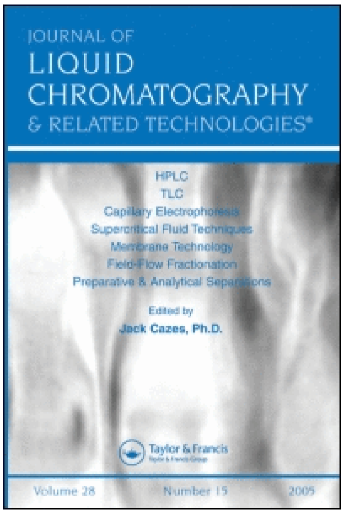

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Model Modification of Binary Competitive Isotherm

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Abstract: Frontal analysis (FA) has enabled the experimental determination of the binary isotherms for 2-phenylethanol and 3-phenylpropanol using an octadecylsilane (ODS) bonded liquid chromatographic column. Existing models were applied and others developed to determine which provided the most accurate prediction of the binary isotherms. The competitive Langmuir was the basic model initially applied for fitting. The results indicated that this classical model provided large relative errors at the upper concentration limit of the range used in these studies. Further improvement of the competitive Langmiur model for predicting adsorption data was obtained using a modified Freundlich equation and the multicomponent Sips equation. Among these three isotherm models, the modified Freundlich equation could be successfully used as an accurate modeling technique through the entire experimental concentration range studied.

Keywords: Adsorption equilibria, Competitive Langmuir, Freundlich-Langmuir model, Frontal analysis, Isotherm modeling, Model modification

INTRODUCTION

Most chromatographic research involves the separation of multicomponent mixtures. At low analyte concentrations a linear relationship exists between analyte distribution in the mobile and stationary phases. However, at higher analyte concentrations, once the column starts to

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become overloaded a nonlinear adsorption distribution exists. Binary component systems are the simplest mixtures system to study to determine multicomponent adsorption isotherms. Once the distribution of the analytes between the stationary phase and mobile phase is determined, optimization of separation parameters for production processes can be applied. Fundamental knowledge of separation parameters is particularly relevant for developing high performance, large scale production procedures, using, for example, simulated moving bed (SMB) technology. For certain target analytes, such as pharmaceuticals, SMB can become an important isolation technique, hence it is very important to know their adsorption isotherms for optimizing the separation process.

Despite binary mixtures being the simplest mixtures to study, due to the potential competition of the adsorbates for the stationary phase, determination of isotherms for the binary components is more complex than if each component is separately studied. Reported methods including frontal analysis,[1–4] perturb methods,[5–6] inverse methods,[7–8] and the Hodograph method[10–11] have been used to determine binary component isotherms. These modeling techniques when applied to the study of binary isotherms, mainly focus on the principle of adsorption, model fitting, and the determination of system errors.[12] The most common model applied is that originally developed by Langmuir.[13] Models based on BET[14–15] and the Freundlich technique[7,16] have also been reported for the study of liquid chromatographic isotherms. Jie et al. compared several binary isotherms models for fitting.[17] Due to its relative simplicity, methods using the Langmuir model are frequently used for solving the isotherms of nonlinear chromatography systems. However, the use of simple Langmuir models often result in significant numerical errors between experimental data and model fitted data for binary component systems.

In this study the adsorption isotherms of 2-phenylethanol (PE) and 3-phenylpropanol (PP), acting as model compounds, using an ODS stationary phase with frontal analysis methodology were investigated. This utilized two mathematical modeling techniques that were applied and/or further developed to determine the most accurate method of predicting the isotherms of the model compounds. The differences between the experimental and predicted binary isotherm values using the mathematical modeling methods were investigated and are compared in this report. The purpose of this current study was to utilize and evaluate classical modeling techniques for determining binary isotherms, and where appropriate, develop modifications to improve predicative performance against experimentally determined data. Accurate knowledge of fundamental adsorption isotherm data for relevant compounds becomes important when designing and economically applying industrial scale isolation and purification processes that need to be optimized for the isolation or refining of commercially valuable products. Examples of such products include pharmaceutical compounds or their chemical precursors. For this study PE and PP were selected as model compounds since other different isotherm studies have been performed using these compounds.[11]

