Transport in Porous Media **8**: 199–225, 1992.

Travelling Waves in the Transport of Reactive Solutes through Porous Media: Adsorption and Binary Ion Exchange – Part 2*

C. J. VAN DUIJN
TU Delft, Faculty of Technical Mathematics and Informatics, PO Box 356, NL-2600 AJ Delft, The Netherlands

and

P. KNABNER
Universität Augsburg, Institut für Mathematik, Universitätsstr. 8, D-8900 Augsburg, Germany

(Received: 10 May 1990; revised: 19 July 1991)

Abstract. We study travelling wave solutions for the model developed in Part 1 of this paper. We develop and discuss a condition characterizing their existence. The possibility of finiteness is investigated. We consider the convergence to various limit cases and point out their different qualitative behaviour. Numerical examples are discussed.

Key words. Travelling wave, self-sharpening front, mathematical analysis, mathematical model, adsorption, ion exchange.

0. Introduction

This paper is a sequel to van Duijn and Knabner (1992a). It contains the analysis of travelling wave solutions for the situations discussed in Part 1. All definitions and notation remain in force and the numbering is continued. A considerably more detailed version of this paper containing further indications of mathematical proofs, case studies and numerical examples is available (van Duijn and Knabner 1990).

The paper is organized as follows: Section 3.1 is devoted to the existence of travelling-wave solutions for problem TW, introduced in Section 1 of van Duijn and Knabner (1992). The existence is characterized by a condition (C), the wave-speed is given by (3.4). In Section 3.2, the relation between the classification of isotherms and condition (C) is discussed and combinations of convex and concave isotherms are investigated with respect to (C). Section 3.3 contains numerical computations of travelling waves. In Section 4, the phenomenon of finiteness is studied. By finiteness we denote the existence of a moving front, beyond which there is no mass. On the contrary, an infinite wave exhibits the physically

*This work was supported by the EC project 'Filtration and Nonlinear Diffusion Processes' (Contract No. SC1-0019-C(TT)).

inconsistent property that mass is distributed all the way downstream. In Section 5.1, the limit process $k \to \infty$ is considered, k being the rate parameter of the nonequilibrium adsorption. The convergence to the limit problem TWE and distinctions between TW and TWE are pointed out. Section 5.2 parallels this analysis for the limit process $D \to 0$, D being the diffusion-dispersion coefficient. The new aspect of the limit problem TWH is the possibility of shocks, i.e. of jumps in the dissolved concentration. Appendix C contains some closed form solutions for limit cases.

The enlarged version (van Duijn and Knabner, 1990) also contains a description of a numerical method for the computation of travelling waves.

3. Travelling Waves

Here we discuss the analysis needed to prove the existence and some properties of solutions of Equations (1.24) and the boundary conditions (BC). This we do first in Section 3.1. For more details and proofs, we refer to van Duijn and Knabner (1991). We recall that all isotherms ψ are assumed to fulfill (1.10) (ii)–(iv) and all rate functions f with their associated isotherm φ are assumed to fulfill (1.10) (i)–(iv) (see also (1.22), (1.23)). In order to carry out the analysis, a crucial condition on the isotherms φ and ψ is needed. This condition is discussed separately in Section 3.2. Some examples are given in Section 3.3.

3.1. THE ANALYSIS

Because the function ψ in Equation (1.24a) need not be differentiable in every point of $[0, u_m]$, solutions of this equation may be nonsmooth. We, therefore, have to interpret solutions of (1.24) in a weak sense. This we do as follows.

We first require that u and v are continuous functions in $\mathbb{R}$ (i.e. belong to the space $C(\mathbb{R})$). From Equation (1.24b) and the continuity of the rate function f, it then follows that v is also continuously differentiable in $\mathbb{R}$. ($v \in C^1(\mathbb{R})$). Using this in (1.24a) gives

$$(q-a)u - a\psi(u) - Du' \in C^1(\mathbb{R}).$$

From this observation and from the continuity of u and $\psi(u)$, we then obtain that u is also continuously differentiable in $\mathbb{R}$. We therefore use the following definition for solutions of problem TW:

DEFINITION 3.1. A triple $\{u, v, a\}$, with u and v being nonnegative functions defined on $\mathbb{R}$ and a a real number, is called a *travelling wave* for the boundary condition (BC) if

$$u, v \in C^1(\mathbb{R}),$$

$$Du' + a\psi(u) \in C^1(\mathbb{R}),$$

$$\left.\begin{aligned} &(Du' + a\psi(u))' = (q-a)u' - av' \qquad (3.1)\\ &-av' = kf(u,v) \qquad (3.2) \end{aligned}\right\} \text{ in } \mathbb{R},$$

u and v satisfy the boundary conditions (BC).

If ψ is a smooth function (e.g. $\psi \in C^1([0, u_m])$), then $\psi(u) \in C^1(\mathbb{R})$ and, thus, $u \in C^2(\mathbb{R})$. For such cases, the pair (u, v) forms a classical solution of Equations (1.24) and of (1.20) as functions of x and t.

We first integrate Equation (3.1). This gives the first-order equation

$$Du' + a\psi(u) = (q - a)u - av + A \quad \text{in } \mathbb{R}, \tag{3.3}$$

where A is a constant of integration. Applying the boundary conditions (BC) yields

$$a\psi(u^*) = (q - a)u^* - av^* + A,$$

$$a\psi(u_*) = (q - a)u_* - av_* + A.$$

We solve these equations for a and A. Using the notation of (1.28), we find for the wave speed

$$a = \frac{\Delta u}{\Delta u + \Delta\psi + \Delta v}\, q \tag{3.4}$$

and for the integration constant

$$A = a\left(-\frac{q - a}{a}\, u_* + v_* + \psi_*\right).$$

Note that in the original variables, the wave speed a reads

$$a = \frac{q^*}{\Theta\{1 + H(\lambda_1(\Delta\Psi/\Delta s) + \lambda_2)\}},$$

where H is given by (1.15) and $\Delta\Psi = \Psi(c^*) - \Psi(c_*)$.

In this expression, q^*/Θ denotes the interstitial water velocity. Observe that the chemicals are being transported at a speed which is reduced by a factor $\{1 + H(\lambda_1\, \Delta\Psi/\Delta s + \lambda_2)\}$ caused by reactions at sites Λ_1 and sites Λ_2.

We are left with the two first-order equations

$$\left.\begin{aligned} u' &= \frac{a}{D}\left\{\frac{\Delta\psi + \Delta v}{\Delta u}(u - u_*) - (\psi(u) - \psi_*) - (v - v_*)\right\} \\ v' &= -\frac{k}{a} f(u, v) \end{aligned}\right\} \quad \text{in } \mathbb{R}, \tag{3.5}$$

where u and v satisfy conditions (BC).

We look for a solution of these equations in the form of an orbit $\{(u(\eta), v(\eta)) \mid -\infty < \eta < \infty\}$ in the u, v plane (i.e. in the phase plane), connecting the boundary points (u^*, v^*) and (u_*, v_*). The existence of this orbit follows from certain invariance properties in the phase plane. To see this, we reverse the 'time' coordinate in (3.5). Setting $\xi = -\eta$ and writing now $'$ for $d/d\xi$, we find

$$\left.\begin{aligned} u' &= \frac{a}{D}\left\{\psi(u) - \psi_* + v - v_* - \frac{\Delta\psi + \Delta v}{\Delta u}(u - u_*)\right\} =: g_1(u, v) \\ v' &= \frac{k}{a} f(u, v) =: g_2(u, v) \end{aligned}\right\} \quad \text{in } \mathbb{R}. \tag{3.6}$$

We now look for an orbit $\{(u(\xi), v(\xi)) \mid -\infty < \xi < \infty\}$ connecting the reverse boundary points (u_*, v_*) and (u^*, v^*). We first consider the sign of u' and v'. For this purpose, we introduce the function

$$\ell(u) := v_* + \frac{\Delta\psi + \Delta v}{\Delta u}(u - u_*) - (\psi(u) - \psi_*) \quad \text{for } 0 \leqslant u \leqslant u^*, \tag{3.7}$$

which satisfies $\ell(u_*) = v_*$ and $\ell(u^*) = v^*$. In general, it is not monotone increasing. For example, if $u_* = 0$ and if ψ is of type (H) or of type (L), with $\psi'(0+)$ sufficiently large, then ℓ is decreasing in a neighborhood of $u_* = 0$ (see Section 5 for more details). Depending on the behaviour of the isotherm ψ, there may also be other intervals in $[u_*, u^*]$ in which ℓ is decreasing. From the first equation in (3.6), we find

$$v > \ell(u) \text{ implies } g_1(u, v) > 0 \text{ and thus } u' > 0$$

and

$$v < \ell(u) \text{ implies } g_1(u, v) < 0 \text{ and thus } u' < 0.$$

From the second equation, we obtain for the isotherm φ related to f according to (1.10)

$$v > \varphi(u) \text{ implies } g_2(u, v) < 0 \text{ and thus } v' < 0$$

and

$$v < \varphi(u) \text{ implies } g_2(u, v) > 0 \text{ and thus } v' > 0$$

Observe that $\varphi(u_*) = \ell(u_*)$ and $\varphi(u^*) = \ell(u^*)$ (use (1.25)). We now make an assumption about the behaviour of the isotherms φ and ψ which we need for the existence. Suppose

$$(C) \quad \begin{cases} \varphi(u) + \psi(u) > \dfrac{\Delta\psi + \Delta v}{\Delta u}(u - u_*) + v_* + \psi_*, & \text{for } u_* < u < u^*, \\ \text{or equivalently} & \\ \varphi(u) > \ell(u), & \text{for } u_* < u < u^*. \end{cases}$$

