

Review

A retrospective on the solution of the ideal model of chromatography

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ABSTRACT

In an attempt to clarify the difficulties encountered in finding solutions of the ideal model of chromatography and to justify these solutions, the history of the theoretical work performed on this model is reviewed. The publications of Wilson, DeVault, Glueckauf, Helfferich, Klein, Rhee, Aris and Amundson are analyzed, the efforts and successes of these authors are discussed and the rationale for this endeavor is explained.

In a special occasion [1], we were credited with the "...tremendous task of solving the ideal chromatography problem for a two-component competitive Langmuir equilibrium" [2]. This flattering statement requires further explanation. In an attempt to clarify this issue and put into perspective our own contribution, we review briefly the history of the ideal model of chromatography.

This model assumes an ideal column, with no axial dispersion and an infinite rate of mass transfer, achieving constant and immediate equilibrium between the two phases of the system. The differential mass balance of chromatography for this model is simply written as

$$\frac{\partial C}{\partial t} + F \cdot \frac{\partial q}{\partial t} + u \cdot \frac{\partial C}{\partial x} = 0 \quad (1)$$

where q and C are the concentrations of the component in the stationary and mobile phases

at equilibrium [$q = f(C)$, isotherm], respectively, t and x are time and length, respectively, F is the phase ratio [$F = (1 - \epsilon)/\epsilon$, ϵ being the total porosity of the packing bed] and u is the mobile phase flow velocity.

The practical importance of the ideal model stems from its ignorance of mass transfer resistance. Its solution explains to us exactly what it is that the thermodynamics of phase equilibrium is trying to accomplish in the column. If we understand that, we can turn it to our own advantage, and achieve almost all what thermodynamics allows, but we can never hope to do better than that. Further, because the model is simple, it has analytical solutions in some instances. These solutions can be used for a study of the migration and separation of high-concentration bands in non-linear chromatography. Because of the finite column efficiency, the features of these solutions will be somewhat blurred, but in most instances they will remain recognizable.

An equation similar to eqn. 1 was derived first by Wicke [3] in 1939, and independently, a year later, by Wilson [4]. In their equations, these

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authors omitted the term $\partial C/\partial t$. Wicke did not pursue the study of the ideal model, but that of the equilibrium-dispersive model [5]. Wilson studied the solution of his equation for a single component with a Langmuir isotherm [4]. He recognized that this equation can propagate concentration discontinuities, a conclusion which is also valid for eqn. 1 (if we replace q by $C + Fq$ in the equation derived by Wicke or Wilson, it becomes identical with eqn. 1; thus, in spite of the error made, the conclusions in ref. 4 remain qualitatively correct). He did not realize, however, that the solution includes also the formation of a diffuse boundary on the rear of the band, even for a rectangular pulse injection. Wilson concluded that both boundaries remain vertical, and that the band width of an injection pulse remains constant, conclusions which are valid only for a linear isotherm.

DeVault [6] considered the solution of eqn. 1 using convex upwards and downwards isotherms. He derived the correct solution for the diffuse boundary and showed that this diffuse boundary appears on the rear of the band in the case of a convex upwards isotherm and on the band front in the case of a convex downwards isotherm (in the rest of this paper, unless mentioned otherwise we assume that the equilibrium isotherms are convex upwards, like the Langmuir isotherms; the rear boundary is diffuse and the front is vertical, *i.e.*, is a concentration shock). He also suggested that the reverse procedure could be used to derive the isotherm from the experimental diffuse boundary, by integration. The classical frontal analysis by characteristic points (FACP) and elution by characteristic points (ECP) methods of isotherm determination are derived from this theoretical result [7–10]. DeVault [6] used the discontinuous solution of Wilson [4] to account for the front of the band, and explained the origin of the concentration shock in physical terms. The area of the profile is conservative and the shock takes place at a length (concentration profile) or time (elution profile) such that the integral of the concentration profile becomes equal to the injected area. Weiss [11] arrived independently at the same description of the band profile for a single component. Later, the solution of the ideal

model for a single component was extended by Glueckauf to the case of a sigmoidal isotherm [12].