EXPERIMENTAL

A Shimazu LC-10A liquid chromatograph with a Shimadzu SPD-10AVP pump equipped with a UV and RI detector and a computer data station were used for all studies. The mobile phase was composed of methanol: water (50:50, v/v). HPLC grade methanol and water were obtained from Tianjin Yong Da Chemical Ltd. Samples of 3-phenylpropanol and 2-phenylethanol were obtained from J&K CHEMICA (Johnson Mattey Company, USA) and Beijing Jinlong Chemical LTD, respectively. All the solvents were filtered using a PTFE membrane of pore size 0.45 µm obtained from Tianjin Yong Da Chemical Ltd., China prior to use. Uracil was used as the non-retained compound and acted as marker. A 4.6×150 mm stainless steel Extend™ 5 micron C_{18} column (Agilent Technologies, USA) was used for all chromatographic studies. The total porosity measured by injecting uracil was determined as $\varepsilon_t = 0.651$. The column holdup time (t_m) was 2.077 min, and the efficiency of the column at a flow rate of 0.80 mL/min was $N = 2880$ theoretical plates. Stock solutions of 2-phenylethanol (PE) and 3-phenylpropanol (PP) were prepared by dissolving 12.2334 g and 13.6283 g of these compounds, respectively, in 100 mL mobile phase to provide volumetric solutions whose concentrations were 1.001 M (PE) and 1.003 M (PP).

RESULTS AND DISCUSSION

Studies Involving the Determination of Isotherms of Single Components

A set of serial volumetric solutions of PE were prepared using 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, 0.70 mL PE stock solutions diluted with 50.00 mobile phase, providing PE solutions of 0.002, 0.004, 0.006, 0.008, 0.010, 0.012, and 0.014 M, respectively, provided the range of concentrations used in these studies. The adsorbed amount of PE in the solid phase, q_{PE}, was determined by step frontal analysis. The same concentration series and the same procedure were applied to determine q_{pp} for PP.

In many cases, the Langmiur model has proven to afford a good or, at least a reasonable empirical equation to which experimental adsorption data can be successfully fitted.[18] This has resulted in the general

Table 1. Isotherm Parameters of PE and PP by FA

Adsorbent	G_i	b_i (M^{-1})	q_i (M)	r_i
2-Phenylethanol	7.26	5.08	1.43	0.9992
3-Phenylpropanol	11.07	8.34	1.33	0.9996

acceptance of the following general adsorption isotherm equation:

$$q = \frac{Gc}{1+bc} = \frac{q_s bc}{1+bc} \tag{1}$$

In this model, q_s is the apparent saturation capacity of the column, G and b are the equilibrium constants relating to adsorption.

Regressing $\frac{1}{q} \sim \frac{1}{c}$ with a least square method (LSM), the parameters G_i and b_i (i=1,2) can be derived and the results are summarized in Table 1.

Experimental Data Obtained for 2-Phenylethanol and 3-Phenylpropanol Components Using FA

If experimental isotherm coefficients of binary components are derived, FA is the only chromatographic method allowing accurate measurements. According to mass balance equations, there are the following relationships:[19]

$$q_1 = \frac{(V_2 - V_0)(c_1^F - c_1^I) - (V_2 - V_1)(c_1^m - c_1^I)}{V_{ads}} \tag{2a}$$

$$q_2 = \frac{(V_2 - V_0)(c_2 - c_2^I)}{V_{ads}} \tag{2b}$$

Where q_1, q_2 are the concentrations of the less strongly retained component and the more strongly retained component in the solid phase, respectively. Terms: V_1, V_2 are the retention volume of the less strongly retained component and the more strongly retained component, respectively. V_0 is the unretained volume. Terms c_1^F, c_1^I, c_1^m are the concentration of initial injection, primary platform, and sub platform, respectively. Term F is the phase ratio, which may be derived using t_m for a non-retained compound using $F = [\pi(\Phi/2)^2 L - Ut_m]/Ut_m$ where Φ is the inner diameter of the column (cm), L is the length of the column (cm), t_m is the non-retained time (min), u is the average linear mobile phase velocity flow rate (mL/min) used to determine t_m.

