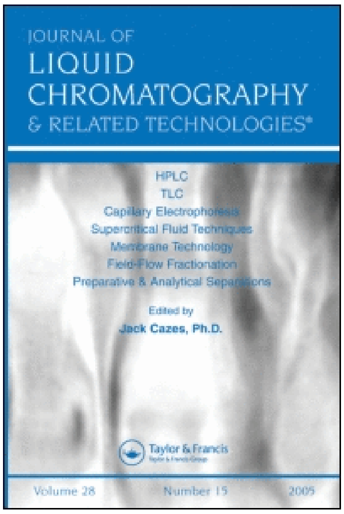

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CONSEQUENCES OF ION-EXCHANGE AND SORPTION EFFECTS ON pH WAVES PROPAGATING IN A STRONG-BASE ANION-EXCHANGE COLUMN

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ABSTRACT

When pH buffers are used in frontal anion exchange chromatography, it is known that important transient pH variations may occur, even if pHs are identical in preequilibration and feed. This effect was earlier studied with the aid of equilibrium theory extended to the case where dissociation reactions are involved. In the present paper, the sodium acetate/acetic acid system has been revisited but accounting for sorption effects. Sorption experiments were performed to determine the ratio between stationary and mobile phases as a function of ionic concentration. Column experiments with respectively alkaline and acid acetate buffers have been performed and modelled (computer program Impact). Sorption effects have been taken into account; a good prediction of pH and acetate breakthrough curves has thus been achieved.

INTRODUCTION

Frontal ion-exchange chromatography is a well-developed technique, increasingly applied to extraction and purification of molecules of biological interest (amino-acids, proteins etc.) [1]. These molecules are very sensitive to pH and , a constant pH value must be imposed in the course of separation: pH buffers are used to achieve this goal. But chromatographic processes generally comport a step where buffer ionic strength is modified. For example, ionic concentration is significantly increased to elute sorbed species. It is commonly believed that the use of a pH buffer imposes pH regardless of any properties of the ion-exchanger. Unfortunately, a modification of ionic concentration may transiently bring important pH alterations as a consequence of ion exchanges between buffer components and adsorbed species.

An experimental and theoretical study of this phenomenon has been proposed by Helfferich and Bennett [2-4]. The first part of this work was concerned with systems composed of a weak acid and its sodium salt (sodium acetate/acetic acid; sodium carbonate/carbonic acid). For each system, two solutions of different ionic concentration were successively injected into a column of strong-base anion exchanger [2] and important pH excursions in the column outflow were observed. The second part of the work dealt with a three-component exchange involving a weak acid and its sodium salt with an additionnal species not undergoing a reaction. The chosen system was sodium acetate/acetic acid/sodium chloride with the same type of ion-exchanger as in the first part [3]. The theoretical interpretation of experiments was based on the so-called "equilibrium theory" essentially developed by Klein, Helfferich and Tondeur [5-10]. The main assumptions of this type of model are: plug-flow inside the column (hydrodynamic dispersion is neglected); no shrinking, no swelling (the volume of each phase is assumed constant); thermodynamic equilibrium attained at any point of the column at any time (local equilibrium assumption); isothermal behavior; description of ion-exchange equilibria by means of constant binary separation factors. From these assumptions, in the case of a coherent wave (instantaneous modification of the composition of the solution entering the column), the resolution of mass balances by the method of characteristics allows the prediction of the number and natures of concentration propagating waves. The first systems (sodium salt/weak acid) were shown to generate two waves, identified as a "sodium wave" and an "ion-exchange wave", and the three-component system three waves, a sodium wave and two ion-exchange ones.

The comparison of equilibrium theory predictions with experimental results [2] shows that this theory allows a semi-quantitative prediction of solute concentration variations observed at the column outflow. Theory fails to precisely describe experiments because of limitations due to hydrodynamic and thermodynamic assumptions and moreover so important reactions as sorption of neutral species or penetration of electrolytes into the resin are mentioned but not taken into account.

A more complete approach to physico-chemical interactions should improve agreement between model and experiments. It is worth underlining that equilibrium theory was first worked out for systems involving only adsorption or ion-exchange reactions and was extended later to cases in which homogeneous reactions like dissociation or heterogeneous reactions like precipitation/dissolution must be considered [11-16]. But it turns out to be very complex and even useless for systems involving too many species and reactions.

Another approach consists in using equilibrium theory on the one hand for a semi-quantitative treatment of problems: analysis of involved species and reactions, computation of wave number and nature [12,13]. On the other hand, a computer code in which physicochemical interactions are coupled with hydrodynamics may be helpful. The Impact computer code worked out by Jauzein et al. [17] has been used in this work.

In this paper, a study about the propagation of pH and acetate waves in a strong-base anion-exchanger column is presented. The column behavior is investigated when the column is equilibrated with a pH buffer and then fed with a solution of the same buffer at a different ionic concentration. The sodium acetate/acetic acid system developed by Helfferich and Bennett is revisited with experimental complements in particular about acetate breakthrough and sorption. Results are modelled by means of the Impact computer program and sorption effects are taken into account.