Because φ is strictly increasing, condition (C) also implies that

$$\varphi(u) > \underline{\ell}(u) = \max\{\ell(s) \mid u_* \leqslant s \leqslant u\}, \quad \text{for } u_* < u < u^*,$$

where $\underline{\ell}$ is now monotonically nondecreasing (see Figure 2). Then we can introduce the set

$$S = \{(u, v) \mid u_* < u < u^*, \ \underline{\ell}(u) < v < \varphi(u)\}.$$

In Lemma 2.3 of van Duijn and Knabner (1991) we proved that S is positive invariant. By this, we mean that if we take any pair $(u_0, v_0) \in S$ and if we consider

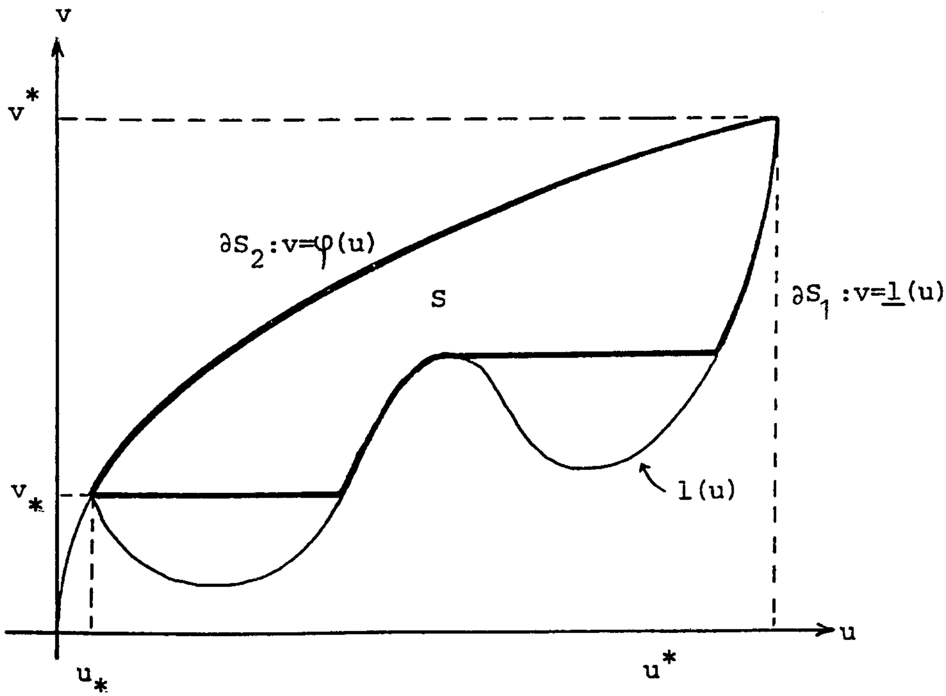


Fig. 2. Construction of the invariant set S.

the initial value problem

$$P\begin{cases} \left.\begin{aligned} u' &= g_1(u, v) \\ v' &= g_2(u, v) \end{aligned}\right\} & \text{for } \xi > 0, \\ u(0) = u_0, \qquad v(0) = v_0, \end{cases}$$

then $(u(\xi), v(\xi)) \in S$ for all $\xi > 0$ (i.e. the emerging orbit lies entirely in the set S). In addition, $u(\xi)$ and $v(\xi)$ are strictly increasing in $\xi > 0$, because $g_1 > 0$ and $g_2 > 0$ in S. With this invariance property, we can now prove the existence of an orbit connecting (u_*, v_*) and (u^*, v^*).

If $(u_*, v_*) = (0, 0)$, then the boundary values may be reached for some finite negative value of ξ. This may happen if the functions ψ or f are not Lipschitz continuous at the origin. This will result in a finite travelling wave. We give precise results about this behaviour in the next section.

Returning to our original variable η we have now the following result.

THEOREM 3.2. *Let condition* (C) *be satisfied. Then for any* $0 \leqslant u_* < u^* \leqslant u_m$ *and* $v_* = \varphi(u_*)$, $v^* = \varphi(u^*)$, *there exists a monotone travelling wave* $\{u, v, a\}$, *with* a *given by* (3.4), *which satisfy* $u' < 0$ *and* $v' < 0$ *on the set where* $u > u_*$ *and* $v > v_*$.

Consequently

$$\lim_{\eta \to -\infty} (u(\eta), v(\eta)) = (u^*, v^*).$$

If $u_* > 0$, *then* $u' < 0$ *and* $v' < 0$ *on the whole real line and*

$$\lim_{\eta \to +\infty} (u(\eta), v(\eta)) = (u_*, v_*).$$

If $u_* = 0$, *then a finite wave may exist, i.e. there may exist a number* L, *with* $-\infty < L < \infty$, *such that*

$$\lim_{\eta \uparrow L} (u(\eta), v(\eta)) = (0, 0),$$

and

$$(u(\eta), v(\eta)) = (0, 0), \quad \text{for } \eta \geqslant L.$$

In van Duijn and Knabner (1991), we showed that in fact condition (C) is not only sufficient but also necessary for the existence of a connecting orbit, i.e. for the existence of a travelling wave.

3.2. THE EXISTENCE CONDITION

In order to carry out the existence proof, we introduced in the previous section a condition on the behaviour of the sum of the isotherms φ and ψ. In terms of the original variables, this condition (C) reads

$$\lambda_1 \Psi(c) + \lambda_2 \Phi(c) > \frac{\lambda_1 \Delta\Psi + \lambda_2 \Delta s}{\Delta c}(c - c_*) + \lambda_1 \Psi(c_*) + \lambda_2 s_*,$$
$$\text{for } c_* < c < c^*.$$

This shows that condition (C) is a condition on the overall averaged isotherm only (compare (2.27)). Moreover, it is a global condition on the interval $[c_*, c^*]$, with the following geometrical interpretation: Given in the boundary conditions c^*, s^* at $x = -\infty$ and c_*, s_* at $x = +\infty$, a travelling wave occurs if and only if the overall averaged isotherm $\lambda_1 \Psi(c) + \lambda_2 \Phi(c)$ is above the chord between c_* and c^* for all intermediate values of concentrations c.

As the classification of isotherms only takes into account their properties at $c = 0$, there can be only a loose relation between the classification and the validity of condition (C) and only for $c_* = 0$. Returning to the scaled variables, we set

$$u_* = 0, \qquad \chi(u) := \varphi(u) + \psi(u).$$

We note some relations:

- If χ is of type (H) or (L), then
  condition (C) holds for small $u^* > 0$.
- If χ is strictly concave for all $u > 0$, in particular of type (H) or (L), then condition (C) holds for any $u^* > 0$ (Figure 1, H/L(a)).
- Assume $\chi \in C^1[0, \infty)$, χ is bounded, strictly concave for large u ($u \geqslant L$ for some $L > 0$), and (3.8)
  $\chi'(u) > 0$ for $u \geqslant 0$, then
  condition (C) holds for large $u^* > 0$.

- If χ is of type (S), then
  condition (C) does not hold for small $u^* > 0$.
  If $\chi'(0) = 0$, then
  condition (C) does not hold for any $u^* > 0$.

The properties described by statement (3.8) are fulfilled by the isotherms arising in both examples of class (S) from Section 2.1.

It is easy to check condition (C) using a plot of χ and a ruler, but possibly difficult by inspecting a formula for χ. The following observations may be helpful. Assume $\chi \in C^1(0, \infty)$ and $u_* = 0$.

- If $\chi'(u) < \chi(u)/u$ for $0 < u < a$, then
  condition (C) holds for $0 < u^* \leqslant a$. (3.9)

Note that $\chi'(u) < \chi(u)/u$ is equivalent with $\mathrm{d}/\mathrm{d}u(\chi(u)/u) < 0$ and, thus, $\chi(u)/u$ is strictly decreasing in $[0, a]$. By an analogous argument, we get

- If $\chi'(u) > \chi(u)/u$ for $a < u < b$, then
  condition (C) does not hold for $a < u^* \leqslant b$. (3.10)

We apply (3.9), (3.10) to the following cases:

Case 1. $\chi(u) = A_1 u^{p_1} + A_2 u^{p_2}$ with $A_1, A_2, p_1, p_2 > 0$.

Using

$$\chi'(u) = A_1 p_1 u^{p_1 - 1} + A_2 p_2 u^{p_2 - 1}, \qquad \chi(u)/u = A_1 u^{p_1 - 1} + A_2 u^{p_2 - 1},$$

we obtain from (3.9) and (3.10):

- $p_1 < 1$, $p_2 \leqslant 1$: Condition (C) holds for any $u^* > 0$.
- $p_1 < 1$, $p_2 > 1$: Set
  $$u_m^* := \left(\frac{(1 - p_1)A_1}{(p_2 - 1)A_2}\right)^{1/(p_2 - p_1)}. \tag{3.11}$$
  Then condition (C) holds for $0 < u^* \leqslant u_m^*$ and does not hold for $u^* > u_m^*$. Here one of the isotherms is of type (H), the other of type (S), χ is of type (H) (Figure 1, H(b)).
- $p_1 \geqslant 1$, $p_2 \geqslant 1$: Condition (C) does not hold for any $u^* > 0$.

For $p_1 < 1$, $p_2 > 1$, the result is a consequence of

$$\chi'(u) \gtreqless \chi(u)/u \Leftrightarrow u \gtreqless u_m^*.$$

Note that for $p_1 < 1$, $p_2 > 1$ χ is strictly concave for $0 \leqslant u \leqslant u_c^*$ and strictly convex for $u > u_c^*$, where

$$u_c^* := \left(\frac{p_1}{p_2}\right)^{1/(p_2 - p_1)} u_m^* \quad (< u_m^*).$$

This shows again that curvature of χ and condition (C) are not strictly related.

