

Travelling Waves in the Transport of Reactive Solutes through Porous Media: Adsorption and Binary Ion Exchange – Part 1 *

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Short title: Travelling Waves: Adsorption and Ion Exchange 1

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

Abstract: We develop a model for solute transport in porous media, which takes into account equilibrium and non-equilibrium multiple-site adsorption. Binary ion exchange is included. Adsorption rate formulations and their isotherms are reviewed and their mathematical properties investigated. This forms the basis of the study of travelling wave solutions in the second part of the paper.

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

Introduction

Solute transport through porous media, where the chemical species undergo *adsorption* or *exchange processes* on the surface of the porous skeleton, are of fundamental importance in different fields. These range e.g. from analytical chemistry and chemical engineering to soil science and hydrology. Corresponding key words are chromatographic separation and mobility of plant nutrients or pollutants, respectively. Since a long time there is experimental evidence that some of these processes may exhibit *self-sharpening* or *compressive fronts*. Consequently, in the soil chemical and chemical engineering literature there appear heuristic arguments concerning the existence and properties of these fronts for corresponding mathematical models (e.g. (Valocchi *et al.*, 1981)). A mathematical model describing the transport and adsorption processes results in (partial) differential equations, where a self-sharpening front is modeled by a *travelling wave solution*. Suppose that the water flow is uniform. Then in case of their existence, travelling waves are the limit profiles for continuous feed in one space dimension and for continuous feed from a line or plane, respectively, in higher space dimensions, if the inflow concentration stabilizes to a fixed value. Therefore it is desirable to study the existence and the qualitative properties of travelling waves and to achieve detailed information, which is unlikely to get in the general case, for this prototype situation. If one restricts to one-species-systems with a nonlinear *equilibrium adsorption reaction*, then it is easy to derive formally an implicit expression for the wave profile, which, in some cases, can be resolved leading to solutions in closed form. This situation changes fundamentally, if in addition to an equilibrium reaction a *non-equilibrium adsorption reaction* is to be considered leading to two differential equations. In the last years such *multiple-site* or *bicontinuum models* have achieved much attention in the experimental literature (e.g. (Boesten, 1986) and the literature cited there).

In (v. Duijn/Knabner 1989) we considered one-species-models of this type taking into account general isotherms and rate functions for the description of the equilibrium and non-equilibrium adsorption reaction, respectively. On the basis of a phase plane analysis, we developed a rigorous mathematical framework for travelling wave solutions including characterization of existence, precise qualitative properties and limit behaviour. In this paper and its sequel we apply our results to various descriptions of adsorption and ion exchange, which are frequently discussed and used. The two-species-system of binary exchange can be put in our framework, as conservation properties allow a reduction to a one-species-system. Adsorption is taken here as a general notion in the sense that the distinction between ionic and nonionic species or cations and anions will play no decisive role. Our aim is to achieve enough *qualitative information* about travelling wave solutions for various models, such that these results may give hints for the proper selection of a model.

In further papers of this series we will address models for surface reactions with threshold effects as fixation or crystal dissolution and models for physical non-equilibrium, respectively.

This paper is organized as follows:

In *section 1* we develop the model in original and scaled variables ((1.7), (1.17) and (1.20)), fix the notions of travelling wave solutions ((1.24)) and of adsorption isotherms ((1.10)) and a classification of isotherms ((1.11), (1.12)). For the convenience of the reader some mathematical notation and results are collected in *Appendix A*.

In *section 2.1 and 2.2* we review some typical adsorption and ion exchange models and derive rigorously the mathematical properties of rate functions and isotherms, relevant for the travelling waves. The properties of the isotherm for binary ion exchange are developed in *Appendix B*, allowing for the general heterovalent case and for Debye-Hückel corrections. In particular, concavity and convexity of the isotherm are characterized ((B.29) – (B.31)). Furthermore, the significance of averaged isotherms is pointed out in *section 2.3* and the construction of rate functions from known isotherms is discussed in *section 2.4*. The analysis of the travelling wave solutions itself is subject of part 2 of this paper.

1. Basic Definitions

We consider the transport and adsorption process at the macroscopic scale appropriate for the measurement of the phenomena, but our macroscale model can be derived in principle from a corresponding micro model at the scale of single grains by averaging or homogenization (compare e.g. (Hornung/Jäger, 1987)).

Conservation of mass yields for c [mol/m³], the *concentration of adsorbate in solution*, and A [mol/kg], the *adsorbed concentration*

$$\frac{\partial}{\partial t}(\Theta c) + \rho \frac{\partial}{\partial t} A - \nabla \cdot (\Theta D \nabla c - q^* c) = 0. \quad (1.1)$$

Hereby t [s], x [m], Θ [-], ρ [kg/m³], D [m²/s], q^* [m/s] denote time, space, the water content, the bulk density, the sum of molecular diffusion and mechanical dispersion matrix and the water flux, respectively (and the spatial dimension is not restricted). We allow for the heterogeneity of the adsorbent surface and describe this by a set Λ . Examples for Λ are $\Lambda = \{1, \dots, m\}$ corresponding to a subdivision of a representative grain surface into m chemically different collections of adsorption sites or a nondiscrete set being a description of a representative, i.e. rescaled, grain surface, e.g. the unit sphere.

Let s_λ [mol/kg] be the *adsorbed concentration at adsorption sites corresponding to λ* , then

$$\begin{aligned} A &= \int_{\Lambda} s_\lambda d\lambda, \\ \frac{\partial}{\partial t} s_\lambda &= k_\lambda F_\lambda(c, s_\lambda) \quad \text{for } \lambda \in \Lambda, \end{aligned} \quad (1.2)$$

where \int_{Λ} denotes a (discrete or continuous) averaging and the second equation is a general rate description of the adsorption reaction with a rate parameter $k_\lambda > 0$ [1/s]. – Compare Appendix A for some mathematical notation and basic mathematical results. –

We consider a subdivision of Λ into Λ_1 and Λ_2 . For $\lambda \in \Lambda_1$ it is assumed that the adsorption reaction is *in equilibrium* because the reaction kinetics are fast compared to the water flow (quasistationary approach). Therefore we have formally

$$\begin{aligned} k_\lambda &= +\infty & \text{for } \lambda \in \Lambda_1, \\ k_\lambda &< +\infty & \text{for } \lambda \in \Lambda_2, \end{aligned}$$

and thus

$$F_\lambda(c, s_\lambda) = 0 \quad \text{for } \lambda \in \Lambda_1.$$

This equation substitutes the rate equation for the sites in Λ_1 . If we can resolve this equation for s_λ , i.e.

$$F_\lambda(c, s_\lambda) = 0 \quad \Leftrightarrow \quad s_\lambda = \Psi_\lambda(c) \quad \text{for } \lambda \in \Lambda_1, \quad (1.3)$$

we call Ψ_λ an (*adsorption*) *isotherm* and equations (1.1), (1.2) take the form

$$\frac{\partial}{\partial t}(\Theta c) + \rho \frac{\partial}{\partial t} \left\{ \lambda_1 \int_{\Lambda_1} \Psi_\lambda(c) d\lambda + \lambda_2 \int_{\Lambda_2} s_\lambda d\lambda \right\} - \nabla \cdot (\Theta D \nabla c - q^* c) = 0, \quad (1.4a)$$

$$\frac{\partial}{\partial t} s_\lambda = k_\lambda F_\lambda(c, s_\lambda) \quad \text{for } \lambda \in \Lambda_2. \quad (1.4b)$$

Here $\lambda_1 := |\Lambda_1|/|\Lambda|$ and $\lambda_2 := |\Lambda_2|/|\Lambda|$, i.e. λ_1, λ_2 are the relative measures of the different sets of adsorption sites.

In particular $\lambda_1 + \lambda_2 = 1$.

Equation (1.4a) shows that the adsorption behaviour of the sites in Λ_1 , possibly being different from one site to the other, only acts through the *averaged isotherm*

$$\Psi(c) := \int_{\Lambda_1} \Psi_\lambda(c) d\lambda. \quad (1.5)$$

Thus the set Λ_1 behaves as a set of homogeneous adsorption sites with the averaged isotherm Ψ .

To reduce the problem to two unknown functions c and s we *assume* that the sites in Λ_2 behave homogeneous, i.e.

$$k_\lambda = k, \quad F_\lambda(c, s) = F(c, s) \quad \text{for } \lambda \in \Lambda_2.$$

Then also s_λ for $\lambda \in \Lambda_2$ becomes independent of λ and we end up with the model, we are going to consider:

$$\frac{\partial}{\partial t}(\Theta c) + \rho \frac{\partial}{\partial t} \left\{ \lambda_1 \Psi(c) + \lambda_2 s \right\} - \nabla \cdot (\Theta D \nabla c - q^* c) = 0, \quad (1.6a)$$

$$\frac{\partial}{\partial t} s = k F(c, s). \quad (1.6b)$$

For a one-dimensional, stationary flow directed from $x = -\infty$ (upstream) to $x = +\infty$ (downstream), i.e. for constant positive Θ, ρ, D, q , equations (1.6) for $c = c(x, t), s = s(x, t)$ read

$$\Theta \frac{\partial}{\partial t} c + \rho \frac{\partial}{\partial t} \left\{ \lambda_1 \Psi(c) + \lambda_2 s \right\} - \Theta D \frac{\partial^2}{\partial x^2} c + q^* \frac{\partial}{\partial x} c = 0, \quad (1.7a)$$

$$\frac{\partial}{\partial t} s = k F(c, s) \quad (1.7b)$$

for $-\infty < x < +\infty$, and $t > 0$.

