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Adsorption Equilibria of Succinic Acid and Lactic Acid on Amberchrom CG300C Resin

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ABSTRACT: One of the prerequisites to the development of a simulated moving bed (SMB) or a temperature-gradient SMB process for separation of succinic acid and lactic acid is to obtain their adsorption equilibrium data on a properly selected adsorbent. It was first found that an Amberchrom CG300C resin could function well as a qualified adsorbent for the separation processes of interest. On the basis of the selected adsorbent, the single-component adsorption equilibria of succinic acid and lactic acid were measured using a staircase frontal analysis method over the temperature range of (30 to 50) °C and the liquid-phase concentrations up to 10 $\text{g}\cdot\text{L}^{-1}$. The resultant adsorption data were correlated with the Langmuir and the bi-Langmuir adsorption models. For these two models, the effect of temperature on the Langmuir and the bi-Langmuir equilibrium constants was examined, which revealed that the adsorption of each acid onto Amberchrom CG300C was exothermic. Such a temperature effect was expressed mathematically, which was then incorporated into each model equation. The resultant temperature-dependent form of the model equation allowed accurate predictions of all the adsorption equilibrium data acquired over the investigated temperature range. The adsorption equilibrium data and the model parameters reported in this study will be of great value in the stage of designing the temperature-gradient SMB process that is packed with the Amberchrom CG300C resin and targeted at separating succinic acid and lactic acid.

INTRODUCTION

Several organic acids with multiple functional groups are highly useful as starting materials for the chemical industry because they can be easily transformed into a variety of valuable substances.[1−3] Such organic acids with potential applicability are therefore called "building-block chemicals" in the literature.[1−3] Among these building-block chemicals, succinic acid (butanedioic acid) has received remarkable attention because it can be widely used as a specialty chemical for the production of surfactants, detergents, forming agents, ion chelators, cosmetics, pharmaceuticals, and antibiotics.[1,2,4]

Currently, succinic acid is obtained from two different sources.[1,4] One is from petroleum, from which succinic acid is produced chemically. The other is from biomass, from which succinic acid is produced by fermentation. Between the two sources, the latter has been drawing a lot of attention because its advantages in both economical and environmental aspects are becoming increasingly important.[1,4]

However, the use of fermentation technology for the production of succinic acid always causes the necessity for the separation of succinic acid and the byproduct components resulting from the fermentation process.[4] In this connection, it is worth noting a recent study,[4] in which a nanofiltration process for resolving such a separation task has been developed. This process was successful to some extent. However, it was reported to have some difficulties in complete removal of lactic acid (2-hydroxypropanoic acid), which was one of the byproduct components. Hence, an additional chromatographic process for separation between succinic acid and lactic acid was needed. Since lactic acid serves as a starting material of the biodegradable plastic polylactide,[1,3] the separated lactic acid from the additional process will also be as useful as succinic acid. For industrial applications, this additional process needs to be designed at the level of a simulated moving bed (SMB) process, which is a well-defined continuous counter-current chromatographic process that can outperform conventional batch chromatographic processes in every respect.[5−7]

The goal of this study was to provide essential data and information that will be a prerequisite for designing such a SMB chromatographic process for separation of succinic acid and lactic acid. For this purpose, a qualified adsorbent for separation between the two acids will be proposed first. The adsorption equilibria of each acid on the proposed adsorbent will then be measured in the temperature range of (30 to 50) °C. This task will be carried out using a staircase frontal analysis (SFA) method,[8−10] which has been recognized to be highly accurate in acquiring adsorption equilibrium data. Furthermore, an appropriate model for predicting the measured equilibrium data over the investigated temperature range will be suggested, and its relevant parameters will also be determined.

The results of this study showed that an Amberchrom CG300 C resin, which is commercially available, possessed sufficient potential as the adsorbent of SMB chromatographic processes for separation of the two acids. It was also found from the measured adsorption equilibrium data that the adsorption affinity of each acid to Amberchrom CG300C was largely affected by temperature. This indicates that the design of a temperature-gradient SMB process, which was reported to surpass a classical SMB in separation performance,[11−13] is also practicable. Finally, the thermodynamic properties of the system under investigation were estimated, which revealed that the adsorption of each acid onto Amberchrom CG300C was exothermic and belonged to the case of physisorption.

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THEORY

Adsorption Equilibrium Model. SMB chromatographic processes consist of multiple columns that are connected in series.[5,6,8,10] Each of these chromatographic columns provides two distinct phases in connection with adsorption equilibrium. One is the solid phase, which is formed by the adsorbent particles contained in each column, and the other is the liquid phase, which is generated by the eluent introduced into the SMB process via its inlet port.

Many industrial-scale SMB processes are operated in an overloaded condition because it is advantageous to attain high productivity. In such an overloaded condition, the relationship between the solid-phase concentration (q) and liquid-phase concentration (C) at equilibrium is known to follow a nonlinear adsorption relationship.[5,10] One of the typical models to account for such an adsorption equilibrium relationship is the Langmuir model, which was established based on the assumption of monolayer coverage of adsorbate over a homogeneous adsorbent surface.[14] The Langmuir model equation for a fixed temperature is given below

$$q = \frac{q_s bC}{1 + bC} \tag{1}$$

where q_s is the saturation capacity and b is the Langmuir equilibrium constant related to the affinity of the adsorbent site and the energy of adsorption.[15] These two (q_s and b) are called Langmuir model parameters, which play an important part in the stage of designing a SMB process.

