Short Communication

Adsorption isotherm of undissociated eluent acid and its relation to the retention of system peaks in non-suppressed ion chromatography

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ABSTRACT

The formation of a system peak in non-suppressed ion chromatography is related to the adsorption of undissociated eluent acid onto the functionalized resin surface. To clarify the elution behaviour of system peaks, a new method for determining the isotherms from the capacity factors of system peaks using low-pH eluents free from sodium ions was developed. The isotherms for adsorption of undissociated salicylic and phthalic acids as eluents onto an IC-Anion-PW column, measured by the present method, showed two-site biLangmuir correlations. The capacity factors of system peaks calculated from the equations based on these isotherms were in good agreement with those from actual chromatograms with the acidic eluent conditions.

INTRODUCTION

In non-suppressed ion chromatography (IC), the injection of a sample may result in an extraneous peak depending on the eluent conditions [1]. This peak is called a system peak. Some attempts to eliminate systems peaks from chromatograms have been made because they distort the baseline [2,3]. In addition, selective peak enhancement analyses for the analyte whose elution is close to the system peak have

also been investigated [4,5]. We have already discovered that the interaction between undissociated, neutral eluent acid and the surface of the column packing material forms the system peak [6]. This formation mechanism suggests that prediction of the retention of system peaks by an equation based on an ion-exchange model is impossible, and that the optimization of chromatographic resolution between analyte and system peaks must be made experimentally. Recently, we established a retention model of a multiple eluent system [7], but the retention volume of the system peak was indispensable for a prediction of analyte peak intensity based on this model. It is no exaggeration to say that the

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only thing left to clarify in non-suppressed IC is the behaviour of the system peak.

Considering that the system peak is formed by the adsorption of an eluent component on the resin surface, the clarification of the isotherm may elucidate its elution behaviours. However, the existence of an ion-exchange resin functional group has made it difficult to accurately determine the adsorption isotherms by a traditional static method. In this paper, we establish a technique to determine the isotherms for adsorption of undissociated eluent acid onto low-capacity, surface-functionalized anion exchangers from the actual chromatograms and attempt to predict theoretically the behaviour of the system peak.

THEORY

In our previous publication [6] we introduced the relationship between the apparent distribution ratio of undissociated acid in the two phases ($K_d \cdot \phi$) and the capacity factor of the system peak (k'_e) with low-pH eluents free from counterions such as the sodium ion when the eluent is a monoprotic acid, EH:

$$K_d \cdot \phi = (2[H^+] + K_{ae})k'_e / 2[H^+] \qquad (1)$$

where K_{ae} is the dissociation constant of the eluent acid, ϕ is the phase ratio of the column and square brackets represent the concentration. The distribution ratio defined in eqn. 1 means the ratio of changed fractions between the undissociated acid adsorbed on the resin and dissolved in the eluent. This is the differential value for the adsorption isotherm of the undissociated eluent with respect to its concentration in the eluent, [EH]. Thus, the integration of the function between the two variables, [EH] and $K_d \cdot \phi$, calculated from actual chromatograms under low-pH eluent conditions, gives the adsorption isotherm. The isotherms obtained from eqn. 1 are related to the quantity of eluent acid, not to the concentration, because eqn. 1 contains the phase ratio.

When the eluent is the diprotic acid, EH_2, k'_e is determined using the following equation:

$$k'_e = d[EH_2]_s \phi / (d[EH_2]_m + d[EH^-]_m + d[E^{2-}]_m)$$

where the subscripts m and s represent the existence of bracketed species in the mobile and stationary phases, respectively. Substitution of K_d into this equation gives:

$$k'_e = d[EH_2]_m K_d \cdot \phi / (d[EH_2]_m$$
$$+ d[EH^-]_m + d[E^{2-}]_m) \qquad (2)$$