Case 2.

$$\chi(u) = A_1 u^p + \frac{A_2 u}{1 + A_2 u} \quad \text{with } A_1, A_2, A_3, p > 0.$$

The analysis of this case is more involved and can be found in van Duijn and Knabner (1990) and in van Duijn *et al.* (1992).

Finally, condition (C) also implies the shock (or entropy) inequalities for the limit case $k \to \infty$ and $D \searrow 0$. This limit case is considered in Section 5. Formally, it results in the hyperbolic partial differential equation (see also (1.20))

$$\frac{\partial}{\partial t}\{u + \psi(u) + \varphi(u)\} + q\frac{\partial}{\partial x}u = 0.$$

Writing $w = u + \psi(u) + \varphi(u)$ and introducing the inverse function $u = h(w)$, we obtain the scalar conservation law

$$\frac{\partial}{\partial t}w + q\frac{\partial}{\partial x}h(w) = 0.$$

We know that equations of this type may have discontinuous solutions. In order to ensure uniqueness and to distinguish the 'physical' solution from all other possible solutions, one introduces an additional condition. In the theory of shock waves, this condition is called the *Oleinik entropy condition.* It has the form

$$\frac{h(s) - h(w_r)}{s - w_r} \leqslant \frac{h(w_\ell) - h(w_r)}{w_\ell - w_r} \tag{3.12}$$

for all s between w_r and w_ℓ. Here w_ℓ and w_r denote the values of w just left and right to the shock.

Observe that our condition (C) corresponds to condition (3.12) with a strict inequality sign and with

$$w_\ell = u^* + \psi(u^*) + \varphi(u^*) \quad \text{and} \quad w_r = u_* + \psi(u_*) + \varphi(u_*).$$

For the limit case $k \to \infty$ and $D \searrow 0$, this means that inequality (C) implies the proper entropy condition at discontinuities.

3.3. EXAMPLES

We show here some typical examples of travelling waves as they arise in the different models. The discussion of further examples covering the whole range of possibilities is contained in van Duijn and Knabner (1990). We give both the representation of the waves as orbits in the phase plane and the more usual representation of the waves as function of the variable $\eta = x - at$. In van Duijn and Knabner (1990) we give some details about the computational method used in these examples to obtain the waves as functions of η and from these the connecting orbit.

As in the preceding subsections, we present here the results in terms of the scaled variables (1.19). In all the examples, we have taken

$$D = 3, \qquad q = 5, \qquad k = 0.5$$

and

$$u_* = 0, \qquad u^* = 1.$$

This implies that

$$v_* = \varphi(0) = 0, \qquad v^* = \varphi(1),$$

and

$$\psi_* = \psi(0) = 0, \qquad \psi^* = \psi(1).$$

Consequently, the wave speed a is given by

$$a = \frac{q}{1 + \psi^* + v^*}.$$

In each of the following examples, we have $\psi^* + v^* = 3$ and, thus, $a = 1.25$.

These and the subsequent parameters are typical for column studies with slow flow and low dispersion length for contaminant transport, if one uses the following units for the unscaled variables: For length [cm] and for time [hr], for concentration in solution a unit in the range 1–100 μg/ml and, correspondingly, for adsorbed concentration 1–100 μg/g. $\Theta = 0.5$ and $\rho = 1.5$, then, corresponds to a representative loam. Note that $K = 0.06$ for the dimensionless rate parameter (1.16), i.e. it is to be expected that nonequilibrium effects are significant. We consider the case

ψ is of type (H): $\psi(u) = 1.5u^{1/2}$, i.e. $\psi^* = 1.5$.

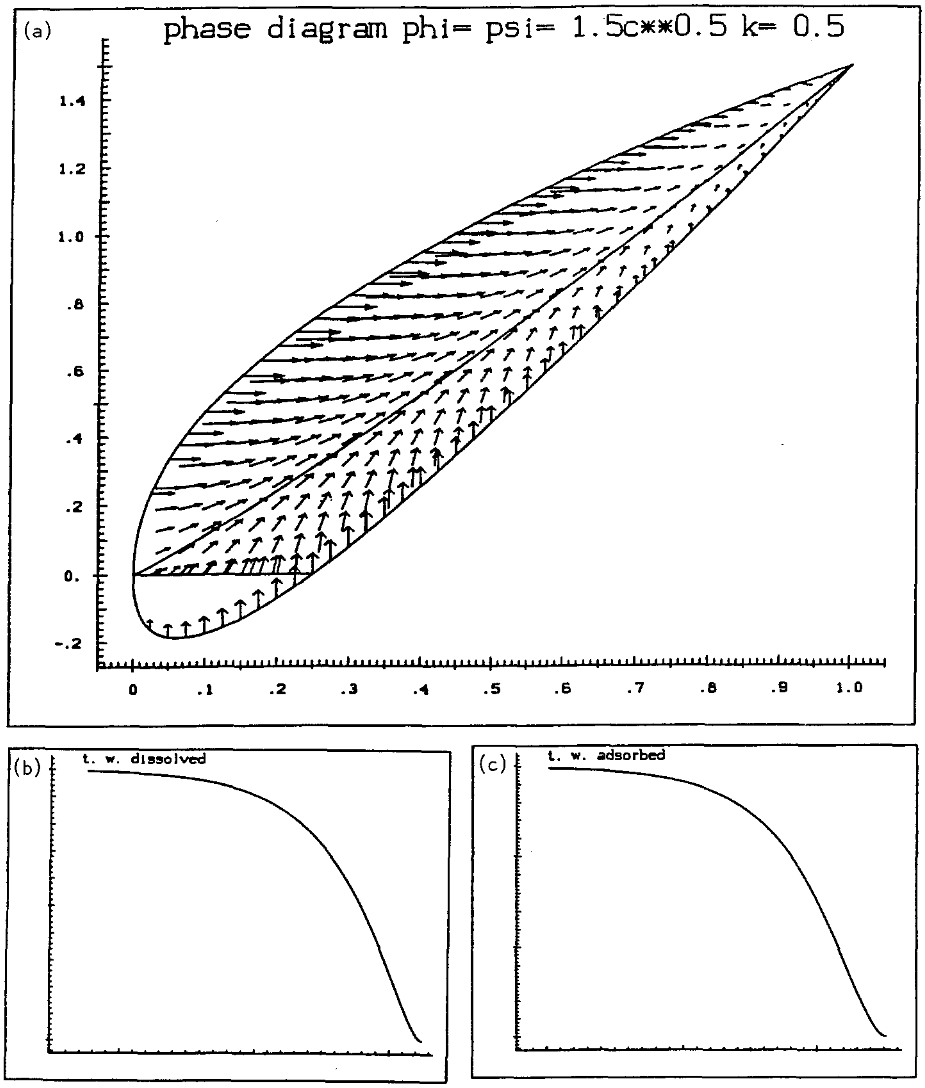
f is of type (E): $f(u, v) = \varphi(u) - v$ with $\varphi(u) = 1.5u^p$, i.e. $v^* = 1.5$.

This choice corresponds to the situation discussed in Case 1 of Section 3.2. We distinguish

(1) $p = 1/2$, i.e. φ is of type (H).
Here condition (C) holds for any $u^* > 0$. In this case, we may use either Theorem 4.3 or Theorem 4.5 to see that finiteness must occur. Referring to the Example in Section 4.1, which applies here with $\mathscr{C} = 1$, we obtain that

$$u(\eta) \leqslant \mathscr{C}_1(L - \eta)^2, \quad \text{for } \eta \leqslant L.$$

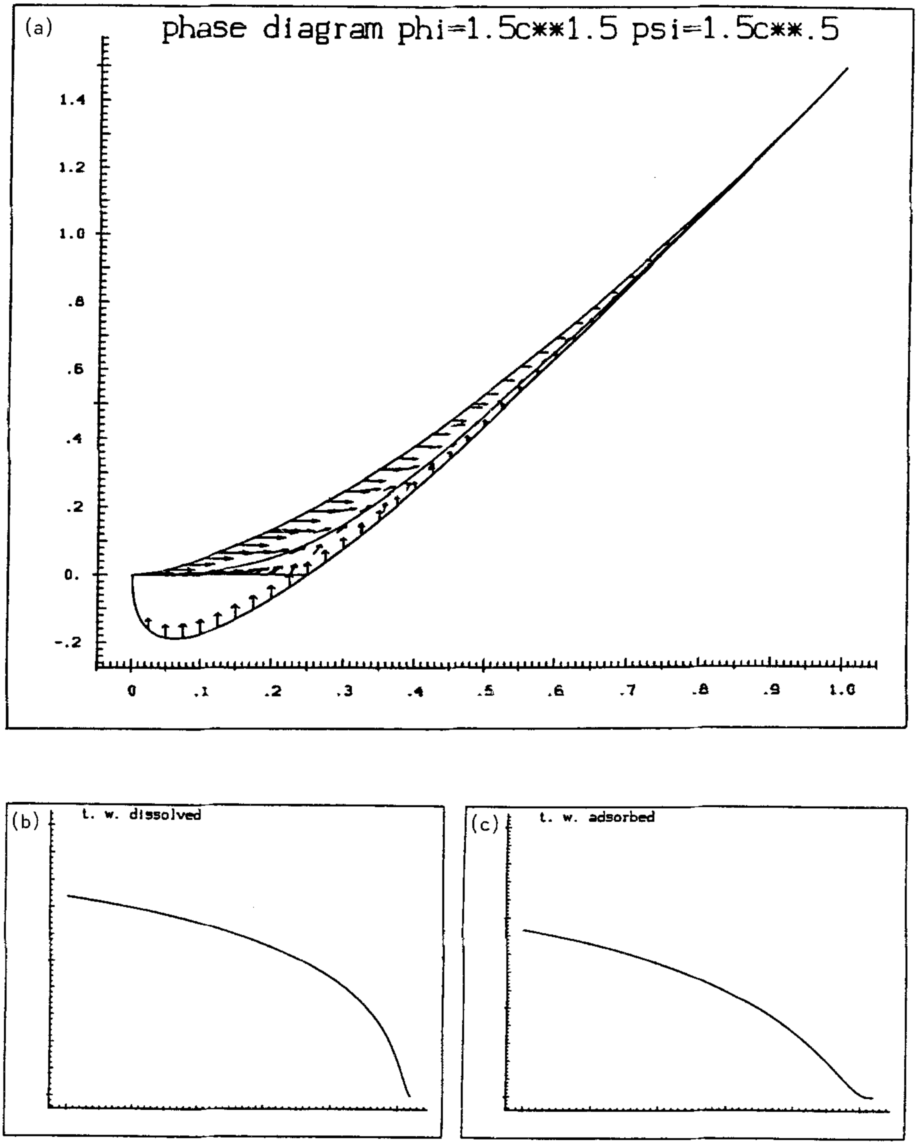
The constant $\mathscr{C}_1$ is given in the Example. Due to this smooth way in which u vanishes the appearance of finiteness is not so prominent. The computational results are given in Figures 3a-c. Note that the arrows in the phase-plane picture (Figure 3a) are pointing in the opposite direction according to the transformation $\xi = -\eta$. It clearly demonstrates the invariance of the set S.



