Effect of Ethanol Content on Adsorption Equilibria of Some Useful Amino Acids in Poly-4-vinylpyridine Chromatography

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One of the prerequisites to the development of solvent gradient simulated moving bed (SG-SMB) chromatography for amino acid separation is to obtain their adsorption equilibrium data on a poly-4-vinylpyridine (PVP) resin under different contents of an additive solvent in the liquid phase. It was first found that ethanol could function well as a qualified additive solvent for the SG-SMB of interest. Then, the adsorption equilibria of 2-amino-3-phenyl-propanoic acid, 2-amino-3-(3-indolyl)-propanoic acid, and 2-amino-3-(4-hydroxyphenyl)-propanoic acid on the PVP resin were measured through a series of staircase frontal experiments while varying the ethanol content in the liquid phase from (0.0 to 0.2) volume fraction. On the basis of the resultant adsorption data, the partition coefficient, which is the ratio of solid-phase and liquid-phase concentrations at equilibrium, was determined for each amino acid. The determined partition coefficient showed a remarkable dependence on the ethanol content. Such a trend was successfully described with the Abel model, which correlated the partition coefficient as a function of the ethanol content. The adsorption data and the model parameters reported in this study will be of great value in the stage of designing the SG-SMB chromatographic process that is packed with the PVP resin and targeted at separating amino acids.

Introduction

Several amino acids have attracted a lot of attention in the food or pharmaceutical industries.[1−5] One of such amino acids with widespread applications is 2-amino-3-phenyl-propanoic acid, which is used as a sweetener in place of sugar.[1] This is also known to be effective in the recovery of a taxol,[2] which is one well-known anticancer drug. Other amino acids with noteworthy applications are 2-amino-3-(4-hydroxyphenyl)-propanoic acid and 2-amino-3-(3-indolyl)-propanoic acid. The former was reported to serve as starting material of a neurotransmitter[3] and the latter to function as a dietary supplement and as an effective sleep aid and particularly shows considerable promise as an antidepressant.[4,5] The common names of these three amino acids, 2-amino-3-phenyl-propanoic acid, 2-amino-3-(4-hydroxyphenyl)-propanoic acid, and 2-amino-3-(3-indolyl)-propanoic acid, are phenylalanine, tyrosine, and tryptophan, respectively. Such common names will be used hereafter for designating the three amino acids of interest throughout this article.

Because of the aforementioned value of the amino acids, their economical production has been a matter of primary concern in a variety of biofrontier industries. One of the important issues for such economical production is the development of a highly efficient process for amino acid separation.[6,7] Such a separation process development has been accomplished in previous research, where well-designed simulated moving bed (SMB) chromatographic processes for amino acid separation were established.[7−10]

In all of these SMB chromatographic processes,[7−10] poly-4-vinylpyridine (PVP) resin and distilled deionized water (DDW) were used as a solid phase (or adsorbent phase) and a liquid phase, respectively. Since the liquid phase used was comprised of only one solvent (DDW), the previous SMBs were all operated under an isocratic mode. To improve their productivities further, their operation modes can be changed from an isocratic to a solvent gradient mode, where the liquid-phase strength is allowed to have a local change along the chromatographic bed. Under this condition, the adsorption affinities of feed components can be varied as a function of local position. Once such variation of adsorption affinities along the position can be controlled properly, a remarkable improvement in process performances can be realized. This is why the solvent gradient mode outperforms the isocratic mode in every respect.[11−13]

The most important requirement in operating an SMB process under a solvent gradient mode (hereafter, "solvent gradient SMB") is to employ a mixture of two different solvents as the liquid phase.[11−13] In addition, the ratio between the employed solvents should have a marked effect on the adsorption equilibria of the feed components to be separated.[11,12,14]

Therefore, it will be a worthwhile task to find an additive solvent that can be mixed with DDW to form a qualified liquid phase for a solvent gradient simulated moving bed (SG-SMB) for amino acid separation. The following task of importance to optimal design of the SG-SMB is to obtain the adsorption equilibrium data of amino acids on the PVP resin by varying the content of an additive solvent in a composite liquid phase. All of these tasks will be performed in this article for the first time. Furthermore, the effects of the chosen additive solvent on the adsorption equilibria of amino acids will be investigated. Such effects will be eventually described with a proper model equation, which will play an important role in the design of the SG-SMB packed with the PVP resin.

Theory

Adsorption Equilibrium in Chromatography. An SMB process uses a series of chromatographic columns that are

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connected in series. Each of these chromatographic columns provides two different phases in connection with the adsorption equilibrium. One is the solid phase (or adsorbent phase), and the other is the liquid phase.

Once solute molecules enter a chromatographic column, they can either stay in the liquid phase and migrate along the direction of liquid flow or approach the solid phase and be adsorbed onto the solid surface. At this time, the adsorbed amount of solute per solid volume (or solid-phase concentration) is always related to the concentration of solute in the liquid phase (or liquid-phase concentration).