The *travelling wave solutions* (c, s) depend on $\eta = x - at$ only, with a *wave speed* a , and have to fulfill the differential equations (1.7) and upstream the boundary conditions

$$c(-\infty, t) = c^*, \quad s(-\infty, t) = s^* \quad \text{for } t > 0, \quad (1.8a)$$

and downstream

$$c(+\infty, t) = c_*, \quad s(+\infty, t) = s_* \quad \text{for } t > 0. \quad (1.8b)$$

A travelling wave can only exist, if the boundary values are in equilibrium, i.e.

$$F(c^*, s^*) = 0 \quad \text{and} \quad F(c_*, s_*) = 0. \quad (1.9)$$

In section 2 we review several derivations of adsorption rate functions F ranging from the Langmuir approach and extensions of it via the binary ion exchange to heuristic forms on the basis of isotherms. It turns out that all the rate functions share the following *basic properties*:

For appropriately chosen $c_m > 0$ and $s_m > 0$, satisfying $F(c_m, s_m) = 0$, we set

$$\Omega := (0, c_m] \times (0, s_m] \quad \text{and} \quad \bar{\Omega} := [0, c_m] \times [0, s_m].$$

Then:

(i) $F \in C(\bar{\Omega}) \cap C^{0,1}(\Omega)$,

(ii) there exists a function $\Phi : [0, c_m] \rightarrow [0, s_m]$ such that

$$\begin{aligned} F(c, \Phi(c)) &= 0 \quad \text{for } c \in [0, c_m], \\ \text{and } F(c, s) &\gtrless 0, \quad \text{if } s \lesseqgtr \Phi(c), \end{aligned} \quad (1.10)$$

(iii) $\Phi \in C([0, c_m]) \cap C^{0,1}((0, c_m))$,

$$\Phi(0) = 0, \quad \Phi(c_m) = s_m,$$

(iv) Φ is strictly increasing in $[0, c_m]$.

In accordance with definition (1.3) we call Φ the *isotherm* related to the rate function F , if (1.10)(i)–(iii) is fulfilled and the *monotone isotherm*, if also (1.10)(iv) is satisfied.

In a heuristic approach, which is widely used in contaminant transport models ((Bolt, 1979), (Enfield *et al.*, 1976)), F takes the explicit form

$$F(c, s) = \Phi(c) - s. \quad (1.11)$$

In this case we call F to be of *explicit type* or of *type (E)*. We will assume throughout our analysis of model (1.7) that the property (1.10) is fulfilled for F and that also the isotherm Ψ satisfies (1.10)(iii),(iv). Analogously to (Giles *et al.*, 1974) we classify isotherms according to their behaviour near $c = 0$. We say

$$\begin{aligned} \Phi \text{ is } & \textit{of Langmuir type} \text{ or } \textit{of type (L)}, \text{ if} \\ & \Phi \text{ is strictly concave near } c = 0 \text{ and } \Phi'(0+) < +\infty, \\ \Phi \text{ is } & \textit{of Freundlich type} \text{ or } \textit{of type (H)}, \text{ if} \\ & \Phi \text{ is strictly concave near } c = 0 \text{ and } \Phi'(0+) = +\infty, \\ \Phi \text{ is } & \textit{of convex type} \text{ or } \textit{of type (S)}, \text{ if} \\ & \Phi \text{ is strictly convex near } c = 0. \end{aligned} \quad (1.12)$$

Figure 1 shows various examples of isotherms according to this classification. In this Figure we also made a distinction with respect to the number of curvature changes.

Figure 1. Isotherm classification.

The occurrence of these types, which will turn out to be of importance with respect to existence of travelling waves and their properties, is investigated in section 2 for the rate functions derived there.

Before proceeding we rescale some quantities. For fixed parameters, the usual way is to change to non-dimensional variables, e.g. by setting

$$\begin{aligned}\hat{x} &:= x/L, & \hat{t} &:= t/T, \\ \hat{u} &:= (c - c_*)/\Delta c, & \hat{v} &:= (s - s_*)/\Delta s, \\ \hat{\psi}(\hat{u}) &:= \Psi(\Delta c \hat{u} + c_*)/\Delta s, \\ \hat{f}(\hat{u}, \hat{v}) &:= F(\Delta c \hat{u} + c_*, \Delta s \hat{v} + s_*)/\Delta s,\end{aligned}\tag{1.13}$$

where L and T have the dimensions [m] and [s], respectively and

$$\Delta c := c^* - c_*, \quad \Delta s := s^* - s_*.$$

Then equations (1.7) transform to

$$\begin{aligned}\frac{\partial \hat{u}}{\partial \hat{t}} + H \frac{\partial}{\partial \hat{t}} \left\{ \lambda_1 \hat{\psi}(\hat{u}) + \lambda_2 \hat{v} \right\} - \\ - \frac{T q^*}{\Theta L} \frac{\partial}{\partial \hat{x}} \left(\frac{\Theta D}{q^* L} \frac{\partial \hat{u}}{\partial \hat{x}} - \hat{u} \right) = 0,\end{aligned}\tag{1.14a}$$

$$\frac{\partial \hat{v}}{\partial \hat{t}} = T k \hat{f}(\hat{u}, \hat{v}),\tag{1.14b}$$

where

$$H := \frac{\rho \Delta s}{\Theta \Delta c} \quad [-].\tag{1.15}$$

If we now choose

$$L := \frac{\Theta D}{q^*}, \quad T := \frac{\Theta^2 D}{q^{*2}},$$

and introduce

$$K := \frac{k \Theta^2 D}{q^{*2}} \quad [-],\tag{1.16}$$

then equations (1.14) reduce to

$$\begin{aligned}\frac{\partial \hat{u}}{\partial \hat{t}} + H \frac{\partial}{\partial \hat{t}} \left\{ \lambda_1 \hat{\psi}(\hat{u}) + \lambda_2 \hat{v} \right\} - \frac{\partial}{\partial \hat{x}} \left(\frac{\partial \hat{u}}{\partial \hat{x}} - \hat{u} \right) = 0, \\ \frac{\partial \hat{v}}{\partial \hat{t}} = K \hat{f}(\hat{u}, \hat{v}).\end{aligned}\tag{1.17}$$

The explicit type for F is invariant under this transformation: F according to (1.11) transforms to

$$\hat{f}(\hat{u}, \hat{v}) = \hat{\varphi}(\hat{u}) - \hat{v}, \quad \hat{\varphi}(\hat{u}) := (\Phi(\Delta c \hat{u} + c_*) - s_*)/\Delta s.\tag{1.18}$$

The drawback of the formulation (1.17) is that it cannot be used to study the limit $D \rightarrow 0$, which is what we are going to do. Therefore we refer to (1.17) only occasionally, but rather use a redefinition, which basically adjusts the dimensions of c and s to $[\text{mol}/\text{m}^3]$. We set

$$\begin{aligned} u &:= c, & v &:= \lambda_2 \rho / \Theta s, \\ q &:= q^* / \Theta, & & \text{the interstitial flux,} \\ \psi(u) &:= \lambda_1 \rho / \Theta \Psi(u), \\ f(u, v) &:= \lambda_2 \rho / \Theta F(u, \Theta / (\lambda_2 \rho) v). \end{aligned} \tag{1.19}$$

Then equations (1.7) and the boundary conditions (1.8) transform to

$$\frac{\partial}{\partial t} u + \frac{\partial}{\partial t} (\psi(u) + v) - D \frac{\partial^2}{\partial x^2} u + q \frac{\partial}{\partial x} u = 0, \tag{1.20a}$$

$$\frac{\partial}{\partial t} v = k f(u, v) \tag{1.20b}$$

$$\text{for } -\infty < x < +\infty, \quad t > 0,$$

$$\begin{aligned} u(-\infty, t) &= u^*, & u(+\infty, t) &= u_*, \\ v(-\infty, t) &= v^*, & v(+\infty, t) &= v_* \text{ for } t > 0. \end{aligned} \tag{1.21}$$

The basic properties (1.10) are exactly the same in the new variables, setting

$$u_m := c_m, \quad v_m := \lambda_2 \rho / \Theta s_m, \quad \varphi(u) := \lambda_2 \rho / \Theta \Phi(u). \tag{1.22}$$

Also the explicit type for F is preserved here. Expression (1.11) reads

$$f(u, v) = \varphi(u) - v, \quad \varphi(u) := \lambda_2 \rho / \Theta \Phi(u). \tag{1.23}$$

We look for *travelling wave solutions* $\{u, v, a\}$ of this problem. By this we mean

$$u = u(\eta), \quad v = v(\eta) \quad \text{with } \eta := x - at,$$

where the functions u and v and the *wave speed* a have to satisfy

$$TW \left\{ \begin{array}{l} -a(u + \psi(u) + v)' - Du'' + qu' = 0 \\ -av' = kf(u, v) \\ u(-\infty) = u^*, \quad u(+\infty) = u_*, \\ v(-\infty) = v^*, \quad v(+\infty) = v_*. \end{array} \right\} \text{ in } \mathbb{R}, \tag{BC}$$

Here $'$ denotes the differentiation with respect to η .

