



Strong anion exchange recovery of aqueous dicarboxylates: Extraction and sorption equilibrium comparison



Camilo S. López-Garzón¹, Luuk A.M. van der Wielen, Adrie J.J. Straathof*

Department of Biotechnology, Delft University of Technology, van der Maasweg 9, 2629 HZ Delft, The Netherlands

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ABSTRACT

Ion-exchange can be used for primary recovery of aqueous dicarboxylic acids at neutral pH, where there is almost complete acid dissociation. The equilibria of anion exchange of aqueous dicarboxylate anions (fumarate, itaconate, malate and succinate) with anions (Cl^- and OH^-) bound to quaternary ammonium compounds (Aliquat extractant and Dowex sorbent) were quantified. All equilibria could be described by the same model. The four dicarboxylates behaved similarly, and were exchanged by two Cl^- or OH^- anions. Sorption gave a much better exchange than extraction and OH^- gave a much better exchange than Cl^- . In batch equilibrium experiments most Cl^- is not exchanged by dicarboxylate, pointing at the importance of column operation.

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1. Introduction

In recent years, interest in bio-based production of dicarboxylic acids has increased as they have shown a clear potential of becoming relevant renewable chemical building blocks. Their diacid functionality provides a versatile platform for different chemical transformations into alcohols, esters, furans, and lactone-related compounds, among others, driving the production of new specialty chemicals, solvents, polymers, detergents and many other intermediate and consumer products [1]. Biotechnological production of dicarboxylic acids has been investigated extensively and has reached technological maturity for some molecules, in particular for succinic acid leading to different industrial ventures worldwide [2]. The economic and sustainability hurdles associated with the feasibility of large scale production of dicarboxylic acids are closely related to the biological host chosen, as it determines the fundamental structure of the production process. During fermentation, production of carboxylic acids will decrease the pH of the medium, creating a challenging acidic environment for most natural producer microorganisms. Neutrophilic microorganisms will require the removal of the produced diacid either by neutralization reaction or other physical or chemical methods. Alternatively, an acid-tolerant microorganism can be used provided it has enough

acid stress resistance. As expected, there is a trade-off in selecting the production microorganism, higher titers and productivities have been observed at neutral pH conditions for most relevant dicarboxylic acids [3].

From a recovery and purification standpoint, neutral pH fermentations will require a more extensive processing and thus might compromise the overall economics of the process, even with a favorable fermentation. At neutral pH, dicarboxylates are present as bivalent salts associated with metal cations originating from the base used during fermentation. During downstream processing, the dicarboxylate should be recovered from the bulk liquid, converted back to its undissociated form, concentrated, and purified to the required grade. Several sequences of operations are possible to achieve this [3], but the choice of the primary recovery method is often critical as it has a great influence on subsequent operations. Different technologies for primary recovery of carboxylates are available. They are mostly based on the transfer of the carboxylate to an extractant or sorbent auxiliary phase. Anion exchangers comprise an interesting class of extractant or adsorbent auxiliary phases, potentially allowing integration of several of the above described downstream steps, possibly resulting in an efficient and sustainable bio-based dicarboxylate process. Recovery by anion exchange at neutral pH can be integrated with subsequent downstream ester formation [4,5].

Although the extraction and sorption of carboxylic acids using ion-exchange has been studied for over three decades, most of the research has been focused on monocarboxylic acid at the time, e.g. lactic acid, at a processing pH below the pK_a where the major-

* Corresponding author.

E-mail address: A.J.J.Straathof@tudelft.nl (A.J.J. Straathof).

¹ Present address: Novozymes A/S, Recovery Development, Krogshoejvej 36, 2880 Bagsvaerd, Denmark.

ity of the acid exists as the undissociated species. There is a limited amount of equilibrium data for capture of dicarboxylates that is, at a pH above their second pK_a . Moreover, a myriad of different models and parameters has been used to characterize the equilibrium phenomena of such operations, impeding thorough and accurate comparisons across the existing literature.

Limiting the scope of the present study to fully dissociated acids produced at neutral pH, favorable chemical interactions for primary recovery occur using strong anion exchangers rather than using weak anion exchange resins. Strong anion exchange materials typically contain a quaternary ammonium-based functional group, so they are capable of ion pairing leading to anion exchange reactions. As a consequence, the target carboxylate can be captured, and depending on the selected displacement and regeneration steps, further acidified and purified. The phase of the exchanger will determine the process technology to be used, liquid exchangers leading to extraction operations and their solid analogues to sorption operations.

In the case of ion exchange extraction of dicarboxylates, the anion exchanger Aliquat 336 Cl^- (Fig. 1a) will be studied as extractant. It is used in many carboxylate extraction studies because of its extracting capacity, low aqueous solubility, and low price. Although it has been reported to be non-toxic to anaerobic bacteria [6], it is a very viscous liquid, limiting its applications in pure form. Thus, diluents and modifiers are commonly used diluted to improve extraction characteristics.