In the acidic eluent free from sodium ion, the charge balance is indicated by:

$$[H^+] = [EH^-]_m + 2[E^{2-}]_m$$

Introduction of the first and second dissociation constants of eluent, K_{ae1} and K_{ae2}, into this equation gives the concentrations for every eluent species:

$$[E^{2-}]_m = [H^+]K_{ae2}/([H^+] + 2K_{ae2})$$

$$[EH^-]_m = [H^+]^2/([H^+] + 2K_{ae2})$$

$$[EH_2]_m = [H^+]^3/K_{ae1}([H^+] + 2K_{ae2})$$

If the hydrogen ion concentration, $[H^+]$, is much larger than K_{ae2}, the following equations are deduced:

$$d[E^{2-}]_m = 0$$

$$d[EH^-]_m = [H^+] - [H^+_x]$$

$$d[EH_2]_m = ([H^+]^2 - [H^+_x]^2)/K_{ae1}$$

where the subscript x represents the existence in the system peak zone. Substitution of these equations into eqn. 2 gives:

$$K_d \cdot \phi = (2[H^+] + K_{ae1})k'_e / 2[H^+] \qquad (3)$$

This equation is the same as eqn. 1, and means that, in cases of triprotic or higher protic acid eluents, the apparent distribution ratio can be calculated from eqn. 3 when $[H^+]$ is much larger than K_{ae2}.

EXPERIMENTAL

The IC system consisted of a Shimadzu (Kyoto, Japan) LC-5A pump, a Rheodyne (Cotati, CA, USA) Model 7125 injector and a Shimadzu SPD-6AV UV–visible detector. Chromatographic separation was performed on a 5 cm × 4.6 mm I.D. column packed with a low-

capacity anion exchanger (Tosoh, Tokyo, Japan, TSK gel IC-Anion-PW, 0.03 mequiv./ml) maintained at 25°C. Salicylic acid solution as a monoprotic eluent and phthalic acid solution as a diprotic one were delivered at various concentrations. k'_e was measured by injecting water and concentrated eluents.

RESULTS AND DISCUSSION

Values for k'_e measured at various concentrations of salicylate and phthalate eluents free from sodium ions and the distribution ratios, which denote the slopes of the isotherm as previously mentioned, calculated from eqns. 1 and 3, are summarized in Tables I and II, respectively. Both isotherms, the slopes of which become steep as the concentrations of the undissociated acids decrease and converge to constants at high concentrations, have the shapes expected of a Langmuir isotherm. Consequently, the relations between $K_d \cdot \phi$ and [EH] were estimated by conforming to the following Langmuir differential equation

$$K_d \cdot \phi = a \cdot b/(1 + b[EH])^2 \qquad (4)$$

where a is a parameter related to maximum adsorption and b is related to heat of adsorption. Eqn. 4 means that $\log (K_d \cdot \phi)$ is $\log a \cdot b$ when

TABLE I

EXPERIMENTAL DATA OF CAPACITY FACTOR FOR SYSTEM PEAK WITH SALICYLATE ELUENT CONCENTRATION AND DISTRIBUTION RATIO CALCULATED FROM EQN. 1

Salicylate concentration (M)	k'_e	Undissociated eluent (M)	$K_d \cdot \phi$
$1.0 \cdot 10^{-4}$	85.2	$7.20 \cdot 10^{-6}$	636
$3.0 \cdot 10^{-4}$	45.0	$5.15 \cdot 10^{-5}$	153
$5.0 \cdot 10^{-4}$	37.3	$1.20 \cdot 10^{-4}$	96.2
$1.0 \cdot 10^{-3}$	31.8	$3.51 \cdot 10^{-4}$	61.1
$1.5 \cdot 10^{-3}$	30.8	$6.30 \cdot 10^{-4}$	52.1
$2.0 \cdot 10^{-3}$	29.6	$9.39 \cdot 10^{-4}$	46.5
$3.0 \cdot 10^{-3}$	27.2	$1.61 \cdot 10^{-3}$	38.9
$5.0 \cdot 10^{-3}$	25.5	$3.08 \cdot 10^{-3}$	33.4

TABLE II

EXPERIMENTAL DATA OF CAPACITY FACTOR FOR SYSTEM PEAK WITH PHTHALATE ELUENT CONCENTRATION AND DISTRIBUTION RATIO CALCULATED FROM EQN. 3