In the case of a temperature-gradient SMB process, the above Langmuir model needs to be extended in such a way that it can become effective over a wide range of temperatures. The usual way of doing so is to determine the values of the model parameters at several discrete temperatures and then utilize the determined values for expressing the model parameters as a continuous function of temperature. Here, there are two different approaches possible. One is to express both q_s and b as a function of temperature, while the other is to express only b as a function of temperature. Between the two, the latter has been the most accepted approach in the area of temperature-gradient separation process development.[11−13] It has also been widely adopted in other areas.[15−17] Furthermore, the latter approach is more faithful to the fundamental theory of the Langmuir model, which is based on the principle that the saturation capacity (q_s) must be independent of temperature.[16] Therefore, the latter approach will be used in this study.

Sometimes, the Langmuir model may fail to describe the adsorption equilibria with reasonable accuracy. In this case, it is customary to employ a more generalized model than the Langmuir model as an alternative. According to the literature, the bi-Langmuir model can be well suited for such an alternative model.[14] The reason is that the bi-Langmuir model contains a larger number of parameters than the Langmuir model, which means that the former is favorable for predicting adsorption equilibria with higher accuracy than the latter.

The bi-Langmuir model was established based on the assumption that the adsorbent surface is covered with two different kinds of sites (A and B) which behave independently.[14] The bi-Langmuir model equation for a fixed temperature is given below

$$q = \frac{q_{s,A} b_A C}{1 + b_A C} + \frac{q_{s,B} b_B C}{1 + b_B C} \tag{2}$$

where $q_{s,A}$ and $q_{s,B}$ are the saturation capacities of the adsorption sites A and B, respectively. In addition, b_A and b_B are the bi-Langmuir equilibrium constants for the sites A and B, respectively, each of which is related to the adsorption affinity of the respective sites. Like the Langmuir model, the above bi-Langmuir model equation can also be applied to a temperature-gradient process by expressing the two equilibrium constants (b_A and b_B) as a continuous function of temperature.

Indexes of Model Accuracy and Efficiency. In the stage of design or simulation of continuous separation processes, the selection of a proper equilibrium model is of importance. This necessitates making a quantitative evaluation of each candidate model in terms of accuracy and efficiency. To facilitate such a model evaluation, the concepts of average relative error (ARE) and standard deviation (σ) will be introduced in this study. First, the ARE of each model is estimated as follows[17]

$$\text{ARE}\ (\%) = \frac{100}{n} \sum_{i=1}^{n} \left(\frac{|q_{\text{cal},i} - q_{\text{exp},i}|}{q_{\text{exp},i}} \right) \tag{3}$$

where q_{exp} and q_{cal} are the experimentally measured solid-phase concentration and the calculated solid-phase concentration from the model equation, respectively, and n is the number of data points. Second, the standard deviation of each model is estimated in the following manner[8]

$$\sigma = \sqrt{\sum_{i=1}^{n} \frac{(q_{\text{cal},i} - q_{\text{exp},i})^2}{n - p}} \tag{4}$$

where p is the number of model parameters. In general, the ARE and σ are used as the indicators of model accuracy and model efficiency, respectively.

EXPERIMENTAL SECTION

Materials. Both succinic acid (butanedioic acid) and lactic acid (2-hydroxypropanoic acid) were purchased from the Sigma-Aldrich Co. (St. Louis, MO). The Amberchrom CG300C resin obtained from the Rohm and Hass Co. (Philadelphia, PA) was used as the adsorbent (solid phase), which has an average diameter of 120 μm. This adsorbent was packed into an omnifit chromatographic column, which was purchased from the Bio-Chem Fluidics Co. (Boonton, NJ). The column has a diameter of 1.5 cm and a packing length of 11.6 cm. The interparticle and intraparticle void fractions of the packed column were 0.376 and 0.723, respectively, which were obtained from a series of tracer-molecule pulse tests. A column jacket supplied from the Bio-Chem Fluidics Co. (Boonton, NJ) was used to control the column temperature.

Apparatus. The experiments were conducted with an HPLC system (Figure 1), which was manufactured by the Young Lin Co. (Anyang, South Korea). This system consisted of two HPLC pumps (Young Lin SP-930D), a refractive index detector (Young Lin 750F), an HPLC mixer from the Analytical Scientific Instruments Co. (El Sobrante, CA), an HST-250WL circulator from the Hanbaek Co. (Bucheon, South Korea), and a BW-20G water bath from the Jeio Tech Co. (Daejon, South Korea). The experimental data from this HPLC system were collected and analyzed with the help of automatic data acquisition software (Young Lin Autochro-3000), which operated in the Windows environment. A Milli-Q system by Millipore (Bedford, MA) was used to obtain distilled deionized water (DDW), which constituted a liquid phase in the adsorption equilibrium experiments performed.