MODELLING OF FLOW AND OF PHYSICOCHEMICAL INTERACTIONS

Flow Description

To describe flow and mass-transfer inside a fixed bed of total volume V_t, it is important to define precisely which phases are taken into account [18] and what their respective volumes are. The bed is represented by two phases (Figure 1), that are:

- one mobile phase or fluid phase of volume V_m, composed of the volume accessible to solution and thus to all ions by convection and diffusion: that is the sum of external or interstitial volume V_e and of internal resin volume accessible to cations V_{ia}.
- one stationary zone of volume V_s including the motionless resin-bound water (volume V_i) from which cations are excluded (except hydronium ions produced by immobile water hydrolysis) and the resin itself, with its true solid phase volume V_r.

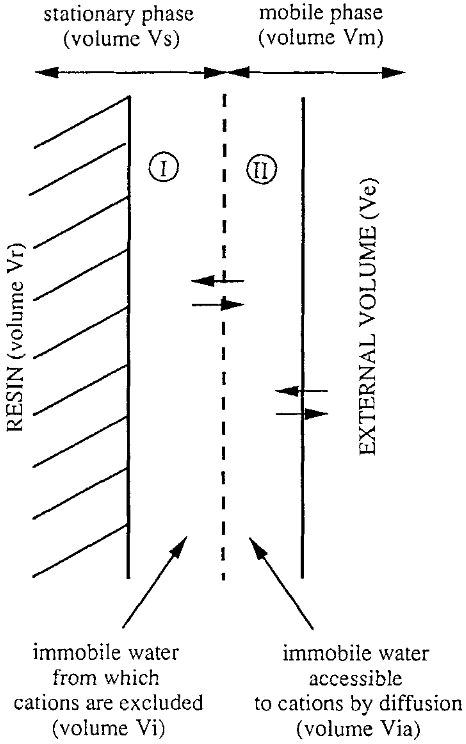

FIGURE 1 : Schematic representation of the different zones of the resin bed

It is important to point out that the borderline between the two zones is located somewhere inside the resin and not right between interstitial and apparent (V_{ap}) resin volume. The relations between these volumes are:

$$V_{ap} = V_r + V_i + V_{ia} \qquad (1)$$

and $$V_t = V_{ap} + V_e = (V_r + V_i) + (V_{ia} + V_e) = V_m + V_s \qquad (2)$$

Usually, the frontier between mobile and stationary zones is imposed by geometric constraints: external or intersticial fluid transported by convection on the one hand and internal fluid accessible to ions by diffusion on the other hand. Here a distinction is made between fluid accessible to cations and fluid inaccessible to cations. The frontier is determined by ionic exclusion: it depends not only on the porous medium geometry but also on the total ionic concentration of the mobile solution.

This description is based on the assumption of local equilibrium. The fluid velocity is slow enough so that mass transfer limitations between phases may be neglected.

Fluid flow in the mobile zone is assumed to be convective-dispersive and one-dimensional. It is modelled by mixing cells in series: the bed is represented by a network composed of J basic identical elements with a constant geometry [18]. In each element, the mobile and stationary phases are respectively located in the volumes V_m/J and V_s/J. The two parameters V_m and J are deduced from sodium breakthrough (see experimental section).

Physicochemical Interactions

For the studied system, three types of reactions are involved [17]: (1) dissociation of neutral species in the mobile phase (homogeneous reaction), (2) anion exchange, (3) sorption of neutral species (heterogeneous reactions). Let R be the number of independent reactions, these reactions can be written in terms of stoichiometric relations as:

$$\sum_{j=1}^{N} \nu_{ij} A_j = 0 \qquad i = 1 \text{ to } R \qquad (3)$$

where N is the number of chemical species, ν_{ij} is the stoichiometric coefficient for species A_j in the reaction i (positive for products, negative for reactants). A_j is a species in a given phase: a species present in two different phases is given by two different numbers or symbols. For instance, hydroxyl ion in the mobile zone is represented by OH^- (species A_1 for example) as hydroxyl ion in the stationary zone is represented by $\overline{OH^-}$ (species A_2 for example).

Equilibria are described by mass-action laws:

$$K_i = \prod_{j=1}^{N} a_j^{\nu_{ij}} \tag{4a}$$

where a_j is the activity of A_j. As a first approximation activities are assimilated to concentrations ; ν_{ij} is the required exponent for homogeneous reactions, it is replaced by zero for species in excess or with an activity equal to unity (pure precipitate).

$$K_i = \prod_{j=1}^{N} (A_j)^{\nu_{ij}} \tag{4b}$$

(A_j): concentration of A_j

All concentrations are expressed in moles per liter of mobile phase, the species being either in the mobile or in the stationary phase.

Set of Assumptions

The set of assumptions can be summed up to:

(1) Ion-exchange, dissociation and sorption equilibria are reached at any point anytime (local equilibrium).

(2) Cations are partially excluded from the interior of the resin.

(3) Neutral species penetrate into the resin.

(4) The bed volume is constant (swelling or shrinking does not exceed 5% in general).

(5) Mass transfer in the bed is dispersive-convective in the flow direction.

(6) The system is isothermal.

(7) Each phase is electrically neutral.

(8) Activity coefficients equal unity.

(9) The separation factors of binary ion-exchanges defined in terms of concentrations are constant.