In the case of solid exchangers, a variety of polymeric matrixes and functional groups are commercially available, but their characteristics are often broadly lumped by the manufacturer and only a few details about their chemical composition are known. Gel type resins have great permeability and allow higher number of functional groups as a true porous structure is absent. Strong anion exchange resins are usually classified by their basicity as Type I or II, the former being the stronger base, thus able to ion pair in a broader pH range. Dowex Marathon A is a gel, type I resin with uniform size, which might provide high capacity for the sorption of dicarboxylates.

As can be concluded from the discussion presented above, the choice of an ion exchange-based primary separation operation will be facilitated by comparing the capture equilibria of extraction and sorption for several model dicarboxylates. Fumaric, itaconic, succinic and malic acid will be used as model compounds as have been considered promising chemical building blocks from biomass [7] and for which bio-based processes are available at neutral pH [2]. The capacity and affinity of such dicarboxylates will be established and compared using the already presented Aliquat 336 and Dowex Marathon A as model ion exchange extractant and sorbent, respectively. Finally, the influence of two typical counter-ions, Cl^-

and OH^- , on the mentioned equilibrium characteristics will be considered.

2. Experimental

2.1. Materials

Fumaric, itaconic, succinic and malic acid used were of analytical grade (Sigma-Aldrich). Aqueous solutions were prepared using deionized water from a Milli-Q water purification system (Millipore Corp.) All the acid solutions were adjusted to $pH\ 7.00 \pm 0.5$ in two steps, using solid sodium hydroxide (Merck) to a pH close to 6 and to neutral pH with 1 mol/L NaOH solution by means of an automatic titrator (Metrohm Titrino system). The prepared solutions were analyzed to determine the exact carboxylate concentration prior to use. Extraction experiments were performed using Aliquat 336 (Sigma-Aldrich), a commercial ion exchange extractant composed of a mixture of trialkylmethylammonium chlorides (C_8 – C_{10} alkyl chains) with an average molecular weight of 404.16 and a density of $884\ kg/m^3$. The extractant was converted to the OH^- form as described in Section 2.2. 1-Decanol 98% (Fluka) and *n*-dodecane (Sigma) were used as modifiers and diluent, respectively. Ion exchange sorption experiments were carried out using the strong anion exchange resin Dowex Marathon A (Sigma-Aldrich), composed by a styrene-DVB matrix with a type I quaternary amine functional group. Both Cl^- and OH^- forms were obtained directly from the supplier. According to the supplier, the moisture retention capacity of the resins varies between 50% and 60% for the Cl^- form to 60–72% for the OH^- ion. As a result of this, shipping density is higher for Cl^- than OH^- , with values of 670 and 640 g/L, respectively. The resin was washed twice and rehydrated with deionized water prior to use.

2.2. Conversion of Aliquat 336 Cl^- into its OH^- form

A solution (500 mL) composed of Aliquat 336 in chloride form (30% v/v), 1-decanol (20% v/v) and *n*-dodecane was contacted with an equal volume of 1.0 mol/L NaOH in a closed flask at 500 rpm using an overhead stirrer during four hours. Preliminary tests showed this time was sufficient to attain exchange equilibrium. After settling, the spent aqueous phase was drained and replaced by fresh hydroxide solution for a new contacting. By the end of the last contacting, and settling overnight in a separation funnel, the yellowish organic phase was centrifuged at 2500 rpm for 15 min, and washed with deionized water until the pH of the aqueous solution was below 7.5, to remove the excess NaOH from the organic phase.

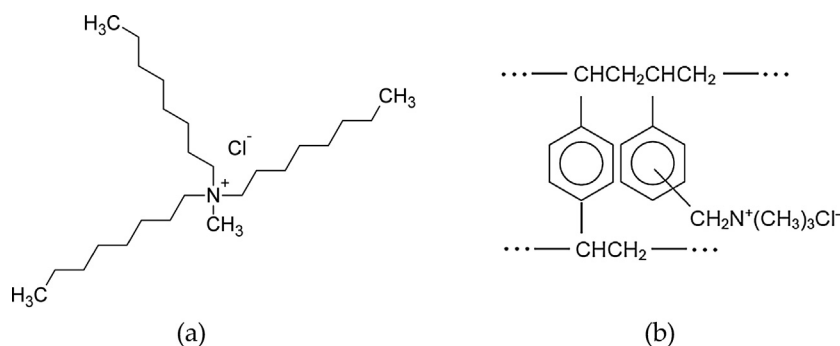


Fig. 1. Strong anion exchangers used in this study. (a) Aliquat 336 Cl^- , although shown as *N*-methyl-*N,N,N*-triocetyl ammonium chloride, its commercially available as a mixture of octyl (predominant) and decyl chains. (b) Dowex Marathon A, a styrene-divinylbenzene gel matrix functionalized with trimethylammonium chloride.

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