Without loss of generality we only consider boundary values

$$0 \leq u_*, u^* \leq u_m, \quad 0 \leq v_*, v^* \leq v_m.$$

Because (1.10)(ii) holds, the necessary condition (1.9) implies

$$v^* = \varphi(u^*), \quad v_* = \varphi(v_*). \quad (1.25)$$

Thus in view of (1.10)(iv) the two possible cases are

$$u^* > u_* \geq 0, \quad v^* > v_* \geq 0, \quad (1.26a)$$

$$u_* > u^* \geq 0, \quad v_* > v^* \geq 0. \quad (1.26b)$$

In the first case we speak of *adsorption waves*, in the second of *desorption waves*. We will concentrate mainly on adsorption waves, as desorption waves can be transformed to adsorption waves by setting

$$\begin{aligned} \tilde{u} &:= u_* + u^* - u, & \tilde{v} &:= v_* + v^* - v, \\ \tilde{\psi}(\tilde{u}) &:= \psi_* + \psi^* - \psi(u_* + u^* - \tilde{u}), \\ \tilde{f}(\tilde{u}, \tilde{v}) &:= -f(u_* + u^* - \tilde{u}, v_* + v^* - \tilde{v}). \end{aligned} \quad (1.27)$$

Here we already used the *abbreviations*:

$$\begin{aligned} \psi^* &:= \psi(u^*), & \psi_* &:= \psi(u_*), \\ \Delta u &:= u^* - u_*, & \Delta v &:= v^* - v_*, & \text{and } \Delta\psi &:= \psi^* - \psi_*. \end{aligned} \quad (1.28)$$

Considering only adsorption waves thus means

$$\Delta u > 0, \quad \Delta v > 0, \quad \text{and } \Delta\psi \geq 0. \quad (1.29)$$

(Note that $\lambda_1 = 0$ is possible).

2. Adsorption Processes

In this section we derive some representative adsorption rate functions (compare (1.2), (1.6)) and study those properties which are of importance for travelling wave solutions. We want to describe at the microscopic level the overall adsorption rate function

$$k \tilde{F}(c, \tilde{s}) \tag{2.1}$$

where $k[1/s]$ is a rate parameter and \tilde{s} [mol/m²] *the surface concentration of the adsorbate*. Here we suppress the dependence of \tilde{F} on $\lambda \in \Lambda$ expressing the microscopic heterogeneity of the adsorption process. Instead of \tilde{s} it is more convenient to consider the *molar concentration relative to mass of adsorbent* s [mol/kg]. If the underlying microscopic spatial structure is periodic as necessary for homogenization, we have

$$\begin{aligned} s &= A/\rho \tilde{s}, \\ F(c, s) &:= A/\rho \tilde{F}(c, \rho/As), \end{aligned} \tag{2.2}$$

where A is the specific surface of a representative grain and ρ the bulk density. The same rate function then appears in the macroscopic equations (1.2) or (1.6b).

A rational description of \tilde{F} usually is based on *collision theory* from kinetic gas theory, i.e. the rate function is formulated at a *discrete molecular level*. To pass to the continuous microscopic level a first "averaging" procedure is necessary which allows us to introduce the concentrations c and s . We implicitly consider this step being carried out.

Below we describe the *adsorption rate* F_a and the *desorption rate* F_d depending on c and s , which leads to

$$k F = F_a - F_d. \tag{2.3}$$

2.1 Adsorption Rate Description based on Molecular Theory.

The classical theory, going back to I. Langmuir, is based on the following assumptions (compare e.g. (Thomas/Thomas, 1967) or (Aris, 1975)):

- The adsorbed particles are located at well-defined adsorption sites, each of which can bind exactly one adsorbed particle.
- A particle in solution breaks up into ℓ particles during the process of adsorption and needs ℓ neighbouring adsorption sites.

Relating the probability that a particle in solution with sufficient energy meets ℓ available neighbouring adsorption sites to the concentrations, one arrives at

$$F_a(c, s) = k_a c (1 - s/s_{\max})^\ell \exp(-E_a/(RT)) \quad \text{for } c \geq 0, 0 \leq s \leq s_{\max}, \tag{2.4a}$$

where s_{\max} is the maximal adsorbed concentration, corresponding to the occupation of all adsorption sites, E_a [J/mol] the activation energy for adsorption, R [J/(K mol)] the gas constant and T [K] the temperature. In the adsorption rate constant $k_a > 0$ all factors are summarized, which define the relation between concentration and particle flux density according to kinetic gas theory. In particular k_a depends on T . Analogously:

$$F_d(c, s) = k_d(s/s_{\max})^\ell \exp(-E_d/(RT)), \quad (2.4b)$$

where E_d is the activation energy for desorption and $k_d > 0$ the corresponding rate constant. We define

$$Q := (E_d - E_a)/(RT), \quad b := k_a/k_d \exp(Q), \quad (2.5)$$

i.e. $Q \cdot R \cdot T$ is the *heat of adsorption*.

A further assumption of the classical theory is:

- E_a, E_d are independent of c and s .

Then F fulfills our basic properties (1.10), if we define

$$\Phi(c) := \frac{s_{\max}(bc)^{1/\ell}}{1 + (bc)^{1/\ell}} \quad \text{for } c \geq 0, \quad (2.6)$$

with $c_m > 0$ and $s_m := \Phi(c_m)$.

For $\ell = 1$, Φ is the well-known *Langmuir-isotherm*.

The function Φ satisfies the additional properties

- ◊ $\Phi(+\infty) = s_{\max}$ and Φ is strictly concave for $c \geq 0$.
- ◊ $\Phi'(0+) < +\infty \Leftrightarrow \ell = 1$.

Thus we have in particular:

- ◊ For $\ell = 1$ Φ is of type (L) and of type (H) otherwise (Figure 1, L/H(a)).

– For our considerations $\ell \geq 1$ could also be a general real number. –

Thus the assumption of constant Q does not lead to isotherms which exhibit a change in curvature, such as isotherms for example of type (S). However it has been conjectured that these cases, which can be observed experimentally, arise if the heat of adsorption Q depends on s . Giles *et al.* (1974) assume that the adsorbed particles bind with each other, which implies that Q increases with s . This is called *cooperative adsorption*.

In contrast, other models lead to a heat of adsorption, which is decreasing with s (cf. e.g. (Wilkinson, 1980)).

In general, if $Q = Q(s)$, there is no explicit form of the isotherm anymore. Instead we have

$$F(c, s) \stackrel{\geq}{\leq} 0 \Leftrightarrow c \stackrel{\geq}{\leq} X(s) \quad \text{for } c \geq 0, s \in [0, s_{\max}),$$

where

$$X(s) := k_d/k_a \exp(-Q(s)) \left(\frac{s}{s_{\max} - s} \right)^\ell.$$

For sufficiently smooth Q , the basic properties (1.10) are fulfilled only if X is strictly increasing in $[0, s_{\max})$. Then Φ can be defined as the inverse of X on $[0, s_{\max})$ with $c_m := X(s_m)$. A simple calculation shows that

$$X'(s) \stackrel{\geq}{\leq} 0 \Leftrightarrow Q'(s) \stackrel{\leq}{\geq} \ell s_{\max} / ((s_{\max} - s)s) \quad \text{for } s \in (0, s_{\max}),$$

which implies the statement

$$\diamond \text{ If } Q'(s) < 4\ell/s_{\max}, \text{ then } X'(s) > 0 \text{ for } s \in (0, s_{\max}). \quad (2.7)$$

To stay within the framework of property (1.10), we assume that statement (2.7) holds. This leads to the strictly increasing isotherm $\Phi := X^{-1}$ satisfying

- $\diamond \Phi(0) = 0, \Phi(+\infty) = s_{\max}.$
- $\diamond \Phi'(0+) < +\infty \text{ exists } \Leftrightarrow \ell = 1.$

For $\ell = 1$ we have $\Phi'(0+) = s_{\max}k_a/k_d \exp(Q(0))$.

Furthermore

$$\begin{aligned} X''(s) \stackrel{\leq}{\geq} 0 \Leftrightarrow Q'^2(s) - Q''(s) \stackrel{\leq}{\geq} \\ -\ell(\ell-1) \frac{s_{\max}^2}{(s_{\max}-s)^2 s^2} - \frac{2s_{\max}\ell}{(s_{\max}-s)s} \left(\frac{1}{s_{\max}-s} - Q'(s) \right) \end{aligned} \quad \text{for } s \in (0, s_{\max}). \quad (2.8)$$

From this we obtain the following properties

- $\diamond X''(s) > 0$ for s near s_{\max} and thus $\Phi''(c) < 0$ for c sufficiently large.

For the case $\ell = 1$:

- \diamond If $Q'(0) < 1/s_{\max}$, then $X''(s) > 0$ near $s = 0$ and thus $\Phi''(c) < 0$ near $c = 0$. This implies that Φ is of type (L).
- \diamond If $Q'(0) > 1/s_{\max}$, then $X''(s) < 0$ near $s = 0$ and thus $\Phi''(c) > 0$ near $c = 0$. This implies that Φ is of type (S).

