ELSEVIER

Journal of Chromatography A, 918 (2001) 13–23

JOURNAL OF CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Determination and comparison of competitive isotherms by rectangular pulse method and frontal velocity analysis method

Sufang Sun, Gengliang Yang*, Hanwen Sun, Dexian Wang, Haixing Liu

College of Chemistry and Environmental Science, Hebei University, Baoding 071002, PR China

Received 4 December 2000; received in revised form 23 February 2001; accepted 1 March 2001

Abstract

Two different approaches, the rectangular pulse method and a new method, the frontal velocity analysis method are applied to the determination of competitive isotherms for two systems on ODS-silica. Both sets of experimental data are found to fit well to the competitive-Langmuir isotherm equation. The data obtained from the rectangular pulse method and the frontal velocity analysis method are in general agreement with each other and the best coefficients of the competitive isotherms obtained with the two methods are close. This shows that the simpler and easier method, the frontal velocity analysis method can be used to determine binary competitive isotherms.

Keywords: Competitive isotherm; Rectangular pulse method; Frontal velocity analysis method; Adsorption isotherms

1. Introduction

Determination of competitive equilibrium isotherms is important in theoretical and experimental studies in order to evaluate the separation process. The isotherm is the fundamental thermodynamic property which has to be measured in order to permit the accurate prediction of the individual band profiles in non-linear chromatography [1]. Although it is commonly realized that the use of the models and the computing facilities now available can allow considerable savings in the optimization of new separations, potential users are still reluctant because of the experimental difficulties encountered in the accurate determination of competitive equilibrium isotherms. Therefore considerable attention is devoted to the development of new methods which should be much more practical and easier than the existing ones while achieving the same level of accuracy.

Several traditional methods have been used to measure competitive isotherms: the static method [2], which is a tedious and time-consuming task and requires considerable amount of chemicals and solvents; the pulse method [3–7], which is impractical for most organic compounds, because labeled molecules are difficult and expensive to synthesize; the simple wave method [1,8,9], which only can be used for the determination of competitive isotherms in cases where the deviation from the Langmuir model is moderate [9]. Another approach of great interest in the determination of competitive isotherms is the composition velocity method presented by Helfferich [10], which is based on the theory of multicomponent chromatography. This is an effective means for determining competitive isotherms, but the draw-

*Corresponding author. Tel.: +86-312-503-2313; fax: +86-312-501-6914.

E-mail address: ygl@mail.hbu.edu.cn (G. Yang).

0021-9673/01/$ – see front matter
PII: S0021-9673(01)00724-5

back is that this method is only applicable to Langmuir-type isotherms or to stoichiometric adsorption, Another disadvantage is its complex mathematical treatment, which is very hard to master.

Apart from these, the most widely used method is the frontal analysis method [1,11–15]. There are two main variants of this method. One is the staircase frontal analysis method [1,11–13] and the other is the rectangular pulse method [1,14,15]. Both methods are well suited to measure competitive isotherms of any type, but only work if the intermediate plateau is well formed for the determination of the two concentrations on the intermediate plateau [13,14]. The former method allows savings in chemicals compared to the rectangular pulse method, but the effluent on the intermediate plateau must be collected and analyzed by another HPLC analytical system. For the rectangular pulse method, a series of wide plug injections of increasing concentration are used, allowing the sample to elute completely from the column. Although more tedious and time-consuming than the staircase frontal analysis, this approach avoids the need for analysis of the composition on the intermediate plateaus. Also, cumulative errors are prevented.

In our previous papers [15,16], a new simple method of competitive isotherm determination, the frontal velocity analysis method, was presented and used for the determination of competitive isotherms of oxazepam. The goal of this paper is to apply this method to the measurement of competitive isotherms for another two systems, and compare the results with those obtained by the classical method, the rectangular pulse method, in an effort to validate the new method's applicability in some more general cases.

2. Theoretical

2.1. Rectangular pulse method

The rectangular pulse method consists of injecting a single step, washing the solution off the column with the pure mobile phase after the elution of the first step is completed, and starting again with a new, higher step. For a binary mixture of A and B, two plateaus are observed in the elution profiles. The first one is pure A (the less retained), the second one is composed of A and B, and their concentrations are the same as that of the sample injected. The schematic is shown in Fig. 1 ($j = 1$).

According to Refs. [1,15], the concentrations of A and B in the stationary phase can be given by the following expressions, component A (the less retained):

$$q^{A} = \frac{(V_2 - V_D)C^{A} - (V_2 - V_1)(C'^{A})}{V_{sp}} \quad (1)$$

Component B (the more retained):

$$q^{B} = \frac{(V_2 - V_D)C^{B}}{V_{sp}} \quad (2)$$

where $q^{M}$and C^{M} are the concentrations of M (A or B) in the stationary phase and in the mobile phase at equilibrium, respectively; C'^{A} is the concentration of A on the intermediate plateau; $V_1$and V_2 are the elution volumes of the two elution plateaus; V_D is the hold-up volume of the column and V_{sp} is the volume of the stationary phase in the column.