Procedure. As mentioned in the Introduction, the adsorption equilibrium data in this study were acquired using the staircase frontal analysis (SFA) method.[8−10] Thus, let us give a brief

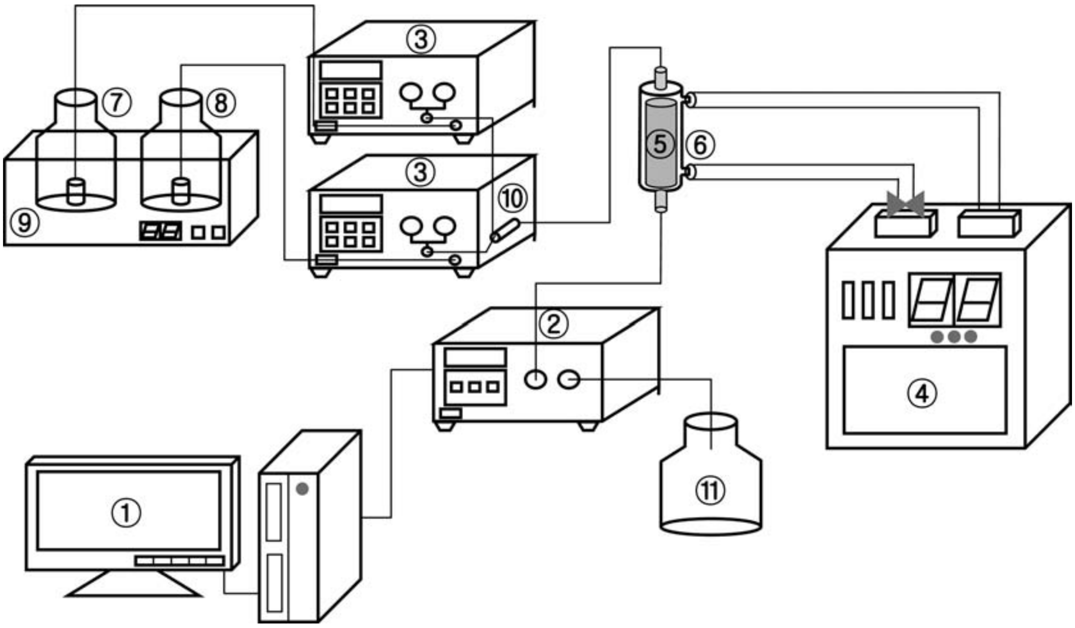

Figure 1. Schematic diagram of the experimental system used in this study. 1, Autochro-3000 software; 2, refractive index detector; 3, HPLC pumps; 4, circulator; 5, chromatographic column packed with Amberchrom CG300C; 6, column jacket; 7, reservoir for a feed solution; 8, reservoir for distilled deionized water; 9, water bath; 10, HPLC mixer; 11, waste reservoir.

summary of the SFA principle prior to explanation of the procedure of the experiments performed. The SFA method usually begins by loading a solution with known concentration into a chromatographic column packed with adsorbent. Such loading is continued until the equilibrium state between solid and liquid phases is attained. While the equilibrium state is maintained inside the column, the liquid-phase concentration is always kept uniform over the entire chromatographic bed, including both interparticle and intraparticle void spaces. Under such circumstances, the equilibrium liquid-phase concentration becomes identical with the concentration of the loaded solution. This means that the equilibrium liquid-phase concentration belongs to the category of controllable variables, which is one of the advantages in the SFA method.

The solid-phase concentration in equilibrium with the uniformed liquid-phase concentration (i.e., the concentration of the loaded solution) can then be estimated through a material balance over the entire bed. This procedure can be repeated by increasing stepwise the concentration of the loaded solution, which can eventually allow the acquisition of a set of adsorption equilibrium data over the investigated range of liquid-phase concentration. Other details including the relevant equations can be found elsewhere.[8]

To realize the aforementioned SFA principle experimentally, the two HPLC pumps in the experimental system (Figure 1) were utilized simultaneously. One pump delivered DDW and the other pump the feed solution containing either succinic acid or lactic acid. The concentration of each acid in the feed solution was kept constant at 10 $\text{g}\cdot\text{L}^{-1}$ throughout the experiments. The two streams were mixed before being loaded into the column packed with Amberchrom CG300C. Such a mixing process was facilitated by the HPLC mixer, which enabled the two streams to attain the state of perfect mixing before being loaded into the packed column. The total flow rate for the mixed stream (i.e., the loaded solution) was kept constant at 2 $\text{mL}\cdot\text{min}^{-1}$. Various feed compositions (20 %, 40 %, 60 %, 80 %, and 100 %) were obtained by changing the ratio of the two streams, which could allow the loaded solution to have five different concentrations. The ratio was changed only after a concentration plateau was fully developed at the column outlet. The column effluent was monitored using the refractive index detector. To maintain constant temperature during the experiments, distilled water at a fixed temperature was continuously circulated through the jacket enclosing the packed column, which was carried out by the HST-250WL circulator (Figure 1). In addition, both reservoirs containing DDW and the feed solution, respectively, were immersed in the BW-20G water bath, which was maintained at constant temperature.

