Journal of Chromatography A, 1458 (2016) 63–69

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Purification of organic acids by chromatography with strong anionic resins: Investigation of uptake mechanisms

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ARTICLE INFO

Article history:
Received 5 February 2016
Received in revised form 15 June 2016
Accepted 16 June 2016
Available online 23 June 2016

Keywords:
Chromatography
Modelling
Anionic resin
Organic acid
Sustainable processing

ABSTRACT

Bio-based organic acids are promising renewable carbon sources for the chemical industry. However energy-consuming purification processes are used, like distillation or crystallization, to reach high purities required in some applications. That is why preparative chromatography was studied as an alternative separation technique. In a previous work dealing with the purification of lactic, succinic and citric acids, the Langmuir model was insufficient to explain the elution profiles obtained with a strong anionic resin.

Consequently the Langmuir model was coupled with a usual ion-exchange model to take into account the retention of their conjugate bases (<2%), which are commonly neglected at low pH (<1.5). Elution simulations with both uptake mechanisms fitted very well with experimental pulse tests. Only two parameters were optimized (equilibrium constant of acid uptake and ion-exchange selectivity coefficient of conjugate base) and their value were coherent with experimental and resin suppliers' data.

These results confirmed that the singular tailing and apparent delay observed with succinic and citric acids can be explained by the high affinity of succinate and citrate for resin cationic sites. The model was implemented in a preparative chromatography simulation program in order to optimize operating parameters of our pilot-scale ISMB unit (Improved Simulated Moving Bed). The comparison with experimental ISMB profiles was conclusive.

1. Introduction

In the frame of sustainable development, biomass valorization as a renewable carbon source for the chemical industry is growing. Indeed, fossil resources are running out in the medium to long term. Moreover carbon balances have to be improved so as to reduce the CO_2 level in the atmosphere, whose rapid rise is linked to global warming. In the famous report of the Pacific Northwest National Laboratory (PNNL) and the National Renewable Energy Laboratory (NREL) [1], bio-based organic acids are identified as very promising sources of renewable carbon. Many compounds can be produced from these molecules in the chemical industry, particularly in the polymer industry. Up to now, the production of bio-based organic acids keeps small because they are still uncompetitive compared to the corresponding petroleum-derived products [2]. That is why the reduction of their production cost is a major concern of the chemical industry.

Bio-based organic acids are usually produced by microbial fermentation for the food industry but further purification techniques are required for others applications which need a much higher purity, particularly polymer synthesis. Currently, distillation [3,4], esterification [5–7] and crystallization [8] are commonly used to reach very high purities (>99.5%) [9]. However, these techniques are energy-consuming and give quite low recovery rates. Preparative chromatography is a promising solution for downstream processes because its energy, chemical and water consumptions are generally quite lower and consequently effluent volumes too. Initially developed for extraction and purification of complex vegetal mixtures [10], this separation method is spreading in different fields: biotechnology [11,12], pharmaceutic [13,14] and the sugar industry [15], for instance. Indeed, the same separation quality may be reached with better yields, lower costs and impacts on the environment. However, for several years now, the state of the world economy has not been favorable to industrial investments for the improvement of downstream purification processes. Moreover,

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http://dx.doi.org/10.1016/j.chroma.2016.06.057
0021-9673/

chromatography needs to prove itself for high purity application (>99.5%) at the industrial scale.

In the frame of organic acids purification in fermentation broths, chromatography is often performed with ion-exchange resins to separate mineral salts, sugars and organic acids. The eluent is an aqueous solution whose pH can be adjusted with the inorganic acid or base corresponding to the counter-ions fixed on the resin so as to keep its composition constant. The separation of compounds is based on affinity differences for the resins. Higher is the affinity, slower migrates the compound along the resin bed. In the sugar industry, cationic resins are used to separate sucrose from salts as well as sugars from each other. The glucose-fructose separation is among the most famous applications of preparative chromatography. Otherwise, anionic resins are performed for the citric acid purification. Uptake and slowdown mechanisms are not well known and complex, coupling size exclusion, ligand exchange, hydrophilic or hydrophobic interactions and ion-exchange [16,17].

In a previous work dealing with the purification of lactic, succinic and citric acids by chromatography with a strong anionic resin (quaternary ammonium), the Langmuir model fitted well with the experimental equilibrium isotherms obtained by frontal analysis [18]. However, the corresponding affinity coefficients were significantly lower than those obtained by pulse tests for succinic and citric acids. Their peaks had a singular tailing and were delayed compared to simulated ones with the Langmuir model and experimental coefficients of isotherms. Indeed, the Langmuir model was insufficient to describe the organic acids retention on the strong anionic resin and frontal analysis gave underestimated affinity coefficients.

These results lead us to suspect the impact of conjugate bases (dissociated organic acids) retention by ion-exchange, despite their very low concentrations. Indeed, the citrate anion affinity is high for quaternary ammonium anionic resin according to selectivity coefficients given by resins producers. Usually, this uptake mechanism is not taken into account because the strong anionic resins are performed at such acid pH (1–1.5) that only 0.2–0.4% of lactic acid, 0.1–0.2% of succinic acid and 1.2–2.3% of citric acid are dissociated. Thus, the organic acids dissociation is generally not considered although such small amount of conjugate bases may have a significant impact if they are strongly retained.