Since only the less retained component is present during the elution of the intermediate plateau, C'^{A} is directly derived from the height of this plateau and no analysis of the effluent is required. Compared with the staircase frontal analysis method, the instrumentation is much simpler, the measurements are more accurate since they rely on the determination of the concentration of the intermediate plateau and of the retention times of the two fronts, and these data are more accurate than a relative concentration measurement [16]. Recently, it was preferred to staircase frontal analysis in the determination of ternary isotherms by Quiñones et al. [17] because it is more accurate.

2.2. Frontal velocity analysis method

A new method called frontal velocity analysis for determining competitive isotherms is described in a previous paper [15]. For each concentration step of the binary solution entering the column, two concentration steps are obtained in the elution profile. A concentration plateau follows each step. The schematic is shown in Fig. 1. The competitive

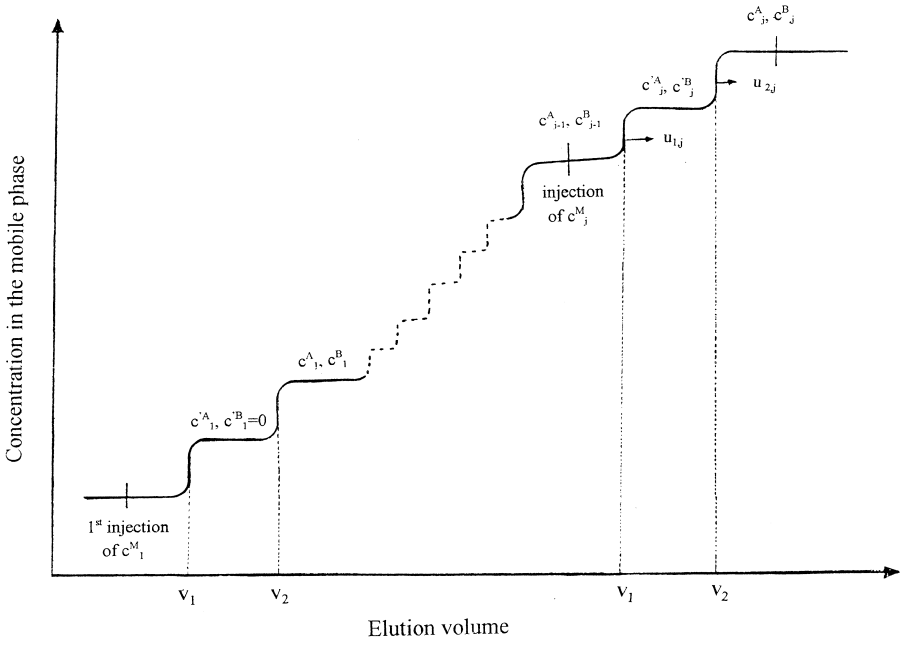

Fig. 1. Schematic depiction of a binary mixture breakthrough profiles where $u_{1,j}$ and $u_{2,j}$ are the frontal velocities of the first and the second fronts of the jth step concentration increase of the solution; V_1 and V_2 are the elution volumes of the first and the second fronts; C^{A}_{j-1}, c^{B}_{j-1} and C^{A}_{j}, c^{B}_{j}, are the concentrations of A and B in the mobile phase before and after the jth concentration increase, respectively C'^{A}_{j}, and c'^{B}_{j} are the concentration of A and B on the intermediate plateau after the jth injection.

isotherms can be readily obtained merely by measurement the frontal velocities of the concentration steps.

According to the equations inferred from Ref. [15], the following expressions can be obtained directly:

$$u_{1,j} = \frac{u_0}{1 + F\dfrac{q'^{\mathrm{A}}_j - q^{\mathrm{A}}_{j-1}}{C'^{\mathrm{A}}_j - C^{\mathrm{A}}_{j-1}}} \quad u_{2,j} = \frac{u_0}{1 + F\dfrac{q^{\mathrm{A}}_j - q'^{\mathrm{A}}_j}{C^{\mathrm{A}}_j - C'^{\mathrm{A}}_j}} \tag{3}$$

Where j is the rank of the concentration step; $u_0$is the linear velocity of the mobile phase; $u_{1,j}$ and $u_{2,j}$ are the front velocities of the first and second fronts of the jth step of concentration increase of the solution; q^{A}_j is the amount of component A adsorbed at equilibrium with the new mobile phase concentration, C^{A}_j; q^{A}_{j-1} is the amount adsorbed at equilibrium with the preceding concentration, C^{A}_{j-1}; q'^{A}_j is the amount adsorbed at equilibrium with the concentration of A on the intermediate plateau, C'^{A}_j; F is the phase ratio ($F = (1-\epsilon)/\epsilon$, ϵ is the packing porosity).