BEHAVIOR OF THE SODIUM ACETATE/ACETIC ACID SYSTEM

Species and Equilibria

This system is relatively simple, giving rise to four independent reactions:

- water dissociation

$$H_2O = H^+ + OH^- \qquad K_w = (H^+)\,(OH^-) \qquad [\mathrm{mol/l}]^2 \qquad (5)$$

- acetic acid dissociation

$$AcOH = AcO^- + H^+ \qquad K_a = \frac{(AcO^-)\,(H^+)}{(AcOH)} \qquad [\mathrm{mol/l}] \qquad (6)$$

- anionic exchange between acetate and hydroxyl ions:

$$AcO^- + \overline{OH^-} = \overline{AcO^-} + OH^- \qquad K_{AcO,OH} = \frac{(\,\overline{AcO^-}\,)}{(AcO^-)}\,\frac{(OH^-)}{(\,\overline{OH^-}\,)} \qquad (7)$$

(adimensional)

- sorption of undissociated acetic acid:

$$AcOH = \overline{AcOH} \qquad K_D = \frac{(\,\overline{AcOH}\,)}{(AcOH)} \qquad \text{(adimensional)} \qquad (8)$$

To be rigorous in what concerns sorption, two additional species and reactions must be considered to describe dissociation occuring in the stationary phase:

$$\overline{H_2O} = \overline{H^+} + \overline{OH^-} \qquad \overline{K_w} = \overline{(H^+)}\;\overline{(OH^-)} \qquad (9)$$

(mol/l of mobile phase)^2

$$\overline{AcOH} = \overline{AcO^-} + \overline{H^+} \qquad \overline{K_a} = \frac{\overline{(AcO^-)}\;\overline{(H^+)}}{\overline{(AcOH)}} \qquad (10)$$

(mol/l of mobile phase)

The following relations between the sorbed species can then be written:

$$\overline{(AcOH)} = \frac{\overline{(AcO^-)}\;\overline{(H^+)}}{\overline{K_a}} = \frac{\overline{(AcO^-)}}{\overline{(OH^-)}}\,\frac{\overline{K_w}}{\overline{K_a}} \qquad (11)$$

From equations (6) and (7):

$$\overline{(AcOH)} = K_{AcO,OH}\,\frac{\overline{K_w}}{\overline{K_a}}\,\frac{(AcO^-)}{(OH^-)} = K_{AcO,OH}\,\frac{\overline{K_w}}{K_w}\,\frac{K_a}{\overline{K_a}}\,(AcOH) \qquad (12)$$

Let us assume the continuity of dissociation constants from one phase to another one. K_w and K_a (resp. $\overline{K_w}$ and $\overline{K_a}$) are relative to homogeneous reactions and should be referred to the phase in which they occur. Thus to express equality between $\overline{K_w}$ and K_w (resp. $\overline{K_a}$ and K_a), it is necessary to introduce the volume ratio V_m/V_i, which gives $\left[\frac{V_m}{V_i}\right]^2 \overline{K_w} = K_w$ and $\left[\frac{V_m}{V_i}\right]\overline{K_a} = K_a$.

Reporting eq. (8) into (12), the Donnan constant K_D becomes:

$$K_D = K_{AcO,OH}\,\frac{\overline{K_w}}{\overline{K_a}}\,\frac{K_a}{K_w} \cong \frac{V_i}{V_m}\,K_{AcO,OH} \qquad (13)$$

Finally, there are only four independent reactions (5) to (8). On the whole, there are:

- 5 species in the mobile phase ($N_l = 5$): AcOH, AcO$^-$, H$^+$, Na$^+$, OH$^-$,
- 3 species in the stationary phase ($N_s = 3$): $\overline{AcO^-}$, $\overline{OH^-}$, $\overline{AcOH}$

Water is eliminated since its activity equals unity. Sodium ion is present as an inert species. The reaction scheme can be written under the form of a stoichiometric matrix with 4 rows and 8 columns:

$$v_{4,8} = \begin{array}{cccccccc|l} \mathrm{H^+} & \mathrm{OH^-} & \mathrm{AcOH} & \mathrm{AcO^-} & \mathrm{Na^+} & \overline{\mathrm{AcO^-}} & \overline{\mathrm{OH^-}} & \overline{\mathrm{AcOH}} & \\ 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & (5) \\ 1 & 0 & -1 & 1 & 0 & 0 & 0 & 0 & (6) \\ 0 & 1 & 0 & -1 & 0 & 1 & -1 & 0 & (7) \\ 0 & 0 & -1 & 0 & 0 & 0 & 0 & 1 & (8) \end{array} \qquad (14)$$

mobile species stationary species

The rank of this matrix equals the number of independent reactions R = 4. The matrix (14) can be separated in two submatrices, associated with mobile and stationary species, the ranks of which being respectively $R_l = 3$ and $R_s = 2$. Following the rules enounced by Schweich et al. [12,13], the number of Stoichiometric Inert Species or SIS is the number of species minus the number of independent reactions:

$$n_{SIS} = N - R = 4 \qquad (15)$$

The number of Stoichiometric Inert Species in the mobile phase, known as stoichiometric tracers is $N_l - R_l = 2$, these stoichiometric tracers are:

- electroneutrality

$$S_1 = (\mathrm{AcO^-}) + (\mathrm{OH^-}) - (\mathrm{H^+}) - (\mathrm{Na^+}) = 0 \qquad (16a)$$

- sodium, as a true inert species:

$$S_2 = (\mathrm{Na^+}) \qquad (16b)$$

In the same way, the number of SIS in the stationary phase is $N_s - R_s = 1$. There is only one stationary SIS, that is actually the electroneutrality in the stationary phase:

$$S_3 = (\overline{\mathrm{OH^-}}) + (\overline{\mathrm{AcO^-}}) - N_E = 0 \qquad (16c)$$

where N_E is the exchange capacity expressed in moles per liter of mobile phase. The fourth SIS is a combination associating species in the mobile phase and in the stationary phase. The total acetate mass balance is a typical example:

$$S_4 = (\mathrm{AcOH}) + (\mathrm{AcO^-}) + (\overline{\mathrm{AcO^-}}) + (\overline{\mathrm{AcOH}}) = (\mathrm{Ac}) \qquad (16d)$$

Consequences of Physicochemistry on the form of Breakthrough Curves

Stoichiometric Matrix and Number of Fronts The number of fronts is obtained from the stoichiometric matrix [12,13], that is the number of combined SIS:

$$F = R_l + R_s - R \tag{17}$$

This number is sometimes called "sorption variance" of the transport problem [11,14]. Moreover, the existence of stoichiometric tracers (SIS depending on the mobile phase exclusively) may give birth to unretarded waves travelling at fluid velocity, if the stoichiometric tracer concentration in the initial solution and in the feed solution are different.

In the case of the sodium acetate/acetic acid system, sodium ion is the only stoichiometric tracer affected by a concentration variation at the time when the feed solution is introduced into the preequilibrated column. It can be used as a flow tracer to determine of the different zone volumes.

The number of retarded fronts is the same as in [2] despite the occurence of the sorption reaction (one new reaction and one new species are added simultaneously), the SIS number remains unchanged. Given the linear relation between AcOH and $\overline{\text{AcOH}}$, S_4 can be written directly as a function of only three species:

$$S_4 = (\text{AcOH})\,(1+K_D) + (\text{AcO}^-) + (\,\overline{\text{AcO}^-}\,) \tag{18}$$

As a conclusion, when a strong-base anion-exchange column equilibrated with a sodium acetate/acetic acid buffer is submitted to a step-wise injection of the same buffer at a different concentration, two waves are observed: an indifferent wave travelling at fluid velocity across which sodium concentration varies and a retarded one in which sodium concentration remains unchanged as reactive species concentrations vary simultaneously. These waves are separated by a constant composition zone or intermediate plateau zone. Knowledge of the composition of this zone and of the nature and location of the retarded wave allows the construction of the breakthrough curves.

Composition Calculation on the Intermediate Zone and Position of the Retarded Wave Before presenting the computation of the intermediate plateau zone composition with Impact, let us recall the basic principles of an a priori calculation with the equilibrium theory. In this problem, the retarded front is self-sharpening ($K_{AcO,OH}$ greater than unity) and the ion-exchange wave travels at the velocity $\mathbf{U}$:

$$\mathbf{U} = \frac{\mathbf{U}_0}{1 + \dfrac{\Delta(\overline{Ac})}{\Delta(Ac)}} \qquad (19)$$

where: $\mathbf{U}_0$ is the fluid velocity (m/s), $(\overline{Ac})$ and (Ac) are the total acetate concentration in the mobile and stationary phases, respectively (mol/l of mobile phase) and Δ represents the difference between the concentrations in the feed solution and in the intermediate zone.

Since the first wave is indifferent, the stationary phase composition remains unchanged from the initial plateau zone to the intermediate one. Conversely, the total ionic concentration in the mobile phase varies because of sodium step. This new sodium concentration (feed concentration) is reported into electroneutrality (16a), which enables us to calculate the mobile phase composition in the intermediate zone.

Case 1: Alkaline Medium The column is equilibrated with a dilute acetate buffer at alkaline pH and fed with a concentrated alkaline acetate buffer. The whole acetate is dissociated and there is no sorption effect. Matrix (14) reduces to N = 6 species and R = 2 reactions:

$$\nu_{2,6} = \begin{array}{cccccccc} & H^+ & OH^- & AcO^- & Na^+ & \overline{AcO^-} & \overline{OH^-} & \\ \left[\right. & 1 & 1 & 0 & 0 & 0 & 0 & \left.\right] (5) \\ & 0 & 1 & -1 & 0 & 1 & -1 & (8) \end{array} \qquad (20)$$

now $N_l = 4$, $R_l = 2$, $N_s = 2$, $R_s = 1$ (same SIS and wave numbers).

The propagation velocity of the ion-exchange wave is:

$$\mathbf{U} = \frac{\mathbf{U}_0}{1 + \dfrac{\Delta\,(\,\overline{AcO^-}\,)}{\Delta(AcO^-)}} \qquad (21)$$

The position of the exchange wave is in terms of reduced eluted volume:

$$V' = L\,\Omega\,\frac{\mathbf{U}_0}{\mathbf{U}} \qquad (22)$$

where L and Ω are the column length (m) and section (m^2) respectively.

