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Ion-exchange equilibrium of N-acetyl-D-neuraminic acid on a strong anionic exchanger

Jinglan Wu [a,b,1], Xu Ke [a,b,1], Xudong Zhang [a,b], Wei Zhuang [a,b], Jingwei Zhou [a,b], Hanjie Ying [a,b,c,*]

[a] College of Biotechnology and Pharmaceutical Engineering, Nanjing Tech University, Nanjing, China
[b] National Engineering Technique Research Center for Biotechnology, Nanjing, China
[c] State Key Laboratory of Materials-Oriented Chemical Engineering, Nanjing, China

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ABSTRACT

N-acetyl-D-neuraminic acid (Neu5Ac) is a high value-added product widely applied in the food industry. A suitable equilibrium model is required for purification of Neu5Ac based on ion-exchange chromatography. Hence, the equilibrium uptake of Neu5Ac on a strong anion exchanger, AD-1 was investigated experimentally and theoretically. The uptake of Neu5Ac by the hydroxyl form of the resin occurred primarily by a stoichiometric exchange of $Neu5Ac^-$ and OH^-. The experimental data showed that the selectivity coefficient for the exchange of $Neu5Ac^-$ with OH^- was a non-constant quantity. Subsequently, the Saunders' model, which took into account the dissociation reactions of Neu5Ac and the condition of electroneutrality, was used to correlate the Neu5Ac sorption isotherms at various solution pHs and Neu5Ac concentrations. The model provided an excellent fit to the binary exchange data for Cl^-/OH^- and $Neu5Ac^-/OH^-$, and an approximate prediction of equilibrium in the ternary system $Cl^-/Neu5Ac^-/OH^-$. This basic information combined with the general mass transfer model could lay the foundation for the prediction of dynamic behavior of fixed bed separation process afterwards.

1. Introduction

N-Acetyl-D-neuraminic acid (CAS Registry No. [131-48-6]), also known as Neu5Ac, is a high value-added product. Fig. 1 shows the molecular structure of Neu5Ac. As an important food additive, Neu5Ac is widely added to dairy products and infant formulas to protect infants against enteric pathogens, provide prebiotic functions and activate the immune system (Bergelson, 1995).

In the past decades, the biotechnological production of Neu5Ac based on the whole-cell bio-catalysis technology has emerged as an important tool for the large-scale synthesis of Neu5Ac (Tao, Zhang, Ma, & Xu, 2010, 2011). In addition to the upstream biosynthesis process, the downstream purification process plays an essential role in the Neu5Ac production as well. Since Neu5Ac is an acidic sugar and the carboxylate group at the 1-carbon position can be ionized at certain pH (see Fig. 1 the molecular structure), the ion-exchange chromatography is extensively used in the purification of Neu5Ac from many sources (Chen, Pan, Liu, Troy, & Wang, 2014; Priego-Capote, Orozco-Solano, Calderon-Santiago, & Luque de Castro, 2014; Zimmermann, Masuck, & Kragl, 2008). The design and efficient operation of an ion-exchange process require equilibrium data for use in kinetic and mass transfer models. Consequently, the acquisition of equilibrium data as well as the equilibrium model is a primary step in the development of an ion-exchange process (Franco et al., 2013).

Mathematical modeling of the ion-exchange equilibrium using Saunders' model (Helfferich, 1962) is a powerful tool for evaluating the equilibrium composition of ionic species among phases. Carta's research group (Dye, DeCarli, & Carta, 1990) used this model to predict the equilibrium uptake of amino acids by a cation-exchange resin, Amberlite 252, in single- and multi-component systems. The model calculations agreed well with the experimental data. Recently, Moreira and Ferreira extended the Saunders' model to evaluate the ion-exchange equilibrium sorption of phenylalanine and tyrosine on both cation- and anion-exchange resins (Moreira & Ferreira, 2005). Moreover, based on this model, they successfully simulated column dynamic breakthrough curves (Moreira & Gando-Ferreira, 2012a) and cyclic adsorption/desorption processes (Moreira & Gando-Ferreira, 2012b). However, until now, few detailed equilibrium studies of Neu5Ac on ion-exchange resins have been reported in literature. Since Neu5Ac is a high

* Corresponding author at: College of Biotechnology and Pharmaceutical Engineering, Nanjing Tech University, Xin Mofan Road 5, Nanjing 210009, China. Tel.: +86 25 86990001; fax: +86 25 58139389.
E-mail address: yinghanjie@njtech.edu.cn (H. Ying).
[1] These authors contributed equally to this work.