If one defines:

$$\Delta u_{1,j} = F\frac{u_{1,j}}{u_0 - u_{1,j}} \quad \Delta u_{2,j} = F\frac{u_{2,j}}{u_0 - u_{2,j}} \tag{4}$$

or

$$\Delta u_{1,j} = F\frac{V_{\mathrm{D}}}{V_1 - V_{\mathrm{D}}} \quad \Delta u_{2,j} = F\frac{V_{\mathrm{D}}}{V_2 - V_{\mathrm{D}}} \tag{5}$$

where V_1 and V_2 are the retention volumes of the two fronts of every step increase, then Eq. (4) can be simplified to:

$$\Delta u_{1,j} = \frac{C'^{\mathrm{A}}_{j-}C^{\mathrm{A}}_{j-1}}{q'^{\mathrm{A}}_j - q^{\mathrm{A}}_{j-1}} \quad \Delta u_{2,j} = \frac{C^{\mathrm{A}}_j - C'^{\mathrm{A}}_j}{q^{\mathrm{A}}_j - q'^{\mathrm{A}}_j} \tag{6}$$

From Eq. (6), the following expression can be derived:

$$q_j^{\mathrm{A}} - q_{j-1}^{\mathrm{A}} = \frac{1}{\Delta u_{1,j}}(C_j^{\mathrm{A}} - C_{j-1}^{\mathrm{A}}) + \left(\frac{1}{\Delta u_{1,j}} - \frac{1}{\Delta u_{2,j}}\right)(C_j^{'\mathrm{A}} - C_j^{\mathrm{A}}) \quad (7)$$

For the more retained component B, the following can be obtained:

$$q_j^{\mathrm{B}} - q_{j-1}^{\mathrm{B}} = \frac{1}{\Delta u_{2,j}}(C_j^{\mathrm{B}} - C_{j-1}^{\mathrm{B}}) + \left(\frac{1}{\Delta u_{1,j}} - \frac{1}{\Delta u_{2,j}}\right)(C_j^{'\mathrm{B}} - C_{j-1}^{\mathrm{B}}) \quad (8)$$

As inferred from Ref. [15], it can be seen that the second terms on the right hand sides of Eqs. (7) and (8) are of higher order of zero and can therefore be neglected when $\Delta C_j = C_j - C_{j-1} \to 0$.

By integration of Eqs. (7) and (8) one obtains:

$$q_{\mathrm{A}}(C_{\mathrm{A}},C_{\mathrm{B}}) = \int_0^{C_{\mathrm{A}}} \frac{1}{\Delta u_{1,j}(C_{\mathrm{A}},C_{\mathrm{B}})}\,\mathrm{d}C_{\mathrm{A}} \quad (9)$$

$$q_{\mathrm{B}}(C_{\mathrm{A}},C_{\mathrm{B}}) = \int_0^{C_{\mathrm{B}}} \frac{1}{\Delta u_{2,j}(C_{\mathrm{A}},C_{\mathrm{B}})}\,\mathrm{d}C_{\mathrm{B}} \quad (10)$$

In practice, when the concentration step is not large, one can neglect the second terms in Eqs. (7) and (8) and Eqs. (11) and (12) can be used to calculate the concentrations in the stationary phase:

$$q_j^{\mathrm{A}} - q_{j-1}^{\mathrm{A}} = \frac{1}{\Delta u_{1,j}}(c_j^{\mathrm{A}} - c_{j-1}^{\mathrm{A}}) \quad (11)$$

$$q_j^{\mathrm{B}} - q_{j-1}^{\mathrm{B}} = \frac{1}{\Delta u_{2,j}}(c_j^{\mathrm{B}} - c_{j-1}^{\mathrm{B}}) \quad (12)$$

By combination of Eqs. (5), (11) and (12), the following can be obtained:

$$q_j^{\mathrm{A}} = q_{j-1}^{\mathrm{A}} + \frac{V_1 - V_{\mathrm{D}}}{FV_{\mathrm{D}}}(C_j^{\mathrm{A}} - C_{j-1}^{\mathrm{A}}) \quad (13)$$

$$q_j^{\mathrm{B}} = q_{j-1}^{\mathrm{B}} + \frac{V_2 - V_D}{FV_{\mathrm{D}}}(C_j^{\mathrm{B}} - C_{j-1}^{\mathrm{B}}) \quad (14)$$

As shown in Eqs. (13) and (14), for the frontal velocity analysis method, the competitive isotherms can be obtained by determining the retention volumes of the two fronts for every concentration step, V_1 and V_2.

The only practical limitation of the method is that the concentration steps achieved should not be too high, and this can be easily realized in the experiment. The advantage of the frontal velocity analysis method over the classical, staircase frontal analysis method is that a second HPLC analytical system is no longer necessary [16]. Thus, the new method is simpler and faster than conventional staircase frontal analysis method although using the same principle. Its advantage over the rectangular pulse method is in requiring smaller amount of chemicals and less time to perform the experiments needed to acquire the data.