Case 2: Acid Medium The column is equilibrated with a dilute acetate buffer at acid pH and fed with a concentrated one at acid pH. Acetic acid is now partially dissociated and all species and reactions must be considered (stoichiometric matrix (14)).

Although theory predicts the existence of an ion-exchange wave independently of sorption effects, the variation of acetate ion concentration in each phase between final and intermediate zones is almost zero. Thus in the absence of sorption, the ion-exchange wave would travel at a velocity very close to fluid velocity. Consequently, the intermediate zone would have a so short duration that it could not be experimentally detected.

If sorption effects are taken into account, $\Delta\,(\,\overline{Ac}\,)$ becomes important because of the sorption of undissociated acid, and wave velocity is strongly affected:

$$U \cong \frac{U_0}{1 + \dfrac{\Delta\,(\,\overline{AcOH}\,)}{\Delta(AcOH)}} \cong \frac{U_0}{1 + K_D} \qquad (23)$$

This relation predicts the occurence of an intermediate zone with a significant length depending only on sorption effects.

Computation with IMPACT

Impact has been worked out [17] with the set of assumptions previously presented. It allows the computation of equilibrium in a batch system as well as the computation of breakthrough curves and profiles in a flow system.

To compute breakthrough curves one must supply:

- the elementary reactions (species, stoichiometric coefficients, equilibrium constants),
- the mechanisms composed of sets of elementary reactions. For column experiments, two mechanisms are required: one including reactions in the mobile phase and one including all the reactions. The former allows the computation of the equilibrium composition of preequilibrant and feed solutions and the latter the equilibrium composition of the two phases along the bed.
- the flow network (number of mixing cells in series J),
- reference compositions of preequilibrant and feed solutions and of the stationary phase. From these reference compositions (corresponding here to experimental values), Impact computes the equilibrium composition of both phases at initial and

final states, that gives actually initial and limit conditions. Impact is then ready to compute all the required breakthrough curves and profiles.

EXPERIMENTS

Experiments were made in two steps: to begin, penetration of electrolytes into the resin as a function of ionic concentration has been measured and then column experiments were performed as an illustration of the presented theory.

Penetration of Cations into a Strong-Base Anion Exchange Resin

The chosen resin is a gel type strongly basic anion-exchange resin Dowex SBR-P with a granulometry 0.6-0.8 mm. This resin is placed in a glass column (diameter: 1.4 cm; bed length: 18 cm). Penetration of cations is evaluated by measuring the volume accessible to a sodium chloride solution by a residence time distribution measurement.

For convenience, volume fractions V_x/V_T will be denoted by ε_x, with x being either m, e, i or ia (see eq. (2)).

A typical experiment consists in stabilizing the column at a given ionic concentration with a sodium chloride feed, the resin being saturated with chloride. At t=0, the feed concentration is slightly modified and the system response measured in the column outflow and amplified (with a conductimetric cell and a zero-annulation conductimeter). The mean residence time of sodium ion in the column is deduced from the mean position of the step response, after correction of apparatus dead volumes: the total volume accessible to sodium ion ($V_m=V_e+V_{ia}$) is thus obtained for each feed concentration.

The same experiments are repeated, the column being saturated with acetate ion and fed with sodium acetate. For both series, ε_m is plotted against the mobile phase concentration (Figure 2).

When ionic concentration tends towards zero, cations are totally excluded: the external porosity ε_e is given by the intersection point of both curves with the ordinate axis (Fig. 2). In the same fashion, a measurement of the total penetration would give the total porosity:

$$\varepsilon_t = \frac{V_t - V_r}{V_t} = \varepsilon_e + \varepsilon_{ia} + \varepsilon_i \qquad (24)$$

The internal porosity β is deduced from ε_t, it is defined as usual by :

$$\beta = \frac{\varepsilon_t - \varepsilon_e}{1 - \varepsilon_e} \qquad (25)$$

In Figure 2, both experimental curves intercept the ordinate axis at the same point: $\varepsilon_e=0.39$ (close to 0.40, usual value for spherical beads).

For the highest sodium chloride concentration (1.9 mol/l), curve 1 begins to reach a plateau: electrolyte penetration is almost totally achieved and the total porosity is about 0.65 (this value is certainly a little underestimated, it could reasonably reach 0.70 and even more). It corresponds to an internal porosity $\beta=0.43$. Acetate, unlike sodium chloride indicates for the same concentration an accessible porosity $\varepsilon_m=0.55$; this suggests that penetration is not yet total. In the following, the value obtained with chloride will be used for K_D estimation.