For the case $\ell \geq 2$:

- $\diamond \Phi''(c) < 0$ for small $c > 0$. Because of $\Phi'(0+) = +\infty$ for these cases we deduce that Φ is of type (H).

From (2.8) we can also derive a sufficient condition for the strict concavity of Φ for all $c > 0$:

- ◇ If $Q''(s) \leq 0$ and $Q'(s) < (2\ell - 1)/s_{\max}$ for $0 < s < s_{\max}$, then $X''(s) > 0$ for $0 < s < s_{\max}$ and consequently $\Phi''(c) < 0$ for all $c > 0$ (Figure 1, L/H(a)).

Giles *et al.* (1974) replace the dependence of Q on s by a dependence of Q on c , because this leads to explicit forms of the isotherm similar to the case of constant Q . For sufficiently smooth $Q = Q(c)$, this gives again a rate function f satisfying (1.10)(i)–(iii) with the isotherm (see also (2.6))

$$\Phi(c) := \frac{s_{\max}(b(c)c)^{1/\ell}}{1 + (b(c)c)^{1/\ell}} \quad \text{for } c \geq 0,$$

where

$$b(c) := \alpha \exp(Q(c)), \quad \alpha := k_a/k_d \quad \text{and } c_m > 0 \quad \text{with } s_m := \Phi(c_m).$$

We illustrate the behaviour of Φ for this case by working out the following example.

Example. $\ell = 1$ and $Q(c) = Q_0 + \beta c^n$ where $Q_0 \in \mathbb{R}$, $\beta \geq 0$ and $n \geq 1$. Then the following is true.

- ◇ $\Phi'(c) > 0$ for $c \geq 0$.
- ◇ $\Phi(0) = 0$, $\Phi(+\infty) = s_{\max}$.

For $n = 1$:

- ◇ $\Phi''(c) < 0$ for c large.
- ◇ If $\alpha \exp Q_0 \geq \beta$ then $\Phi''(c) < 0$ for all $c > 0$ and in particular Φ is of type (L).
- ◇ $\alpha \exp Q_0 \leq \beta \Leftrightarrow \Phi''(0) \geq 0$. Thus in particular if $\alpha \exp Q_0 < \beta$ then $\Phi''(c) > 0$ for small c and φ is of type (S).

For $n \geq 2$:

- ◇ $\Phi''(c) < 0$ for small c and for large c , i.e. Φ is of type (L).
- ◇ If $n \geq 6$ then there exists a $\hat{c} > 0$ at which $\Phi''(\hat{c}) > 0$. In this case the curvature of the isotherm changes sign at least twice (Figure 1, L(c)).

2.2 Binary Ion Exchange.

We now consider ion exchange in the sense that the binding on the grain surface, the *exchange complex*, is due to electric charges carried by the solutes and the exchange complex. One assumes that all sites on the exchanges are covered at all times. Therefore a variation in the concentration of one of the species at the exchange complex can only be due to the

competition of another species. Consequently one has to consider at least two species. The two species case is called *binary ion exchange*. We discuss it below in two parts.

In the first part, under appropriate assumptions, we reduce this two-species-system to a one-species-system, whose dynamics is described in the form (1.6). This relation between binary ion exchange and adsorption is known in principle in soil science (cf. e.g. (Sposito, 1979)). In the second part we describe some variants of rate functions and study their properties. The considerations below apply both to cation and to anion exchange.

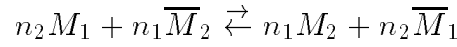
For $i = 1, 2$ let

M_i denote the ion i in solution,

\overline{M}_i denote the ion i attached to the exchange complex,

n_i denote the valence of ion i .

Then the exchange reaction has the form



in order to maintain electroneutrality. Let the rate from left to right be denoted by \tilde{k}_1 and from right to left by \tilde{k}_2 .

If c_i and s_i denote the concentrations of M_i and \overline{M}_i , respectively, then mass conservation yields analogously to (1.6)

$$\begin{aligned} \frac{\partial}{\partial t}(\Theta c_i) + \rho \frac{\partial}{\partial t} \{ \lambda_1 \psi_i(c_i) + \lambda_2 s_i \} - \nabla \cdot (\Theta D \nabla c_i - q^* c_i) &= 0, \\ \frac{\partial}{\partial t} s_i &= F_i(c_1, s_1, c_2, s_2), \quad i = 1, 2, \\ F_1 &= n_2(\tilde{k}_1 - \tilde{k}_2), \\ F_2 &= n_1(\tilde{k}_2 - \tilde{k}_1). \end{aligned} \tag{2.9}$$

Note that we also allow for an additional adsorption reaction described by ψ_i . If we define

$$\overline{s}(x, t) := n_1 s_1(x, t) + n_2 s_2(x, t) \tag{2.10}$$

as the *ion exchange capacity*, (2.9) implies

$$\frac{\partial \overline{s}}{\partial t} = 0. \tag{2.11}$$

If one considers an initial-boundary value problem for (2.9), then \overline{s} is determined directly by the initial values of s_1 and s_2 . Here we are interested in travelling wave solutions

$$c_i = c_i(x - at), \quad s_i = s_i(x - at),$$

a being the wave speed, which fulfill the boundary conditions

$$\begin{aligned} c_i(-\infty) &= c_i^*, & c_i(+\infty) &= c_{i*}, \\ s_i(-\infty) &= s_i^*, & s_i(+\infty) &= s_{i*}. \end{aligned}$$

Then also \bar{s} depends only on $x - at$ and thus due to (2.11) has to be constant. Thus we get as a necessary condition for the existence of travelling waves:

$$n_1 s_1^* + n_2 s_2^* = n_1 s_{1*} + n_2 s_{2*} =: \bar{s} \quad (2.12)$$

and (2.10) holds as an equality.

From now on we neglect differences in molecular diffusivities and take the same linear adsorption isotherm, i.e.

- $D_1 = D_2 =: D, \quad \psi_i(c) = \psi(c) := Ac, \quad A > 0.$

Defining

$$\bar{c}(x, t) := n_1 c_1(x, t) + n_2 c_2(x, t)$$

this leads to the equation

$$\frac{\partial}{\partial t}((\Theta + \lambda_1 A)\bar{c}) - \nabla \cdot (\Theta D \nabla \bar{c} - q^* \bar{c}) = 0. \quad (2.13)$$

In the case of travelling waves of (2.9), we also have a travelling wave solution of (2.13). This wave has a given speed a , determined by (2.9), and satisfies the boundary conditions $n_1 c_1^* + n_2 c_2^*$ at $-\infty$ and $n_1 c_{1*} + n_2 c_{2*}$ at $+\infty$. However, (2.13) is a linear convection-diffusion equation. Therefore the only travelling wave that can occur is the trivial (=constant) wave. Hence we have as a necessary condition for the existence of travelling waves:

$$n_1 c_1^* + n_2 c_2^* = n_1 c_{1*} + n_2 c_{2*} =: \bar{c}. \quad (2.14)$$

In what follows we assume that (2.12) and (2.14) holds. Then we can reduce the four unknown concentrations to the pair

$$c := c_1, \quad s := s_1$$

by setting

$$c_2 := \frac{n_1}{n_2} \left(\frac{\bar{c}}{n_1} - c_1 \right) \quad \text{and} \quad s_2 := \frac{n_1}{n_2} \left(\frac{\bar{s}}{n_1} - s_1 \right).$$

It is convenient to define

$$\bar{c} := \frac{\bar{c}}{n_1} \quad \text{and} \quad \bar{s} := \frac{\bar{s}}{n_1}. \quad (2.15)$$

Then the equations for c and s resulting from (2.9) have the form of (1.6). We still have to specify the rate functions \tilde{k}_1 and \tilde{k}_2 , leading to the overall rate function $F := F_1$. We set according to (2.3)

$$F_a := n_2 \tilde{k}_1 \quad \text{and} \quad F_d := n_2 \tilde{k}_2.$$

A rate description analogously to section 2.1 yields

$$\begin{aligned} \tilde{k}_1 &= \hat{k}_2 [M_1]^{n_2} [\overline{M}_2]^{n_1}, \\ \tilde{k}_2 &= \hat{k}_2 [M_2]^{n_1} [\overline{M}_1]^{n_2}, \end{aligned}$$

when $\hat{k}_i > 0$ are constants and where $[M]$ denotes the *activity of M*. Different variants of f are caused by different definitions of $[M_i]$ or $[\overline{M}_i]$.

In *dilute solutions* one usually defines

$$\bullet [M_i] = \gamma_i c_i, \quad [\overline{M}_i] = \delta_i s_i \tag{2.16}$$

with constants $\gamma_i, \delta_i > 0, i = 1, 2$.

This assumption has been used e.g. by Rubin/James (1973) and Cederberg *et al.* (1985).

As \overline{s} is a constant here, the Gaines-Thomas approach, used e.g. by Valocchi *et al.* (1981), fits into the formulation (2.16) by

$$\delta_i = \hat{\delta}_i / \overline{s} \tag{2.17}$$

with new constants $\hat{\delta}_i$.