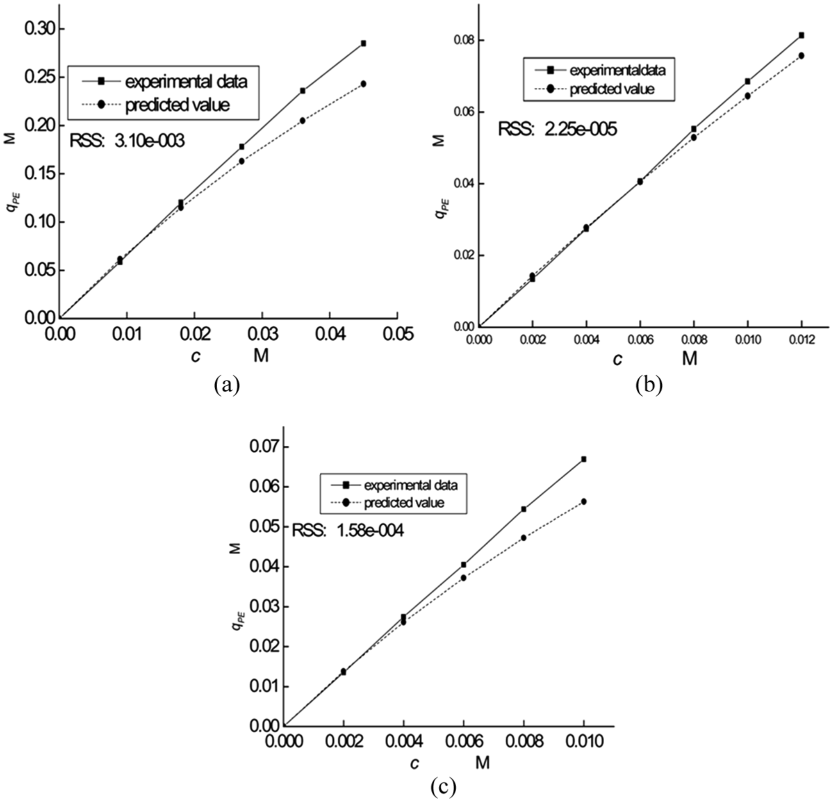
In most case, retention time t_{Ri} is used to replace retention volume V_{Ri} for convenience. The Equations (2a) and (2b) become:

$$q_1 = \frac{(t_{R,2} - t_m)(c_1^F - c_1^I) - (t_{R,2} - t_{R,1})(c_1^m - c_1^I)}{Ft_m} \tag{3a}$$

$$q_2 = \frac{(t_{R,2} - t_m)(c_2 - c_2^I)}{Ft_m} \tag{3b}$$

where t_{R1}, t_{R2} are the retention times of the less strongly retained component and the more strongly retained component, respectively.

Different solute concentration ratios composed of 3:1, 1:1, and 1:3 (PE: PP) were investigated by FA, and q_{PE}, q_{pp} were obtained. The results are summarized in Figures 1–6 and are separately discussed.



(a) (b)

(c)

Figure 1. Comparison of experimental results and competitive Langmuir model derived values for fitting q_{PE} for various concentrations ratio PE to PP 3:1(a), 1:1 (b) and 1:3(c).

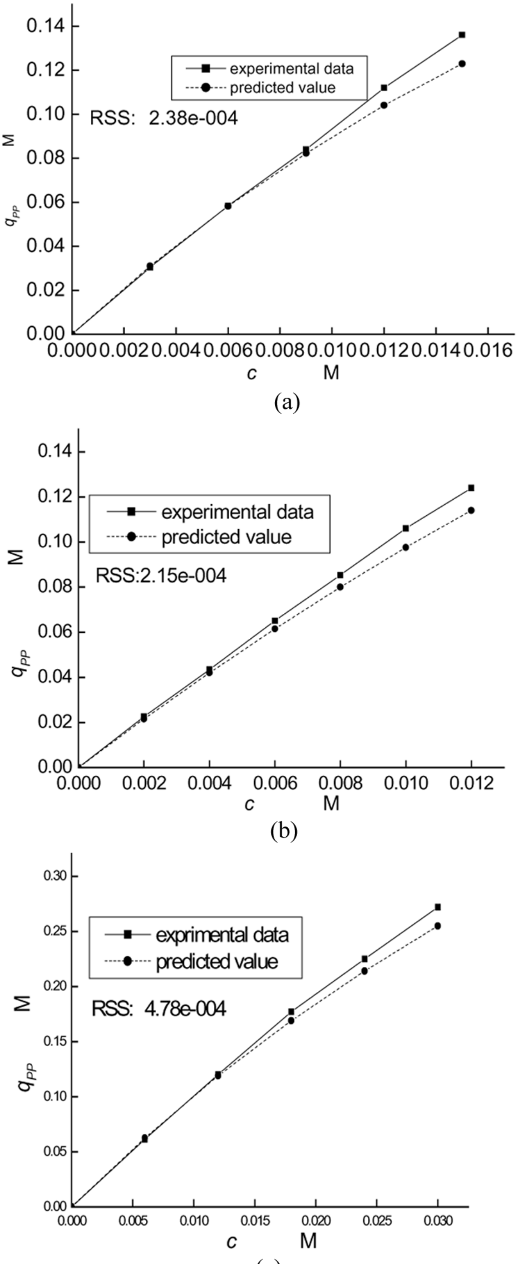


Figure 2. Comparison of experimental results and competitive Langmuir model derived values for fitting q_{PP} for various concentrations ratio PE to PP 3:1(a), 1:1 (b) and 1:3(c).