Column Experiments

The apparatus was composed of a tank containing the feed solution, a peristaltic pump, a small volume cell containing the bulbe of a pH electrode and a fraction

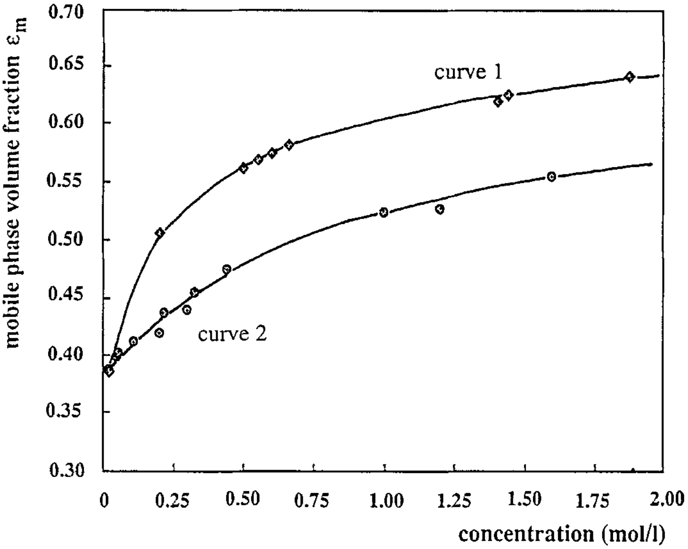

FIGURE 2 : Variations of the mobile phase volume fraction with concentration
◇ curve 1: sodium chloride
⊗ curve 2 : sodium acetate

collector. The characteristics of the system are: total exchange capacity 1.22 eq per liter of column; bed volume: 45.4 ml; flowrate: 2 ml/mn; column diameter: 1.4 cm. The dead liquid volume between injection and detection (independently on porous medium) was evaluated to 8 ml. pH was measured with a high-alcalinity electrode. Analysis were made by atomic absorption spectrometry for sodium ions (λ = 330.3 nm) and by ion chromatography for anions (Dionex 4000 I, CS2 column, eluent: sodium borate for total acetate).

The experiments performed at alkaline and acid pH are presented in Table 1.

The raw values of elution volume are corrected by substraction of the dead volume and reported to the mobile phase volume. Experimental curves of Figure 3 and 4 are thus obtained and compared with the results predicted by equilibrium model and by numerical simulations.

TABLE 1: Experimental compositions of the preequilibrant and feed solutions for Cases 1 and 2.

	Case 1: alkaline pH		Case 2: acid pH	
	Preequilibrant	Feed	Preequilibrant	Feed
total acetate (mol/l)	0.016	0.480	0.104	1.068
sodium (mol/l)	0.022	0.530	0.048	0.504
pH	11.75	12.70	4.66	4.71

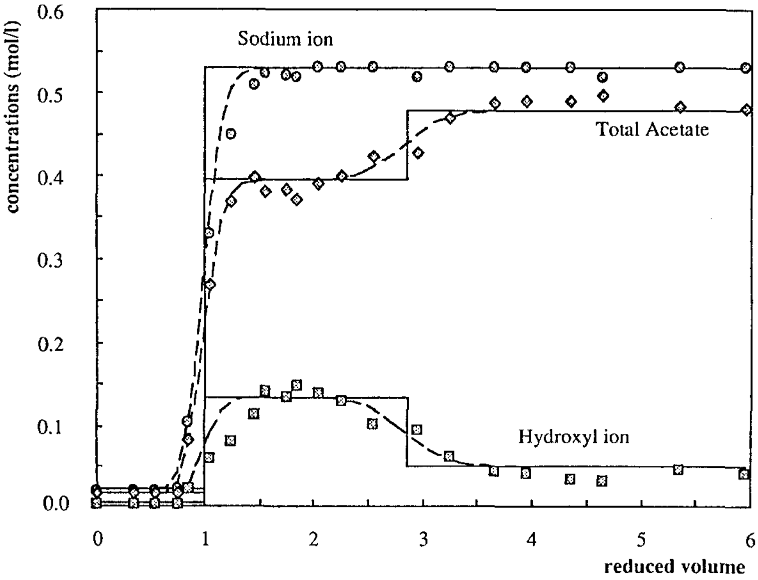

FIGURE 3a : Case 1 - Experimental and modelled breakthrough curves of total acetate, sodium ion and hydroxyl ion

Experimental curves : ◇ total acetate, ⊙ sodium ion , ⊠ hydroxyl ion
Modelled curves : — Equilibrium Theory predictions, — — Impact results

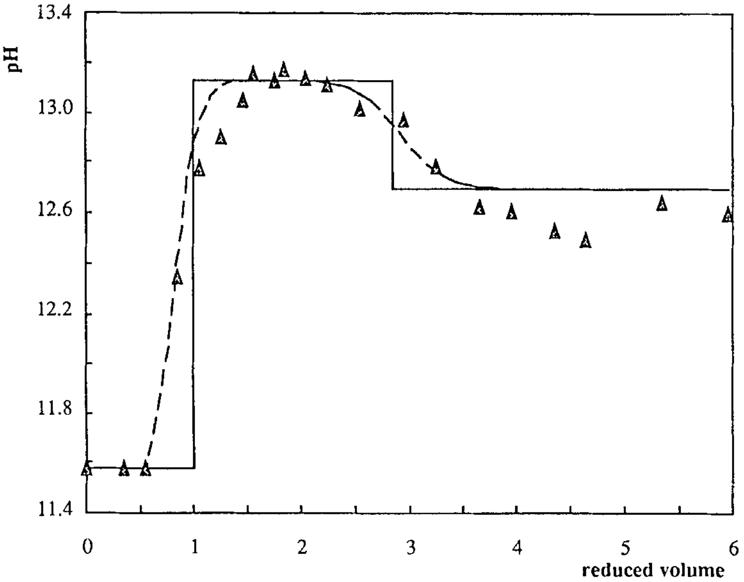

FIGURE 3b : Case 1 - Experimental and modelled variations of pH in the column effluent
Experimental curve : ▲ pH
Modelled curves :— Equilibrium Theory predictions,– – Impact results