Such a relationship between the liquid-phase and the solid-phase concentrations at equilibrium is referred to as an adsorption isotherm, which has a crucial effect on the linear velocities of solute molecules migrating through a chromatographic column.[15] Hence, in the initial stage of designing a chromatographic separation process, it is of utmost importance to acquire a series of adsorption equilibrium data, that is, a set of solid-phase concentrations in equilibrium with a given range of liquid-phase concentrations.

One of the simplest methods of acquiring adsorption equilibrium data is to keep loading a feed solution into a chromatographic column until the liquid-phase concentration is uniform over the entire chromatographic bed, including the intraparticle void (or pore) space as well as the interparticle void space.[14−16] Since the uniformed liquid-phase concentration is eventually equalized with the feed concentration, the liquid-phase concentration belongs to the category of controllable variables in the experiments associated with this method.

The solid-phase concentration in equilibrium with the uniformed liquid-phase concentration (i.e., the feed concentration) can then be estimated through a material balance over the entire bed. This procedure can be repeated by increasing stepwise the feed concentration, which can eventually allow the acquisition of a set of adsorption equilibrium data in the investigated range of liquid-phase concentration.[14−17]

The aforementioned procedure, which was designated as a staircase frontal analysis (SFA) method in the literature, has been well-established in previous research.[14−17] As far as the measurement of adsorption equilibria in a chromatographic process is concerned, the SFA method is regarded as the most accurate.[14−16] The detailed equations associated with the SFA method can be found elsewhere.[14] Among the reported equations, the core one that will be exploited in this study is given below.

$$q_j = q_{j-1} + \frac{C_j F(t_j - t_{j-1}) - F\int_{t_{j-1}}^{t_j} C_{\text{effluent}}\,\mathrm{d}t - (C_j - C_{j-1})(V_0 + V_D)}{V_S} \quad (1)$$

where the subscript j indicates the step number; C_j is the feed concentration employed during the j^{th} step; q_j is the solid-phase concentration in equilibrium with C_j; F is the flow rate; C_{effluent} is the concentration of effluent from the column; and V_D is the extra-column dead volume. In addition, V_0 and V_S are the entire void volume and the total solid (or adsorbent) volume within the column, respectively, each of which can be expressed as a function of column porosities and bed volume (BV) as follows:

$$V_0 = BV[\varepsilon_b + (1 - \varepsilon_b)\varepsilon_p] \quad (2a)$$

$$V_S = BV\cdot(1 - \varepsilon_b)(1 - \varepsilon_p) \quad (2b)$$

where ε_b and ε_p are the bed porosity and the particle porosity, respectively.

The adsorption data measured using the aforementioned SFA method can be characterized by a partition coefficient (K), which is the ratio of solid-phase concentration (q) to liquid-phase concentration (C) at equilibrium.

Physical Models for Describing the Effect of an Additive Solvent on Adsorption Equilibrium. Sometimes, the liquid phase in a chromatographic separation process consists of two different solvents, one of which corresponds to the main solvent and the other an additive solvent. Under such circumstances, the relative composition of an additive solvent in the liquid phase can have a significant effect on the adsorption equilibria. To clarify this effect in a quantitative manner, the above-mentioned SFA procedure and the estimation of the relevant partition coefficient (K) can be repeated while varying the liquid-phase composition (ϕ), which is usually expressed by the volume percentage of an additive solvent in the liquid phase (main solvent + additive solvent).

To correlate the resultant K value as a function of ϕ, one of the following two models[12,18,19] can be utilized.

$$K = p_1 \exp(-p_2\phi) \quad \text{for the Snyder model} \quad (3a)$$

$$K = \frac{p_1}{(1 + p_2\phi)^{p_3}} \quad \text{for the Abel model} \quad (3b)$$

where p_1, p_2, and p_3 are the model parameters to be obtained by fitting the model-predicted results with experimental data. For each of the two models, the following criterion (standard deviation) can be evaluated to determine which model is the most pertinent to experimental data.

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

where K^{cal} and K^{exp} are the model-predicted partition coefficient and the experimentally determined partition coefficient respectively; n is the number of data points; and p is the number of model parameters fitted. Obviously, the model with the smallest σ is considered to make the most accurate description of a given adsorption system.

Experimental Section

Materials. The three amino acids under investigation were all purchased from the Sigma-Aldrich Co. (St. Louis, MO). Sodium chloride, which was used as a tracer molecule for the measurement of column void fraction, was also purchased from the Sigma-Aldrich Co. (St. Louis, MO). Ethanol was obtained from the Burdick & Jackson Co. (Muskegon, MI) and used as an additive solvent. The liquid phase was prepared by mixing DDW and ethanol.