Figs. 3a–c. Phase diagram and travelling wave as function of η for Example 1 (scaling factor vector field: 0.25).

(2) $p = 3/2$, i.e. φ is of type (S).
Using Equation (3.11), one finds that $u^* = 1$ is precisely the maximal value for which condition (C) holds. This accounts for the cusp in the invariant set S (see Figure 4a). Here Theorem 4.3 tells us that the wave is finite. The computations are shown in Figures 4b and c. Note that both the dissolved and the adsorbed concentration reach their equilibrium value very slowly. For this reason, we show here an η interval of the length 52, while in Figure 3, the length of the η-interval is 26.

In both cases the displayed u-interval is [0, 1], the v-interval is [0, 1.5].



Figs. 4a–c. Phase diagram and travelling wave as function of η for Example 2.

4. Finiteness

In Section 3, we constructed a solution to problem TW in the sense of Definition 3.1. This solution was obtained by considering the two first-order equations (3.5) and by studying their solutions in the u, v-phase plane. From the Picard–Lindelöf theorem (Appendix A), we obtain that through each point (u_0, v_0) of the phase plane, with $0 < u_0 < u_m$ and $0 < v_0 < v_m$, a unique orbit $(u(\eta), v(\eta))$ passes where the functions u and v satisfy Equations (3.5) in an appropriately chosen interval. This follows directly from the Lipschitz continuity of the functions ψ and f near (u_0, v_0). However, when $(u_0, v_0) = (0, 0)$, this may no longer be true. In particular, when $u_* = 0$ and, thus, $\psi_* = \psi(0) = \varphi(0) = 0$, Equations (3.5) have the solutions $u \equiv 0$ and $v \equiv 0$. However, the construction in Section 3 shows that there may also exist a solution (u, v) which passes through the origin and which is nontrivial. This will lead to *finite* travelling waves. We examine this phenomenon in detail in this section. Again we refer to van Duijn and Knabner (1991) for the mathematical proofs.

Throughout this section, we assume that $u_* = 0$ and that condition (C) is satisfied, so that the results of Theorem 3.2 hold.

We first note that if $u(\eta_0) = 0$ for some $\eta_0 \in \mathbb{R}$, then, since $u \geqslant 0$, also $u'(\eta_0) = 0$. The first equation in (3.5) gives $v(\eta_0) = 0$ and the monotonicity $u(\eta) = v(\eta) = 0$ for $\eta \geqslant \eta_0$. Conversely, if $v(\eta_0) = 0$, then $v'(\eta_0) = 0$ and the second equation in (3.5) gives $0 = f(u(\eta_0), 0)$. Consequently, $0 = \varphi(u(\eta_0))$ and, thus, $u(\eta_0) = 0$. This leads to the following definition.

DEFINITION 4.1. A travelling wave $\{u, v, a\}$ is called *finite* if

$$L = \sup\{\eta \in \mathbb{R} \mid u(\eta) > 0\} = \sup\{\eta \in \mathbb{R} \mid v(\eta) > 0\} < \infty.$$

We first consider finiteness for general rate functions f of the form (1.10). Thereafter, we treat the case where f is of explicit type (E). This latter case, being of a special form, allows us to obtain more detailed information and sharper results concerning the occurrence of finiteness and the behaviour of u near the point L. Our conditoins will be in terms of the integrability near $u = 0$, i.e. on an interval $(0, \varepsilon)$ for some small number $\varepsilon > 0$, of the reciprocal of a function $\sigma = \sigma(u)$, fulfilling $\sigma(0) = 0$. Then $1/\sigma$ is singular at $u = 0$ and the integrability condition restricts the growth of $1/\sigma$ or, equivalently, the decay of σ for $u \to 0$. Consider the example $\sigma(u) = u^p$ for $p > 0$, where

$1/\sigma$ is integrable near $u = 0$ exactly in the case $p < 1$.

The proofs of the following result are worked out in van Duijn and Knabner (1990). The functions χ and ℓ are defined as in Section 3.

4.1. GENERAL RATE FUNCTIONS

- Finiteness can only occur if the isotherms φ and ψ do not tend to zero too fast: we have

THEOREM 4.2. *Let* $L < \infty$. *Then* $1/\chi$ *is integrable near* $u = 0$.

- If the isotherm ψ, describing the equilibrium adsorption, tends to zero sufficiently slow, then finiteness occurs. We have

THEOREM 4.3. *Let* ψ *be of Freundlich type* (H). Then

$1/\psi$ *integrable near* $\mathrm{u} = 0 \Rightarrow \mathrm{L} < \infty$.

Note that this situation occurs in the examples of Section 3.3. Whenever ψ is of the form $\psi(u) = Au^p$ with $A > 0$ and $p \in (0, 1)$, then

$$\int_0^u \frac{1}{\psi(s)}\,\mathrm{d}s = \frac{1}{A(1-p)}\,u^{1-p} < \infty$$

and finiteness appears. This is independent of the behaviour of the nonequilibrium adsorption isotherm φ (that is, as long as condition (C) holds). Note, however, that the figures displaying u and v, do not clearly demonstrate the finiteness. This is due to the fact that when $\eta \nearrow L$, $u(\eta)$ tends to zero rather smoothly. There is an upper bound for the rate of decay of the function u near the point L (if it exists):

COROLLARY 4.4. *Let $L < \infty$ and let*

$$w(\eta) := \int_0^{u(\eta)} \frac{1}{\chi(s)}\,\mathrm{d}s, \quad \textit{for } \eta \in \mathbb{R}. \tag{4.1}$$

Then

$$w(\eta) \leqslant \frac{a}{D}(L-\eta), \quad \textit{for } \eta \leqslant L$$

and in particular,

$$w'(L-) \geqslant -\frac{a}{D}. \tag{4.2}$$

EXAMPLE. Let $\psi(u) = Au^p$ with $A > 0$ and $p \in (0, 1)$ and let there exist a constant $\mathscr{C} > 0$ such that $\varphi(u) \leqslant \mathscr{C}\psi(u)$. Further, let condition (C) be satisfied. Then

$$\chi(u) \leqslant (1+\mathscr{C})\psi(u) = (1+\mathscr{C})Au^p$$

and, thus,

$$w(\eta) \geqslant \frac{1}{A(1-p)(1+\mathscr{C})}\,(u(\eta))^{1-p}, \quad \text{for } \eta \in \mathbb{R}.$$

Corollary 4.4 now implies

$$u(\eta) \leqslant \left\{\frac{aA(1-p)(1+\mathscr{C})}{D}\right\}^{1/(1-p)} (L-\eta)^{1/(1-p)}, \quad \text{for } \eta \leqslant L,$$

which shows the smooth behaviour of u near L.

Due to the smoothness of u, the difference between finiteness and nonfiniteness in practical terms is not so big: from the computations the distinction is hard to make.

4.2. RATE FUNCTIONS OF EXPLICIT TYPE (E)

In this case the equation for v in (3.5) becomes

$$v' = \frac{k}{a}(v - \varphi(u)) \quad \text{in } \mathbb{R}.$$

This equation is linear in v. Then the two first-order equations for u and v can be combined into one second-order equation for u only. The result is

$$(Du' + a\psi(u))' = \left(q - a + \frac{kD}{a}\right)u' + k\left(\chi(u) - \frac{q-a}{a}u\right) \quad \text{in } \mathbb{R}. \tag{4.3}$$

In Section 3 of van Duijn and Knabner, (1991), a detailed analysis based on Equation (4.3) is given to characterize the finiteness for this special case. The result is presented in the next theorem.

THEOREM 4.5. *Let there exist a* $\delta \in (0, u^*)$ *such that* χ *is concave in* $(0, \delta)$. *Then*

$L < \infty \Leftrightarrow 1/\{(P\chi)^{1/2} + \psi\}$ *is integrable on* $(0, \delta)$.