3. Experimental

3.1. Instrumental

The schematic of the HPLC system used by the frontal velocity analysis method is shown in Fig. 2. Compared with the instrumental used in Ref. [16], it is unnecessary to use another on-line analytical HPLC system. The sample introduction in the frontal velocity analysis is achieved by simultaneously switching the two valves, 1 and 2, interconnected in such a way that when loop A is flushed into the column, loop B can be filled with the solution at the next higher concentration. The pump is Waters 510, loops A and B are of 2 ml volume and the injection valves are Rheodyne 7125. The column (200×2.0 mm I.D.) is packed with 5-μm spherical ODS-silica particles from Hypersil and thermostated at 35°C. The variable wavelength UV detector is Shimadzu SPD-6AV and it is set at 275 nm in order to determine the steps even at high concentrations. The flow-rate is 0.3 ml min^{-1}. The signals of the detector are recorded on a PC computer and evaluated with JS-3030 workstation.

3.2. Chemicals

2-Phenylethanol, 3-phenylpropanol, *p*-dihydroxy-

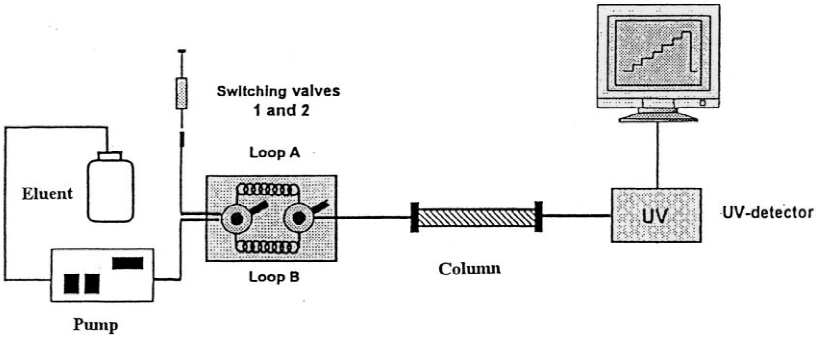

Fig. 2. Schematic depiction of a chromatographic system for measuring competitive isotherms by the frontal velocity analysis method.

benzene, resorcinol, and methanol were all of analytical grades from Beijing Chemical Reagent Factory (Beijing, China). All reagents were applied without further purification. Doubly distilled water was used. The mobile phase was methanol–water (50:50) for homologues of 2-phenylethanol and 3-phenylpropanol, and methanol–water (20:80, pH 6.0, adjusted by 0.01 *M* HCl) for isomers of *p*-dihydroxybenzene and resorcinol. Concentrations are reported in mg ml^{-1}.

3.3. Chromatographic measurement

The column hold-up volume, V_D, is measured with methanol as the unretained marker. The volume of the stationary phase V_{sp} is calculated from the column volume and the dead volume. The stability of the volume flow-rate of the effluent is checked periodically by measuring the volume of column effluent collected over a measured time. The retention volumes of the steps are calculated from the inflection points of the breakthrough curves. In the frontal velocity analysis, first loop A is filled with the lowest concentration planned in the run, then injected onto the column by simultaneously switching valves 1 and 2. Meanwhile, loop B is filled with the solution of the next higher concentration. The corresponding new concentration step is injected at the proper time, by turning both valves simultaneously again. Other injections required are performed in the same way.

4. Results and discussion

4.1. Experimental data

Competitive isotherm data were obtained under conditions of increasing total sample concentration at constant mass ratios of the two components using the two methods described above. The ratios of 2-phenylethanol (PE) to 3-phenylpropanol (PP) or *p*-dihydroxybenzene to resorcinol concentration investigated are 3:1, 1:1 and 1:3. The experimental data are shown in Figs. 3–8 respectively (symbols). Circles represent the data obtained from the frontal velocity analysis method and crosses are the data from the rectangular pulse method. The experimental data obtained from the two different methods are in general agreement.

4.2. Determination of the isotherms and coefficients of the isotherms

The experimental values obtained for the two homologues and two isomers, with either method mentioned above, are fitted to the equations of the competitive Langmuir isotherms.