The PVP resin (cross-linked, Reillex HP polymer) from Reilly Industries Inc. (Indianapolis, IN) was used as the adsorbent, which has an average radius of 181 μm. This adsorbent was packed into an omnifit chromatographic column, which was purchased from Bio-Chem Fluidics Co. (Boonton, NJ). The column has a diameter of 1.5 cm and a packing length of 11.6 cm.

Equipment. The experiments were conducted with an ÄKTA fast protein liquid chromatography (FPLC) system (Figure 1), which was manufactured by Amersham Biosciences Co. (Piscataway, NJ). This system consists of two pumps (Amersham Biosciences P-920), a high-performance monitor (Amersham Biosciences UPC-900), an injection valve (Amersham Biosciences INV-907), and a mixer (Amersham Biosciences M-925). Effluent from the column was monitored using a single-

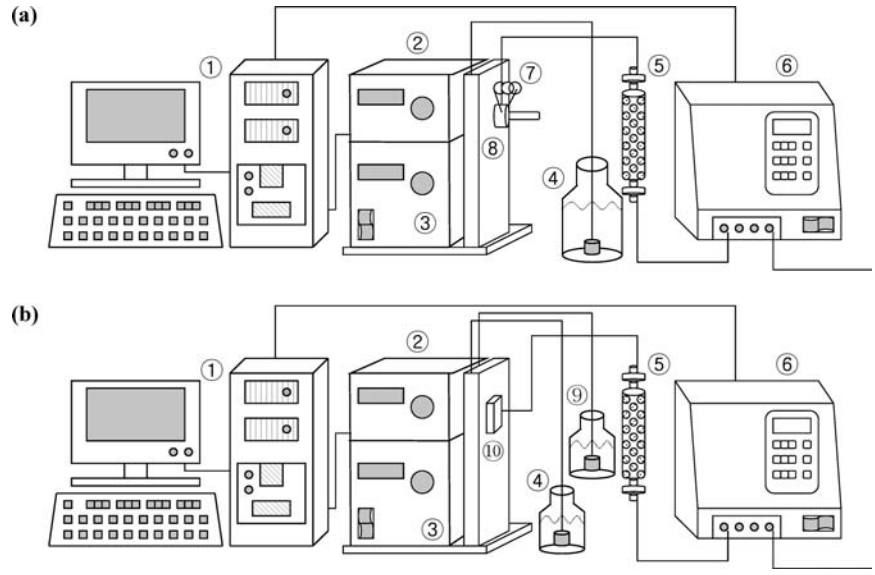

Figure 1. Schematic diagram of the experimental system used in this study. (a) Experimental system for pulse tests; (b) experimental system for staircase frontal tests. ①, UNICORN 5.1 software; ②, high performance monitor (UPC-900); ③, FPLC pumps (P-920); ④, liquid-phase reservoir; ⑤, chromatographic column; ⑥, single-wavelength detector (waters 486); ⑦, sampling loop; ⑧, injection valve (INV-907); ⑨, feed reservoir; (10), mixer (M-925).

wavelength detector (Waters 486). The experimental data from the FPLC system were collected and analyzed with the help of automatic data acquisition software (Amersham Biosciences UNICORN 5.1), which operated in the Windows environment.

Methods. Two kinds of chromatographic experiments, which included pulse and staircase frontal tests, were carried out in this study. The former test was used to measure the column void fraction or test the suitability of an additive solvent, while the latter test was used to obtain adsorption equilibrium data under different contents of an additive solvent in the liquid phase. Both experiments were conducted with the aforementioned FPLC system at room temperature.

For pulse tests, a sampling loop with the volume of 100 μL was connected to the injection valve (INV-907) as shown in Figure 1a. This test began with setting the injection valve to the load position, followed by filling the loop with a feed solution (amino acid solution). The flow rate was controlled by the Unicorn software. Then the feed solution was introduced into the column by switching the valve to the inject position. Data acquisition was started simultaneously and continued until the attainment of a pulse chromatogram.

To perform staircase frontal tests, both FPLC pumps (P-920) were used (Figure 1b). One pump delivered the liquid-phase solvent and the other pump the feed solution (amino acid solution). The feed concentration was kept constant throughout the experiments as follows: phenylalanine (1 g·L^{-1}), tyrosine (0.2 g·L^{-1}), and tryptophan (0.4 g·L^{-1}). The two streams were mixed before entering the column, which was equilibrated with the liquid-phase solvent prior to the experiments. The total flow rate for the mixed stream was kept constant at 2 mL·min^{-1}. The output ratio of the two streams was changed to generate solutions of different concentrations, which were loaded into the column in series. The ratio was changed only after a concentration plateau was fully developed at the column outlet. The column effluents of phenylalanine and tyrosine were monitored at the wavelength of 254 nm each, with the column effluent of tryptophan at the wavelength of 304 nm.