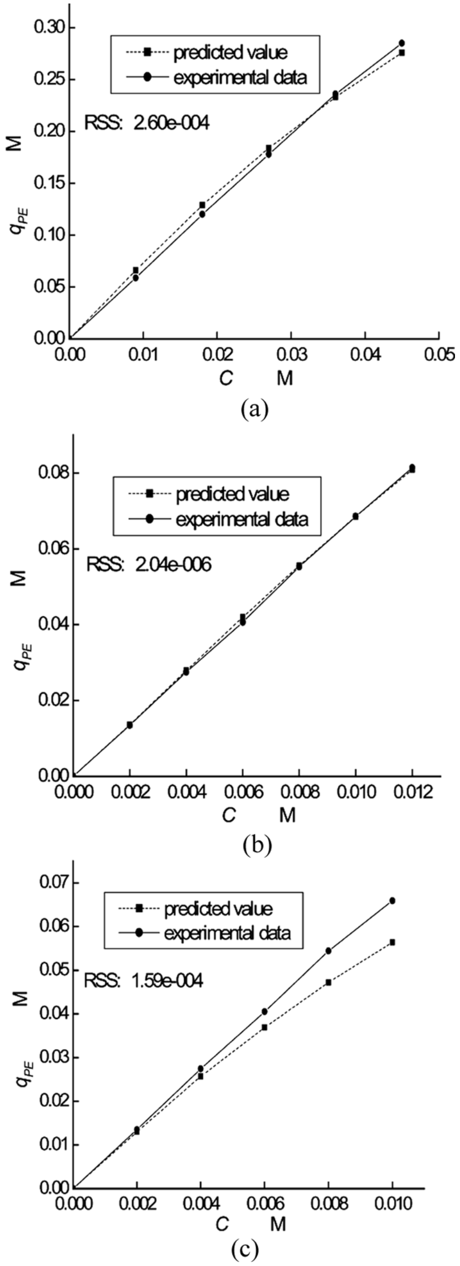
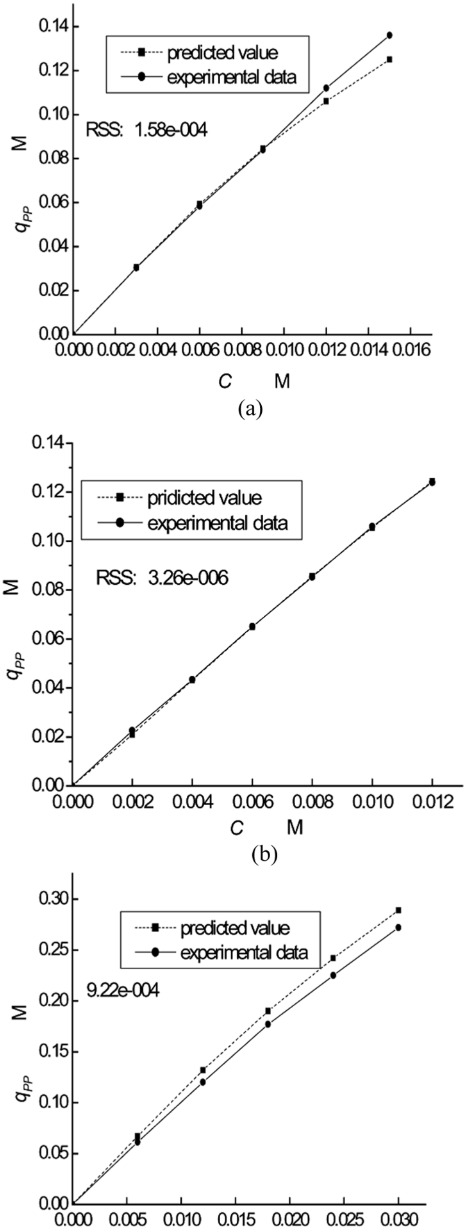


Figure 3. Comparison of experimental results and modified Freundlich equation derived values for fitting q_{PE} for various concentrations ratio PE to PP 3:1 (a), 1:1 (b) and 1:3 (c).