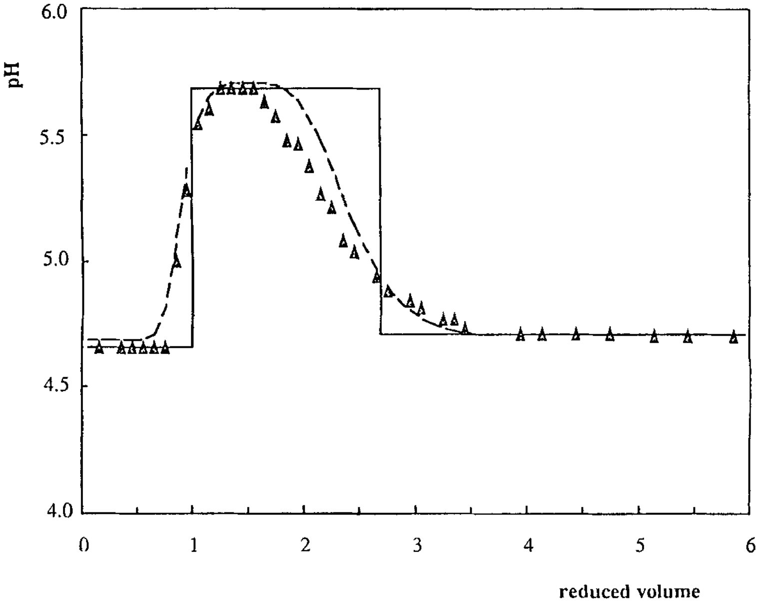

FIGURE 4a: Case 2- Experimental and modelled breakthrough curves of total acetate and sodium ion.
Experimental curves : ◇ total acetate, ⊙ sodium ion
Modelled curves : — Equilibrium Theory predictions, – – Impact results

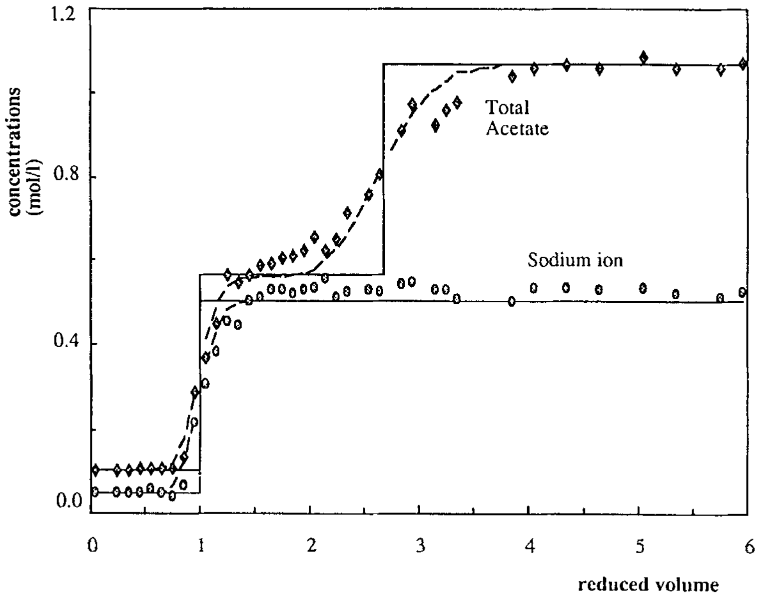

FIGURE 4b : Case 2 - Experimental and modelled variations of pH in the column effluent
Experimental curve : ♦ pH
Modelled curves :— Equilibrium Theory predictions,— — Impact results

Hydrodynamic Dispersion As a first approximation, hydrodynamic dispersion is estimated by mean of the inflection tangent method applied to the sodium concentration curve. J equals 53 in Case 1 and 71 in Case 2 (values used in simulations).

RESULTS AND DISCUSSION

The discussion will not focus on the occurence of a pH excursion in a strong-base anion exchanger [2] but rather on the comparison between experimental data and the results obtained from equilibrium theory and from simulations.

TABLE 2 Experimental and computed composition of the intermediate zone and of the position of the ion-exchange wave

	Case 1: alkaline pH		Case2: acid pH	
	experiment	simulation	experiment	simulation
Composition of the intermediate zone				
total acetate (mol/l)	0.395	0.395	0.580	0.560
pH	13.14	13.13	5.63	5.71
Position of the retarded wave				
reported to V_m	2.875	2.850	2.680	2.475

The experimental and computed composition of the intermediate zone and position of the ion-exchange wave are presented in Table 2. Dissociation and exchange constants were taken from litterature: $K_w = 1.0\ 10^{-14}$ $(mol/l)^2$, $K_a = 1.76\ 10^{-5}$ mol/l, $K_{AcO,OH} = 2.95$ [2]; K_D was estimated, a convenient K_D value is 1.475.