Results and Discussion

Measurement of Column Porosities. One of the prerequisites for estimating adsorption equilibria from the aforementioned SFA method is to measure the porosities of a chromatographic column that serves as the adsorption system of investigation. The porosities to be measured include bed porosity (ε_b) and particle porosity (ε_p). The former is the ratio of interparticle void volume to bed volume, while the latter is the ratio of intraparticle void volume to total solid (or adsorbent) volume.

The particle porosity of the adsorbent used (PVP resin) was provided by the resin manufacturer, which was reported to be 0.55. To determine the remaining porosity, that is, bed porosity, a sodium chloride pulse was injected into the packed column. Since the sodium chloride molecule is sufficiently small to penetrate the entire void space while being nonadsorbed onto the resin particles, the first moment of the sodium chloride pulse chromatogram can be used to estimate the total porosity (ε_t) from the following equation.

$$\varepsilon_t = \left(F \frac{\int_0^\infty t C_{out}\, dt}{\int_0^\infty C_{out}\, dt} - V_D - \frac{V_p}{2} \right) / BV \qquad (5)$$

where C_{out} is the concentration of sodium chloride in the outlet stream; t is the exit time; and V_p is the loading volume. The total porosity was then combined with the reported particle porosity ($\varepsilon_p = 0.55$) to calculate the bed porosity as follows:

$$\varepsilon_b = \frac{\varepsilon_t - \varepsilon_p}{1 - \varepsilon_p} \qquad (6)$$

The resulting bed porosity value for the column packed with the PVP resin was found to be 0.31.

Selection of a Proper Additive Solvent for the Liquid Phase in the Chromatographic System of Interest. In all of the previous chromatographic systems for amino acid separation using PVP resin,[7−10] the liquid phase employed was pure DDW, and thus the liquid-phase strength was uniform over the entire bed. To implement a solvent gradient operation of our interest, the liquid phase should contain an additive solvent that can change the liquid-phase strength.

To become a proper additive solvent, it should have several requirements. First, the content of an additive solvent in the liquid phase is to have a marked effect on the adsorption equilibria of amino acid on the PVP resin. Second, the volatility

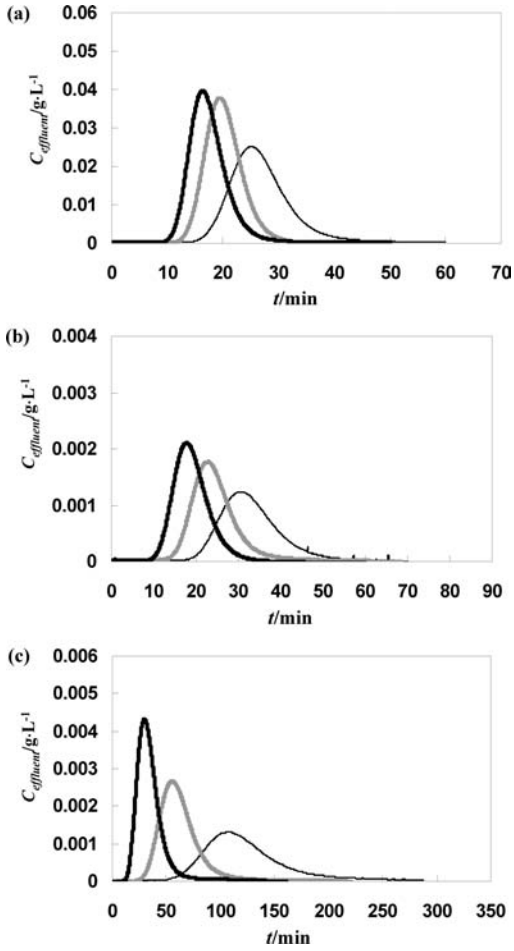

Figure 2. Effect of ethanol content on the amino acid chromatograms from the pulse tests where the effluent concentration $C_{effluent}$ was monitored as a function of time t. (a) Phenylalanine, (b) tyrosine, (c) tryptophan. Lines: thin black line, $\phi = 0$; thick gray line, $\phi = 0.05$; thick black line, $\phi = 0.2$, where ϕ is the ethanol volume fraction in the liquid phase.

