

# Sorption of levulinic acid onto weakly basic anion exchangers: Equilibrium and kinetic studies

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## Abstract

The equilibrium and dynamics of levulinic acid sorption on two weakly basic anion exchangers, in free base form, in single-component aqueous solutions were investigated. Adsorption isotherms such as Langmuir, Sips, Radke–Prausnitz, and Toth were applied to correlate the experimental data in the temperature range 285–315 K. Modeling results showed that the Toth model is the best one to correlate the sorption isotherms. The resulting Toth equations were used with the Clausius–Clapeyron equation to determine the isosteric heat of sorption. The sorption kinetics was experimentally measured via a completely stirred finite-bath batch experiment under different initial concentrations and at varying solution temperatures. The pseudo-second-order kinetic model and the Elovich equation were used to represent the kinetic data and the equation parameter values were also evaluated. The pseudo-second-order equation cannot simulate the experimental kinetic data, while the Elovich equation fitted the sorption dynamic data very well under all the operating conditions studied. Finally, the apparent activation energy of sorption was also determined.

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*Keywords:* Levulinic acid; Anion exchanger; Sorption equilibrium; Batch kinetics; Toth; Elovich; Pseudo-second order; Isosteric heat

## 1. Introduction

Levulinic acid (LA, 4-oxopentanoic acid), a short-chain non-volatile fatty acid, has a ketone carbonyl group and an acid carboxyl group. It can be used as a basic chemical raw material to react with a wide range of chemicals to synthesize different products [1,2]. LA and its derivatives have versatile applications as fuel extender, solvent, biodegradable herbicide, monomer, polymer resin, ink, and coating. Recently, LA has been proposed as a platform chemical because it can be produced cost-effectively and in high yield from renewable biomass [3]. Numerous patents and articles have been reported for the manufacture of LA. The most widely used approach is the hydrolysis or decomposition of biomass or sugars with acids [4–6]; however, there are few published researches concerned with the recovery of LA from hydrolysate.

Weakly basic ion exchangers are frequently used for recovery of carboxylic acid from aqueous hydrolysate or fermentation broth. Tong et al. [7] reported the purification of lactic acid from fermentation broth with paper sludge as feedstock using Amberlite IRA-92, a weak anion exchanger. Takatsuji and Yoshida [8] found out that DIAION WA30 was a good adsorbent for recovery of organic acids from wine, which contained glucose, ethanol, and various acids. Kanazawa et al. [9, 10] investigated sorption equilibria of nine organic acids including monocarboxylic and monosulfonic acids on 16 anion exchangers. Acid separation behavior on a different resin type and basicity [11] and carboxylic acid transport in porous anion exchangers [12,13] were also studied.

In this work, the sorption behavior of weakly basic anion exchangers for the uptake of LA from aqueous solution is investigated. The amounts adsorbed at equilibrium sorption were measured at different temperatures. The sorption rate and kinetics in a completely stirred finite-bath vessel have been experimentally determined. Finally, the change of heat of sorption with amount adsorbed and the apparent activation energy was also analyzed.

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## 2. Materials and methods

### 2.1. Levulinic acid and anion exchangers

LA (purity greater than 98%) was supplied by Langfang Sanwei Chemical Co., Ltd. (Hebei Province, China) and used as received without further purification. All aqueous LA solutions were prepared in distilled, deionized water from a Milli-Q water treatment system (Millipore Corp., Bedford, MA), and the resultant solution pH was called the natural pH. LA concentrations in aqueous solutions were measured by high performance liquid chromatography (Waters 1525 binary HPLC pump, 717 Plus auto sampler) equipped with Waters 2487 dual absorbance detector at a wavelength of 270 nm and Discovery C<sub>18</sub> column (25 cm × 4.6 mm, 5 μm). The column temperature was maintained at 40 °C and the mobile phase was water/methanol/acetic acid (88/12/0.1, v/v/v).

Weakly basic anion exchangers D301 and D315 were purchased from Shanghai Huazhen Science & Technology Co., Ltd. (Shanghai, China). The fresh resins were sieved several times and the fraction 0.74–0.9 mm in diameter was collected and used in this work. The sieved media samples were pretreated in a column by washing with 1.0 mol/l HCl, deionized water and 1.0 mol/l NaOH in turn and finally washed thoroughly with deionized water to pH around 7. The anion exchangers were in free base form for this pretreatment. Following pretreatment, the samples were suctioned dry (no drop) under vacuum and stored in sealed containers and ready for use. The total water content of each media sample was determined from the mass loss on vacuum drying at 60 °C to constant weight. The physical characteristics of the exchangers are summarized in Table 1.

### 2.2. Equilibrium experiments

Sorption equilibrium experiments of LA on the anion exchangers were conducted using the batch adsorption method. Fixed amount of 200 mg resin particles were weighed and added into each of the 250-ml glass flasks containing 100 ml of LA solution with different concentrations (0.862–25.862 mmol/l). Then the flasks were shaken at 180 rpm and the desired temperature in a temperature-controlled shaker for 24 h (48 h for 285 K), which is confirmed to be sufficient to reach adsorption equilibrium. Upon equilibrium, shaking was stopped and the supernatants from each flask were sampled and analyzed by HPLC. The amount adsorbed was calculated by mate-

rial balance,

$$q_e = \frac{V(C_0 - C_e)}{M}, \quad (1)$$

where  $q_e$  is the amount of LA adsorbed per gram of medium (mmol/g),  $V$  is the volume of solution (l),  $M$  is the wet mass of the resin (g), and  $C_0$  and  $C_e$  are respectively the initial and equilibrium concentration in solution (mmol/l).

### 2.3. Batch kinetics experiments

Sorption rate studies were carried out in a stirred finite-bath batch contactor. Exactly 1.0 g of resin beads were weighed and added into a 500-ml flask containing 250 ml of deionized water, and then the flask was immersed in a water bath to control the temperature. After the required temperature was reached, the solution in the flask was stirred with a Teflon impeller, which was driven by a motor equipped with a speed controller at 800 rpm to completely suspend the resin particles. At time 0, 250 ml of preheated LA aqueous solution was added quickly into the flask to obtain the desired initial concentration; the total volume in the flask was 500 ml. Fixed-volume samples of 1 ml were withdrawn at different time intervals using glass syringes (equipped with needles to ensure that no resin bead was taken out during sampling) and analyzed by HPLC. The total solution volume reduction due to sampling was less than 3% for all experiments, so that sorption rates were measured under essentially constant liquid volume. The adsorbed amount of LA at different times was calculated by material balance. The amounts adsorbed at time  $t$  and at equilibrium were expressed in terms of the mass of wet particles.

## 3. Results and discussion

### 3.1. Sorption equilibrium

The sorption of carboxylic acids onto weakly basic anion exchangers can be regarded as an acid/base neutralization reaction [14],



where R-N denotes a tertiary amine fixed in the resin phase and HA is the carboxylic acid. The neutralization reaction can be described by the equilibrium constant  $K_L$ ,

$$K_L = \frac{q_e}{(q_L - q_e)C_e}. \quad (3)$$

Table 1  
Physical properties of weakly basic anion exchangers used in this study

Ion exchanger	D301	D315
Matrix	Polystyrene-divinylbenzene macroreticular	Polyacrylic-divinylbenzene macroreticular
Water content (%)	57.5	53.2
Apparent density (g of wet resin/ml of wet resin)	1.05	1.09
Functional groups	Tertiary amine	Tertiary amine
Ionic form	Free base (FB)	Free base (FB)
Particle size (mm)	0.74–0.90	0.74–0.90

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