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Nomenclature

C_0	initial concentration of Neu5Ac in aqueous solution (mmol l^{-1})
$C_{0,NaCl}$	initial concentration of NaCl in aqueous solution (mmol l^{-1})
C_e	concentration of Neu5Ac at equilibrium (mmol l^{-1})
C_{e,Cl^-}	concentration of Cl^- in solution at equilibrium (mmol l^{-1})
C_{H^+}	concentration of hydrogen ions (mmol l^{-1})
C_{Na^+}	concentration of sodium in aqueous solution (mmol l^{-1})
C_{Neu5Ac}	concentration of non-ionized form of Neu5Ac (mmol l^{-1})
C_{Neu5Ac^-}	concentration of Neu5Ac present in negatively charged form (mmol l^{-1})
C_{OH^-}	concentration of hydroxyl ions (mmol l^{-1})
C_t	total concentration of Neu5Ac (containing both ionized and non-ionized Neu5Ac) (mmol l^{-1})
p	skewness parameter
q_0	ion-exchange capacity of AD-1 resin (mmol g^{-1})
q_e	mass of Neu5Ac adsorbed per unit mass of adsorbent at equilibrium (mmol g^{-1})
q_{e,Cl^-}	mass of Cl^- adsorbed per unit mass of adsorbent at equilibrium (mmol g^{-1})
S_{Cl^-,OH^-}	apparent selectivity coefficient for ion exchange of Cl^- and OH^- ions
S_{Neu5Ac^-,OH^-}	apparent selectivity coefficient for ion exchange of $Neu5Ac^-$ and OH^- ions
$\bar{S}_{i,j}$	average selectivity coefficient for ion exchange of i and j
V	volume of Neu5Ac solution (ml)
$W_{i,j}$	heterogeneity parameter
X_{Cl^-}	ionic fraction of chloride in solution
X_{Neu5Ac^-}	ionic fraction of $Neu5Ac^-$
Y_{Cl^-}	ionic fraction of chloride in resin phase
Y_{Neu5Ac^-}	ionic fraction of Neu5Ac in resin phase
Y_{OH^-}	ionic fraction of OH^- in resin phase

Greek symbol

ρ_s	dry resin density (g of dry resin/g of hydrated resin)

value-added product, investigation of the sorption behaviors of Neu5Ac on ion-exchangers is of great importance.

Therefore, the aim of this paper is to obtain the equilibrium data as well as the equilibrium model for ion-exchange of Neu5Ac on a tailor-made anion-exchanger AD-1 resin. This basic information will be incorporated into a general mass transfer model for the prediction of the dynamic behavior of fixed-bed separation process in the future work. To achieve the aim, the equilibrium uptake of Neu5Ac by the hydroxyl form of the AD-1 resin was determined using batch experiments. The equilibrium uptake was measured as a function of the Neu5Ac concentration and the solution pH. Moreover, the Saunders' model which took into account the dissociation reaction of Neu5Ac and the ion-exchange reaction was discussed and validated by comparing the model predictions with the experimental results at various solution pHs and Neu5Ac concentrations as well.

2. Theory

The Saunders' model (Saunders, Vierow, & Carta, 1989) was developed based on the mass action law to represent variable selectivities in ion exchange. The main assumptions of the model include: (i) interactions among counterions can be neglected, and (ii) due to the structural irregularity of the random polymeric matrix, the functional groups on the resin have different specific selectivities. The apparent selectivity ($S_{i,j}$) exhibited by the resin is thus the result of a combination of the individual ion-exchange reactions occurring on each different functional groups. According to this model, the conterions A, which is assumed to be the "preferred ion", is first bounded by the functional groups with high selectivity, resulting in a high $S_{i,j}$. Then, as the resin becomes saturated with A, the exchange reaction will occur on the less selective groups, yielding a reduced $S_{i,j}$. Consequently, in general, the $S_{i,j}$ for the preferred ion will decrease as the loading of that ion in the resin is increased. The details of the model equations are discussed elsewhere (Saunders et al., 1989) and are briefly discussed here. Considering N counterions and selecting ion j as the reference counterion, the apparent selectivity coefficient for ion i is given by

$$S_{i,j} = \frac{Y_i X_j}{Y_j X_i} = \bar{S}_{i,j} \frac{\sum_{k=1}^{N} \left\{ \bar{S}_{k,j} X_k W_{k,j}^{U+V} \left[(1-p) W_{i,k}^{U} + p W_{i,k}^{V} \right] \right\}}{\sum_{k=1}^{N} \left\{ \bar{S}_{k,j} X_k W_{k,j}^{U+V} \left[(1-p) W_{j,k}^{U} + p W_{j,k}^{V} \right] \right\}} \quad (1)$$

$$U = \frac{-p}{\sqrt{p(1-p)}} \quad (2)$$

$$V = \frac{1-p}{\sqrt{p(1-p)}} \quad (3)$$

where X and Y is the ionic fraction of ion in solution and in the resin, respectively. $\bar{S}_{i,j}$ is the average selectivity, p represents the skewness parameter, which indicates the probability of finding one type of site, and $W_{i,j}$ is the heterogeneity parameter, which is related to the variations in energy distributions on exchange sites. For binary exchange, these three parameters need to be determined. Once all the $S_{i,j}$ have been obtained, the uptake of ion i can be calculated from

$$Y_i = \frac{q_i}{q_0} = \frac{X_i S_{i,j}}{\sum_{K=1}^{N} X_K S_{K,j}} \quad (4)$$

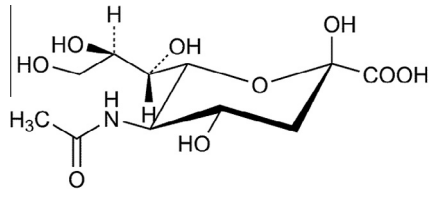

Fig. 1. Molecular structure of Neu5Ac.

3. Materials and methods

3.1. Materials

Neu5Ac was purchased from Sigma–Aldrich. All the chemicals used were of analytical grade. Neu5Ac solutions were prepared by dissolving precisely measured amounts (±0.1 mg) of Neu5Ac in deionized water. The ion exchanger, AD-1, kindly provided by National Engineering Research Center for Biotechnology, consisted of a crosslinked (7%) styrene–poly(vinylbenzene) resin matrix.