Table 1. Single-Component Adsorption Equilibrium Data for the Case Where the Ethanol Volume Fraction ϕ Ranges from 0.0 to 0.2 in the Liquid Phase

phenylalanine		tyrosine		tryptophan	
C	q	C	q	C	q
g·L^{-1}	g·L^{-1}	g·L^{-1}	g·L^{-1}	g·L^{-1}	g·L^{-1}
		$\phi = 0.0$			
0.25	0.4686	0.05	0.1478	0.10	1.2836
0.50	0.9419	0.10	0.2971	0.20	2.4547
0.75	1.4148	0.15	0.4510	0.30	3.5155
1.00	1.8791	0.20	0.6079	0.40	4.5717
		$\phi = 0.03$			
0.25	0.2916	0.05	0.0980	0.10	0.8955
0.50	0.5981	0.10	0.2048	0.20	1.7819
0.75	0.9115	0.15	0.3141	0.30	2.5603
1.00	1.2130	0.20	0.4159	0.40	3.2544
		$\phi = 0.05$			
0.25	0.2312	0.05	0.0819	0.10	0.6945
0.50	0.4872	0.10	0.1698	0.20	1.3699
0.75	0.7533	0.15	0.2668	0.30	1.9993
1.00	1.0190	0.20	0.3634	0.40	2.6445
		$\phi = 0.07$			
0.25	0.1998	0.05	0.0761	0.10	0.5114
0.50	0.4266	0.10	0.1467	0.20	1.1479
0.75	0.6673	0.15	0.2277	0.30	1.7043
1.00	0.8847	0.20	0.3116	0.40	2.2970
		$\phi = 0.10$			
0.25	0.1728	0.05	0.0564	0.10	0.5015
0.50	0.3712	0.10	0.1284	0.20	0.9959
0.75	0.5818	0.15	0.2047	0.30	1.4599
1.00	0.7878	0.20	0.2743	0.40	1.9765
		$\phi = 0.15$			
0.25	0.1368	0.05	0.0453	0.10	0.3285
0.50	0.2943	0.10	0.0980	0.20	0.7178
0.75	0.4603	0.15	0.1564	0.30	1.1016
1.00	0.6090	0.20	0.2096	0.40	1.4917
		$\phi = 0.20$			
0.25	0.1046	0.05	0.0362	0.10	0.2886
0.50	0.2387	0.10	0.0778	0.20	0.6115
0.75	0.3871	0.15	0.1317	0.30	0.8327
1.00	0.5183	0.20	0.1658	0.40	1.1139

of an additive solvent is to be higher than that of DDW. This is to reduce the load of evaporation, which is the process subsequent to a chromatographic separation step. Third, an environmentally benign solvent is preferred.

In consideration of the second and third issues, ethanol was selected as a promising additive solvent. To examine further the remaining issue for ethanol, a series of amino acid pulses were injected into the PVP column while varying the ethanol content in the liquid phase. As shown in the resultant chromatograms in Figure 2, the retention time of each amino acid is strongly affected by the ethanol content in the liquid phase. All things considered, ethanol was chosen as an additive solvent for the liquid phase of this study.

Adsorption Equilibria of Amino Acids on the PVP Resin. A series of chromatographic experiments in accordance with the SFA method were carried out for the acquisition of the adsorption equilibrium data for the three amino acids, including phenylalanine, tyrosine, and tryptophan. The solid phase employed in such an adsorption system of investigation was PVP resin, while the liquid phase employed was a mixture of DDW and ethanol. Under such circumstances, the adsorption equilibria of each amino acid were measured by varying the ethanol content in the liquid phase from (0.0 to 0.2) volume fraction.

The resulting single-component adsorption data are presented in Table 1. To analyze the pattern of these adsorption data, the solid-phase and liquid-phase concentrations at equilibrium (q and C) are plotted in Figure 3. One of the interesting observations is that the solid-phase concentration becomes lower as the ethanol content increases. This means that the addition of ethanol to the liquid phase weakens the adsorption affinities of the amino acids for the PVP resin. Another noteworthy phenomenon is that the adsorption pattern of each amino acid component follows a linear isotherm relation in the investigated range of liquid-phase concentration.

For each such adsorption data set, the partition coefficient (K) was determined using a linear regression based on a least-squares analysis, and the resultant value is summarized in Table 2 together with its related regression coefficient, R^2. On the basis of the obtained partition coefficient, the solid-phase concentrations in equilibrium with liquid-phase concentrations were calculated. The calculation results were then compared with the experimental data in Figure 3, which shows a close agreement between them. In addition, the standard deviations between the experimentally measured solid-phase concentrations and the calculated solid-phase concentrations were estimated, and they are listed in Table 2. The standard deviation values (Table 2), the regression coefficient values (Table 2), and the comparison result (Figure 3) indicate that a linear isotherm equation ($q = KC$) is the most reliable in describing the adsorption equilibria of each amino acid on the PVP resin in its investigated range of concentration.