$$q_A = \frac{b_A q_{s,A} C_A}{(1 + b_A C_A + b_B C_B)} \quad (15)$$

$$q_B = \frac{b_B q_{s,B} C_B}{(1 + b_A C_A + b_B C_B)} \quad (16)$$

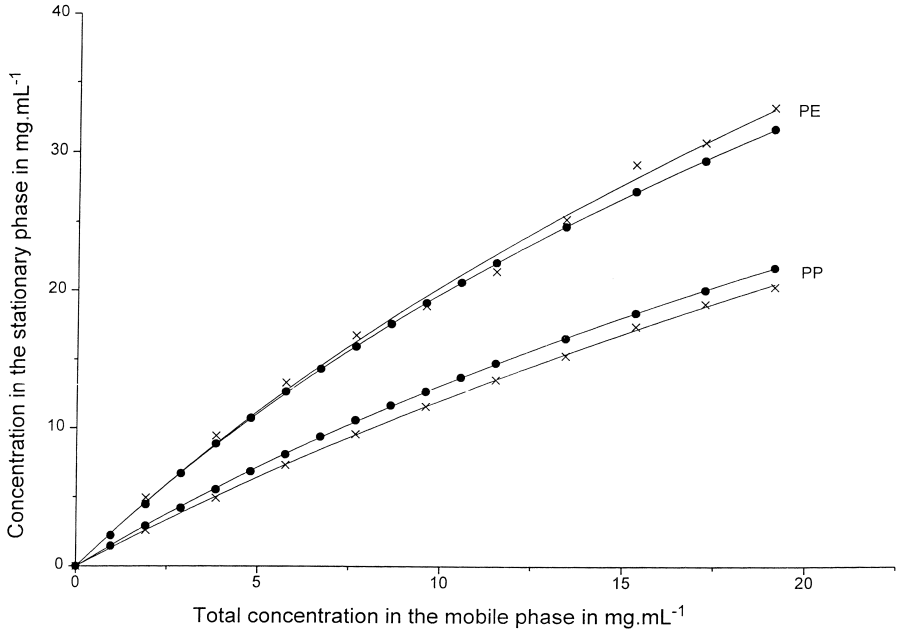

Fig. 3. Competitive isotherms for 2-phenylethanol (PE) and 3-phenylpropanol (PP) (the mass ratio of PE to PP is 3:1) on ODS-silica, which are calculated by two different methods. Crosses (×) represent the data obtained from rectangular pulse method, and circles (●) are the data from frontal velocity analysis method.

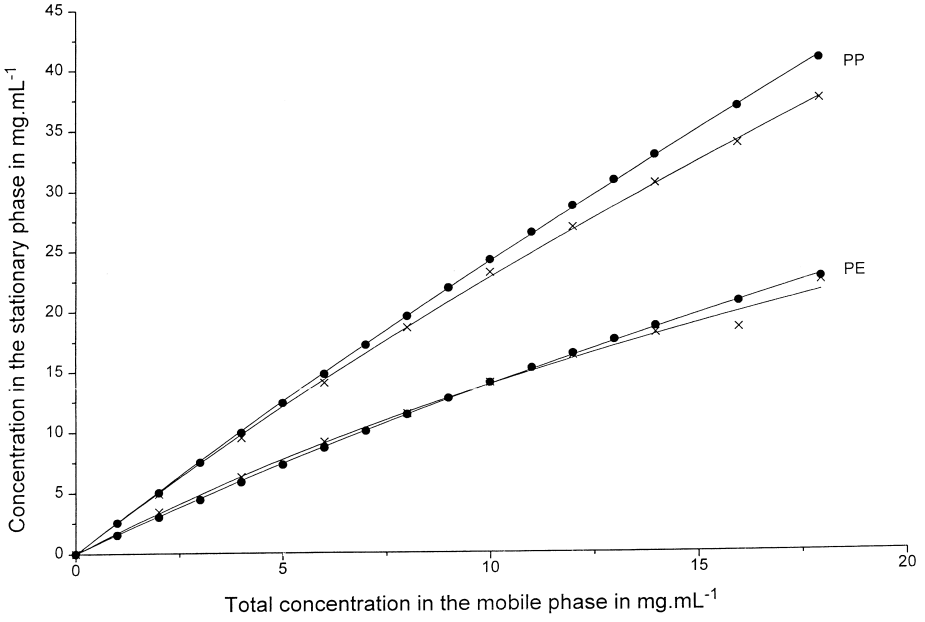

Fig. 4. Competitive isotherms for 2-phenylethanol (PE) and 3-phenylpropanol (PP) (the mass ratio of PE to PP is 1:1) on ODS-silica, which are calculated by two different methods. Crosses (×) represent the data obtained from rectangular pulse method, and circles (●) are the data from frontal velocity analysis method.

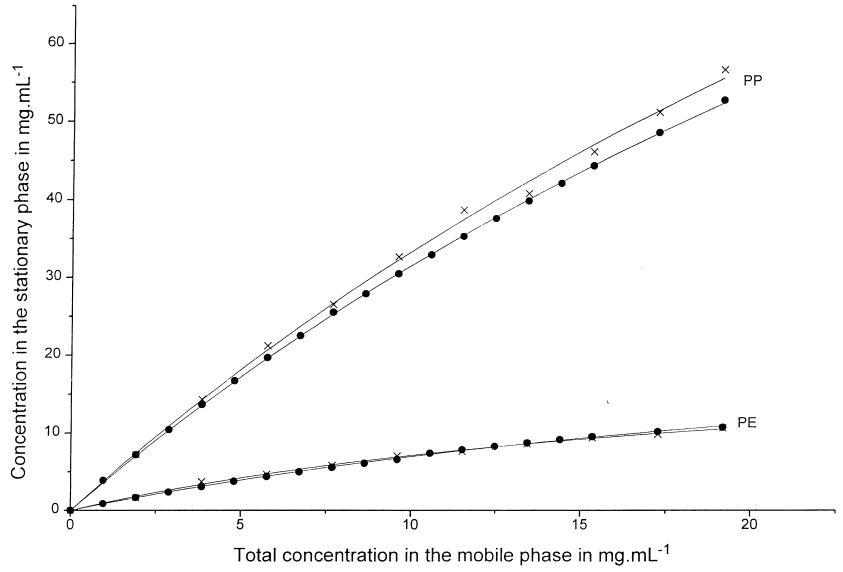

Fig. 5. Competitive isotherms for 2-phenylethanol (PE) and 3-phenylpropanol (PP) (the mass ratio of PE to PP is 1:3) on ODS-silica, which are calculated by two different methods. Crosses (×) represent the data obtained from rectangular pulse method, and circles (●) are the data from frontal velocity analysis method.