Now the rate functions take the form

$$\begin{aligned} F_a(c, s) &= k_1 c^{n_2} (\overline{s} - s)^{n_1} \\ F_d(c, s) &= k_2 (\overline{c} - c)^{n_1} s^{n_2} \quad \text{for } c \in [0, \overline{c}], s \in [0, \overline{s}], \\ \text{where } k_1 &:= n_2 \hat{k}_1 \gamma_1^{n_2} \delta_2^{n_1} \left(\frac{n_1}{n_2} \right)^{n_1}, \\ k_2 &:= n_2 \hat{k}_2 \gamma_2^{n_1} \delta_1^{n_2} \left(\frac{n_1}{n_2} \right)^{n_1}. \end{aligned} \tag{2.18}$$

For *strong electrolyts* the Debye-Hückel-theory takes into account the interaction of the different ions in solution (cf. e.g. (Sposito, 1981) or (Garrels/Christ, 1965)). Let the *ion strength I* be defined by

$$I := \frac{1}{2} (n_1^2 c_1 + n_2^2 c_2 + \hat{c}),$$

where \hat{c} is a constant representing the concentrations of all ions in solution different from M_1 and M_2 . Then (2.16) is modified into

$$\bullet [M_i] = \gamma_i c_i, \quad \gamma_i = \exp(-n_i^2 \sigma(I)),$$

$$[\overline{M}_i] = \delta_i s_i, \quad \delta_i > 0 \text{ constant}, \quad i = 1, 2. \quad (2.19)$$

Hereby σ has the form

$$\sigma(I) := \frac{a_1 I^{1/2}}{1 + a_2 I^{1/2}} - a_3 I, \quad (2.20)$$

where $a_1 > 0$, $a_2, a_3 \geq 0$.

Accordingly (2.18) becomes

$$\begin{aligned} F_a(c, s) &= k_1 (\gamma_1(c) c)^{n_2} (\overline{s} - s)^{n_1} \\ F_d(c, s) &= k_2 (\gamma_2(c) (\overline{c} - c))^{n_1} s^{n_2} \end{aligned} \quad \text{for } c \in [0, \overline{c}], s \in [0, \overline{s}], \quad (2.21)$$

$$\text{where } k_1 := n_2 \hat{k}_1 \delta_2^{n_1} \left(\frac{n_1}{n_2}\right)^{n_1} \quad \text{and} \quad k_2 := n_2 \hat{k}_2 \delta_1^{n_2} \left(\frac{n_1}{n_2}\right)^{n_1}.$$

Here γ_i is defined by (2.19) and (2.20) and

$$I := \frac{1}{2} (n_1 (n_1 - n_2) c + n_1 n_2 \overline{c} + \hat{c}). \quad (2.22)$$

There are only a few explicit isotherms available: In the *homovalent case* $n_1 = n_2 =: n$ properties (1.10) are fulfilled for $c_m := \overline{c}$, $s_m := \overline{s}$ and

$$\Phi(c) := \frac{\overline{s} c}{K^{1/n} \overline{c} + (1 - K^{1/n}) c}, \quad (2.23)$$

where $K := k_2/k_1$.

The similarity with (2.6) for $K < 1$ is well-known.

The general cases (2.18) and (2.21) are analysed in Appendix B. The main results are, setting $c_m := \overline{c}$ and $s_m := \overline{s}$:

- ◇ Property (1.10)(i)–(iii) is fulfilled with an isotherm $\Phi \in C^1([0, \overline{c}])$.
- ◇ For γ_i according to (2.18) (=constant), Φ is strictly increasing. (2.24)
- ◇ For γ_i according to (2.21), Φ is strictly increasing, if $a_1 \leq a_2$ and $|n_1 - n_2| \leq 3$, or if (B.27) holds.
- ◇ For γ_i according to (2.18) and for $K := k_2/k_1$, we have:

$$\text{If } K = \left(\frac{\overline{s}}{\overline{c}}\right)^{n_1 - n_2}, \text{ then } \Phi(c) = \frac{\overline{s}}{\overline{c}} c \text{ for } c \in [0, \overline{c}].$$

If $K < \left(\frac{\overline{s}}{\overline{c}}\right)^{n_1 - n_2}$, then Φ is strictly concave in $[0, \overline{c}]$, in particular Φ is of type (L) (Figure 1, L(a)). (2.25)

If $K > \left(\frac{\overline{s}}{\overline{c}}\right)^{n_1 - n_2}$, then Φ is strictly convex in $[0, \overline{c}]$, in particular Φ is of type (S) (Figure 1, S(a)).

2.3 Isotherms by Averaging Procedures.

In section 1 we divided the surface Λ of a representative grain into a part Λ_1 , related to equilibrium adsorption, and a part Λ_2 , related to non-equilibrium adsorption. For sites assembled in Λ_1 we introduced the averaged isotherm

$$\Psi(c) = \int_{\Lambda_1} \Psi_\lambda(c) d\lambda.$$

For sites assembled in Λ_2 we considered the reaction equations

$$\frac{\partial}{\partial t} s_\lambda = k_\lambda F_\lambda(c, s_\lambda), \quad \lambda \in \Lambda_2.$$

Assuming that F_λ satisfies (1.10)(ii) for each $\lambda \in \Lambda_2$, this leads to a family of isotherms $\{\Phi_\lambda \mid \lambda \in \Lambda_2\}$. Averaging then gives

$$\Phi(c) = \int_{\Lambda_2} \Phi_\lambda(c) d\lambda \tag{2.26}$$

as the *averaged isotherm for sites Λ_2* . For the total grain surface we now introduce

$$\lambda_1 \Psi(c) + \lambda_2 \Phi(c) \tag{2.27}$$

as the (*overall*) *averaged isotherm*. It is interesting to note that the existence of a travelling wave solution is solely determined by the isotherm in (2.27) (see condition (C) in section 3) in the cases we consider here.

If the adsorption sites in Λ_2 are homogeneous, i.e. Φ_λ is independent of λ , then the averaging in (2.26) is trivial. This relates to a situation as presented in the introduction and leads to equations (1.6). If the rate functions F_λ are of explicit type (E) with the same rate constant k , we can proceed as follows. Consider

$$\frac{\partial}{\partial t} s_\lambda = k(\Phi_\lambda(c) - s_\lambda) \tag{2.28}$$

and set

$$s(x, t) := \int_{\Lambda_2} s_\lambda(x, t) d\lambda.$$

Then we have

$$\frac{\partial}{\partial t} s = k(\Phi(c) - s), \tag{2.29}$$

where Φ is given by (2.26). Thus we have reduced the system consisting of $\{c, s_\lambda \mid \lambda \in \Lambda_2\}$ to a two-component-system $\{c, s\}$, which satisfies (1.6a) and (2.29). Having determined the concentration $c = c(x, t)$, one could try to resolve the $s_\lambda = s_\lambda(x, t)$ from the ordinary differential equations (2.28) for $\lambda \in \Lambda_2$. This would lead to a solution of the original

problem (1.4). We will develop this point in a subsequent paper. We observe here again that the averaged isotherm Φ for the sites in non-equilibrium together with the isotherm Ψ determines the existence of a travelling wave solution by means of the overall averaging according to (2.27).

Finally, a related averaging of isotherms has been developed to justify isotherms with properties different from the classical Langmuir form, i.e. from (2.6) for $\ell = 1$ (cf. e.g. (Aris, 1975)). The averaging is carried out with respect to a parameter $r \in \mathbb{R}$ which is weighted with a specific measure, in general given by a distribution function α , i.e.

$$\Psi(c) = \int_{\mathbb{R}} \Psi_r(c) \alpha(r) dr. \quad (2.30)$$

Usually ψ_r is taken according to Langmuir ((2.6), $\ell = 1$) and r corresponds to the heat of adsorption (compare (2.5)). For some specific distribution functions α the integral in (2.30) can be resolved in closed form, which leads to the following examples (cf. e.g. (Aris, 1975) and (Riemsdijk *et al.*, 1986)):

$$\Psi(c) = s_{\max} \frac{(Kc)^p}{1 + (Kc)^p}, \quad (2.31)$$

$$\Psi(c) = s_{\max} \left(\frac{Kc}{1 + Kc} \right)^p, \quad (2.32)$$

$$\Psi(c) = s_{\max} \frac{Kc}{(1 + (Kc)^p)^{1/p}}, \quad (2.33)$$

where in all cases $K > 0$, $0 < p \leq 1$. These parameters are related to the form of the distribution function α .

All the cases (1.5), (2.26) and (2.30) fit into the general form

$$\Psi(c) = \int_M \psi_\lambda(c) d\lambda, \quad (2.34)$$

where M is a set with a measure $d\lambda$, being compact with the possible exception of (2.30). Some immediate conclusions with respect to the classification of isotherms are:

- ◇ If Ψ_λ is concave (convex) for all $\lambda \in M$, then Ψ is concave (convex).
- ◇ To conclude strict concavity (convexity) of Ψ from the corresponding property of Ψ_λ for all $\lambda \in M$ requires additional conditions as e.g. the compactness of M and the continuity of $\Psi_\lambda(c)$ in λ for fixed c .