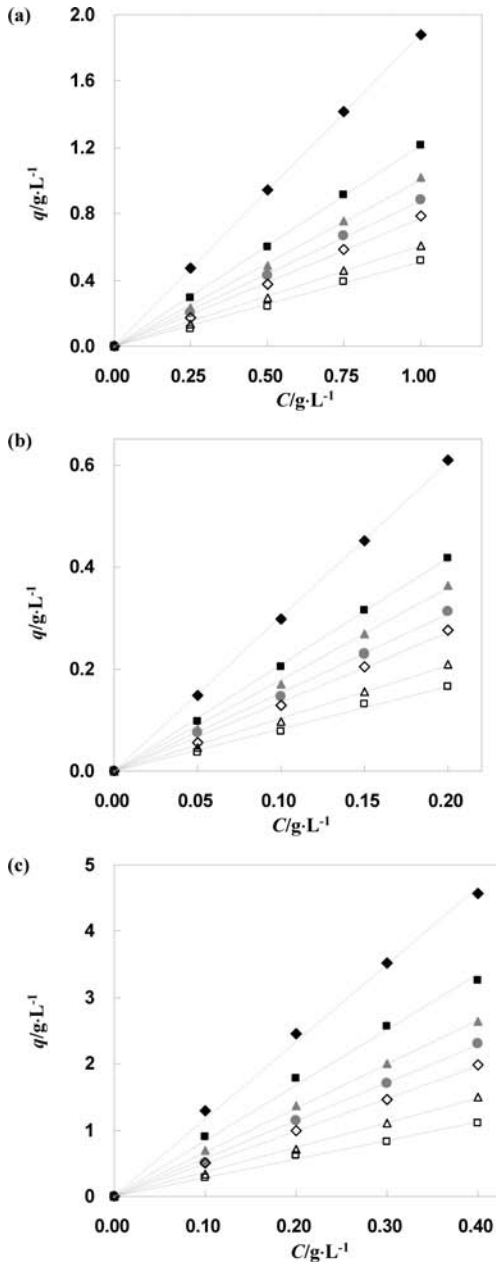

Figure 3. Single-component adsorption equilibria (plot of solid phase concentration q versus liquid phase concentration C at equilibrium) of each amino acid in the range of ethanol volume fraction $\phi = 0$ to 0.2 in the liquid phase. (a) Phenylalanine; (b) tyrosine; (c) tryptophan. Symbols: ◆, $\phi = 0$; ■, $\phi = 0.03$; ▲, $\phi = 0.05$; ●, $\phi = 0.07$; ◇, $\phi = 0.1$; △, $\phi = 0.15$; □, $\phi = 0.2$. Lines calculated from a linear isotherm equation ($q = KC$).

Determination of a Proper Model and Its Related Parameters for Predicting the Partition Coefficients of Amino Acids as a Function of Ethanol Content in the Liquid Phase. The partition coefficients determined in the previous section were plotted with respect to the liquid-phase composition, that is, the ethanol fraction in the liquid phase. The plotting results are presented in Figure 4, which shows a strong dependency of the partition coefficient on the liquid-phase composition. Obviously, such a trend is of great advantage to the realization of the merits of the SG-SMB method.

To utilize the aforementioned partition coefficient data and trend for the design of the SG-SMB for amino acid separation, a proper model equation that can describe the partition coefficient as a function of liquid-phase composition is needed. For this purpose, the Snyder and the Abel models that were reported in the literature[12,18,19] were tested. As indicated by eqs 3a and 3b, their corresponding model equations contain several parameters to be specified. Such model parameters were determined by a nonlinear least-squares fitting of the model equation to the experimentally determined partition coefficients. The nonlinear least-squares fitting process was performed with a well-known optimization program. In this study, a genetic algorithm, which has been known as a highly efficient optimization tool,[20,21] was employed to minimize the sum $\sum_{j=1}^{7}(K_j^{exp} - K_j^{cal})^2$. The resulting parameter values from the optimization are listed in Table 3.

The parameter values in Table 3 were then plugged into the model equations, which were used to predict the partition coefficient of each amino acid as a function of ethanol fraction in the liquid phase. The model-predicted results are compared with the experimentally determined partition coefficients in

Table 2. Partition Coefficient K, Regression Coefficient R^2, and Standard Deviation σ for the Case Where the Ethanol Volume Fraction ϕ Ranges from 0.0 to 0.2 in the Liquid Phase

ϕ	K	R^2	σ^a / g·L^{-1}
		Phenylalanine	
0.00	1.8817	1.0000	0.0024
0.03	1.2099	0.9998	0.0069
0.05	1.0055	0.9987	0.0144
0.07	0.8791	0.9987	0.0129
0.10	0.7749	0.9978	0.0147
0.15	0.6057	0.9986	0.0091
0.20	0.5089	0.9950	0.0148
		Tyrosine	
0.00	3.0178	0.9998	0.0036
0.03	2.0757	0.9995	0.0035
0.05	1.7836	0.9979	0.0065
0.07	1.5328	0.9988	0.0043
0.10	1.3496	0.9961	0.0069
0.15	1.0325	0.9972	0.0045
0.20	0.8334	0.9942	0.0052
		Tryptophan	
0.00	11.6750	0.9971	0.0970
0.03	8.3860	0.9961	0.0809
0.05	6.6701	0.9994	0.0255
0.07	5.7026	0.9989	0.0309
0.10	4.9263	0.9998	0.0117
0.15	3.6786	0.9984	0.0239
0.20	2.8218	0.9965	0.0259