Finally, DeVault [6] recognized the effect of competition between the two components of a binary mixture. He made several qualitative observations of importance. For example, he showed that with a convex upwards isotherm the individual band fronts of the two components are self-sharpening, and he explained the origin of the displacement effect. He also suggested that the concentration of the first (*i.e.*, less retained) component in the first band, where it is pure, is higher than in the original solution, while the concentration of the second, slower moving component in the rear band, where it is pure, tends to be smaller than in the mixed band. However, he could not give a solution to the two-component problem.

Further important progress was made by Offord and Weiss [13], who assumed, without demonstration, that the velocities associated with the concentrations C_1 and C_2 found simultaneously on a diffuse boundary are equal (this assumption is equivalent to the concept of coherence, a concept of critical importance for further progress, introduced by Helfferich [14]; it states that coherence is a state of stability that develops from arbitrary non-coherent conditions, so distance–time regions of non-coherence are finite). All the successful work dealing with the solution of the two-component problem is based on this postulate, although only Klinkenberg [15] realized its importance before the work of Helfferich [14]. This relationship provides the key to the calculation of the diffuse boundaries in the mixed zone, when the bands of the two components are not yet separated. The second part of their work, however, was marred by an unfortunate error [16–18].

Hence there is no doubt that Glueckauf [8,19] was the first to solve the ideal model of chromatography for two components with competitive Langmuir isotherms and to obtain an analytical solution. He determined the two individual profiles during their migration and their progressive separation. He showed the existence of two stable concentration discontinuities, one in front of each component band and of a concentration

plateau on the rear diffuse boundary of the second band. By writing an independent mass balance for these discontinuities, he could study their migration and decay. He also described the band profiles in frontal analysis and in displacement chromatography of a binary mixture [8]. This paper was considerably in advance on its time, and it remained largely ignored by chromatographers, for several reasons.

First, the presentation of Glueckauf's solution is complex [8,19], in part because the mathematics available to him were incomplete, partly because of an unfortunate choice of the variables and symbols used, and partly because of the lack of a considerable amount of the details which are needed by those who have a more modest understanding of mathematics. More importantly, the rapid development of instrumentation in the late 1940s and 1950s and the availability of sensitive on-line detectors caused analytical chromatography to be more and more often carried out under linear conditions. In linear chromatography, peaks are symmetrical and do not interact. Chromatograms are easy to account for and a sophisticated theory is unnecessary. The renewed interest in preparative chromatography observed in the recent years has rekindled concern for the ideal model of chromatography.

Like the solutions of DeVault [6] and Weiss [11] for the single-component problem, and although it is correct from the point of view of physical chemistry, Glueckauf's handling of the concentration discontinuities [8] was based on physical intuition. It was not and could not have been founded on a rigorous mathematical derivation. The relevant fundamental results of the theory of partial differential equations had not yet been derived and published. As shown by DeVault [6] and Weiss [11], the definition of a solution of the equations of the ideal model is not easy. These equations can propagate discontinuities [20,21]. This is due to the fact that a velocity is associated with each concentration. With a Langmuir isotherm, the velocity associated with a concentration increases with increasing concentration. The rear profile is continuous and spreads because the higher a concentration, the faster it moves along the column. On the

front, however, the high concentrations cannot pass the low concentrations, and all the concentrations pile up into a discontinuity. A solution of a system of partial differential equations which cannot be continuously differentiated everywhere (*e.g.*, which contains a discontinuity) is called a weak solution. The theory of characteristics [22] explains the appearance, growth, decay and collapse of these discontinuities or shocks. It also accounts for the continuous parts of the solution.

The concept of weak solutions and the shock theory were developed around 1950 by Courant and Friedrichs [23] and by Lax [24]. The difficulty is that, from the mathematical point of view, there is an infinite number of weak solutions to the equation of the ideal model. For example, as a discontinuity can be propagated at a certain velocity, a function only of its height [22], and a constant concentration is a trivial solution of eqn. 1, any rectangular plug is a weak solution. Only one of this infinity of weak solutions is acceptable from a physical point of view, however. The proper solution of eqn. 1 is not uniquely determined until the entropy condition [23,25] is introduced to regulate the direction (*i.e.*, sign) of the concentration jump across a discontinuity. Later, Oleinik [26] formulated the generalized entropy condition, valid for any isotherm. Rhee *et al.* [27] also proposed the use of a diffusional term whose coefficient tends towards zero. The application of the mathematical entropy condition has been discussed by Rhee and co-workers [20,22,27] and recently reviewed by Rouchon *et al.* [28]. In the single-component case, all the conditions have been shown to be equivalent [26,29]. To be acceptable as a solution of a physical problem, a weak solution should contain diffuse parts which all satisfy the partial differential equation(s) of the problem, while its discontinuity satisfies the entropy or shock condition.

