed by Martin and Synge in 1945 [11], and Van Deemter et al. in 1956 [12]. Together with the mass balance model proposed by Lapidus and Amundson in 1952 [9,10] and Glueckauf in 1955 [13], they are still the basis on which modern column theories have been built. In addition, for nonlinear chromatography, the coherence state theory, developed by Helfferich, has been successfully applied [14].

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