■ RESULTS AND DISCUSSION

Suitability of the Adsorbent under Consideration. Prior to the measurement of adsorption equilibria for the system of interest, it was a matter of primary concern to clarify whether the Amberchrom CG300C resin was suitable for the adsorbent of an SMB chromatographic process for separation of succinic acid and lactic acid. For this task, a preliminary pulse test was performed, where a small amount of each acid was injected through the column packed with the Amberchrom CG300C resin. The result of this pulse test is presented in Figure 2. It is clearly seen that the retention time of succinic acid is quite different from that of lactic acid. This indicates the existence of an explicit discrepancy between the adsorption affinities of the two acids to Amberchrom CG300C, which is obviously favorable for facilitating the use of Amberchrom CG300C as the adsorbent of a targeted SMB process.

Adsorption Equilibria of Succinic Acid and Lactic Acid on Amberchrom CG300C. The single-component adsorption equilibrium data of succinic acid and lactic acid on Amberchrom CG300C were obtained using the SFA method in the temperature range of (30 to 50) °C. The obtained equilibrium data are presented in Table 1. First, a comparison between the two acids

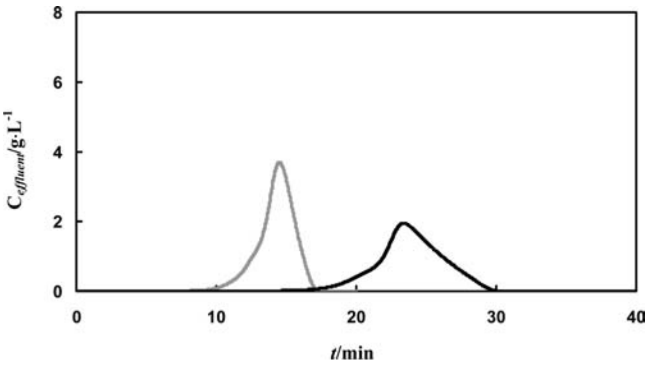

Figure 2. Result of the preliminary pulse test that was performed for the purpose of confirming the suitability of Amberchrom CG300C as the adsorbent of chromatographic processes for separation of succinic acid and lactic acid. In this test, the effluent concentration C_{effluent} was monitored as a function of time *t*. The gray and the black lines indicate lactic acid and succinic acid, respectively.

Table 1. Single-Component Adsorption Equilibrium Data of Succinic Acid and Lactic Acid on Amberchrom CG300C in the Temperature Range from $T = (30 \text{ to } 50)$ °C

succinic acid		lactic acid	
C / g·L^{-1}	q / g·L^{-1}	C / g·L^{-1}	q / g·L^{-1}
	T = 30 °C		
2	16.565	2	6.174
4	27.656	4	11.944
6	36.838	6	17.414
8	44.524	8	22.437
10	51.368	10	26.999
	T = 40 °C		
2	13.273	2	5.436
4	23.205	4	10.608
6	31.409	6	15.363
8	38.386	8	19.765
10	44.250	10	23.826
	T = 50 °C		
2	11.114	2	4.582
4	19.762	4	9.118
6	27.164	6	13.519
8	33.659	8	17.722
10	39.453	10	21.502

was made in terms of the equilibrium solid-phase concentrations (q) at 30 °C for the purpose of confirming again the result from the previous section. The comparison in Figure 3 reveals that there is a marked difference in equilibrium solid-phase concentration (q) between the two acids. This result supported the aforementioned statement that the selection of Amberchrom CG300C as the adsorbent for separation between the two acids was appropriate.

The experimental data in Table 1 were also used to examine the effect of temperature on the adsorption equilibrium of each acid. For this task, the adsorption data acquired at three different temperatures were plotted collectively in Figure 4a for succinic acid and in Figure 4b for lactic acid. It is clearly seen from these figures that the adsorption equilibrium of each acid is largely affected by temperature. In particular, it is worth noting that the solid-phase concentration, i.e., the

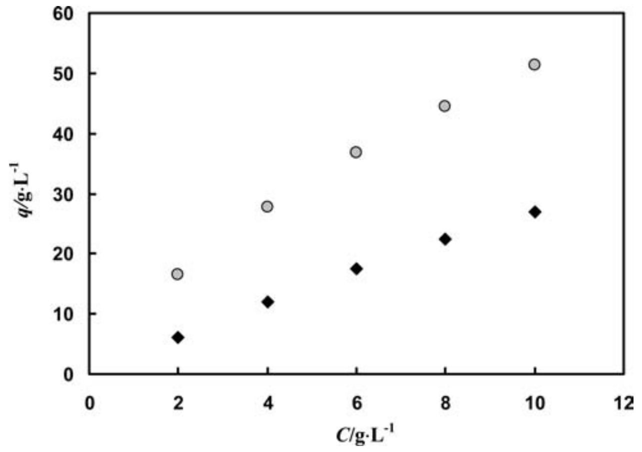

Figure 3. Comparison of succinic acid and lactic acid in terms of the solid-phase concentration (q) that is in equilibrium with the liquid-phase concentration (C) at 30 °C. Symbols: ○, succinic acid; ◆, lactic acid.