The present work aimed at modelling uptake mechanisms on a strong anionic resin. The Langmuir model, commonly used for the retention of organic acids, was coupled with a usual ion-exchange model for the retention of conjugate bases. Simulation results were compared with experimental pulse tests to check the model. The final goal was to improve the accuracy of a preparative chromatography simulation program in order to optimize the operating parameters of our pilot-scale ISMB unit (Improved Simulated Moving Bed).

2. Chromatography modelling

2.1. Mass transfer model

The Martin and Synge plate model [19] was chosen to describe the elution of organic acids through a strong anionic resin bed. In each plate of volume V, the mobile phase takes up a volume εV and the stationary phase a volume $(1-\varepsilon)$V, with ε the bed voidage. Usually, for preparative chromatography, volumes are expressed in BV (bed volume) [20–22], corresponding to the ratio of volume to the resin bed volume. Both phases are always supposed in equilibrium in all plates (nonlinear equilibrium in our case). The axial dispersion is characterized by the plate number N.

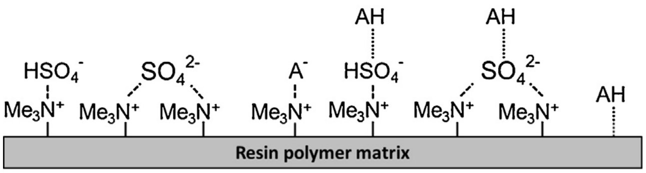

Fig. 1. Illustration of the six compounds considered in the stationary phase.

2.2. Uptake mechanisms—reactions in stationary phase

The strong anionic resin is a styrene-divinylbenzene resin functionalized with quaternary ammonium groups RMe_3N^+. The amount of these cationic sites corresponds to the ion-exchange capacity $q_{RMe_3N^+}$ of the resin, expressed in mol L^{-1}_{resin}. The resin is initially in the sulfate form, namely with the counteranions $HSO_4{}^-$ and $SO_4{}^{2-}$ in equilibrium. The proportion of both forms depends on their concentration in the mobile phase, so on its pH. The concentrations of hydroxyl anion OH^- in both phases were considered negligible at pH <1.5.

The proposed model was based on two classical uptake mechanisms, with some assumptions:

- Uptake of the organic acid in the dissociated form A^- by ion-exchange with resin counteranions $HSO_4{}^-$ and $SO_4{}^{2-}$.
- Retention of the organic acid in the molecular form AH according to the Langmuir model, by weak bonds (hydrogen or van der Waals), on free sites either on counteranions $HSO_4{}^-$ and $SO_4{}^{2-}$ (weak nucleophiles, *cf.* UOP patents [23,24]) or on the polymer matrix whose capacity q_{mat} is also expressed in mol L^{-1}_{resin}. We supposed that the AH retention does not modify the selectivity coefficients of counteranions.

Consequently, 6 compounds were considered in the stationary phase: $HSO_4{}^-$, $SO_4{}^{2-}$, A^-, AH-site($HSO_4{}^-$), AH-site($SO_4{}^{2-}$) and AH-site(matrix) (Fig. 1).

The ion-exchange reactions correspond to the following equilibria:

$$\left(RMe_3N^+\right)_2SO_4^{2-}+2A^- \leftrightarrow 2\left(RMe_3N^+\right)A^- + SO_4^{2-}$$

$$\left(RMe_3N^+\right)_2SO_4^{2-}+2HSO_4^- \leftrightarrow 2\left(RMe_3N^+\right)HSO_4^- + SO_4^{2-}$$

$$\left(RMe_3N^+\right)HSO_4^- + A^- \leftrightarrow \left(RMe_3N^+\right)A^- + HSO_4^-$$

Since the affinity of counteranions $HSO_4{}^-$ and $SO_4{}^{2-}$ for resin cationic sites was supposed not influenced by AH uptake, their equilibrium constants can be written as follows:

$$Ke_{A^-/SO_4^{2-}} = \frac{\left[SO_4^{2-}\right]q_{A^-}^2}{\left[A^-\right]^2 q_{SO_4^{2-}}} \tag{1}$$

$$Ke_{HSO_4^-/SO_4^{2-}} = \frac{\left[SO_4^{2-}\right]q_{HSO_4^-}^2}{\left[HSO_4^-\right]^2 q_{SO_4^{2-}}} \tag{2}$$

$$Ke_{A^-/HSO_4^-} = \frac{\left[HSO_4^-\right]q_{A^-}}{\left[A^-\right]q_{HSO_4^-}} = \sqrt{\frac{Ke_{A^-/SO_4^{2-}}}{Ke_{HSO_4^-/SO_4^{2-}}}} \tag{3}$$

where $q_{HSO_4^-}$ and $q_{SO_4^{2-}}$ represent the $HSO_4{}^-$ and $SO_4{}^{2-}$ contents in the stationary phase (free or bound to AH), q_{A^-} the A^- content and [X] the concentration of X in the mobile phase.

The ion-exchange equilibrium constants Ke can be estimated from data of resin suppliers by Equations (5)–(7). For example, the Dow Chemical Company gives the selectivity coefficients of anions