Short communication

Stoichiometric mass-action ion-exchange model
Explicit isotherms for mono-, di-, tri- and tetrameric ions

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Abstract

Analytical isotherms for the unhindered stoichiometric mass-action ion exchange of monomeric, dimeric, trimeric and tetrameric ions are derived. The linear increase in oligomer charge from 1 to 4 leads to an exponential increase in the affinity for the stationary phase which, in turn, results in a rapid change in the isotherm shape from hyperbolic to square. The utility of the developed explicit equations is not restricted by the limits imposed by the assumption for absence of steric hindrances because these analytical isotherms can facilitate the use of detailed numerical chromatographic models.

1. Introduction

The work of Brooks and Cramer [1,2] has recently led to the refinement of the stoichiometric mass-action model for polyelectrolyte ion exchange, originally proposed by Boardman and Partridge [3] and subsequently expanded by Regnier and co-workers [4,5] and Velayudhan and Horváth [6]. Two of Brooks and Cramer's contributions to the above theory are most important: first, the introduction of the steric factor defined as the number of column sites per adsorbed polyelectrolyte molecule which are inaccessible to the adsorbate due to steric hindrances; second, the formulation of the non-Langmuirian mass-action isotherm based on the requirement for electroneutrality on the station-ary phase at all times. The concepts of the steric factor and the mass-action isotherm have been verified experimentally [7,8].

The developed mass-action isotherms are implicit in terms of the concentration of bound polyelectrolyte [1]. The purpose of this paper is to present the derivation of explicit forms of these isotherms in certain cases, namely, for the ion exchange of monomeric, dimeric, trimeric and tetrameric ions, in the absence of steric effects. The small size of the adsorbates dealt with in this study justifies the neglect of steric hindrances arising from adsorbate bulkiness as well as from inter-adsorbate electrostatic surface repulsion. Moreover, other steric effects can be avoided by using isotactic adsorbates (bearing charged side-groups with common orientation), and by choosing the appropriate stationary phase such that the charge spacing on the matrix is identical to that of the adsorbate. Isotactic oligo(methacrylic acid)s with degrees of poly-

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merization ranging from 2 to 10 adsorbing on a methacrylate-based stationary phase will experience minimal steric hindrances and shall provide a good model system to test our theory. Despite the restrictions imposed by our assumption for absence of steric effects, the explicit isotherms presented below can facilitate the use of detailed numerical chromatographic models by providing time-saving initial values.

2. Theory

Although the analysis that follows deals with anion exchange, a very similar treatment can be performed for cation exchange.

Polyanion $P^{\nu-}$ comprises ν identical groups each bearing a single negative charge. All ν of the charges of the polyanion are assumed to be free of steric hindrances and be able to interact directly with the stationary phase; ν is called the characteristic charge of the polyanion. The exchange of $P^{\nu-}$ with the column counterion C^- can be described by the reaction:

$$\nu R^+ C^- + P^{\nu-} \rightleftharpoons (R^+)_\nu P^{\nu-} + \nu C^- \qquad (1)$$
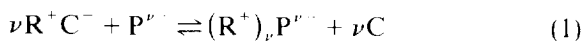
where R^+ is the functional cationic group of the stationary phase and R^+C^- and $(R^+)_\nu P^{\nu-}$ represent the bound counterion and bound polyelectrolyte, respectively. In the following, $(R^+)_\nu P^{\nu-}$ will be written as $R_\nu^{\nu+} P^{\nu-}$. The mass-action equilibrium constant for the anion-exchange reaction, K, is then:

$$K = \beta [R_\nu^{\nu+} P^{\nu-}][C^-]^\nu / (\beta^\nu [R^+ C^-]^\nu [P^{\nu-}]) \qquad (2)$$

where β is the phase ratio (the ratio of the volumes of the stationary phase to the mobile phase), and where the brackets indicate molar concentrations; concentrations are used instead of activities under the assumption of ideal behavior both in the mobile phase and the stationary phase.