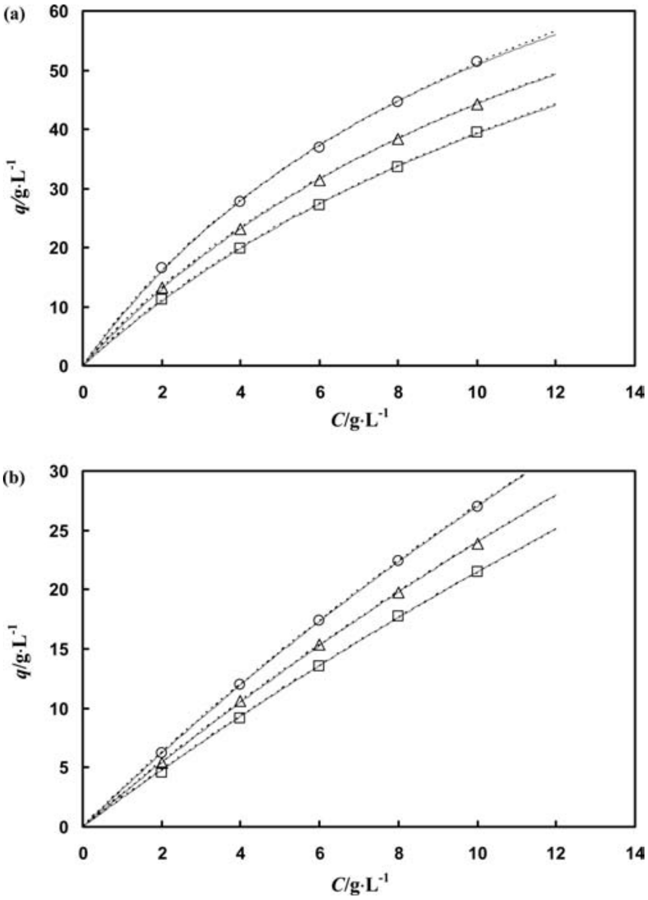

Figure 4. Single-component adsorption equilibria (plot of solid-phase concentration (q) versus liquid-phase concentration (C) at equilibrium) of each acid in the temperature range of (30 to 50) °C. (a) Succinic acid and (b) lactic acid. Symbols (experimental): ○, T = 30 °C; Δ, T = 40 °C; □, T = 50 °C. The solid and the dashed lines indicate the predicted results from the Langmuir and the bi-Langmuir adsorption models, respectively.

Table 2. Parameters of the Langmuir Adsorption Model and the Corresponding Average Relative Error (ARE) and Standard Deviation (σ)

	T	q_s	b	ARE	σ^a
	°C	$g \cdot L^{-1}$	$L \cdot g^{-1}$	%	$g \cdot L^{-1}$
succinic acid	30	112.7448	0.0823	0.99	0.33
	40		0.0647		
	50		0.0534		
lactic acid	30	167.7283	0.0192	0.80	0.12
	40		0.0167		
	50		0.0147		

[a] The σ value was calculated from eq 4, where $n = 15$ and $p = 4$.

Table 3. Parameters of the Bi-Langmuir Adsorption Model and the Corresponding Average Relative Error (ARE) and Standard Deviation (σ)

	T	$q_{s,A}$	$q_{s,B}$	b_A	b_B	ARE	σ^a
	°C	$g \cdot L^{-1}$	$g \cdot L^{-1}$	$L \cdot g^{-1}$	$L \cdot g^{-1}$	%	$g \cdot L^{-1}$
succinic acid	30	86.6985	75.0255	0.0166	0.1066	0.76	0.33
	40			0.0125	0.0857		
	50			0.0111	0.0689		
lactic acid	30	89.7355	83.5682	0.0141	0.0236	0.79	0.14
	40			0.0114	0.0215		
	50			0.0107	0.0180		

[a] The σ value was calculated from eq 4, where $n = 15$ and $p = 8$.

adsorbed amount of each acid onto Amberchrom CG300C, has a pronounced reduction as the temperature increases. Such a strong dependence of the adsorption equilibria on temperature ensures that the Amberchrom CG300C resin deserves to be a potential adsorbent of a temperature-gradient SMB process.

Determination of a Proper Adsorption Equilibrium Model. For an effective application of the above-reported equilibrium data (Table 1) to the optimal design of SMB or other adsorption processes, it is important to establish the most appropriate correlation for the acquired equilibrium data. Such a correlation task is usually accomplished by selecting a proper adsorption equilibrium model (or isotherm model) and determining its relevant parameters (i.e., saturation capacities and equilibrium constants).

Close examination of the adsorption data in Figure 4 reveals that the rate of increase in solid-phase concentration (q) decreases gradually with increasing the liquid-phase concentration (C). Since this is one of the typical phenomena occurring in the Langmuir-type adsorption systems, we employed the Langmuir and the bi-Langmuir adsorption models (eqs 1 and 2) for correlating the adsorption data measured at three different temperatures in Table 1.