Nevertheless the examples show that the averaging may change the type of isotherm. Expressions (2.31) – (2.33) are all averages of the Langmuir-isotherm, i.e. of type (L). They are all strictly increasing and strictly concave for $c > 0$, but we have

- ◇ Ψ according to (2.31) or (2.32) satisfy:

$$\Psi'(0+) < +\infty \Leftrightarrow p = 1,$$

- i.e. they are of type (H) for $p < 1$.
- ◇ Ψ according to (2.33) always satisfies
 - $\Psi'(0+) = s_{\max} K^{2-p} < +\infty$, i.e.
 - Ψ is of type (L).

Observe that (2.31) is of the same form as (2.6) with $p = 1/\ell$.

2.4 Heuristic Adsorption Rate Description.

The descriptions of the rate function kF in sections 2.1 and 2.2 are on a chemico-physical basis, but they require parameters, whose experimental determination may be difficult. On the other hand, the adsorption isotherm Φ can be determined easily by batch equilibrium experiments.

Therefore a common approach is to compose a rate function from Φ such that

$$F(c, \Phi(c)) = 0 \quad \text{and} \quad F(c, s) \begin{cases} \geq 0 \\ \leq 0 \end{cases}, \quad \text{if } s \begin{cases} \leq \\ \geq \end{cases} \Phi(c),$$

i.e. (1.10)(ii) is satisfied. A popular approach fulfilling this condition is (1.11), i.e.

$$F(c, s) = \Phi(c) - s.$$

Many possibilities exist fulfilling the same afore-mentioned sign conditons.

An example is, assuming (1.10)(iv) holds:

$$F(c, s) = c - \Phi^{-1}(s). \tag{2.35}$$

– This formulation appears more justified in chemical engineering to describe a physical non-equilibrium caused by the adsorption rate limitation due to diffusion through a stagnant water film surrounding the grain. Therefore it will be studied in more detail in a subsequent paper. –

Although there may be no chemical or physical reasons to prefer (1.11) or (2.35) or any other form, the specific formulation is significant for the *qualitative* properties of the travelling wave solutions. This will be developed in section 4.

Appendix A: Mathematical Notation and Basic Results

Definition of intervals:

$$\begin{aligned}
 x \in [a, b] &\Leftrightarrow a \leq x \leq b, \\
 x \in (a, b) &\Leftrightarrow a < x < b, \\
 x \in (a, b] &\Leftrightarrow a < x \leq b, \\
 x \in [a, b) &\Leftrightarrow a \leq x < b \quad \text{for real numbers } a, b, x.
 \end{aligned}
 \tag{A.1}$$

For a function f defined on (a, b) :

$$\begin{aligned}
 f(a+) &\text{ is the limit from the right at } x = a, \\
 f(b-) &\text{ is defined analogously.}
 \end{aligned}
 \tag{A.2a}$$

For a function f defined on $[a, b]$:

$$\begin{aligned}
 f'(a+) &\text{ is the derivative from the right at } x = a, \\
 f'(b-) &\text{ is defined analogously.}
 \end{aligned}
 \tag{A.2b}$$

Let $\Omega = [a, b]$ or $\Omega = [a, b] \times [c, d]$ for real numbers a, b, c, d or $\Omega = \mathbb{R}$ (the whole real line), then:

$$\begin{aligned}
 &C(\Omega) \text{ is the space of continuous functions defined on } \Omega, \\
 &\text{let } k \text{ be a natural number:} \\
 &C^k(\Omega) \text{ is the space of continuous functions defined on } \Omega, \\
 &\text{whose } \ell\text{-th derivative for } 1 \leq \ell \leq k \text{ exists on } \Omega \text{ and is continuous} \\
 &\text{(derivatives in e.g. } x = a \text{ have to be understood one-sided)}.
 \end{aligned}
 \tag{A.3}$$

Let Ω be a set in \mathbb{R} or $\mathbb{R} \times \mathbb{R}$, respectively, then consider arbitrary numbers $\alpha < \beta$ and $\gamma < \delta$ such that $\tilde{\Omega} := [\alpha, \beta]$ or $\tilde{\Omega} := [\alpha, \beta] \times [\gamma, \delta]$, respectively, belongs to Ω :

$C^{0,1}(\Omega)$ is the space of functions f defined on Ω , such that there is a constant $L > 0$, possibly depending on $\alpha, \beta, \gamma, \delta$, and

$$\text{for arbitrary } z_1, z_2 \in \tilde{\Omega} : \quad |f(z_1) - f(z_2)| \leq L|z_1 - z_2|.
 \tag{A.4}$$

Example: $f(x) := Ax^p$ for $A > 0$, $0 < p < 1$ belongs for $b > 0$ to $C^{0,1}((0, b])$, but not to $C^1([0, b])$.

Let Ω be an interval from (A.1) and f a function defined on Ω :

$$\begin{aligned}
 &f \text{ is called } \textit{increasing}, \text{ if } f(x) \leq f(y) \text{ for } x, y \in \Omega \text{ and } x < y. \\
 &f \text{ is called } \textit{strictly increasing}, \text{ if } f(x) < f(y) \text{ for } x, y \in \Omega \text{ and } x < y.
 \end{aligned}
 \tag{A.5}$$

Note: For $f \in C^1(\Omega)$ the property: $f'(x) > 0$ for all $x \in \Omega$

implies that f is strictly increasing, but only: (A.6)
 $f'(x) \geq 0$ for all $x \in \Omega$ is necessary.

The properties *decreasing* and *strictly decreasing* are defined analogously.

f is called *convex*, if for arbitrary $x, y \in \Omega$, $x < y$, the chord connecting $(x, f(x))$ and $(y, f(y))$ has no points below the graph of f , i.e.

$$f(z) \leq \frac{f(y) - f(x)}{y - x}(z - x) + f(x) \quad \text{for all } z \in (x, y). \quad (\text{A.7})$$

f is called *strictly convex*, if the chord lies above the graph of f , i.e. \leq in (A.7) is substituted by $<$.

The properties *concave* and *strictly concave* are defined analogously with \leq in (A.7) substituted by \geq or $>$, respectively.

The remark (A.6) applies for f'' and strict convexity.

So (strict) convexity or concavity refer to the corresponding property of the set *above* the graph of f .

Consider integration on a set Λ with respect to a "general" finite measure. This includes in particular a finite set, i.e.:

$$\Lambda = \{1, \dots, m\} \quad \text{and} \quad \int_{\Lambda} f \, d\lambda = \sum_{i=1}^m a(i)f(i), \quad a(i) \geq 0 \quad \text{defining the measure.}$$

Define for $M \subset \Lambda$

$$|M| := \int_{\Lambda} i_M d\lambda \quad \text{with} \quad i_M(x) = \begin{cases} 1 & \text{for } x \in M \\ 0 & \text{for } x \notin M \end{cases}, \quad (\text{A.8})$$

$$\int_{\Lambda} f \, d\lambda := \int_{\Lambda} f \, d\lambda / |\Lambda|.$$

The Theorem of Picard-Lindelöf (special case):

Let $\Omega := (a, b) \times (c, d)$, g_1, g_2 be functions defined on $[a, b] \times [c, d]$, and $g_1, g_2 \in C^{0,1}(\Omega)$. For $(u_0, v_0) \in \Omega$ and $\xi_0 \in \mathbb{R}$ we consider the initial value problem

$$\begin{aligned} \frac{d}{d\xi} u &= g_1(u, v), \\ \frac{d}{d\xi} v &= g_2(u, v), \end{aligned} \quad (\text{A.9})$$

$$u(\xi_0) = u_0, \quad v(\xi_0) = v_0. \quad (\text{A.10})$$

If for some $\Delta\xi > 0$ $u, v \in C^1([\xi_0, \xi_0 + \Delta\xi])$ and u, v satisfy (A.10) and (A.9) pointwise in $[\xi_0, \xi_0 + \Delta\xi]$, (u, v) is called a *(local) positive half-orbit*.

Analogously (u, v) is a *(local) negative half-orbit*, if the interval is substituted by $[\xi_0 - \Delta\xi, \xi_0]$. The following holds true:

- ◇ There is at most one local positive (negative) half-orbit.
- ◇ There exists a local positive and a local negative half-orbit.
- ◇ The length of existence $\Delta\xi$ can be enlarged as long as $(u(\xi), v(\xi)) \in \Omega$.

Appendix B: The Isotherm for Binary Ion Exchange

We consider the isotherm of the following rate function, defined by

$$\begin{aligned} F_a(c, s) &= k_1(\gamma_1(c)c)^{n_2}(\bar{s} - s)^{n_1} \\ F_d(c, s) &= k_2(\gamma_2(c)(\bar{c} - c))^{n_1}s^{n_2} \end{aligned} \quad (B.1)$$

for $(c, s) \in \bar{\Omega} := [0, \bar{c}] \times [0, \bar{s}]$ and real $\bar{c}, \bar{s}, k_1, k_2 > 0, n_1, n_2 \geq 1$, and functions $\gamma_i \in C^1[0, \bar{c}]$ such that $\gamma_i(c) > 0$ for $c \in [0, \bar{c}]$. (B.1) generalizes (2.18) and (2.21).

It is equivalent to investigate the isotherm of

$$g(c, s) := (\gamma_1(c)c)^{n_2}(\bar{s} - s)^{n_1} - K(\gamma_2(c)(\bar{c} - c))^{n_1}s^{n_2} \quad (B.2)$$

for $(c, s) \in \bar{\Omega}$, where

$$K := k_2/k_1. \quad (B.3)$$

First we show the existence of an isotherm in the sense of (1.10) for $c_m := \bar{c}, s_m := \bar{s}$.