The free energy of ion exchange, ΔG, is:

$$\Delta G = -RT \ln K \qquad (3)$$

Since all ν of the negatively charged groups of the polyelectrolyte are identical, Martin's addi-

tive theory (see [9]) suggests that the total free energy of ion exchange is equal to the product of the number of charged groups, ν, with the free energy of ion exchange of a single charged group, Δg:

$$\Delta G = \nu \Delta g \qquad (4)$$

which implies that the ion-exchange constant of polyanion $P^{\nu-}$ is equal to the ion-exchange constant of the corresponding monomer, κ, raised to the polyanion characteristic charge, ν:

$$K = \kappa^\nu \qquad (5)$$

Eq. 5 suggests that the adsorbate affinity for the stationary phase, as expressed by the ion-exchange constant K, increases exponentially with oligomer size.

Electroneutrality on the stationary phase requires that every functional group R^+ be bound by $P^{\nu-}$ or C^-, resulting in the stoichiometric condition:

$$\Lambda = [R^+ C^-] + \nu [R_\nu^{\nu+} P^{\nu-}] \qquad (6)$$

where Λ is the binding capacity of the column in monovalent anions, expressed in mol per volume of stationary phase.

Using Eq. 2, the concentration of bound polyanion $P^{\nu-}$, $[R_\nu^{\nu+} P^{\nu-}]$, can be expressed as:

$$[R_\nu^{\nu+} P^{\nu-}] = K \beta^{\nu-1} [R^+ C^-]^\nu [P^{\nu-}] / [C^-]^\nu \qquad (7)$$

Using Eq. 6, the concentration of bound counteranion C^-, $[R^+ C^-]$, can be expressed as:

$$[R^+ C^-] = \Lambda - \nu [R_\nu^{\nu+} P^{\nu-}] \qquad (8)$$

Eq. 8 implies that at complete saturation of the column by $P^{\nu-}$ (which requires that $[R^+ C^-] = 0$ and this is practically accomplished when $[P^{\nu-}]$ is very high) the limiting concentration of bound polyelectrolyte, $[R_\nu^{\nu+} P^{\nu-}]$, is:

$$[R_\nu^{\nu+} P^{\nu-}] = \Lambda / \nu \text{ for high } [P^{\nu-}] \qquad (9)$$

Using Eq. 8 to eliminate $[R^+ C^-]$ in Eq. 7, and substituting K from Eq. 5 leads to an expression which is implicit in $[R_\nu^{\nu+} P^{\nu-}]$:

$$[R_\nu^{\nu+} P^{\nu-}] = \kappa^\nu \beta^{\nu-1} (\Lambda - \nu [R_\nu^{\nu+} P^{\nu-}])^\nu [P^{\nu-}] / [C^-]^\nu \qquad (10)$$

This is the stoichiometric mass-action anion-exchange isotherm for $R_\nu^{\nu+} P^{\nu-}$. This equation can be explicitly solved only for two types of limiting cases: for oligomeric anion-exchange, i.e. for $\nu = 1, 2, 3$ and 4, which is the subject of this work, and for the anion exchange of analytical amounts of anions, i.e. for $\nu[R_\nu^{\nu+} P^{\nu-}] \ll \Lambda$, which leads to [1]:

$$[R_\nu^{\nu+} P^{\nu-}] = \kappa^\nu \beta^{\nu-1} [P^{\nu-}] \Lambda^\nu / [C^-]^\nu$$

$$\text{for } \nu[R_\nu^{\nu+} P^{\nu-}] \ll \Lambda \tag{11}$$

We continue by solving Eq. 10 for monomeric ($\nu = 1$), dimeric ($\nu = 2$), trimeric ($\nu = 3$) and tetrameric ($\nu = 4$) anions. In the following, to illustrate better the composition of the oligomers by identical units, we represent them as A^-, $(A^-)_2$, $(A^-)_3$ and $(A^-)_4$ rather than P^-, P^{2-}, P^3 and P^{4-}.

In the case of the adsorption of monomeric anion A^- by exchange for C^-, ν is set equal to 1 in Eq. 10 and solving for $[R^+A^-]$ results in the isotherm:

$$[R^+A^-] = \frac{\Lambda}{1 + \dfrac{[C^-]}{\kappa[A^-]}} \tag{12}$$

It can be easily verified that in the cases of high and low concentrations of adsorbate A^-, Eq. 12 correctly yields the limiting expressions of Eqs. 9 and 11, respectively.