The parameters involved in these adsorption models were determined by minimizing the sum of squared deviations between the experimental data (in Table 1) and the calculated values (from eq 1 or 2), which was assisted by a well-known optimization program based on a genetic algorithm.[6,18] First, in the case of the Langmuir model of each acid, a total of four parameters including q_s, b (30 °C), b (40 °C), and b (50 °C) were optimized simultaneously. Second, in the case of the bi-Langmuir model of each acid, a total of eight parameters including $q_{s,A}$, $q_{s,B}$, b_A (30 °C), b_B (30 °C), b_A (40 °C), b_B (40 °C), b_A (50 °C), and b_B (50 °C) were optimized simultaneously. In each optimization run, a total of 15 experimental data, which included the adsorption equilibrium data of each acid at 30 °C, 40 °C, and 50 °C (Table 1), were used as the objects to be fitted by the model equation.

The resultant parameter values from such optimizations are summarized in Tables 2 and 3. It can be seen first from Table 2 that the Langmuir equilibrium constant (b) of succinic acid is larger than that of lactic acid, which means that succinic acid has a stronger adsorption onto Amberchrom CG300C. Another noteworthy observation in Table 2 is that the b values of the two acids decrease with increasing temperature. This implies that the adsorption affinities of both acids to Amberchrom CG300C are reduced as the temperature increases. Similar trends can also be found for the bi-Langmuir equilibrium constants, b_A and b_B, in Table 3.

The above-reported parameter values in Tables 2 and 3 and the model equations (eqs 1 and 2) were used to predict the solid-phase concentrations in equilibrium with liquid-phase concentrations. The predicted results were then compared with the experimental data in Figure 4. It is clearly seen that the predicted results from both models agree well with the experimental data. To make a quantitative comparison between the two models in terms of model accuracy in predicting the adsorption equilibria of interest, the average relative error (ARE) was estimated for each model using eq 3, and the results are listed in Tables 2 and 3. Note first that the ARE values of the Langmuir and the bi-Langmuir models are both less than 1 %, which means that these two models are highly accurate in predicting the adsorption equilibria of interest. Between the two models, the bi-Langmuir model appears to give a slightly better accuracy than the Langmuir model (Tables 2 and 3).

However, this does not necessarily mean that the bi-Langmuir model is more efficient in the application to process design or simulation than the Langmuir model because the number of parameters involved is different between the two models. To make a fair comparison between the two models while reflecting a discrepancy in the number of fitting parameters, one can evaluate the standard deviation (σ) of each model according to eq 4. As reported in Tables 2 and 3, the σ value of the Langmuir model is equal to or smaller than that of the bi-Langmuir model. These results indicate that the use of the Langmuir model in the stage of process design or simulation can be a little more profitable in consideration of both computational efficiency and accuracy.

Analysis of the Temperature Dependence of the Langmuir and the Bi-Langmuir Equilibrium Constants. In the previous section, the Langmuir equilibrium constant (b) values were reported discretely with respect to temperature. Such types of presentations, however, can place some limitations on the application of the Langmuir model to design of a temperature-gradient SMB process, particularly if the process is based on a trailing-wave mode.[12,13] This is because in such a process the temperature is varied continuously along the axial distance. Hence, the Langmuir equilibrium constant (b) needs to be expressed as a continuous function of temperature, which will result in a temperature-dependent form of the Langmuir model that is effective over a wide range of temperatures.

In general, the temperature dependency of the Langmuir equilibrium constant is known to obey an Arrhenius form as follows[15]

$$b = b_0 \exp\left(-\frac{\Delta H}{RT}\right) \tag{5}$$

where b_0 is a pre-exponential factor; R (8.314 $J \cdot K^{-1} \cdot mol^{-1}$) is the gas constant; T (K) is the temperature; and ΔH is the heat of adsorption. To clarify the values of b_0 and ΔH, the above equation can be rearranged into the following form that allows

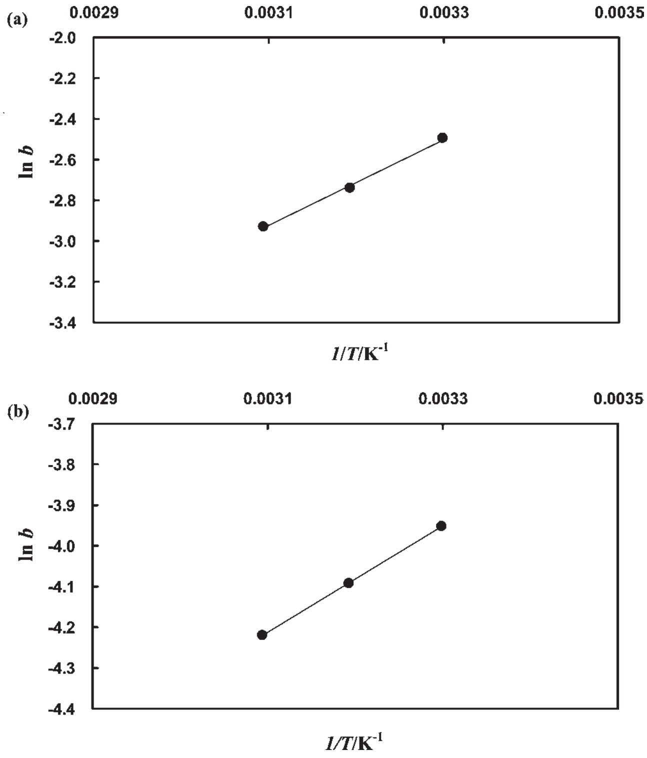

Figure 5. Relationship between the natural logarithm of Langmuir equilibrium constant (b) and the reciprocal of temperature (T). (a) Succinic acid and (b) lactic acid.