Let us compare this K_D value with the result of equation (13). For a concentration of 0.59 mol/l of total acetate (mean value between preequilibrant and feed concentration in case 2), one can read ε_m=0.48 on Curve 2 (Fig. 2). That gives ε_i=0.22 (with ε_L=0.70) and K_D=1.35. This calculated K_D is not far from the value used in simulations. The difference may be due to different reasons: experimental error (difficulties in evaluating ε_m), assumptions leading to a simple K_D expression (13) in particular continuity assumptions, or perhaps a specific adsorption of acetate ion.

The work made by Helfferich et al. [2] has shown that equilibrium theory offers a good prediction of the number of waves and of the intermediate zone pH. The exchange wave velocity is fairly good predicted in Case 1 but the experimental wave is more dispersed than the expected shock. In Case 2, it was shown that ion-exchange was almost non-existent and equilibrium theory indicates that the ion-exchange wave travels at about fluid velocity. Nevertheless, a broad intermediate zone is experimentally observed that theory fails to predict: actually this wave is mainly due to sorption effects and these effects are neglected in the theory premises.

The point is that in Case 1 the retarded wave is really an ion-exchange wave, as in Case 2 it is a combined ion-exchange/sorption wave. Its location is imposed by the sorption phenomenon, as anion-exchange determines the intermediate zone composition.

The use of Impact, in which sorption and hydrodynamic dispersion are taken into account, allows a very good agreement between experiments and predictions. In this way, it is shown that the assumptions constituting the model bases have an excellent prediction power in what concerns intermediate zone composition, ion-exchange wave velocity and hydrodynamic dispersion.

In particular, the preliminary experiments realized about electrolyte penetration into resin give the volumes of each phase with a fair precision. From that point, a reasonable estimation of a sorption constant used in a simple linear sorption law can be made and the prediction of the ion-exchange wave position is really improved ; especially in Case 2.

To obtain a perfect agreement between experimental and computed values, a sensitivity study of the different factors would have to be made. For instance the intermediate zone composition depends uniquely on sodium feed concentration as the ion-exchange wave velocity is sensitive simultaneously to sodium feed concentration, total exchange capacity and ion-exchange constant.

CONCLUSION

1. The study of the penetration of electolyte into a strong anion-exchanger allowed the determination of the mobile phase volume, from the point of total exclusion to the one where total penetration of cations is almost reached. The variations of the mobile phase volume fraction were plotted against concentration for sodium chloride and for sodium acetate. The volume phase ratio allowed an estimation of K_D.

2. When a strong anion exchange column is preequilibrated with a sodium acetate/acetic acid solution and fed with a solution of the same buffer at a different concentration at the same or at a close pH, a transient pH-acetate coupled variation is observed along the fixed bed: pH presents an excursion up to one unit and acetate concentration in the effluent varies in two steps.

3. In the case of alkaline solutions, the retarded wave position and the intermediate zone composition depend only on ion-exchange. In the case of acid buffers, the wave location is a function of Donnan equilibrium as the intermediate zone composition is fixed by ion-exchange. An a priori estimation of the Donnan constant is made assuming that undissociated acetic acid concentration in the stationary phase is determined by the acetate ion concentration in the same phase. Consequently, the sorption constant depends directly on the ion-exchange constant.

A model based on these premises offers a very good prediction of breakthrough curves.

LIST OF SYMBOLS

Ac	total acetate
A_j	chemical species j

a_j	activity of species A_j
J	number of mixing cells
K_a	acetic acid dissociation constant (mol/l of mobile phase)
$\overline{K_a}$	dissociation constant of acetic acid in volume V_i (mol/l of mobile phase)
$K_{AcO,OH}$	separation factor of acetate and hydroxyle ions (-)
K_D	Donnan constant of AcOH sorption (-)
K_i	conditional thermodynamic constant of reaction i
K_w	water dissociation constant (mol/l of mobile phase)^2
$\overline{K_w}$	dissociation constant of immobile water (volume V_i) (mol/l of mobile phase)^2
L	column length (m)
N	number of chemical species
R	number of independent reactions
U	ion exchange wave velocity (m/s)
V'	reduced volume (reported to V_m) where the exchange wave appears (-)
U_0	fluid velocity (m/s)
V_{ap}	apparent resin volume (l)
V_e	external volume (l)
V_i	volume of immobile water (l)
V_{ia}	internal volume accessible to cations (l)
V_m	volume of mobile phase (l)
V_r	volume of the resin skeleton (l)
V_s	volume of stationary phase (l)
V_t	total column volumn (l)
(X)	concentration of species X (mol/l of mobile phase)
$(\overline{X})$	concentration of X in the stationary phase (mol/l of mobile phase)
β	internal porosity (-)
ε_e	fraction of external volume (V_e/V_t) (-)
ε_i	fraction of internal volume (V_i/V_t) (-)
ε_{ia}	fraction of internal volume accessible to cations (V_{ia}/V_t) (-)
ε_m	fraction of mobile phase volume (V_m/V_t) (-)
ε_t	total porosity (-)
ν_{ij}	stoichiometric coefficient for species A_j in reaction i
Ω	column section (m^2)

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