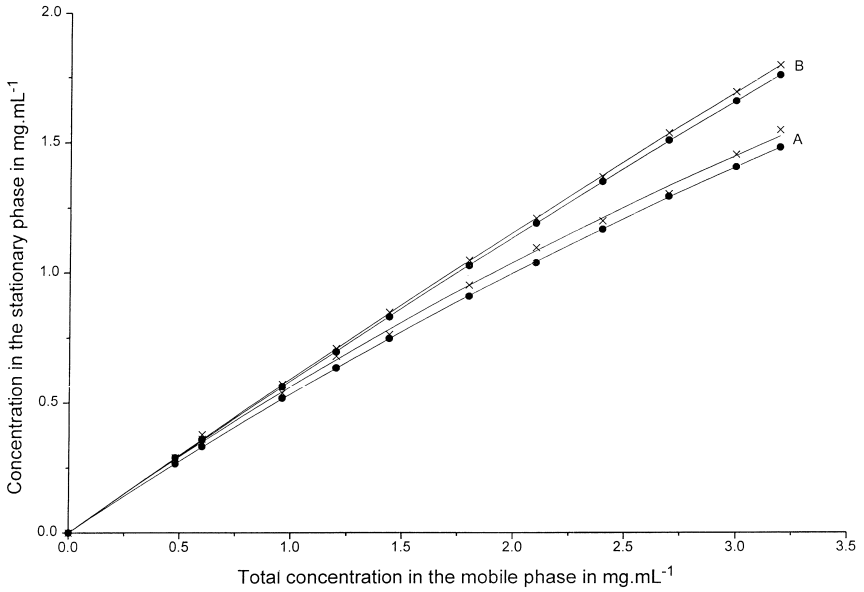

Fig. 6. Competitive isotherms for *p*-dihydroxybenzene (A) and resorcinol (B) (the mass ratio of A to B is 3:1) on ODS-silica, which are calculated by two different methods. Crosses (×) represent the data obtained from rectangular pulse method, and circles (●) are the data from frontal velocity analysis method.

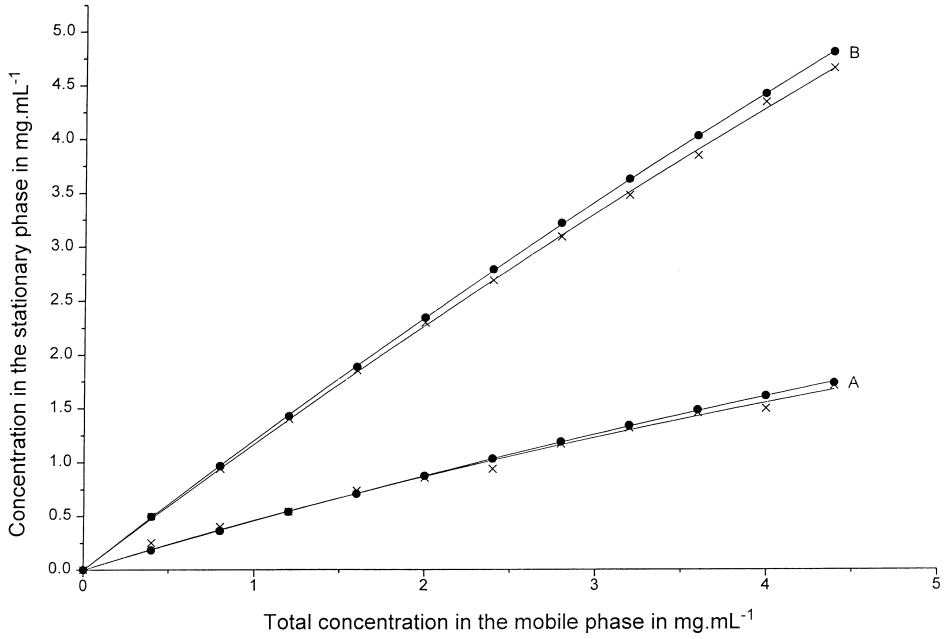

Fig. 7. Competitive isotherms for p-dihydroxybenzene (A) and resorcinol (B) (the mass ratio of A to B is 1:1) on ODS-silica, which are calculated by two different methods. Crosses (×) represent the data obtained from rectangular pulse method, and circles (●) are the data from frontal velocity analysis method.