The extension to multi-component systems of the results obtained for the single-component eqn. 1 seems reasonable from the physical viewpoint, but is not always without dangers when there are no solid mathematical proofs. In the multi-component case, very few results are available, although Di Perna [30] has shown the

existence of a solution for some specific systems and for a finite boundary condition.

A turning point in the study of the solutions of the ideal model of chromatography occurred in 1970, with the publication of two major works, by Helfferich and Klein [31] and by Rhee *et al.* [20], which basically ended the fundamental study of this model. Whereas the former is more comprehensive and is dedicated more directly to ion-exchange chromatography, the latter is more mathematically rigorous and its rationale is better suited to the study of adsorption chromatography. However, the results of these two works are essentially equivalent [32,33].

Rhee *et al.* [20] incorporated all the acquisitions of the theory of partial differential equations and supplied the first really rigorous solution of the problem. Later, this work was extended to the case of displacement chromatography [34], giving results equivalent to those of Helfferich and Klein [31]. In this work, they analyzed the separation of multi-component mixtures using the theory of characteristics and studied the interactions between the concentration shocks and centered simple waves. Given the mathematical intricacy of the problem [4,16–18], we must admire the intuition of DeVault [6] and Glueckauf [8] which let them find their way to the correct physical solution. As did Glueckauf [8], Rhee *et al.* [20] included in their paper chromatograms that illustrate the major features of the solution. The presence of concentration shocks, the formation and decay of concentration plateaux, the origins of the displacement and the tag-along effects are clearly illustrated. Unfortunately, this paper does not contain a detailed explanation of the derivation of the various equations describing the complete individual profiles, and leaves the reader with the task of rediscovering these details.

Meanwhile, Helfferich and Klein [31] had developed a theory of interference based on the ideal model of chromatography, the competitive Langmuir isotherm, the coherence concept [14] and the use of the *h*-transform. They used this theory to calculate the individual band profiles during the progressive formation of the isotachic train in displacement chromatography, and during the elution and separation of pulses in

elution chromatography. The results of Helfferich and Klein have been widely used in the literature to account for experimental results in displacement chromatography. This method allowed the first calculated separation of a fifteen-component rare earth mixture by displacement, which was a remarkable achievement [35,36]. Although real columns have a finite efficiency and actual chromatograms always exhibit mixed zones and steep individual profiles (or “shock layers”) where the ideal model predicts sharp vertical boundaries (or shocks), the agreement reported [37] is often more than satisfactory.

Confronted with the need to compare the results of the ideal and the equilibrium-dispersive models of chromatography for high concentration band profiles, we found that the equations giving the coordinates of the characteristic points of the profile and the equations of its continuous parts were not available anywhere. We derived them using first [38] the characteristic method of Rhee *et al.* [20], and later [39] the *h*-transform of Helfferich and Klein [31]. These equations are now available for the separation chemist to calculate solutions with any set of parameters.

The practical importance of the ideal model of chromatography should not be underestimated. This model is relatively simple and it has an analytical solution. This solution is easy to calculate for any practical case, once the isotherm has been measured. It gives profiles that are in good agreement with the experimental band profiles at high column efficiencies or at high values of the loading factor (ratio of sample size to the amount needed for a complete monolayer) [40]. Thus, the solution of the ideal model, which is easy to derive from the equations we have reported, gives an excellent first approximation of the kind of individual band profiles to expect [38–41]. This can serve as a basis for an approximate optimization of the experimental conditions [42].

Deviations of actual chromatograms from the prediction of the ideal model are due as much to the finite column efficiency [40] as to deviations of the competitive isotherm from the competitive Langmuir model [43]. This latter behavior is prone to happen as soon as the two components studied, albeit both following the Langmuir

model for single-component isotherms, have different column saturation capacities. There is no analytical solution for any competitive isotherm more complex than the Langmuir model.

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