Here we use the notation $P\chi$ for the primitive

$$P\chi(u) := \int_0^u \chi(s)\,\mathrm{d}s = \int_0^u \{\varphi(s) + \psi(s)\}\,\mathrm{d}s.$$

This theorem gives the necessary and sufficient condition for finiteness. In this respect, it is much stronger than Theorem 4.3 which it contains as a special case: Since $\psi \leqslant (P\chi)^{1/2} + \psi$, we have

$$1/\psi \text{ integrable} \Rightarrow 1/\{(P\chi)^{1/2} + \psi\} \text{ integrable} \Rightarrow L < \infty. \tag{4.4}$$

Theorem 4.5 can be reformulated into a statement involving one isotherm only if we can control the decay near $u = 0$ of the other: in particular, if the other isotherm is of type (L) of (S).

COROLLARY 4.6. *Let there exist a* $\delta \in (0, u^*)$ *such that* χ *is concave in* $(0, \delta)$ *and let* φ *be Lipschitz continuous at* $u = 0$ (*for example of type* (L) *or* (S)). *Then*

$L < \infty \Leftrightarrow 1/\psi$ *is integrable on* $(0, \delta)$.

COROLLARY 4.7. *Let there exist a* $\delta \in (0, u^*)$ *such that* χ *is concave in* $(0, \delta)$ *and let* ψ *be Lipschitz continuous at* $u = 0$ (*for example of type* (L) *or* (S)). *Then*

$L < \infty \Leftrightarrow 1/(P\varphi)^{1/2}$ *is integrable on* $(0, \delta)$.

Here $P\varphi(u) := \int_0^u \varphi(s)\,\mathrm{d}s$ *for* $u \geqslant 0$.

One can also use Equation (4.3) to obtain a precise result about the behaviour of u near L (if it exists) in the absence of equilibrium adsorption, that is, when $\psi \equiv 0$. Let φ be such that the finiteness condition of Corollary 4.7 holds. Define the function

$$\bar{w}(\eta) := \int_0^{u(\eta)} \frac{1}{\{P\varphi(s)\}^{1/2}}\,\mathrm{d}s, \quad \text{for } \eta \in \mathbb{R}, \tag{4.5}$$

where u satisfies Equation (4.3). Clearly, $\bar{w}$ is well-defined and $\bar{w}(\eta) = 0$ for $\eta \geqslant L$. In Theorem 3.4 of van Duijn and Knabner (1991), the following two results for the function $\bar{w}$ are given

$$\bar{w}'(\eta) > -\left(\frac{2k}{D}\right)^{1/2}, \quad \text{for } \eta < L \tag{4.6a}$$

$$\bar{w}'(L-) = -\left(\frac{2k}{D}\right)^{1/2}. \tag{4.6b}$$

Consequently,

$$\bar{w}(\eta) < \left(\frac{2k}{D}\right)^{1/2}(L-\eta), \quad \text{for } \eta < L \tag{4.6c}$$

and

$$\lim_{\eta \uparrow L} \frac{\bar{w}(\eta)}{L-\eta} = \left(\frac{2k}{D}\right)^{1/2}. \tag{4.6d}$$

EXAMPLE. Let $\psi \equiv 0$ and let $\varphi(u) = Au^p$ with $A > 0$ and $p \in (0, 1)$. In this case, we compare the results for the function w from (4.1) and the function $\bar{w}$ from (4.5). We have

$$w = \frac{1}{A(1-p)} u^{1-p}, \tag{4.7a}$$

and

$$\bar{w} = \frac{2}{1-p}\left(\frac{1+p}{A}\right)^{1/2} u^{(1-p)/2}. \tag{4.7b}$$

This implies

$$\bar{w}^2 = 4\frac{1+p}{1-p} w$$

and with (4.6b), it follows that $w'(L-) = 0$.

This shows that the estimate (4.2) for w' is far from optimal. Note, however, that the estimate of (4.6) becomes worse when $k \to \infty$ and has no meaning for the limit case $k = \infty$, whereas estimate (4.2) for w is independent of k. In Section 5, we show for the limit case $k = \infty$ that the function w satisfies the lower bound in (4.2), i.e. $w'(L-) = a/D$. This clearly illustrates the regularizing effect of the nonequilibrium adsorption. We return to this subject in Section 5.

In the case when $\bar{w}$ is given by (4.7b), we obtain from (4.6c, d) for u

$$u(\eta) < \mathscr{C}_0(L-\eta)^{2/(1-p)}, \quad \text{for } \eta < L$$

and

$$\lim_{\eta \uparrow L} \frac{u(\eta)}{(L-\eta)^{2/(1-p)}} = \mathscr{C}_0,$$

where

$$\mathscr{C}_0 = \left(\frac{2Ak}{(1+p)D}\right)^{1/(1-p)} \left(\frac{1-p}{2}\right)^{2/(1-p)}.$$

It implies that u tends to zero very smoothly: for instance, $p = 1/2$ gives $u(\eta) \sim (L-\eta)^4$. This behaviour confirms an earlier remark that the difference between finiteness and nonfiniteness, although of great mathematical interest, is small as far as the practical implication and computation are concerned.

It is possible to expand $\bar{w}$ near $\eta = L$. The result is

$$\bar{\omega}(\eta) = \alpha(L-\eta) + \beta(L-\eta)^2 + \cdots, \quad \text{for } \eta \leqslant L, \tag{4.8}$$

where

$$\alpha = \left(\frac{2k}{D}\right)^{1/2} \quad \text{and} \quad \beta = -\frac{1-p}{2(3+p)}\left(q - a + \frac{kD}{a}\right)\left(\frac{2k}{D^3}\right)^{1/2}.$$

Again, this can be translated in terms of the solution u.

In terms of the original variables $c = c(x, t)$, $s = s(x, t)$ in Equations (1.7), the phenomenon of finiteness leads to regions in the x, t-plane, where $c = s = 0$. Finite travelling waves, with $c_* = s_* = 0$, give a linear front in the x, t plane across which the concentrations vanish, for example

$$c(x, t),\ s(x, t) > 0, \quad \text{for} \quad x < at + L$$

and

$$c(x, t) = s(x, t) = 0, \quad \text{for} \quad x \geqslant at + L.$$

In this respect, we speak of a *free boundary problem*, the free boundary being the line $x = at + L$. Note the speed a of the free boundary only appears in the higher-order terms of the expansion of $\bar{w}$.

5. Limit Cases

In this section, we study the limit cases

(1) $k \to \infty$, $D > 0$: In this limit we expect both kinds of adsorption sites to be in equilibrium and call this situation the *equilibrium limit case.*

(2) $k < \infty$, $D \to 0$: In this limit we neglect molecular diffusion and mechanical dispersion and call this the *hyperbolic limit case.*

In particular we want to justify the formal limit equation, and examine the change in the qualitative behaviour of the solutions. If it is also possible, we estimate the rate of convergence. This leads to quantitative criteria for the feasibility of the limit formulation. Closed-form solutions are available for some typical examples. The most simple ones are reviewed in Appendix C.

We assume throughout the section that condition (C) is satisfied. We will consider those solutions of the problem TW ((1.24)), whose existence is guaranteed by the considerations of Section 3.1. To distinguish this travelling wave from the limit problems, we will speak of a *travelling wave for* $k < \infty$ or *for* $D > 0$, respectively.

5.1. THE EQUILIBRIUM LIMIT CASE

Formally, we expect for $k \to \infty$ the limit equations

$$f(u, v) = 0 \quad \text{and thus} \quad v = \varphi(u) \quad \text{by (1.10)},$$

and (1.20a) to remain unchanged, i.e.

$$\frac{\partial}{\partial t} u + \frac{\partial}{\partial t}(\psi(u) + \varphi(u)) - D \frac{\partial^2}{\partial x^2} u + q \frac{\partial}{\partial x} u = 0. \tag{5.1}$$

We consider the problem TW defined in Section 1, where all data with the exception of the rate parameter k are fixed. For k, we take a sequence $k = k_n \to \infty$ and the corresponding travelling wave solutions u_n, v_n, which all have the wave speed a according to (3.4). As travelling waves are only unique up to translations, we cannot expect convergence of u_n, v_n in general. Therefore, some $\tilde{u} \in (u_*, u^*)$ is chosen and u_n is translated such that

$$u_n(0) = \tilde{u}, \quad \text{for all } n. \tag{5.2}$$

In the phase plane, all orbits (u_n, v_n) belong to the same bounded set S (compare Section 3.1) and the $v_n = v_n(\eta)$ are decreasing. There is a mathematical argument which leads to the convergence of u_n and v_n to some functions u and v. The limit functions satisfy the first equation in (3.5), which we write with (3.7) as

$$u' = \frac{a}{D}(\ell(u) - v)$$

and

$$f(u, v) = 0, \quad \text{i.e.} \quad v = \varphi(u).$$

Consequently,

$$u' = \frac{a}{D}(\ell(u) - \varphi(u)). \tag{5.3}$$

Clearly, the limit orbit (u, v) belongs to $\partial S_2 \cup \{(u_*, v_*), (u^*, v^*)\}$. The boundary conditions (BC) can be verified.

A more rigorous version of this argument (cf. van Duijn and Knabner, 1991) leads to:

THEOREM 5.1. *Consider a sequence* $\{u_n, v_n, a\}$ *of travelling waves for rate parameters* $k_n \to \infty$ *and all other data being the same, which satisfies* (5.2). *Then*

$$\lim_{n\to\infty} u_n(\eta) = u(\eta), \qquad \lim_{n\to\infty} v_n(\eta) = v(\eta), \quad \textit{for all } \eta \in \mathbb{R}.$$

The triple $\{u, v, a\}$ *is a travelling wave solution for* $k = \infty$ *in the sense*:

$$\text{TWE} \begin{cases} u \in C^1(\mathbb{R}), \qquad v \in C(\mathbb{R}), \\ Du' + a\psi(u) + a\varphi(u) \in C^1(\mathbb{R}), \\ (Du' + a\psi(u) + a\varphi(u))' = (q-a)u' \quad \text{in } \mathbb{R}, \\ u \textit{ and } v = \varphi(u) \textit{ satisfy the boundary conditions } (\mathrm{BC}). \end{cases} \tag{5.4}$$

u and v are strictly decreasing as long as $u(\eta) > 0$.