[a] $\sigma = [(\sum_{i=1}^{n}(q_i^{cal} - q_i^{exp})^2)/(n - p)]^{1/2}$, where q^{cal} and q^{exp} are the calculated solid-phase concentration and the experimentally measured solid-phase concentration respectively; n is the number of data points ($n = 5$); and p is the number of model parameters fitted ($p = 1$).

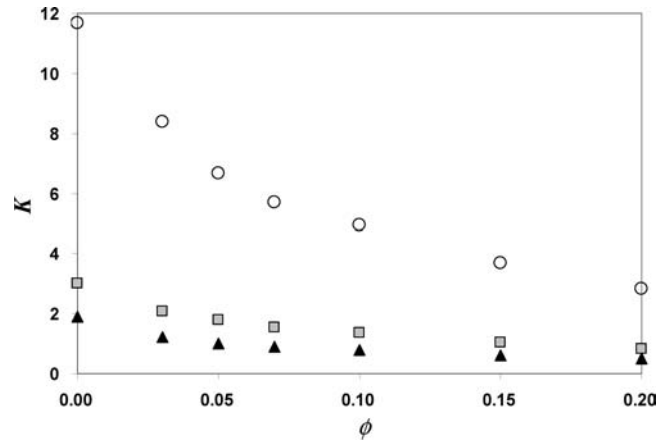

Figure 4. Partition coefficient K of each amino acid as a function of ethanol volume fraction ϕ in the liquid phase. ▲, Phenylalanine; ■, tyrosine; ○, tryptophan.

Table 3. Snyder and Abel Model Parameters p_1, p_2, and p_3 Resulting from Fitting the Model Equations (eqs 3a and 3b) to the Experimentally Determined Partition Coefficients in the Range of Ethanol Volume Fraction $\phi = 0.0$ to 0.2 in the Liquid Phase

Snyder model			Abel model			
p_1	p_2	σ^a	p_1	p_2	p_3	σ^a
Phenylalanine						
1.7021	8.0002	0.1497	1.8817	34.043	0.623	0.0162
Tyrosine						
2.7896	7.3487	0.1826	3.0178	19.025	0.794	0.0367
Tryptophan						
11.0358	8.1827	0.6053	11.6750	11.980	1.140	0.1644

[a] The standard deviation σ was calculated according to eq 4, where $n = 7$ for both the models, while $p = 2$ for the Snyder model and $p = 3$ for the Abel model.

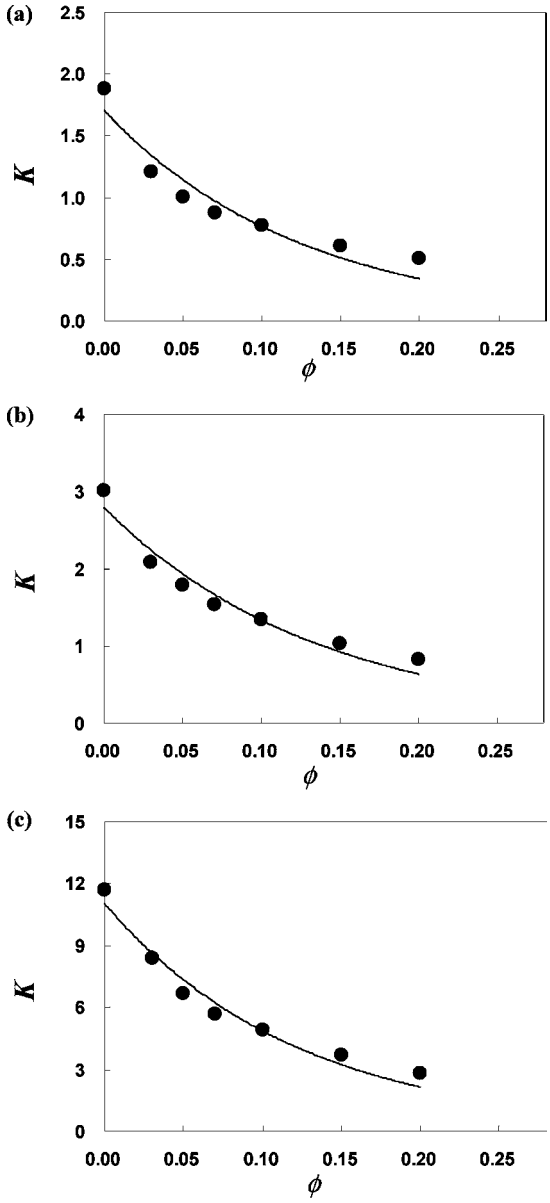

Figure 5. Comparison of the experimentally determined partition coefficients K, ●, and the predicted partition coefficients K, solid line, from Snyder model for the case where the ethanol volume fraction $\phi = 0$ to 0.2 in the liquid phase. (a) Phenylalanine; (b) tyrosine; (c) tryptophan.