Adsorption isotherm 12 can be re-written in terms of the fractional saturation of the column by A^-, $\theta = [^+A^-]/\Lambda$:

$$\theta = \frac{1}{1 + \dfrac{[C^-]}{\kappa[A^-]}} \tag{13}$$

It should be reminded that this anion-exchange isotherm is derived for a system with two components, A^- and C^-, whose adsorption is dictated by the requirement for complete saturation of the stationary phase at all times [2]. It is interesting to note that in Langmuir adsorption, there is no requirement for complete saturation of the adsorbent [2]. It is worth comparing ion-exchange isotherm 13 with the one- and two-

component Langmuir isotherms [10], in Eqs. 14 and 15, respectively:

$$\theta = \frac{1}{1 + \dfrac{1}{K_A[A]}} \tag{14}$$

$$\theta_A = \frac{1}{1 + \dfrac{1 + K_C[C]}{K_A[A]}} \tag{15}$$

where the negative valence superscripts have been dropped, and K_A and K_C represent the equilibrium binding constants for components A and C, respectively. It can be seen that Eq. 13 is intermediate to Eqs. 14 and 15, which can be understood considering the fact that the number of components in ion exchange is something between one and two: there are two adsorbing components and their adsorption is connected by the requirement that they completely saturate the stationary phase. In other words, the fact that Eq. 13 is equally similar to Eqs. 14 and 15 suggests that the mass-action theory does not ignore the presence of the second adsorbing component: the salt counterion.

In the case of the ion-exchange of dimeric anion A_2^{2-}, ν is set equal to 2 in Eq. 10 and rearranging terms results in the quadratic:

$$[R_2^{2+} A_2^{2-}]^2 - \left(\Lambda + \frac{[C^-]^2}{2^2 \kappa^2 [A_2^{2-}] \beta} \right)$$

$$\cdot [R_2^{2+} A_2^{2-}] + \frac{\Lambda^2}{2^2} = 0 \tag{16}$$

which can be easily solved for $[R_2^{2+} A_2^{2-}]$ to give:

$$[R_2^{2+} A_2^{2-}] = \frac{\Lambda}{2} + \frac{[C^-]^2}{2^3 \kappa^2 [A_2^{2-}] \beta}$$

$$\cdot \left(1 \pm \sqrt{1 + 2^3 \cdot \frac{\kappa^2 [A_2^{2-}] \beta \Lambda}{[C^-]^2}} \right) \tag{17}$$

It is necessary now to determine which of the two solutions presented in Eq. 17 is acceptable. This will be done by using Eq. 17 to obtain the expressions for $[R_2^{2+} A_2^{2-}]$ at the high and low concentration limits and comparing the results with the predictions of Eqs. 9 and 11, respectively. At the limit of high concentration of A_2^{2-},

Eq. 17 yields the correct saturation capacity of $\Lambda/2$, as predicted by Eq. 9, for both the positive and the negative values of the square root term. At the low concentration limit of A_2^{2-}, however, calculated by expanding the square root and keeping the first three terms of the resulting polynomial, only the solution with the negative sign in front of the square root yields the expression predicted by Eq. 11. The accepted solution is therefore:

$$\left[R_2^{2+}A_2^{2-}\right] = \frac{\Lambda}{2} + \frac{[C^-]^2}{2^3\kappa^2\left[A_2^{2-}\right]\beta}$$

$$\cdot\left(1 - \sqrt{1 + 2^3 \cdot \frac{\kappa^2\left[A_2^{2-}\right]\beta\Lambda}{[C^-]^2}}\right) \quad (18)$$

In the case of the ion-exchange of trimeric anion A_3^{3-}, ν is set equal to 3 in Eq. 10 and rearranging terms results in the equation:

$$\left[R_3^{3+}A_3^{3-}\right]^3 - \Lambda\left[R_3^{3+}A_3^{3-}\right]^2$$

$$+ \left(\frac{\Lambda^2}{3} + \frac{[C^-]^3}{3^3\kappa^3\left[A_3^{3-}\right]\beta^2}\right) \cdot \left[R_3^{3+}A_3^{3-}\right] - \frac{\Lambda^3}{3^3} = 0 \quad (19)$$