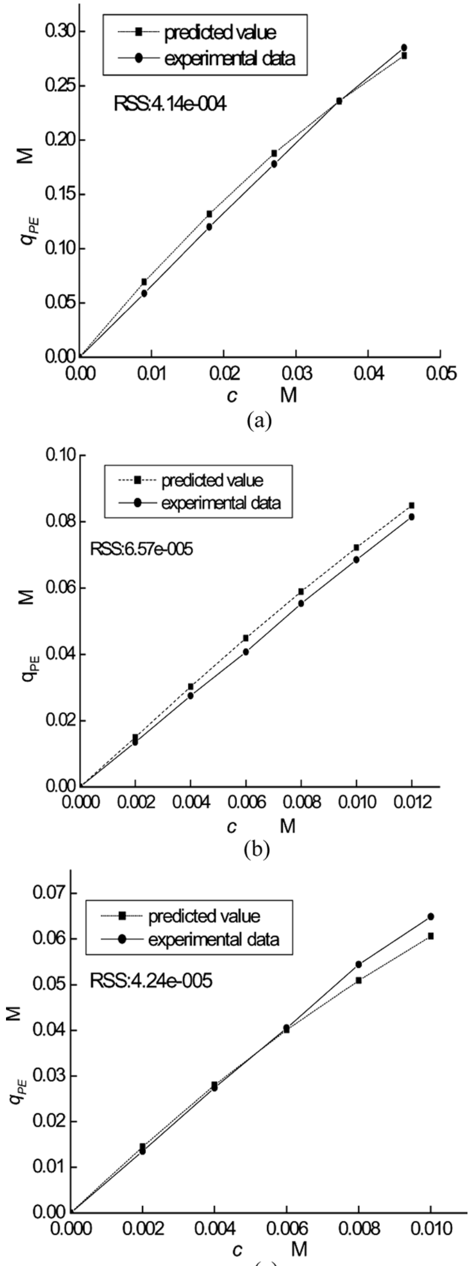


(a)

(b)

(c)

Figure 4. Comparison of experimental results and modified Freundlich equation derived values for fitting q_{PP} for various concentrations ratio PE to PP 3:1 (a), 1:1 (b) and 1:3 (c).



(a)

(b)

(c)

Figure 5. Comparison of experimental results and multicomponent Sips equation derived values for fitting q_{PE} for various concentrations ratio PE to PP 3:1 (a), 1:1 (b) and 1:3 (c).

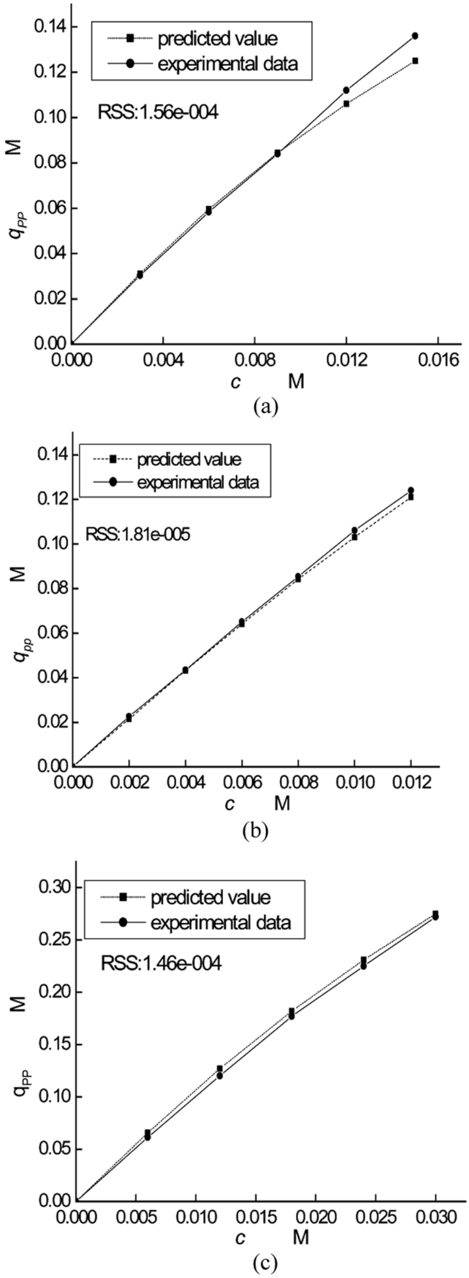


Figure 6. Comparison of experimental results and multicomponent Sips equation derived values for fitting q_{PP} for various concentrations ratio PE to PP 3:1 (a), 1:1 (b) and 1:3 (c).

Comparison of Experimental Data with Predicted Values Using Three Model Equations

Competitive Langmuir Model

With this approach, the simultaneous adsorption of more than one component at a given temperature is described by a multi-component isotherm function. In general, the multi-component function must be fitted to equilibrium adsorption data obtained over the entire composition range of interest. However, only a few measurements have been made of multi-component adsorption isotherms in liquid chromatographic systems. For the most part, simple methods are employed to predict adsorption isotherms using parameters obtained from single component data. For the binary component system, the competitive Langmuir model is often used for fitting the experimental data, the equations are as follows:[20]

$$q_1 = \frac{G_1 c_1}{1 + b_1 c_1 + b_2 c_2} \tag{4a}$$

$$q_2 = \frac{G_2 c_2}{1 + b_1 c_1 + b_2 c_2} \tag{4b}$$

where G_1, b_1 and G_2, b_2 are the results from single isotherms of PE and PP, respectively. $G_i = q_s \cdot b$, q_s is the apparent saturation capacity of the column. In this experiment, the competitive Langmuir model can be expressed as:

$$q_{PE} = \frac{7.26c_1}{1 + 5.08c_1 + 8.34c_2}, \quad q_{PP} = \frac{11.07c_2}{1 + 5.08c_1 + 8.34c_2}$$