Phthalate concentration (M)	k'_e	Undissociated eluent (M)	$K_d \cdot \phi$
$2.0 \cdot 10^{-4}$	106	$2.27 \cdot 10^{-5}$	502
$3.0 \cdot 10^{-4}$	73.4	$4.65 \cdot 10^{-5}$	268
$5.0 \cdot 10^{-4}$	47.8	$1.10 \cdot 10^{-4}$	141
$7.0 \cdot 10^{-4}$	30.8	$1.89 \cdot 10^{-4}$	78.9
$1.0 \cdot 10^{-3}$	21.4	$3.28 \cdot 10^{-4}$	43.3
$1.2 \cdot 10^{-3}$	17.2	$4.30 \cdot 10^{-4}$	33.0
$1.5 \cdot 10^{-3}$	14.4	$5.94 \cdot 10^{-4}$	24.8
$3.0 \cdot 10^{-3}$	9.0	$1.51 \cdot 10^{-3}$	13.2
$4.5 \cdot 10^{-3}$	7.8	$2.60 \cdot 10^{-3}$	9.4

[EH] is small enough to be negligible and converges to a line having a slope of -2 as [EH] becomes large. The values in Tables I and II are plotted as the logarithm of $K_d \cdot \phi$ versus the logarithm of [EH] in Fig. 1. However, neither plot showed the tendency predicted by eqn. 4. On the other hand, the solid lines in Fig. 1 are the values calculated from the following equations based on a two-site biLangmuir model.
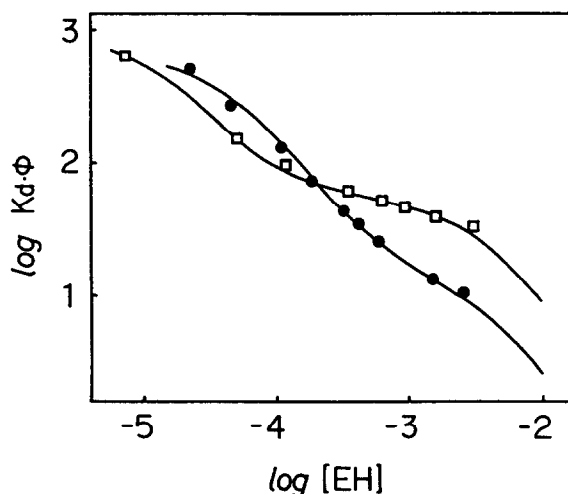

Fig. 1. Fit of differential value (solid lines) of adsorption isotherm based on biLangmuir model to calculated distribution ratio (points). ● = Phthalate eluent; □ = salicylate eluent.

They are in good agreement with the observed results:

$$\{SaH\}_s = 1010\{SaH\}_m/(1 + 44700\{SaH\}_m)$$
$$+ 62.0\{SaH\}_m/(1 + 161\{SaH\}_m)$$

$$\{PhH\}_s = 700\{PhH\}_m/(1 + 12500\{PhH\}_m)$$
$$+ 18.1\{PhH\}_m/(1 + 166\{PhH\}_m)$$

where the braces (curly brackets) represent the quantities of undissociated salicylic (SaH) and phthalic acid (PhH) eluents. The adsorption isotherms of these acids on the unfunctionalized IC-Anion-PW packing material were found to obey the Langmuir equation in the previous publication [6]. These isotherms and the second terms in the above-stated biLangmuir equations had a similar tendency, though different in their dimensions. This result suggested that the functionalization of resin produced a different, stronger adsorption site for the undissociated eluent.

By using these isotherms obtained from the present technique, the prediction of elution behaviours of a system peak was attempted. k_e' for a monoprotic eluent is calculated from the following equation:

$$k_e' = d[EH]_m K_d \cdot \phi/(d[EH]_m + d[E^-]_m) \qquad (5)$$

In the acidic eluent, where $[OH^-]$ is negligible, since $[H^+] = [E^-] - [Na^+]$, $[EH]_m$ is defined by the following equation:

$$[EH]_m = (K_{ae} + 2[ET]_m - [Na^+]$$
$$- (([Na^+] - K_{ae})^2 + 4[ET]_m K_{ae})^{1/2})/2$$

where [ET] is the concentration of the total eluent species. When [ET] is higher than K_{ae}, since $([Na^+] - K_{ae})^2 \ll 4[ET]K_{ae}$, the numeration in eqn. 5 is simplified to:

$$d[EH]_m \doteqdot [ET]_m - [ET_x]_m$$
$$- K_{ae}^{1/2}([ET]_m^{1/2} - [ET_x]_m^{1/2})$$

On the other hand, since the denominator in eqn. 5 is $[ET]_m - [ET_x]_m$, eqn. 5 is rearranged by substituting these equations as follows;

$$k_e' = K_d \cdot \phi(1 - (K_{ae}/[ET]_m)^{1/2}/2) \qquad (6)$$

This equation means that, in the monoprotic eluent, k_e' depends on the distribution ratio.