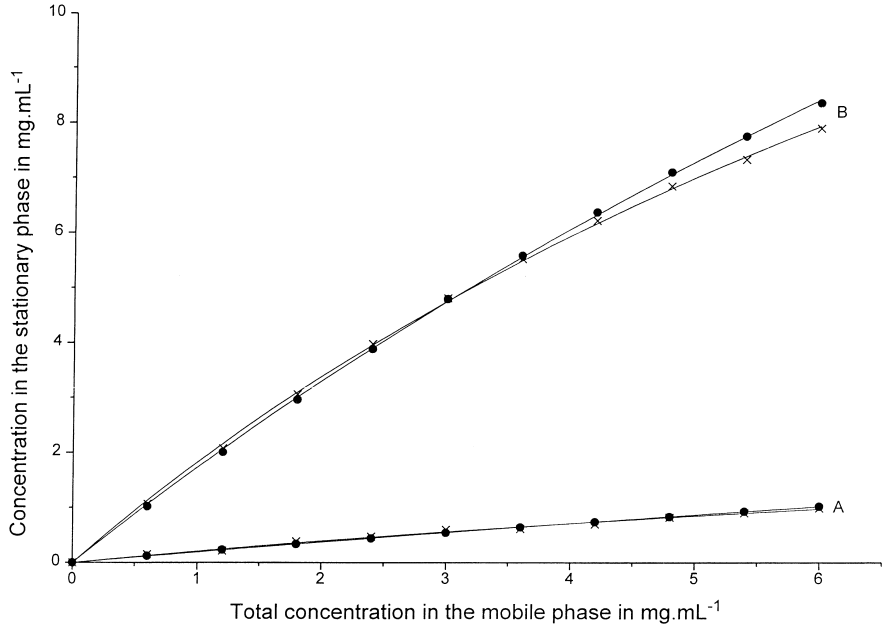

Fig. 8. Competitive isotherms for *p*-dihydroxybenzene (A) and resorcinol (B) (the mass ratio of A to B is 1:3) on ODS-silica, which are calculated by two different methods. Crosses (×) represent the data obtained from rectangular pulse method, and circles (●) are the data from frontal velocity analysis method.

Table 1
Langmuir constants determined by both methods for the system of 2-phenylethanol (PE) and 3-phenylpropanol (PP)[a]

m(PE): m(PP)	Frontal velocity analysis method				Rectangular pulse method			
	PE		PP		PE		PP	
	a_1	b_1	a_2	b_2	a_1	b_1	a_2	b_2
3:1	2.5253	0.02761	1.5849	0.02095	2.5180	0.02398	1.3907	0.01573
1:1	1.5734	0.01340	2.5986	0.00791	1.7339	0.02504	2.5700	0.01302
1:3	0.9128	0.03150	3.8081	0.02051	1.0441	0.04719	4.0035	0.01988

[a] a_i, b_i in ml mg^{-1}.

Where $q_{s,M}$ is the maximum column loadability for M (A or B) and $b_M$is numerical coefficient. When the ratios of $C_A/C_B$are constant, Eqs. (15) and (16) are simplified and become the following expressions:

$$q_A = \frac{a_1 C}{(1 + b_1 C)} \quad (17)$$

$$q_B = \frac{a_2 C}{(1 + b_2 C)} \quad (18)$$

Here C is the total concentration in the mobile phase, a_i and $b_i$are apparent parameters, and they are simply related to the coefficients in Eqs. (15) and (16) and the ratio of the two concentrations in the corresponding feed.

For the investigated ratios of PE and PP and *p*-dihydroxybenzene and resorcinol, the experimental data obtained from the two different methods are fitted to Eqs. (17)–(18). Figs. 3–5 show the competitive isotherms for PE and PP (3:1, 1:1, 1:3) on ODS-silica respectively (solid line), and Figs. 6–8 illustrate the competitive isotherms for *p*-dihydroxybenzene and resorcinol (3:1, 1:1, 1:3) on the same stationary phase (solid line). There is an excellent agreement between the experimental data got from the two different methods and the best Langmuir isotherms obtained from the regression. Meanwhile, the values of the four coefficients a_1, b_1, a_2 and b_2 are also obtained, and the results are reported in Tables 1 and 2, respectively.

4.3. Comparison of the two methods

The experimental data obtained using the frontal velocity analysis method and the rectangular pulse method are in general agreement but with some significant differences which somewhat exceed those expected. Table 1 shows the relative differences between the values of the corresponding coefficient a_i are between 0.3 and 14%, for the coefficient b_i, these relative differences are between 3 and 46%. Similar conclusions can be derived from Table 2. These phenomena can be explained by the following aspect. Although only one set of the instrument is used whether in the rectangular pulse method or in the frontal velocity analysis method, the systematic

Table 2
Langmuir constants determined by both methods for the system of *p*-dihydroxybenzene and resorcinol

m(A): m(B)	Frontal velocity analysis method[a,b]				Rectangular pulse method[a,b]			
	A		B		A		B	
	a_1	b_1	a_2	b_2	a_1	b_1	a_2	b_2
3:1	0.5763	0.0761	0.6034	0.0301	0.6156	0.0911	0.6094	0.0265
1:1	0.4812	0.0480	1.2480	0.0316	0.4958	0.0690	1.2116	0.0325
1:3	0.1957	0.0252	1.8191	0.0491	0.2201	0.0593	1.9766	0.0820