The solutions of TWE are less regular than the solutions of TW (cf. (3.1)): Here $v = \varphi(u)$ satisfies $v \in C^1(\mathbb{R})$ only for smooth φ, e.g. $\varphi \in C^1([u_*, u^*])$. The limit functions are a classical solution of (5.1), if both φ and ψ are smooth. Lacking smoothness of φ or ψ has the following consequences: Kinks in φ or ψ at some $\bar{u} \in (u_*, v^*)$ lead to jumps of u'' at $\bar{\eta}$, where $u(\bar{\eta}) = \bar{u}$.

In the case $u_* = 0$, the possible finiteness of u is another source of lacking smoothness. So we first turn to the *characterization of finiteness* for TWE. In van Duijn and Knabner (1990), we prove:

THEOREM 5.2. *Let* χ *be of type* (H) *and let* $u_* = 0$. *Then if u satisfies* TWE

$$L < \infty \Leftrightarrow 1/\chi \quad \textit{is integrable near } u = 0. \tag{5.5}$$

Since $1/\chi$ is bounded above by either $1/\varphi$ or $1/\psi$, we have as an immediate corollary

COROLLARY 5.3. *Let* χ *be of type* (H). *Then*

$$1/\varphi \textit{ or } 1/\psi \quad \textit{integrable near } u = 0 \Rightarrow L < \infty. \tag{5.6}$$

Again the singular behaviour of one of the isotherms is sufficient for finiteness. For φ or ψ being of the form Au^p with $A > 0$ and $p > 0$, the integrability condition is equivalent to $p < 1$. Consequently, $p < 1 \Rightarrow L < \infty$. In general, the requirements for finiteness are stronger for $k < \infty$.

COROLLARY 5.4. *Let* χ *be of type* (H). *If a travelling wave for* $k < \infty$ *is finite, then the travelling wave for* $k = \infty$ *is also finite.*

The assertion is a consequence of Theorems 4.2 and 5.2.

The reversed implication is generally wrong. A counter example is worked out in van Duijn and Knabner (1990).

As in Section 4, we can investigate the behaviour of a finite wave, with $k = \infty$, near the front. To this end, we write Equation (5.3) as

$$u' = \frac{q-a}{D}\left(u - u_* - \frac{a}{q-a}(\chi(u) - \chi(u_*))\right). \tag{5.7}$$

In van Duijn and Knabner (1990), we conclude from this for the transformation w, defined in (4.1):

PROPOSITION 5.5. *Let u be a finite wave for $k = \infty$. For w, given by* (4.1), *we have*

$$w'(\eta) > -\frac{a}{D}, \quad \text{for } \eta < L \quad \text{and} \quad w'(L-) = -\frac{a}{D}. \tag{5.8}$$

The wave profiles for $k = \infty$ are steeper than for $k < \infty$, as can be seen from the following proposition.

PROPOSITION 5.6. *Let $\{u_k, v_k, a\}$ and $\{u, v, a\}$ be travelling waves for the same data for $k < \infty$ and $k = \infty$, respectively, such that $u_k(0) = u(0) =: \tilde{u} \in (u_*, u^*)$. Then*:

$$\begin{aligned} &u(\eta) > u_k(\eta), \quad \text{for } \eta < 0,\\ &u(\eta) < u_k(\eta), \quad \text{for } \eta > 0 \quad \text{and} \quad u_k(\eta) > 0, \quad \text{and} \\ &u(\eta) = u_k(\eta) = 0, \quad \text{otherwise.} \end{aligned} \tag{5.9}$$

We prove this proposition as follows: Let

$$\rho(u) := \frac{a}{D}(\varphi(u) - \ell(u)), \quad \text{for } u \in [u_*, u^*], \tag{5.10}$$

then, by (5.3) and the discussion of Section 3.1,

$$\begin{aligned} u'(\eta) &= -\rho(u(\eta)),\\ u_k'(\eta) &= -\rho(u_k(\eta)) + \frac{a}{D}(\varphi(u_k(\eta)) - v_k(\eta)) > -\rho(u_k(\eta)), \end{aligned} \tag{5.11}$$

for η such that $u_k(\eta) > 0$.

Thus $u'(0) < u_k'(0)$ implying the assertion.

For the explicit type (1.11) a convergence rate can be established in a typical special case. The assumptions are the same as in Proposition 5.6.

THEOREM 5.7. *If, in addition, f is of explicit type*, i.e. $f(u, v) = k(\varphi(u) - v)$, *and ρ from* (5.10) *is increasing in $[u_*, \tilde{u}]$ and decreasing in $[\tilde{u}, u^*]$, then*

$$|u(\eta) - u_k(\eta)| \leqslant \frac{a^2}{kD}(v^* - v_*) \quad \text{for all } \eta \in \mathbb{R}. \tag{5.12}$$

For a proof, consider $\eta > 0$. From (5.9)–(5.11), we get

$$\begin{aligned} 0 &\leqslant u_k(\eta) - u(\eta)\\ &= \int_0^\eta (u_k' - u')(s)\, \mathrm{d}s\\ &= -\int_0^\eta \rho(u_k(s)) - \rho(u(s))\, \mathrm{d}s + \frac{a}{D}\int_0^\eta \left(-\frac{a}{k} v_k'(s)\right) \mathrm{d}s\\ &\leqslant \frac{a^2}{kD}(v_k(0) - v_k(\eta)) \leqslant \frac{a^2}{kD}(v^* - v_*), \end{aligned}$$

as $u(s) \leqslant u_k(s) < \tilde{u}$ for $s > 0$. The argument for $\eta < 0$ is similar.

In unscaled variables, (5.12) reads

$$|c(\eta) - c_k(\eta)| \leqslant \frac{\lambda_2 H}{[1 + H(\lambda_1(\Delta\Psi/\Delta s) + \lambda_2)]^2} \frac{1}{K} \Delta c,$$

where H and K are defined in (1.15) and (1.16). Therefore, the magnitude of the dimensionless parameter K is significant for the feasibility of a *kinetic approximation* or a *quasi-stationary approximation*. Here, we denote, with the first notion, the substitution of an equilibrium model, i.e. (5.1), by a nonequilibrium model, i.e. (1.20) with f being of explicit type and the corresponding isotherm φ. Analogously, the second notion denotes the reversed procedure.

For $|v(\eta) - v_k(\eta)|$, we get an estimate similar to (5.12) only for smooth φ. For $\varphi(u) = Au^p$, $A > 0$, $0 < p < 1$, for example, $a^2/(kD)$ has to be substituted by $(a^2/kD)^p$ (compare van Duijn and Knabner (1991) for details).

5.2. THE HYPERBOLIC LIMIT CASE

Here we expect for $D \to 0$ the limit equation

$$\frac{\partial}{\partial t} u + \frac{\partial}{\partial t} \psi(u) + \frac{\partial}{\partial t} v + q \frac{\partial}{\partial x} u = 0 \tag{5.13}$$

and (1.20b) to remain unchanged, i.e. we arrive at a first-order system. The argument for the convergence parallels, in principle, the one of Section 5.1 with the roles of u, v interchanged. Now the limit orbit (u, v) satisfies (1.20b) and belongs to $\partial S_1 \cup \{(u_*, v_*), (u^*, v^*)\}$, i.e. $v = \underline{\ell}(u)$. If ℓ is not strictly increasing, there are subintervals of $[u_*, u^*]$, on which $\underline{\ell}$ is constant. If u would run smoothly along these parts, v would be constant for the corresponding η-interval. This leads to a contradiction: $v =$ constant and (1.20b) imply $f(u, v) = 0$ and with (1.10) $v = \varphi(u)$. On the other hand, $v = \underline{\ell}(u)$. This contradicts condition (C). Thus, in this situation, u has to be discontinuous, i.e. to develop shocks. To express this fact, we consider the inverse ℓ^{-1} of $\underline{\ell}$. For a (maximal) subinterval of $[u_*, u^*]$ on which $\underline{\ell}$ is constant, we take the left boundary point, i.e.

$$\ell^{-1}(v) := \min\{u \in [u_*, u^*] \mid \ell(u) = v\}, \quad \text{for } v \in [v_*, v^*]. \tag{5.14}$$

We assume that ℓ has, at most, finitely many changes from increasing to decreasing and vice-versa. Then ℓ^{-1} is strictly increasing and continuous with the possible exception of finitely many jumps, where it is left-sided continuous.

The sketched argument ends up with

THEOREM 5.8. *Consider a sequence $\{u_n, v_n, a\}$ of travelling waves for diffusion/dispersion coefficients $D_n \to 0$, and all other data being the same, which satisfy the normalization*

$$v_n(0) = \tilde{v}, \quad \textit{for all } n \textit{ and some } \tilde{v} \in (v_*, v^*).$$

Then there are functions u and v, defined on $\mathbb{R}$, such that

$v \in C(\mathbb{R})$, u and v' are continuous in $\mathbb{R}$ with the possible exception of finitely many points, where they are continuous from the right

and

$$\lim_{n\to\infty} v_n(\eta) = v(\eta), \quad \textit{for all } \eta \in \mathbb{R},$$

$$\lim_{n\to\infty} u_n(\eta) = u(\eta), \quad \textit{with the exception of the}$$

points of discontinuity.