Table 4. Parameters of the Temperature-Dependent Langmuir Adsorption Model and the Corresponding Average Relative Error (ARE) and Standard Deviation (σ)

	T	q_s	b_0	ΔH	ARE	σ^a
	°C	$g \cdot L^{-1}$	$L \cdot g^{-1}$	$kJ \cdot mol^{-1}$	%	$g \cdot L^{-1}$
succinic acid	30	112.7448	$7.4995 \cdot 10^{-5}$	−17.6303	1.10	0.38
	40					
	50					
lactic acid	30	167.7283	$2.5633 \cdot 10^{-4}$	−10.8771	0.80	012
	40					
	50					

[a] The σ value was calculated from eq 4, where $n = 15$ and $p = 3$.

the use of linear regression based on a least-squares method.

$$\ln b = \ln b_0 - \frac{\Delta H}{RT} \tag{6}$$

The values of b_0 and ΔH in eq 6 were determined through the slope and y-intercept, which were generated by the linear regression of $\{\ln b\}$ versus $\{1/T\}$ as shown in Figure 5. The resulting values of b_0 and ΔH are listed in Table 4. Note that the ΔH values of succinic acid and lactic acid are both of negative sign, which means that the adsorption of each acid onto Amberchrom CG300C is exothermic. It is also observed from Table 4 that the absolute value of ΔH of succinic acid is larger than that of lactic acid. This result implies that succinic acid has a higher adsorption affinity to Amberchrom CG300C than lactic acid.

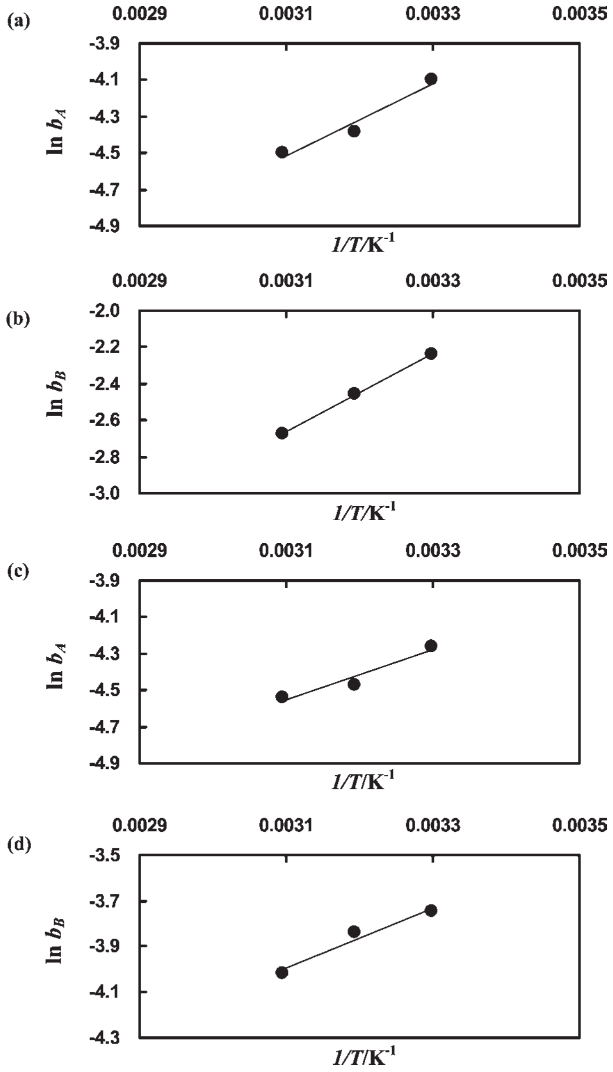

Figure 6. Relationship between the natural logarithms of bi-Langmuir equilibrium constants (b_A and b_B) and the reciprocal of temperature (T): (a) succinic acid ($\ln b_A$ versus $1/T$), (b) succinic acid ($\ln b_B$ versus $1/T$), (c) lactic acid ($\ln b_A$ versus $1/T$), (d) lactic acid ($\ln b_B$ versus $1/T$).