Because the coefficients of the $\left[R_3^{3+}A_3^{3-}\right]$ terms in Eq. 19 are real and because the discriminant of Eq. 19 is positive, there is only one real root [11]. Using the formulas given by Spiegel [11] and performing the appropriate simplifications, the solution to Eq. 19 is:

$$\left[R_3^{3+}A_3^{3-}\right] = \frac{\Lambda}{3} - \frac{[C^-]}{3}\cdot\sqrt[3]{\frac{\Lambda}{6\kappa^3\left[A_3^{3-}\right]\beta^2}}$$

$$\cdot\left(\sqrt[3]{1 + \sqrt{1 + \frac{2^2}{3^4}\cdot\frac{[C^-]^3}{\kappa^3\left[A_3^{3-}\right]\beta^2\Lambda^2}}}\right.$$

$$\left.+ \sqrt[3]{1 - \sqrt{1 + \frac{2^2}{3^4}\cdot\frac{[C^-]^3}{\kappa^3\left[A_3^{3-}\right]\beta^2\Lambda^2}}}\right) \quad (20)$$

It can be observed that in the case of high concentration of adsorbate A_3^{3-}, Eq. 20 correctly yields the saturation capacity of $\Lambda/3$, as predicted by Eq. 9. It can also be shown that at the low concentration limit of A_3^{3-}, calculated by successively expanding the square and cube roots, Eq. 20 behaves as predicted by Eq. 11.

For the ion exchange of tetrameric anion A_4^{4-}, ν is set equal to 4 in Eq. 10 and rearranging terms results in the equation:

$$\left[R_4^{4+}A_4^{4-}\right]^4 - \Lambda\left[R_4^{4+}A_4^{4-}\right]^3 + \frac{3\Lambda^2}{2^3}\cdot\left[R_4^{4+}A_4^{4-}\right]^2$$

$$-\left(\frac{\Lambda^3}{4^2} + \frac{[C^-]^4}{4^4\kappa^4\left[A_4^{4-}\right]\beta^3}\right)\cdot\left[R_4^{4+}A_4^{4-}\right] + \frac{\Lambda^4}{4^4} = 0 \quad (21)$$

which can be solved using the formulas given by Spiegel [11] to yield four roots for the concentration of bound tetramer, $[R_4^{4+}A_4^{4-}]$:

$$\left[R_4^{4+}A_4^{4-}\right] = \frac{\Lambda}{4} + \frac{\sqrt{\Xi}}{2}$$

$$\cdot\left(1 \pm \sqrt{-1 \mp \frac{\Lambda}{\sqrt{\Xi}} + 2\sqrt{1 + \frac{\Lambda^2}{4\Xi}}}\right) \quad (22)$$

where Ξ is given by:

$$\Xi = \sqrt[3]{\frac{[C^-]^8}{2\cdot 4^8\kappa^8\left[A_4^{4-}\right]^2\beta^6}}$$

$$\cdot\left(\sqrt[3]{1 + \sqrt{1 + \frac{4^5}{3^3}\cdot\frac{\kappa^4\left[A_4^{4-}\right]\beta^3\Lambda^3}{[C^-]^4}}}\right.$$

$$\left.+ \sqrt[3]{1 - \sqrt{1 + \frac{4^5}{3^3}\cdot\frac{\kappa^4\left[A_4^{4-}\right]\beta^3\Lambda^3}{[C^-]^4}}}\right) \quad (23)$$

The only solution in Eq. 22 that behaves correctly at low adsorbate concentrations is the one with the negative big square root term and the positive $\Lambda/\Xi^{1/2}$ term leading to the acceptable form of the isotherm:

$$\left[R_4^{4+}A_4^{4-}\right] = \frac{\Lambda}{4} + \frac{\sqrt{\Xi}}{2}$$

$$\cdot\left(1 - \sqrt{-1 + \frac{\Lambda}{\sqrt{\Xi}} + 2\sqrt{1 + \frac{\Lambda^2}{4\Xi}}}\right) \quad (24)$$