The triple $\{u, v, a\}$ is a travelling wave solution for $D = 0$ in the sense

$$\text{TWH}\begin{cases} -av' = kf(u,v) \text{ in } \mathbb{R}, & (5.15\text{a})\\ u = \ell^{-1}(v) \text{ in } \mathbb{R}, & (5.15\text{b})\\ -av' + (-a\psi(u) + (q-a)u)' = 0 \text{ in } \mathbb{R}, & (5.15\text{c})\\ u \text{ and } v \text{ satisfy the boundary conditions (BC).} \end{cases}$$

u and v are strictly decreasing as long as $v_* < v(\eta) < v^*$.

More explicitly: In equation (5.15c) the functions $-a\psi(u) + (q-a)u$ is continuous on $\mathbb{R}$, i.e. the jumps of u and $-a/(q-a)\psi(u)$ cancel, and the derivative has to be understood in the same piecewise sense as v'. The points of discontinuity are the same for u and v' and they are exactly those $\hat{\eta}$, for which ℓ^{-1} is discontinuous at $\hat{v} := v(\hat{\eta})$. The jumps are

$$u(\hat{\eta}) - u(\hat{\eta}-) = \ell^{-1}(\hat{v}) - \ell^{-1}(\hat{v}+),$$

$$v'(\hat{\eta}) - v'(\hat{\eta}-) = -\frac{k}{a}(f(\ell^{-1}(\hat{v}), \hat{v}) - f(\ell^{-1}(\hat{v}+), \hat{v})). \tag{5.16}$$

Obviously, the solutions of TWH are less regular than the solutions of TW: At points where u and v' are continuous, u is continuously differentiable only if ψ is smooth. The more significant distinction, however, is the possibility of jumps of u and v'. This we will examine here. We will concentrate on such profiles for ψ, which appear in adsorption models according to Section 2. For simplicity, we assume that $\psi \in C^1((u_*, u^*])$, i.e. isotherms of the Freundlich type are allowed. Before we consider the various possibilities, we make two general observations. One is that condition (C) implies that $\ell'(u^*) \geqslant 0$ and ℓ is strictly increasing near u^*. In particular, ℓ^{-1} is continuous at $v = v^*$. The other is that ℓ is (strictly) convex if and only if ψ is (strictly) concave and the same vice-versa.

Below, we distinguish a number of possibilities for the function ψ. To illustrate the effect in the phase plane, in Figure 5 we present small sketches of the function ℓ involved.

Let ψ be convex in $[u_*, u^*]$. This implies that $\ell'(u) > 0$ for $u_* < u < u^*$ and, thus,

- If ψ is convex in $[u_*, u^*]$, then no jumps in ℓ^{-1} appear (Figure 5a and Figure 1, S(a) for ψ).

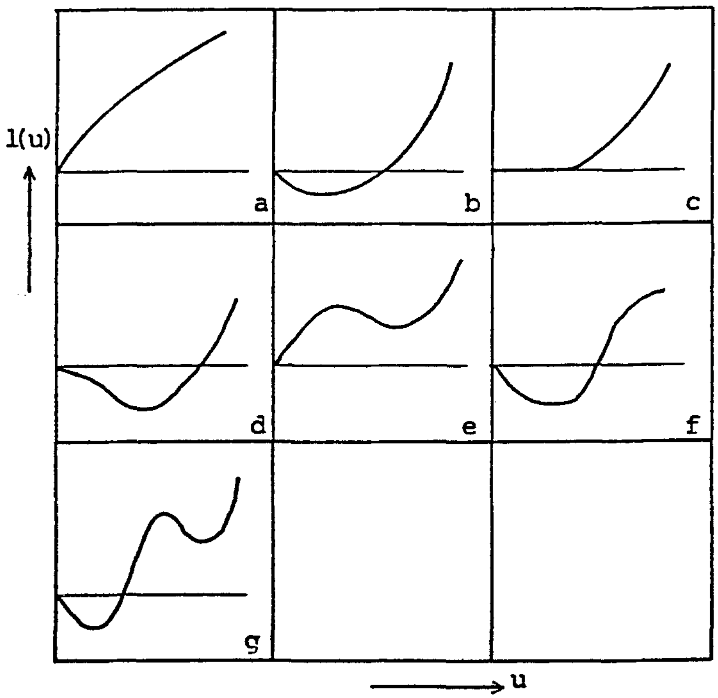


Fig. 5. Possible shapes of ℓ.

For concave ψ a jump of ℓ^{-1} at $v = v_*$ is possible depending on $\ell'(u_*) = (\Delta\psi + \Delta v)/\Delta u - \psi'(u_*)$. But for $u > \bar{u} := \ell^{-1}(v_* +)$ we have $\ell'(u) > 0$ and, thus, no further jump is possible. In detail:

- Let ψ be concave in $[u_*, u^*]$ (Figure 1, L/H(a)).
  The only possible jump of ℓ^{-1} is at $v = v_*$.
  There is a jump in each of the following cases: (5.17)
  $\psi'(u_*) > (\Delta\psi + \Delta v)/\Delta u$ (Figure 5b) or
  $\psi'(u_*) = (\Delta\psi + \Delta v)/\Delta u$ and ψ is linear near $u = u_*$ (Figure 5c).
  There is no jump in the remaining cases.

Note that in particular $\psi'(u_*) = +\infty$ leads to a jump.
In simple cases, $\bar{u}$ can be explicitly calculated, e.g. for $\psi(u) = Au^p$, A, $p > 0$, and $u_* = 0$. We have: There is no jump for $p \geqslant 1$ and a jump at $v = 0$ with $\bar{u} = (Au^*/(\psi(u^*) + v^*))^{1/(1-p)}$ for $p < 1$. Computations for this example are displayed in Figures 6a–c. For a sequence of decreasing D ($D = 3, 0.3, 0.03$) and all other data the same as in example 1 of Section 3.3, the orbits are shown in Figure 6a together with the curves φ, ℓ and $\underline{\ell}$. Figures 6b and c show the corresponding u and v components in dependence of η, translated such that $u(0) = 0{\cdot}25$ and $v(0) = 0{\cdot}75$. $\ell^{-1}(0+) = 0{\cdot}25$ is the height of jump to be expected for $D = 0$ and the convergence to such a discontinuous limit is clearly to be seen.

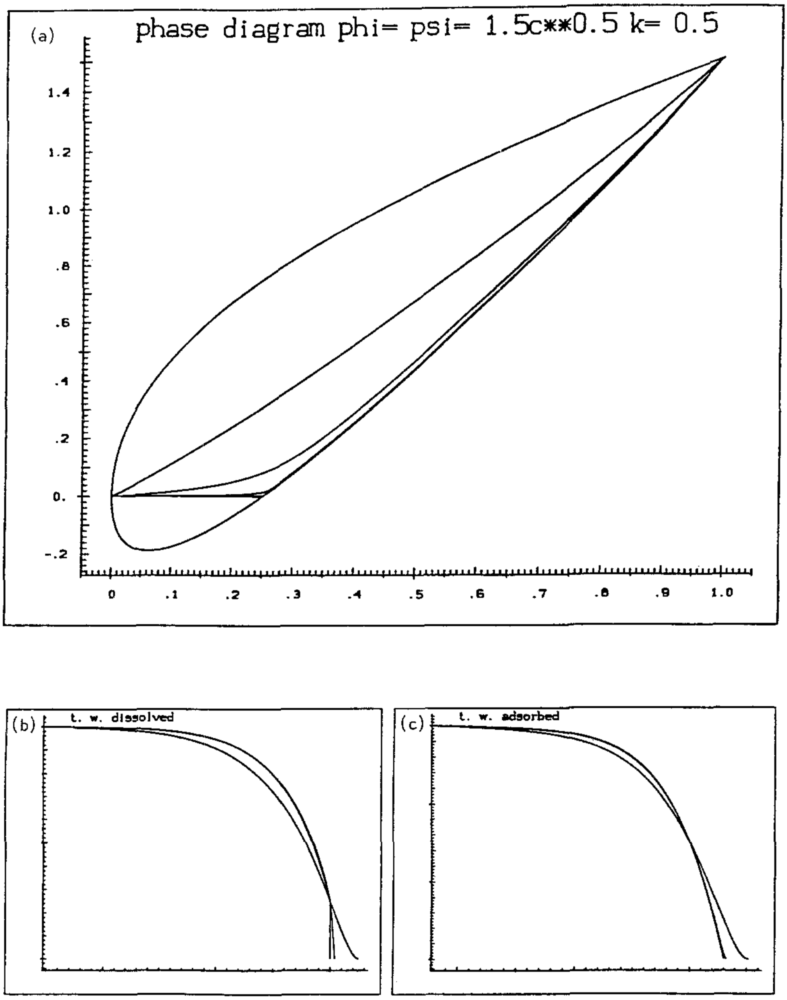


Fig. 6. (a) Phase diagram for decreasing D. Dissolved phase (b) and adsorbed phase (c) for decreasing D.

A typical isotherm ψ of type (S) is often convex-concave, i.e. ψ is convex in $[u_*, \tilde{u}]$ and concave in $[\tilde{u}, u^*]$ for some $\tilde{u} \in (u_*, u^*)$. Then:

- Let ψ be convex-concave (Figure 1, S(b)).
  Then ℓ^{-1} has a jump at $v = v_*$ if and only if $\psi'(u_*) \geqslant (\Delta\psi + \Delta v)/\Delta u$ (Figure 5d).
  In this case no further jump is possible.
  If $\psi'(u_*) < (\Delta\psi + \Delta v)/\Delta u$, then ℓ^{-1} may have one jump at a point $v = \hat{v} \in (v_*, v^*)$ (Figure 5e). The characterizing condition is:

$$\begin{aligned} &\hat{v} = \ell(\hat{u}),\ \psi'(\hat{u}) = (\Delta\psi + \Delta v)/\Delta u, \\ &\psi'(u) < (\Delta\psi + \Delta v)/\Delta u \quad \text{for } u \in [u_*, \hat{u}), \quad \text{and} \\ &\text{there is a } \tilde{u} > \hat{u} \text{ such that } \psi'(\tilde{u}) = (\Delta\psi + \Delta v)/\Delta u. \end{aligned} \tag{5.18}$$

To the contrary, a concave-convex isotherm exhibits the same behaviour as a concave isotherm:

- Let ψ be concave-convex (Figure 1, L/H(b)).
  The only possible jump of ℓ^{-1} is at $v = v_*$ and the characterization is given by (5.17) (Figure 5f).