In a similar manner to the above analysis, the dependences of the bi-Langmuir equilibrium constants (b_A and b_B) on temperature were investigated. Due to the assumption inherent in the bi-Langmuir model, the two equilibrium constants (b_A and b_B) need to be related to the heats of adsorption for two different adsorption sites A and B, respectively. Such a relationship can be represented by applying the aforementioned Arrhenius-type equation (eq 5) to each of the adsorption sites A and B as follows

$$b_A = b_{A,0} \exp\left(-\frac{\Delta H_A}{RT}\right) \tag{7a}$$

$$b_B = b_{B,0} \exp\left(-\frac{\Delta H_B}{RT}\right) \tag{7b}$$

where ΔH_A and ΔH_B are the heats of adsorption for the sites A and B, respectively. To determine these two values along with $b_{A,0}$ and $b_{B,0}$, the plots of $\{\ln b_A\}$ versus $\{1/T\}$ and $\{\ln b_B\}$ versus $\{1/T\}$ were carried out in Figure 6. The resulting parameter values from the linear regressions of the plots in Figure 6 are presented in Table 5. It is evident that the adsorption of each acid to the two adsorption sites A and B is exothermic. It is also worth noting that the absolute values of ΔH_A and ΔH_B of succinic acid

Table 5. Parameters of the Temperature-Dependent Bi-Langmuir Adsorption Model and the Corresponding Average Relative Error (ARE) and Standard Deviation (σ)

	T / °C	$q_{s,A}$ / $g \cdot L^{-1}$	$q_{s,B}$ / $g \cdot L^{-1}$	$b_{A,0}$ / $L \cdot g^{-1}$	$b_{B,0}$ / $L \cdot g^{-1}$	ΔH_A / $kJ \cdot mol^{-1}$	ΔH_B / $kJ \cdot mol^{-1}$	ARE / %	σ^a / $g \cdot L^{-1}$
succinic acid	30	86.6985	75.0255	$2.3660 \cdot 10^{-5}$	$9.2749 \cdot 10^{-5}$	−16.4552	−17.7667	0.89	0.38
	40								
	50								
lactic acid	30	89.7355	83.5682	$1.5583 \cdot 10^{-4}$	$3.0594 \cdot 10^{-4}$	−11.2976	−10.9905	0.80	0.13
	40								
	50								

[a] The σ value was calculated from eq 4, where $n = 15$ and $p = 6$.

are both larger than those of lactic acid, which means that succinic acid has higher affinities to both adsorption sites A and B than lactic acid.

Temperature-Dependent Adsorption Equilibrium Model. On the basis of the above results, the Langmuir and the bi-Langmuir equations that are effective in the temperature range of (30 to 50) °C can be prepared simply as follows

$$\text{Langmuir equation}: q = \frac{q_s b_0 \exp(-\Delta H/RT)C}{1 + b_0 \exp(-\Delta \mathrm{H}/\mathrm{RT})\mathrm{C}} \qquad (8)$$

$$\text{Bi-Langmuir equation}: q = \frac{q_{s,A} b_{A,0} \exp(-\Delta H_A/RT)C}{1 + b_{A,0} \exp(-\Delta \mathrm{H}_A/\mathrm{RT})\mathrm{C}} + \frac{q_{s,B} b_{B,0} \exp(-\Delta H_B/RT)C}{1 + b_{B,0} \exp(-\Delta \mathrm{H}_B/\mathrm{RT})\mathrm{C}} \qquad (9)$$

where all the relevant parameter values are reported in Tables 4 and 5. On the basis of these model equations and the reported parameter values, the adsorption equilibria of each acid at all three temperatures investigated were predicted at once. The resulting predictions were found to be in close agreement with the experimental data (not shown), which can be confirmed by the ARE values listed in Tables 4 and 5. The ARE values were around 1.0 % for the Langmuir model (Table 4), while the ARE values were less than 1.0 % for the bi-Langmuir model (Table 5). These results indicate that the above temperature-dependent model equations based on the reported parameter values are sufficiently applicable to design or simulation of a temperature-gradient SMB process based on a trailing-wave mode as well as a direct mode. Here, it should be mentioned that the reported model parameters are effective only in the range of liquid-phase concentration (0 to 10) $g \cdot L^{-1}$. This is because the adsorption equilibrium data that served as the basis for determining the model parameters of interest were obtained at the liquid-phase concentrations up to 10 $g \cdot L^{-1}$.

■ CONCLUSIONS

The single-component adsorption equilibria of succinic acid and lactic acid on the Amberchrom CG300C resin were measured in the temperature range of (30 to 50) °C and the liquid-phase concentrations up to 10 $g \cdot L^{-1}$. There was a marked difference between the equilibrium solid-phase concentrations of the two acids for the investigated range of liquid-phase concentration. This indicated that Amberchrom CG300C was sufficiently qualified as the adsorbent of SMB chromatographic processes for separation of the two acids. To correlate the measured adsorption equilibrium data, the Langmuir and the bi-Langmuir models were applied and their relevant parameters such as saturation capacities and equilibrium constants determined using a highly robust optimization program. The resulting equilibrium constants were found to decrease with increasing temperature, which indicated that the adsorption of each acid onto Amberchrom CG300C was exothermic. Such a temperature dependency of the equilibrium constants was described with an Arrhenius-type equation, whose relevant parameters were effective over the investigated range of temperatures. The Langmuir and the bi-Langmuir models based on such a temperature-dependent equilibrium constant were found to be highly successful in predicting collectively all the equilibrium data measured at three different temperatures. The results of this study will pave the way for the development of a temperature-gradient SMB process for separation of succinic acid and lactic acid, both of which can have valuable applications in many industries after separation.

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