We have $g \in C^1(\bar{\Omega})$ and

$$\frac{\partial g}{\partial s}(c, s) = -n_1(\gamma_1(c)c)^{n_2}(\bar{s} - s)^{n_1-1} - Kn_2(\gamma_2(c)(\bar{c} - c))^{n_1}s^{n_2-1}$$

i.e.

$$\frac{\partial g}{\partial s} \leq 0 \text{ in } \bar{\Omega} \text{ and } \frac{\partial g}{\partial s}(c, s) < 0 \text{ for } (c, s) \neq (0, 0) \text{ and } \neq (\bar{c}, \bar{s}). \quad (B.4)$$

Furthermore

$$\begin{aligned} g(c, 0) &= (\gamma_1(c)c)^{n_2}\bar{s}^{n_1} > 0 \text{ for } c \in (0, \bar{c}], \\ g(c, \bar{s}) &= -K(\gamma_2(c)(\bar{c} - c))^{n_1}\bar{s}^{n_2} < 0 \text{ for } c \in [0, \bar{c}), \end{aligned} \quad (B.5)$$

therefore (B.4) implies:

For $c \in (0, \bar{c})$ there is a unique $s \in [0, \bar{s}]$, $s \neq 0$, $s \neq \bar{s}$, such that

$$g(c, s) = 0 : \quad \text{Set } \Phi(c) := s. \quad (B.6)$$

We have $\Phi \in C^1(0, \bar{c})$ and

$$\Phi'(c) = -\frac{\partial g}{\partial c}(c, \Phi(c)) / \frac{\partial g}{\partial s}(c, \Phi(c)) \text{ for } c \in (0, \bar{c}). \quad (B.7)$$

Because of

$$g(0, s) = 0 \Leftrightarrow s = 0, \quad g(\bar{c}, s) = 0 \Leftrightarrow s = \bar{s} \text{ for } s \in [0, \bar{s}]$$

we set

$$\Phi(0) := 0, \quad \Phi(\bar{c}) := \bar{s}. \quad (B.8)$$

So far we have verified (1.10)(i) and (ii) due to (B.5). To conclude (1.10) (iii) we show

$$\Phi \in C^1[0, \bar{c}]. \quad (B.9)$$

In a first step we show the continuity of φ at $c = 0$ (and analogously at $c = \bar{c}$):

For a sequence $c \searrow 0$ we have (for a subsequence) $\Phi(c) \rightarrow a \in [0, \bar{s}]$ and by (B.2), (B.6)

$$0 = -K(\gamma_2(0)\bar{c})^{n_1} a^{n_2} \Rightarrow a = 0 = \Phi(0), \quad \text{i.e. } \Phi(c) \searrow \Phi(0).$$

In a second step we compute $\Phi'(0)$ and $\Phi'(\bar{c})$:

(B.6) implies

$$\left(\frac{\Phi(c)}{c}\right)^{n_2} = \frac{1}{K} \gamma_1(c)^{n_2} \left(\frac{\bar{s} - \Phi(c)}{\gamma_2(c)(\bar{c} - c)}\right)^{n_1} \quad \text{for } c \in (0, \bar{c}). \quad (B.10)$$

Let $c \searrow 0$, then $\Phi(c) \searrow 0$ and thus by (B.8), (B.10):

$$\Phi'(0) = \lim_{c \searrow 0} \frac{\Phi(c)}{c} = \frac{1}{K^{1/n_2}} \gamma_1(0) \left(\frac{\bar{s}}{\gamma_2(0)\bar{c}}\right)^{n_1/n_2} > 0, \quad (B.11)$$

and in the same way:

$$\Phi'(\bar{c}) = K^{1/n_1} \gamma_2(\bar{c}) \left(\frac{\bar{s}}{\gamma_1(\bar{c})\bar{c}}\right)^{n_2/n_1} > 0. \quad (B.12)$$

Finally for $c \searrow 0$ we conclude from (B.7), dividing $\frac{\partial g}{\partial c}$ and $\frac{\partial g}{\partial s}$ by c^{n_2-1} , and using (B.11)

$$\Phi'(c) \rightarrow \gamma_1(0)^{n_2} \bar{s}^{n_1} / (K \Phi'(0)^{n_2-1} (\gamma_2(0)\bar{c})^{n_1}) = \Phi'(0)$$

and analogously we get for $c \nearrow \bar{c}$, now dividing $\frac{\partial g}{\partial c}$, $\frac{\partial g}{\partial s}$ by $(\bar{c} - c)^{n_1-1}$:

$$\Phi'(c) \rightarrow \Phi'(\bar{c}).$$

This ends the proof of (B.9).

Next we want to investigate under which conditions also (1.10)(iv) is satisfied.

For the case of (2.18), where γ_1, γ_2 are constants, we have

$$\frac{\partial g}{\partial c}(c, s) > 0 \quad \text{for } (c, s) \neq (0, 0) \quad \text{and} \quad \neq (\bar{c}, \bar{s})$$

and thus, using (B.7), (B.11), (B.12):

$$\Phi'(c) > 0 \quad \text{for } c \in [0, \bar{c}]. \quad (B.13)$$

For variable γ_1, γ_2 we restrict ourselves to the relevant case (2.21), i.e. we assume

$$\begin{aligned}\gamma_i(c) &:= \exp(-n_i^2 \sigma(I)), \quad i = 1, 2, \\ I &:= \frac{1}{2}(n_1^2 c + n_1 n_2 (\bar{c} - c) + \hat{c})\end{aligned}\tag{B.14}$$

for some $\hat{c} \geq 0$ and $\sigma \in C^1(0, \infty)$ to be specified later on.

Because of (B.7), (B.11), (B.12) it is sufficient for (B.13) to establish

$$\frac{\partial g}{\partial c}(c, \Phi(c)) > 0 \quad \text{for } c \in (0, \bar{c}).\tag{B.15}$$

We have

$$\begin{aligned}\frac{\partial g}{\partial c}(c, s) &= n_2 (\gamma_1(c)c)^{n_2} (\bar{s} - s)^{n_1} \left(\frac{1}{c} - n_1^2 \frac{\partial}{\partial c} \sigma(I) \right) + \\ &\quad + n_1 K(\gamma_2(c)(\bar{c} - c))^{n_1} s^{n_2} \left(\frac{1}{\bar{c} - c} + n_2^2 \frac{\partial}{\partial c} \sigma(I) \right) \\ &\quad \text{for } c \in (0, \bar{c}).\end{aligned}$$

Because of (B.6) this leads to

$$\begin{aligned}\frac{\partial g}{\partial c}(c, \Phi(c)) &= (\gamma_1(c)c)^{n_2} (\bar{s} - s)^{n_1} \left\{ \frac{n_2}{c} + \frac{n_1}{\bar{c} - c} + n_1 n_2 (n_2 - n_1) \frac{\partial}{\partial c} \sigma(I) \right\} \\ &\quad \text{for } c \in (0, \bar{c}).\end{aligned}\tag{B.16}$$

If nothing else is noted, we always assume $c \in (0, \bar{c})$. We consider as in section 2

$$\sigma(I) := \frac{a_1 I^{1/2}}{1 + a_2 I^{1/2}} - a_3 I,\tag{B.17}$$

where $a_1 > 0, a_2, a_3 \geq 0$, therefore

$$\begin{aligned}\sigma'(I) &= \frac{1}{2} \frac{a_1}{I^{1/2} + 2a_2 I + a_2^2 I^{3/2}} - a_3, \\ \frac{\partial}{\partial c} \sigma(I) &= \frac{1}{2} n_1 (n_1 - n_2) \sigma'(I).\end{aligned}\tag{B.18}$$

We want to conclude that the curly bracket in (B.16) is positive by establishing a positive lower bound. We have

$$\frac{n_2}{c} + \frac{n_1}{\bar{c} - c} \geq \frac{1}{\bar{c}} (n_1^{1/2} + n_2^{1/2})^2.\tag{B.19}$$

(B.18) implies for $a_2 > 0$

$$\sigma'(I) \leq \frac{a_1}{4a_2 I}.\tag{B.20}$$

Without loss of generality we can assume

$$n_1 \geq n_2\tag{B.21}$$

which implies

$$I(c) \geq I(0) = \frac{1}{2}(n_1 n_2 \bar{c} + \hat{c}) \geq \frac{1}{2} n_1 n_2 \bar{c}. \quad (\text{B.22})$$

For $n_1 > n_2$ this inequality is strict. From (B.18) – (B.22) we end up with the following sufficient conditions for (B.15) and thus for (B.13), if $a_2 > 0$:

$$4(n_1^{1/2} + n_2^{1/2})^2 \geq \frac{a_1}{a_2} \max(n_1, n_2)(n_1 - n_2)^2. \quad (\text{B.23})$$

A wide range of substances fulfill (compare (Klotz/Rosenberg, 1972), p. 385 –386)

$$a_1 \leq a_2. \quad (\text{B.24})$$

In this situation it is sufficient for (B.23) to have

$$4(n_1^{1/2} + n_2^{1/2})^2 \geq \max(n_1, n_2)(n_1 - n_2)^2. \quad (\text{B.25})$$

This condition is satisfied by pairs (n_1, n_2) fulfilling

$$n_2 \leq n_1 \leq n_2 + 3, \quad (\text{B.26})$$

i.e. for example

$$\begin{aligned} (n_1, 1), & \quad 1 \leq n_1 \leq 4, \\ (n_1, 2), & \quad 2 \leq n_1 \leq 5, \\ (n_1, 3), & \quad 3 \leq n_1 \leq 6. \end{aligned}$$

This seems to cover all relevant cases.