k_e' for the diprotic eluent is calculated from eqn. 2. From the mass and charge balances in the acidic eluent:

$$[EH_2]_m = ([H^+]^3 + [Na^+][H^+])/(K_{ae1}[H^+]$$
$$+ 2K_{ae1}K_{ae2})$$

$$[ET]_m = ([H^+] + [Na^+])([H^+]^2 + K_{ae1}[H^+]$$
$$+ K_{ae1}K_{ae2})/(K_{ae1}[H^+] + 2K_{ae1}K_{ae2})$$

Substitution of these equations into eqn. 2 gives:

$$k_e' = K_d \cdot \phi(2[H^+]^3 + (6K_{ae2} + [Na^+])[H^+]^2$$
$$+ 4K_{ae2}[Na^+][H^+])/(2[H^+]^3 + (K_{ae1} + 6K_{ae2}$$
$$+ [Na^+])[H^+]^2 + 4K_{ae2}(K_{ae1} + [Na^+])[H^+]$$
$$+ K_{ae1}K_{ae2}(2K_{ae2} + [Na^+]))$$

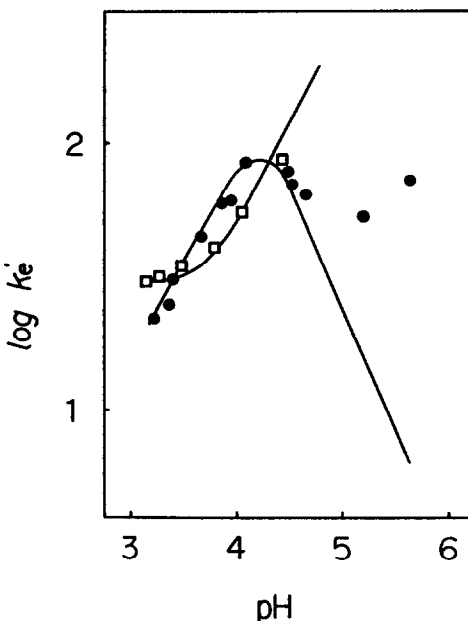Solving for the factors by ignoring the smaller factors, this equation is simplified to:

Fig. 2. Comparison between the calculated (solid lines) and experimental (points) capacity factors of system peak by changing the eluent pH. $\bullet = 1$ mM phthalate eluent; $\square = 2$ mM salicylate eluent.

$$k'_e = K_d \cdot \phi(2[H^+]^2 + [Na^+][H^+])/(2[H^+]$$

$$+ (K_{ae1} + [Na^+])[H^+]$$

$$+ K_{ae1}K_{ae2}[Na^+]/([H^+] + 4K_{ae2})) \qquad (7)$$

This equation means that, in the diprotic eluent, k'_e is strongly affected by pH.

With 2 mM salicylate as a monoprotic acid eluent and 1 mM phthalate as a diprotic acid eluent, comparison between the actual and calculated capacity factors of system peak by changing the eluent pH is shown in Fig. 2. In the salicylate eluent, the elution behaviour of system peak was well elucidated by eqn. 6. In the phthalate eluent, changes in the eluent pH produced curious changes in k'_e. This observation (● in Fig. 2) is in agreement with that by Jackson and Haddad [8]. Calculation from eqn. 7 showed a convex curve that was in close agreement with the observed values at pH values below 4.7. But the increase in k'_e observed at pH values above 4.7, when the concentration of undissociated phthalic acid is less than 10^{-5} M, cannot be explained by eqn. 7. In this pH region, the adsorption of dissociated acid such as the Donnan dialysis may be considered. For the prediction of k'_e, however, it is of little importance in this region, because the elution of system peak was very delayed and the response of the analyte peak reached a state of "standardization" in the indirect photometric detection [9].

Overall, it is possible to determine the adsorption isotherms of undissociated eluent acid onto the functionalized resin of an ion-exchange column by using k'_e in the low-pH eluent. The equations based on the isotherms thus obtained elucidate the behaviour of a system peak in non-suppressed IC with usual eluents in which counter-ions such as sodium ion exist. This result contributes much to the optimization of non-suppressed ion chromatographic separation in cooperation with our latest investigation on the prediction of the analyte capacity factor and intensity in a multiple eluent system [7].

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