The equilibrium adsorbent amounts of q_{PE}, q_{pp} were determined using FA. The experimental results were compared with those derived using competitive Langmuir model fittings and are summarized in Figures 1 and 2.

From Figures 1 and 2, it is established that the competitive Langmuir model fits accurately for the low concentration range. However, when applied for fitting higher concentrations, the relative error becomes larger. Also the relative errors increase with increasing concentration. The greatest relative error point for both 2-phenylethanol and 3-phenylpropanol is obtained at highest concentration, and this trend was observed throughout the concentration ratios 3:1, 1:1, and 1:3 (PE:PP). The largest absolute relative error is 15.90%. Generally, the predicted values, Figures 1 and 2, were lower than those experimentally determined. A probable source of error stems from the fact that the competitive Langmuir is derived from a single isotherm model. Thus, the single Langmuir isotherm model is not able to consider the influence of competition of two solutes on the adsorbate; it depends on the solute-solvent interaction energy between molecules, solute size and shape differences.

The Modified Freundlich Equation

As the competitive Langmiur model deviated a lot from the experimental data, especially for higher concentration points, the modified Freundlich equation was applied and derived from the model

$$q = q_s\left(\frac{bc}{1+bc}\right)^{\gamma}, 0 < \gamma \leq 1,$$

which is a special case of multi-parameters Langmiur isotherm

$$q_i = \frac{q_s(bc)^{\gamma}}{[1+(bc)^K]^{\frac{\gamma}{K}}}, (0 < \gamma \leq 1, 0 < K \leq 1)$$

when K is equals to one. For binary competitive isotherm, the isotherm model was defined as:

$$q_i = q_{s,i}\left(\frac{b_i c_i}{1+\sum\limits_{i=1}^{n} b_i c_i}\right)^{\gamma}, 0 < \gamma \leq 1, i = 1, 2 \tag{5}$$

where $q_{s,i}$ is the column saturation capacity of each pure component i, b_i ($i = 1$, 2) is the equilibrium constants relating to adsorption. γ is the exponent constant. Application of the modified Freundlich equation resulted in an increase for the predicted q_i values. Hence, the upper concentrations could now be fitted and taken into account. This resulted in an increasing value of the constant γ, such that intercept became positive rather than negative.

Expressing $(q/q_s)^{\frac{1}{\gamma}}$ as a function of $1/c$ a linear graph was obtained, such that the values of b_i ($i = 1$, 2) could be determined using a least square method. γ was a trial from 0.90 to 1.20 with every other 0.01 until the intercept became positive. For different equation groups which can be combined with different concentration ratios, the models:

$$q_1 = 1.43\left(\frac{7.52c_1}{1+7.52c_1+11.56c_2}\right)^{\gamma} \text{and}$$

$$q_1 = 1.33\left(\frac{11.56c_2}{1+7.52c_1+11.56c_2}\right)^{\gamma}, (\gamma = 1.10)$$

provided better modeled predictions than the competitive Langmiur model. The results following application of these equations are summarized in Figures 3 and 4.

The results of Figures 3 and 4 demonstrate that with the exception of the 1:3 (PE:PP) concentration ratio for upper concentration range studied, an excellent fit to the experimental data was obtained using the modified Freundlich equation. For the 1:1 mixture through whole concentration investigated, the average absolute relative error of PE and PP is only 1.09% and 1.42%, respectively. Among the data points of predicted, three were the same as those measured.

The Multicomponent Freundlich-Langmuir Equation

Multicomponent Freundlich-Langmuir (Sips) equation is often used to describe binary component competitive isotherm.[21,22] The equations are as follows:

$$q_i = q_{s,i} \frac{(b_i c_i)^{\frac{1}{\gamma}}}{1 + (b_i c_i)^{\frac{1}{\gamma}} + (b_i c_i)^{\frac{1}{\gamma}}}, (i = 1, 2) \tag{6}$$