Another sufficient condition for (B.13) is achieved in the same way, but without the use of (B.20). It incorporates all the appearing constants and also assumes (B.21):

$$\begin{aligned} \frac{1}{\bar{c}}(n_1^{1/2} + n_2^{1/2})^2 \geq \frac{1}{2} n_1^2 n_2 (n_1 - n_2)^2 \left(\frac{1}{2} \frac{a_1}{\tilde{I}^{1/2} + 2a_2 \tilde{I} + a_2^2 \tilde{I}^{3/2}} - a_3 \right) \\ \text{for } \tilde{I} := \frac{1}{2}(n_1 n_2 \bar{c} + \hat{c}). \end{aligned} \quad (\text{B.27})$$

This can also be satisfied in the case $a_2 = 0$, if a_3 or \bar{c} or \hat{c} are large enough.

Because of (B.9) Φ cannot be of Freundlich type (H). For constant γ_1, γ_2 we are able to characterize the occurrence of Langmuir type (L) and of convex type (S). As in (2.18) we incorporate γ_1, γ_2 in k_1, k_2 , respectively, i.e. we consider

$$\gamma_1 = \gamma_2 = 1. \quad (\text{B.28})$$

We will show:

$$\text{If } K = \left(\frac{\bar{s}}{\bar{c}}\right)^{n_1 - n_2}, \text{ then } \Phi(c) = \frac{\bar{s}}{\bar{c}} c \text{ for } c \in [0, \bar{c}]. \quad (\text{B.29})$$

$$\begin{aligned} \text{If } K < \left(\frac{\bar{s}}{\bar{c}}\right)^{n_1-n_2}, \text{ then } \Phi''(c) < 0 \text{ for } c \in (0, \bar{c}), \\ \text{in particular } \Phi \text{ is of type (L)}. \end{aligned} \quad (B.30)$$

$$\begin{aligned} \text{If } K > \left(\frac{\bar{s}}{\bar{c}}\right)^{n_1-n_2}, \text{ then } \Phi''(c) > 0 \text{ for } c \in (0, \bar{c}), \\ \text{in particular } \Phi \text{ is of type (S)}. \end{aligned} \quad (B.31)$$

(B.29) is a consequence of the uniqueness of the isotherm and

$$g(c, \frac{\bar{s}}{\bar{c}}c) = 0 \quad \text{for } c \in [0, \bar{c}].$$

We have

$$\begin{aligned} g(c, s) &= \bar{s}^{n_1} \bar{c}^{n_2} \left(\alpha^{n_2} (1 - \beta)^{n_1} - K \left(\frac{\bar{s}}{\bar{c}}\right)^{n_2-n_1} (1 - \alpha)^{n_1} \beta^{n_2} \right) \\ \text{for } \alpha &:= \frac{c}{\bar{c}}, \quad \beta := \frac{s}{\bar{s}}. \end{aligned} \quad (B.32)$$

Let $c \in (0, \bar{c})$ and $s := \Phi(c)$, then (B.6), (B.32) imply

$$\Phi(c) = \bar{s} f^{-1} \left(\gamma f \left(\frac{c}{\bar{c}} \right) \right), \quad (B.33)$$

where

$$\gamma := \frac{1}{K} \left(\frac{\bar{s}}{\bar{c}} \right)^{n_1-n_2} \quad (B.34)$$

and

$$f(x) := \frac{x^{n_2}}{(1-x)^{n_1}} \quad \text{for } x \in [0, 1). \quad (B.35)$$

f is strictly increasing and therefore f^{-1} well-defined, as

$$f'(x) = \left(\frac{n_2}{x} + \frac{n_1}{1-x} \right) f(x) > 0 \quad \text{for } x \in (0, 1). \quad (B.36)$$

We have

$$\begin{aligned} \Phi''(c) &= \gamma \frac{\bar{s}}{\bar{c}^2} \left\{ f''(a)/f'(b) - \gamma f'(a)^2 f''(b)/f'(b)^3 \right\} \\ \text{for } c &\in (0, \bar{c}), \quad \text{where } a := \frac{c}{\bar{c}}, \quad b := \frac{\Phi(c)}{\bar{s}} \text{ i.e. } a, b \in (0, 1), \end{aligned}$$

and thus because of (B.36)

$$\Phi''(c) \stackrel{\leq}{\geq} 0 \quad \Leftrightarrow \quad f''(a)/f'(a)^2 \stackrel{\leq}{\geq} \gamma f''(b)/f'(b)^2. \quad (B.37)$$

From (B.36) we conclude furthermore

$$f''(x) = \left[\left(\frac{n_2}{x} + \frac{n_1}{1-x} \right)^2 - \frac{n_2}{x^2} + \frac{n_1}{(1-x)^2} \right] f(x)$$

for $x \in (0, 1)$ and therefore

$$\begin{aligned} f''(x)/f'(x)^2 &= \left(1 + \frac{n_1 x^2 - n_2(1-x)^2}{(n_1 x + n_2(1-x))^2}\right) / f(x) \\ &=: (1 + r(x))/f(x). \end{aligned}$$

This identity and (B.37) imply

$$\begin{aligned} \Phi''(c) \stackrel{\leq}{\geq} 0 &\Leftrightarrow (1 + r(a))/f(a) \stackrel{\leq}{\geq} \gamma (1 + r(b))/f(b) \\ &\Leftrightarrow r(a) \stackrel{\leq}{\geq} r(b) \end{aligned} \tag{B.38}$$

for $c \in (0, \bar{c})$, $a := c/\bar{c}$, $b := \Phi(c)/\bar{s}$ because of

$$f(b) = \gamma f(a)$$

as a consequence of (B.33).

The function r is strictly increasing, as

$$r'(x) = 2n_1 n_2 / (n_1 x + n_2(1-x))^3 \quad \text{for } x \in (0, 1).$$

Because of (B.38) the assertions (B.30), (B.31) are a consequence of

$$a \stackrel{\leq}{\geq} b \Leftrightarrow \gamma \stackrel{\geq}{\leq} 1.$$

This holds due to (1.10)(ii) (compare (B.4), (B.5)) and (B.32), as

$$\begin{aligned} a \stackrel{\leq}{\geq} b &\Leftrightarrow \frac{\bar{s}}{\bar{c}} c \stackrel{\leq}{\geq} \Phi(c) \\ &\Leftrightarrow g(c, \frac{\bar{s}}{\bar{c}} c) \stackrel{\geq}{\leq} 0 \\ &\Leftrightarrow \alpha^{n_2} (1 - \beta)^{n_1} - \frac{1}{\gamma} (1 - \alpha)^{n_1} \beta^{n_2} \stackrel{\geq}{\leq} 0 \\ &\quad \text{for } \alpha = \frac{c}{\bar{c}} = \beta, \quad \text{i.e.} \\ a \stackrel{\leq}{\geq} b &\Leftrightarrow \left(1 - \frac{1}{\gamma}\right) \alpha^{n_2} (1 - \alpha)^{n_1} \stackrel{\leq}{\geq} 0 \\ &\Leftrightarrow \gamma \stackrel{\geq}{\leq} 1. \end{aligned}$$

This completes the proof of (B.30) and (B.31).

Using the constants of section 2, the condition in (B.29)–(B.31) takes the form

$$\begin{aligned} K \stackrel{\leq}{\geq} \left(\frac{\bar{s}}{\bar{c}}\right)^{n_1 - n_2} &\Leftrightarrow \hat{K} \left(\frac{\gamma_2}{\delta_2}\right)^{n_1} \left(\frac{\delta_1}{\gamma_1}\right)^{n_2} \stackrel{\leq}{\geq} \left(\frac{\bar{s}}{\bar{c}}\right)^{n_1 - n_2} \\ \text{with } \hat{K} &:= \hat{k}_2 / \hat{k}_1. \text{ For} \end{aligned} \tag{B.39}$$

$$\delta_i = \hat{\delta}_i / \bar{s}, \quad i = 1, 2, \quad (B.40)$$

taking into account (2.15), this leads to

$$K \stackrel{\leq}{\geq} \left(\frac{\bar{s}}{\bar{c}}\right)^{n_1 - n_2} \Leftrightarrow \hat{K} \left(\frac{\hat{\gamma}_2}{\hat{\delta}_2}\right)^{n_1} \left(\frac{\hat{\delta}_1}{\hat{\gamma}_1}\right)^{n_2} \stackrel{\leq}{\geq} \bar{c}^{n_2 - n_1}, \quad (B.41)$$

where \bar{c} is the overall electric charge in solution according to (2.13). This generalizes the results of Valocchi *et al.* (1981) for $n_1 = 1$, $n_2 = 2$, derived from the explicit form available for this special case (compare (B.33)).

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