The developed stoichiometric mass-action isotherms shown in Eqs. 12, 18, 20 and 24 are plotted in Fig. 1 where both the mobile and stationary phase concentrations of the adsorbate are expressed in terms of concentration of monomer segments (equivalents). The concentration
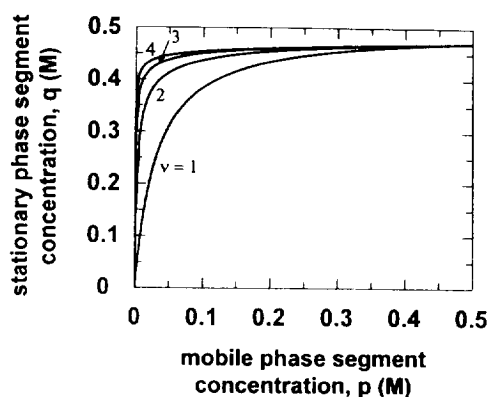
Fig. 1. Stoichiometric mass-action ion-exchange isotherms of monomeric, dimeric, trimeric and tetrameric ions on a stationary phase with a ligand density of 0.50 M and a phase ratio of 1, and a mobile phase uni-univalent salt concentration of 0.25 M. The equilibrium ion-exchange constant of the monomer is taken to be 8.341. The concentrations of the adsorbates in both the mobile and stationary phases are expressed in equivalents.

of monomer segments in the mobile phase, p, is calculated from:

$$p = 1[A^-] = 2[A_2^{2-}] = 3[A_3^{3-}] = 4[A_4^{4-}]$$
$$= \nu[A_\nu^{\nu-}] \tag{25}$$

while the concentration of monomer segments on the stationary phase, q, is given by:

$$q = 1[R^+A^-] = 2[R_2^{2+}A_2^{2-}] = 3[R_3^{3+}A_3^{3-}]$$
$$= 4[R_4^{4+}A_3^{3-}] = \nu[R_\nu^{\nu+}A_\nu^{\nu-}] \tag{26}$$

This transformation is useful because, as implied by Eqs. 9 and 26, it results in a saturation concentration of monomer segments on the stationary phase of Λ, which is independent of polyanion characteristic charge [9]. The values of the parameters utilized in the figure were $[C^-] = [Cl^-] = 0.25$ M, $\Lambda = 0.50$ M, $\kappa = 8.341$ and $\beta = 1$. The column capacity, Λ, of 500 mM was typical of a Waters Protein-Pak Q-8HR strong anion-exchange column [7]. The monomer anion-exchange constant was calculated as the 31st root of the anion-exchange constant of a dextran sulphate fraction with a characteristic charge of 31 [7], according to Eq. 5. The figure clearly shows that by increasing the number of

negatively charged residues on the oligomers from 1 to 4, the isotherm shape rapidly changes from hyperbolic to square. This is a direct result of the exponential increase in the adsorbate affinity for the stationary phase with oligomer size as well as of the constant saturation capacity in terms of monomer segments.

3. Conclusions

Analytical expressions for the ion-exchange isotherms of monomeric, dimeric, trimeric and tetrameric ions, based on the stoichiometric mass-action model of Brooks and Cramer [1] in the absence of steric effects, were developed and presented. Owing to the exponential increase in oligomer affinity for the adsorbent with adsorbate size, the derived isotherms steepen abruptly by increasing the number of charged units from 1 to 4. The utility of the developed analytical isotherms extends beyond the limits set by the assumption for absence of steric hindrances because these explicit equations can provide time-saving initial values to detailed numerical chromatographic models.

Future work will focus on the experimental verification of Martin's additive theory for ion exchange by determining the anion-exchange free energies of a series of monodisperse oligo(methacrylic acid)s [12,13]. Drager and Regnier's [14] data on oligonucleotide anion exchange indicate that by increasing the number of groups per molecule from 5 to 14, the free energy of ion exchange per group gradually decreases, suggesting an increase in group affinity with oligomer size.

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