[a] a_i, b_i in ml mg^{-1}.
[b] A, *p*-dihydroxybenzene; B, resorcinol.

errors introduced by the experimental measurement are different for the two methods. In general, because no any other assumption is put forward in the rectangular pulse method, the data acquired should be less affected by errors. However, for the frontal velocity analysis method, as the isotherm data of higher concentration relates with that of lower concentration, hence, it may suffer from the possibility of a systematic drift of the isotherm data due to cumulative errors. As can be seen in Eqs. (13) and (14), the cumulative errors can be decreased by correctly determining the retention volumes of the two elution fronts for every concentration step, which requires a more precise pump. Meanwhile, the accuracy of the new method can be improved by increasing the number of concentration steps.

Either the rectangular pulse method or the frontal velocity analysis method is suitable for measuring any kind of isotherm if there are discontinuities in the fronts, and both can give the same accurate results, but the economics are different. For the rectangular pulse method, before each individual concentration step increases, the column must be eluted to emptiness. This is a time-consuming and solvent-wasting process. For the new method, the process of it is realized by continuous injection, i.e. the lower concentration sample is eluted by the higher concentration sample, the solvent does not enter into the column during the whole process until the last injection is finished. Thus, the frontal velocity analysis method is much faster and more economical than the rectangular pulse method.

In the rectangular pulse method, the concentration of the intermediate plateau can be calculated from the adsorption curve of the less retained component; this is superior to the staircase frontal analysis method, where the concentration of the intermediate plateau is determined by another analytical HPLC system. However, because the width of the intermediate plateau decreases with increasing concentration of the two components in the mobile phase [13], when the injection concentration is much higher, the intermediate plateau almost disappears and it is very difficult to calculate the concentration of the component in it. In the frontal velocity analysis method, the only parameter needed to calculate the isotherm is the retention volume of the elution front (see Eqs. (13) and (14), the injection concentration is known). If only does the front shock associated with the intermediate plateau concentration appears, the competitive isotherm can be calculated by the new method.

5. Conclusions

The competitive isotherms of 2-phenylethanol and 3-phenylpropanol, *p*-dihydroxybenzene and resorcinol on ODS-silica, obtained from the rectangular pulse and the frontal velocity analysis methods, show that the results acquired from the two methods are in general agreement. The frontal velocity analysis method not only has the advantages of a greater experimental simplicity, of being fast, and of requiring small amounts of material to acquire the necessary data but also gives reliable results for the determination of binary competitive isotherms.

Acknowledgements

This work is supported by funds from the National Natural Science Foundation of China (Grant No. 20075005) and the Natural Science Foundation of Hebei Province (Grant No. 200077).

References

[1] G. Guiochon, S. Golshan Shirazi, A.M. Katti, Fundamentals of Nonlinear and Preparative Chromatography, Academic Press, Boston, MA, 1994.
[2] W. Fritz, E.U. Schluende, Chem. Eng. Sci. 29 (1972) 1279.
[3] F. Helfferich, D.L. Peterson, Science 142 (1963) 661.
[4] F.I. Stalkup, D.L. Kobayashi, AICHE J. 9 (1963) 121.
[5] S.H. Hyun, R.P. Danner, AICHE J. 31 (1985) 1077.
[6] W.A. Ruff, C.J. Glover, A.T. Watson, AICHE J. 32 (1986) 1948.
[7] P. Rouchon, M. Schoenauer, P. Valentin, C. Vidal-Madjar, G. Guiochon, J. Phys. Chem. 89 (1985) 2076.
[8] B. Lin, Z. Ma, S. Golshan-Shirazi, G. Guiochon, J. Chromatogr. 500 (1990) 185.
[9] Z. Ma, A.M. Katti, B. Lin, G. Guiochon, J. Phys. Chem. 94 (1990) 6911.
[10] F. Helfferich, G. Klein, Multicomponent Chromatography, Theory of Interference, Dekker, New York, 1970.
[11] J.M. Jacobson, J.H. Frenz, Cs. Horváth, Ind. Eng. Chem, Res. 26 (1987) 43.

[12] J.M. Jacobson, J.H. Frenz, J. Chromatogr. 499 (1990) 5.
[13] Z. Ma, G. Guiochon, Chromatography 603 (1992) 13.
[14] S.C. Jacobson, A. Felinger, G. Guiochon, Biotechol. Progr. 8 (1992) 533.
[15] G.L. Yang, Chromatography 50 (9/10) (1999) 621.
[16] D. Burger, R. NeumÜller, G.L. Yang, H. Engelhardt, I. Quinones, G. Guiochon, Chromatography 51 (9/10) (2000) 517.
[17] I. Quiň-ones, J. Ford, G. Guiochon, Chem. Eng. Sci. 55 (2000) 909.