Figures 5 and 6. Notice that the Abel model fits the experimental results much better than the Snyder model. This can also be confirmed quantitatively from the standard deviations between

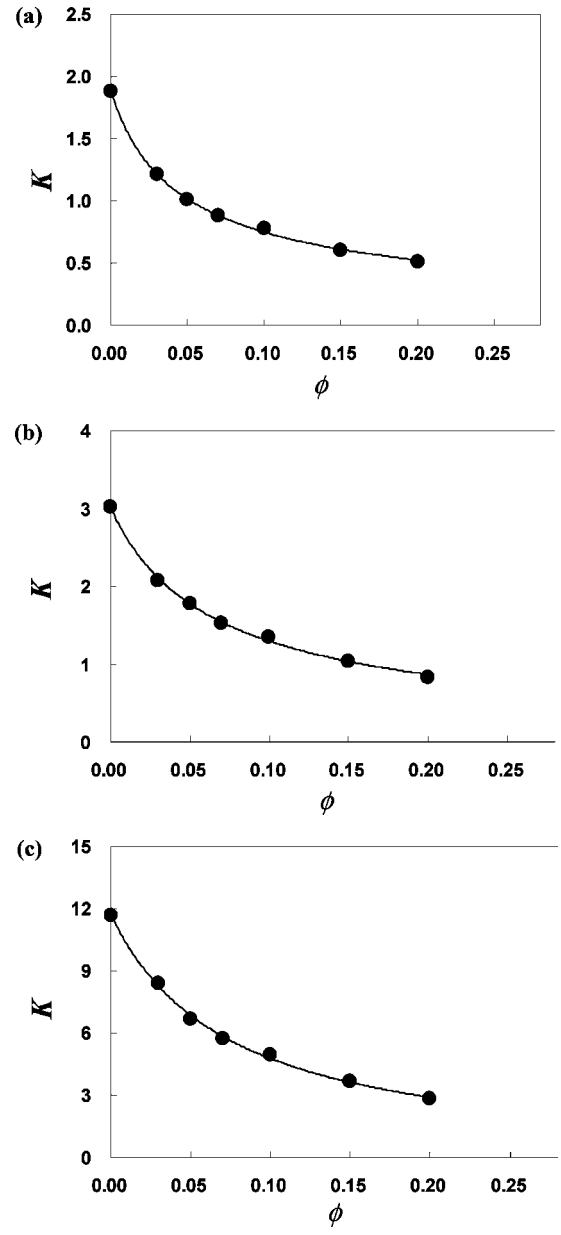

Figure 6. Comparison of the experimentally determined partition coefficients K, ●, and the predicted partition coefficients K, solid line, from Abel model for the case where the ethanol volume fraction $\phi = 0$ to 0.2 in the liquid phase. (a) Phenylalanine; (b) tyrosine; (c) tryptophan.

the experimental and the model-predicted partition coefficients, as listed in Table 3. Therefore, it can be concluded that the Abel model and its related parameter values are suitable for predicting instantaneously the partition coefficient of each amino acid at every location in the SG-SMB packed with the PVP resin, where the ethanol fraction in the liquid phase varies continuously along the bed.

Conclusions

A series of staircase frontal experiments were conducted to measure the adsorption equilibria of amino acids on PVP resin, which were performed by varying the ethanol content in the liquid phase. The amino acids under investigation included 2-amino-3-phenyl-propanoic acid, 2-amino-3-(4-hydroxyphenyl)-propanoic acid, and 2-amino-3-(3-indolyl)-propanoic acid, which are commonly called phenylalanine, tyrosine, and tryptophan, respectively, in industry. A close examination of the

resulting adsorption equilibrium data revealed that the adsorption affinities of these amino acids for the PVP resin were largely affected by the ethanol content in the liquid phase. To characterize such adsorption behavior, a partition coefficient was determined for each set of adsorption data, and the resultant partition coefficients were then correlated as a function of the ethanol content. In such a correlation task, the Snyder and the Abel models were utilized, and the parameters associated with these models were obtained with the help of the optimization program based on a genetic algorithm. According to the correlation results, the Abel model was much more accurate in predicting the partition coefficient of each amino acid as a function of the ethanol content. The adsorption data and the model parameters reported in this study will serve as important information in the future development of an SG-SMB chromatographic process for amino acid separation.

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