An example of this type is $\psi(u) = A_1 u^{p_1} + A_2 u^{p_2}$ with $A_1, A_2 > 0$, $0 < p_1 < 1 < p_2$, discussed in Section 3.2: Here the jump always appears.

In general, an additional convex part does not change the possibility of jumps in ℓ^{-1}, while an additional concave part makes an additional jump possible. For example:

- Let ψ be concave-convex-concave (Figure 1, L/H(c)).
  Then ℓ^{-1} may have a jump at $v = v_*$, characterized by (5.17), and a jump at a point $v = \hat{v} \in (v_*, v^*)$, characterized by (5.18) (Figure 5g).

An isotherm of this type appears in the Example of Section 2.1 (for $n \geqslant 6$).

Next we consider the *characterization of finiteness* for TWH. We get immediately for $u_* = 0$:

- If ℓ^{-1} has a jump at $v = 0$, then a solution of TWH is finite ($L < \infty$ according to Definition 4.1).
  If ℓ^{-1} is continuous at $v = 0$, then:

$$L < \infty \Leftrightarrow 1/f(\ell^{-1}(\,\cdot\,), \cdot\,) \text{ is integrable near } v = 0. \tag{5.19}$$

Restricting ourselves to f being of explicit type (E) and for $\psi \in C^1(0, \delta)$ for some $\delta > 0$, (5.19) implies the more accessible condition

- $L < \infty \Leftrightarrow \ell'/(\varphi - \ell)$ is integrable near $u = 0$.

From this, assuming in addition that, χ is of type (H), we obtain here the same results as in (5.5), Corollary 5.3 and 5.4 (with '$k = \infty$' substituted by '$D = 0$'). In particular, this applies to $\psi \equiv 0$. In this case, (5.12) can be rewritten as

$$u' = \frac{k}{a}\left(u - u_* - \frac{a}{q-a}(\chi(u) - \chi(u_*))\right). \tag{5.20}$$

This equation is identical with (5.7) after the substitution of $(q-a)/D$ by k/a. Thus, we conclude in the same way about the behaviour near the front for w defined by (4.1):

$$w'(\eta) > -\frac{u^*}{v^*}\frac{k}{a}, \quad \text{for } \eta < L,$$

$$w'(L-) = -\frac{u^*}{v^*}\frac{k}{a}. \tag{5.21}$$

Returning to the case of general f, again we can compare the shapes for $D > 0$ and

$D = 0$, but here for v instead of u (cf. Proposition 5.9 in van Duijn and Knabner (1990)).

Finally, we can consider the limit $D \to 0$ also after the limit $k \to \infty$, i.e. for the solutions of TWE. A scaling argument (van Duijn and Knabner, 1989), shows that the travelling waves then reduce to piston flow profiles.

6. Conclusions

We investigated a general model for transport and adsorption in porous media including most of the aspects discussed nowadays. We concentrated on a prototype situation by studying travelling wave solutions which correspond to the limit profiles for continuous feed and uniform water flow.

Due to the nonlinear nature of the problem, also in this restricted situation, no closed form solutions are available, apart from some simple examples for limit cases. Nevertheless, by means of contemporary mathematical analysis, travelling wave solutions can be completely studied. The knowledge gained about their qualitative behaviour is as detailed as that obtained by considering closed form solutions.

Finiteness is a qualitative aspect which strengthens the consistency of the model, although it may not be prominent in numerical terms. It can only occur if the overall averaged isotherm and the rate function have some singular behaviour near zero concentration. In particular, different rate functions, e.g. Langmuir-type rate functions versus explicit type rate functions with the same isotherms, may lead to different conclusions with respect to finiteness.

The relation to the limit problems $k \to \infty$ and $D \to 0$ is clarified, including the precise order of the convergence estimates. This gives a criterion to estimate the validity of an approximation of one situation by the other (quasi-stationary approximation and kinetic approximation, respectively).

Finally, travelling waves can be numerically approximated with minor efforts to high accuracy. Thus, they can serve as 'explicit' solution, e.g. to check numerical algorithms designed for general complications.

Appendix C: Some Closed Form Solutions

In (5.7) and (5.20), we arrive at

$$\begin{aligned} &u' = \gamma \left(u - u_* - \frac{u^* - u_*}{\chi(u^*) - \chi(u_*)} (\chi(u) - \chi(u_*)) \right), \\ &u(-\infty) = u^*, \qquad u(+\infty) = u_*, \end{aligned} \tag{C.1}$$

where we have the two cases

(i) $k = \infty$: $\gamma = \dfrac{q - a}{D}$, $\chi = \varphi + \psi$,

(ii) $D = 0$, f of explicit type, $\psi \equiv 0$: $\gamma = \dfrac{k}{a}$, $\chi = \varphi$.

For $u_* = 0$, $\chi(u) = Au^p$, $A > 0$, $0 < p < 1$, the solution of (C.1) up to translation is

$$u(\eta) = u^*(1 - \exp((1-p)\gamma\eta))^{1/(1-p)}, \quad \text{for } \eta \leqslant 0,$$

$$u(\eta) = 0, \quad \text{for } \eta > 0. \tag{C.2}$$

This can be easily seen, as for $w(\eta) := u(\eta)^{1-p}$, (C.1) becomes linear:

$$w' = (1-p)\gamma(w - u^{*(1-p)}).$$

For (ii) and the Langmuir isotherm (see (2.6) for $\ell = 1$) $\chi(u) = v_{\max} bu/(1 + bu)$ with $v_{\max}$, $b > 0$, we have

$$u' = \gamma b \frac{(u - u_*)(u - u^*)}{1 + bu}$$

and from this, by the method of separation of variables, we obtain

$$\begin{aligned} &-\gamma b\ \Delta u(\eta_2 - \eta_1) \\ &\quad = (1 + bu_*)\ln\left(\frac{u(\eta_2) - u_*}{u(\eta_1) - u_*}\right) - (1 + bu^*)\ln\left(\frac{u^* - u(\eta_2)}{u^* - u(\eta_1)}\right) \\ &\quad \text{for arbitrary } \eta_1, \eta_2, \end{aligned} \tag{C.3}$$

where $\Delta u = u^* - u_*$.

It is instructive to compare this result with the solution obtained from the 'original' Langmuir formulation, (2.4) for $\ell = 1$, for the same situation $D = 0$, $\psi \equiv 0$. The rate function in this case is

$$\begin{aligned} kf(u, v) &= k_a(1 - v/v_{\max})u - k_d v/v_{\max} \\ &= k(b(v_{\max} - v)u - v), \end{aligned} \tag{C.4}$$

where $k := k_d/v_{\max}$, $b := k_a/k_d$. The reason for this definition of k is to have at least the same desorption rate, if in (ii), with the same isotherm, this rate parameter is used.

Let $u_* = 0$. Because of $v(\eta) = v^*/u^* u(\eta)$, (C.4) leads to

$$u' = \gamma(bu^2 - bu^* u), \tag{C.5}$$

again with $\gamma = k/a$. From this we conclude

$$-\gamma bu^*(\eta_2 - \eta_1) = \ln\left(\frac{u(\eta_2)}{u(\eta_1)}\right) - \ln\left(\frac{u(\eta_2) - u^*}{u(\eta_1) - u^*}\right) \quad \text{for arbitrary } \eta_1, \eta_2. \tag{C.6}$$

Comparing (C.3) and (C.6) with respect to their behaviour near u^* and $u_* = 0$, we see that in both cases

$$u(\eta) \sim \exp(-\gamma bu^*\eta), \quad \text{for } \eta \to +\infty,$$

but

$$\text{for (C.3):}\quad u^* - u(\eta) \sim \exp(\gamma b u^*/(1 + b u^*)\eta), \quad \text{for } \eta \to -\infty,$$

$$\text{for (C.6):}\quad u^* - u(\eta) \sim \exp(\gamma b u^* \eta), \quad \text{for } \eta \to -\infty.$$

Observe that, in the first case, the convergence of towards u^* is slower than in the second case.

These results could also have been derived directly from the differential equations, without going through the solution procedure.

Similar remarks can be found in Ruthven (1984).

References

van Duijn, C. J. and Knabner, P., 1990, Travelling waves in the transport of reactive solutes through porous media: Adsorption and binary ion exchange – Part 2 (extended version), Report No. 205, SPP Applied Optimization, Augsburg.

van Duijn, C. J. and Knabner, P., 1991, Solute transport with equilibrium and non-equilibrium multiple site adsorption: Travelling Waves, *J. Reine Angew. Math.* **415,** 1–49.

van Duijn, C. J. and Knabner, P., 1992, Travelling waves in the transport of reactive solutes through porous media: Adsorption and binary ion exchange – Part 1, *Transport in Porous Media.* **8,** 167–194.

van Duijn, C. J., Knabner, P., and van der Zee, S.E.A.T.M., 1992, Travelling waves in transport of reactive solutes through porous media: Effect of adsorption model, in preparation.

Ruthven, D. M., 1984, *Principles of Adsorption and Adsorption Processes*, Wiley, New York.