where $q_{s,i}$ is the column saturation capacity of each pure component i, b_i ($i = 1$, 2) is the isotherm coefficient, c_i is the concentration in mobile phase, and γ is the exponent constant. Generally, $q_{s,i}$ can be acquired by FA of pure component, and the problem to be solved is to get suitable parameters b_i and γ. As the modified Freundlich equation has acquired a satisfactory fitting result, b_i ($i = 1, 2$) in the modified Freundlich equation may also be used for the multicomponent Freundlich-Langmuir equation. Therefore, the adjustment of γ is the most critical. The method of getting γ is to change γ from 0.90 to 1.00 every other 0.01 to make the least relative error of fitting results and experimental values. During this process, when γ is settled to 0.95, we got the satisfactory results. The models:

$$q_1 = 1.43 \frac{(7.52 c_i)^{\frac{1}{\gamma}}}{1 + (7.52 c_i)^{\frac{1}{\gamma}} + (11.56 c_2)^{\frac{1}{\gamma}}} \text{ and}$$

$$q_2 = 1.33 \frac{(11.56 c_i)^{\frac{1}{\gamma}}}{1 + (7.52 c_i)^{\frac{1}{\gamma}} + (11.56 c_2)^{\frac{1}{\gamma}}}, (\gamma = 0.95)$$

also provided better modeled predictions than the competitive Langmiur model. For three concentration ratio of 3:1, 1:1, and 1:3 of mixture of 2-phenylethanol and 3-phenylpropanol, the multicomponent Freundlich-Langmuir equation got excellent fitting results either for 2-phenylethanol or 3-phenylpropanol. The results following application of these equations are summarized in Figures 5 and 6.

From Figures 5 and 6, we can see for concentration ratios of 3:1, 1:1, and 1:3, in the whole range concentration investigated, the multicomponent Freundlich-Langmuir equation got good fitting results. For 1:3 mixtures of 2-phenylethanol and 3-phenylpropanol, the multicomponent Freundlich-Langmuir equation improves significantly more than the modified Freundlich equation. The average absolute relative errors of 2-phenylethanol and 3-phenylpropanol are only 4.96% and 4.00% rather than 9.32% and 8.06%. However, for 3:1 and 1:1 mixture, the average absolute relative errors of 2-phenylethanol and 3-phenylpropanol are larger than the modified Freundlich equation.

Authors recommend the extended Sips equations which are rigorous based on the IAS theory,[23] the equations are as follows:

$$q_i = q_s \frac{b_i c_i (b_1 c_1 + b_2 c_2)^{\frac{1}{\gamma - 1}}}{1 + (b_1 c_1 + b_2 c_2)^{\frac{1}{\gamma - 1}}} (i = 1, 2) \tag{7}$$

where the parameters q_s, b_i and γ retain the same physical meanings as in Equation (6), and the values of b_i follow those in Equation (5). Unfortunately, Equation (7) failed to fit the experimental data though γ is larger enough. They gave substantial disagreement fitting results for 2-phenylethanol and 3-phenylpropanol.

Justification of the fitting models investigated involved calculating the residual sum of square errors (*RSS*) which is given as:

$$RSS = \sum_{i=1}^{N} (q^i_{exp\,erimental} - q^i_{theoretical})^2$$

for the results obtained for each set of experimental data obtained. The results were shown in Table 2. From Table 2 we could see that the competitive Langmuir model gave a larger *RSS*. However, the modified Freundlich and the multicomponent Freundlich-Langmuir equation decrease *RSS* a lot. Both models got excellent results. Compared with the modified Freundlich equation and the multicomponent Freundlich-Langmuir equation, the modified Freundlich equation for 3:1, 1:1, and 1:3 mixture, the *RSS* of PE and PP were both less than that of multicomponent Freundlich-Langmuir equation, except for the 1:3 mixture. However, this kind of difference is not so obvious.

Overall, the modified Freundlich equation and multicomponent Freundlich-Langmuir equation could describe the binary competitive isotherm very well, especially the modified Freundlich equation. Among three fitting models, the modified Freundlich equation got the best fitting results. When γ is equal to one, the modified Freundlich equation can reduce to the competitive Langmuir model.

Table 2. Residual sum of square (*RSS*) of three fitting model of PP and PE under different concentration ratio

	3:1		1:1		1:3	
Fitting model	PE	PP	PE	PP	PE	PP
Competitive model	3.10×10^{-3}	2.38×10^{-4}	2.25×10^{-5}	2.15×10^{-4}	1.58×10^{-4}	4.78×10^{-4}
Modified Freudlich equation	2.60×10^{-4}	1.58×10^{-4}	2.04×10^{-6}	3.26×10^{-6}	1.59×10^{-4}	9.22×10^{-4}
Multicomponent Sips equation	4.18×10^{-4}	1.56×10^{-4}	6.57×10^{-5}	1.81×10^{-5}	4.24×10^{-5}	1.46×10^{-4}

CONCLUSIONS

The results of this study demonstrate the difficulty of accurately modeling the experimentally determined binary isotherms for 2-phenylethanol and 3-phenylpropanol using an ODS column. The results of determining the single isotherm parameters of 2-phenylethanol and 3-phenylpropanol using the Langmuir isotherm model demonstrated that the loading capacity of the ODS stationary phase was nearly the same for 2-phenylethanol and 3-phenylpropanol, that is to say for both model compounds, thermodynamic characteristics exhibit consistency in that they satisfied the Gibbs-Duhem equation.[19–20] Initially, this indicated that application of the competitive Langmuir model for studying this binary component system should have provided potential for accurate modeling. However, the fitted results showed that the competitive Langmuir model was not appropriate for the whole concentration range. The competitive Langmuir model did not perform well at upper concentrations. Improvements were made with a modified Freundlich equation and a multicomponent Freundlich-Langmuir equation using the least square regression method such that predictions could be made through the entire concentration range studied.

The modified Freundlich equation fitted three PE: PP concentration ratios of 3:1, 1:1, 1:3, from low concentration to high concentration with the fitted results providing close correlation with the experimental data. The multicomponent Sips equation also got a good model predicted data, especially for the concentration ratio of 1:3 mixtures. However, the modified Freundlich equations give less relative error for PE: PP concentration ratios of 3:1 and 1:1 than the multicomponent Sips equation (see Table 2). The parameter $q_{s,i}$ is from single components results, and b_i is determined using competitive experimental data. In these studies it was determined that both the modified Freundlich equation and multicomponent Sips equation can be reduced to the general competitive Langmuir model when γ is equal to one.

For the model compounds used in these studies, satisfactory fitting results are seldom acquired using direct application of the competitive Langmiur isotherm model. The Langmiur model suggests that there is only monolayer adsorption and no interaction between the adsorbates. For a binary component system, the adsorbates often compete with each other for the stationary phase retention sites. There also exists an energy distribution on the surface of the adsorbent. Hence, in practice, many derived competitive Langmiur isotherms are developed for various chromatographic systems. Consequently, as regards FA methods, the central points which stands for the retention time have to be measured exactly when the adsorbed amounts q_i were acquired for different c_i. In an ideal case, the central points of the breakthrough front of various concentrations should be focused on a single point. However, with the effect of diffusion, the breakthrough front central points cannot be focused together. When calculating q_i by Equations (3a) and (3b), the system error may be invoked, particularly for the relatively higher concentration areas. Hence, at the higher concentration, as the results of these studies indicate, system error increases. Hence, applying a larger value for exponent γ provides a means to help compensate for system errors that relate to the Langmuir isotherm model and the FA method itself. Finally, the authors wish to acknowledge, though beyond the remit of these current studies primarily involving comparison of mathematical modeling techniques for predicting adsorption isotherms of model compounds, that in practice particularly when adsorption isotherms are being studied to develop commercial separation processes, relevant compounds and a range of adsorbents should be initially studied and where possible the results checked against those previously published before introducing manufacturing scale processes.

NOMENCLATURE

b_1	Absorption coefficient of rapid component (L/mol)
b_2	Absorption coefficient of rapid component (L/mol)
c_1^I	The concentration of main plat of rapid component (mol/L)
c_1^F	The inject concentration of rapid component (mol/L)
c_1^m	The sub-plat concentration of rapid component (mol/L)
F	Phase ratio
G_1	Isotherm constant of rapid component
G_2	Isotherm constant of slow component
k_i'	Capacity factors of component ($i = 1, 2$)
L	Length of column (cm)
q_1	Adsorbed concentration of rapid component in solid- phase (mol/L)
q_2	Adsorbed concentration of slow component in solid-phase (mol/L)
q_s	The column saturation capacity (mol/L)
t_m	Unretained time (min)
$t_{R,i}$	The adjusted retention time of components ($i = 1, 2$), (min)
u	The flow rate (mL/min)
V_0	Unretained volume (mL)
V_1	The retention volume of rapid component in accordance to central point of through curve (mL)
V_2	The retention volume of slow component in accordance to central point of through curve (mL)
t_{R1}	The retention time of rapid component in accordance to central point of through curve (min)

t_{R2}	The retention time of slow component in accordance to central point of through curve (min)
V_{ads}	Solid-phase volume (mL)
Φ	Inner semidiameter of column (cm)
ε_t	Total porosity of column
γ	Coefficient of exponential function
$q^i_{exp\,erimentai}$	The experimental determination value of the *i*th isotherm point (mol/L)
$q^i_{theoretical}$	The model calculation value of the *i*th isotherm point (mol/L)
N	The number of isotherm points

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