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Effect of Batch Factor on a Binary Ion Exchange Equilibrium

Koichi Tanihara
Government Industrial Research Institute, Kyushu; Shuku-machi, Tosu 841
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The relation between the distribution coefficient of Cs^+ on M^{n+} form exchanger and the ratio of the solution volume to the exchanger weight (batch factor) at a constant loading of Cs^+ has been investigated while taking the activity coefficients of ionic species into consideration when the initial concentration of Cs^+ is changed.

The effects of the batch factor on a binary ion exchange equilibrium have often been observed elsewhere[1–6] under specific experimental conditions. Until quite recently, though, very little attention has been devoted to its elucidation.[7]

There are two degrees of freedom in a binary cation exchange system at a constant temperature and pressure[8] where an ion exchanger having a constant exchange capacity is in equilibrium with an aqueous solution of two cations and one common anion. An ion exchange experiment for such a system, therefore, is usually carried out under the one degree of freedom by introducing relevant constant parameters. Taking the effects of the batch factor into consideration, the experimental conditions at a constant temperature and pressure for a binary cation exchange system can be divided into three cases depending on how one specifies the initial concentrations of two cations in the solution.

(1) The sum of the initial equivalent concentrations of two cations is kept constant, while changing the ratio:

In this case, the sum of equivalent concentrations of two cations in equlibrium with the ion exchanger is invariably constant, irrespective of the batch factor. The usual thermodynamic treatments for a binary exchange equilibrium have been conducted under this restriction.[9]

(2) The initial concentration (varied) of the "ingoing" cationic species into an exchanger is much smaller than that (kept constant) of the cationic species displaced from it:

In this case, the ingoing cationic species is a micro component and the equilibrium concentration of the displaced cationic species can be taken as being approximately constant. The distribution coefficient of the ingoing ionic species is virtually invariant with respect to the batch factor, as previously reported.[7]

(3) The initial concentration of either of the two cations is kept constant, changing that of the other:

This is the case when the effects of the batch factor are often observed. By introducing the batch factor as a second parameter, on the other hand, the present author derived a theoretical relationship between the loading of the ingoing ionic species and its equilibrium concentration in the solution, and successfully related it to the distribution coefficient of the ingoing ionic species, as previously reported.[7]

In the present paper, a refined form of theoretical equation previously reported for case (3) is derived in order to elucidate the effect of the batch factor while taking the activity coefficients into consideration.

Theoretical

The present paper is concerned with the case of an exchange involving two cations only, where a single electrolyte solution of cesium chloride is allowed to react with an ion exchanger of M^{n+} form, while changing the initial concentration at a given batch factor. The exchange reaction may be written as

$$n\mathrm{Cs}^+ + \overline{\mathrm{M}^{n+}} \rightleftarrows \overline{n\mathrm{Cs}^+} + \mathrm{M}^{n+}, \tag{1}$$

(overbar: the exchanger phase)

When the initial concentration of M^{n+} in the solution is zero, a "theoretical adsorption isotherm," as previously reported,[7] is given by

$$\frac{Q}{[\mathrm{Cs}^+]_\mathrm{s}} = \frac{1}{n}\sqrt[n]{\frac{n\beta(C_\mathrm{CEC} - Q)(C_\mathrm{CEC} + (n-1)Q)^{n-1}}{Q} K_{\mathrm{M}^{n+}}^{\mathrm{Cs}^+}}, \tag{2}$$

where Q is the Cs^+ loading (mequiv g^{-1}), β the batch factor (cm^3 g^{-1}), C_CEC the cation exchange capacity (mequiv g^{-1}), $[\mathrm{Cs}^+]_\mathrm{s}$ the equilibrium concentration of Cs^+ in the solution, and $K_{\mathrm{M}^{n+}}^{\mathrm{Cs}^+}$ a selectivity coefficient which is defined by the molarities and the mole fractions for cations in the solution and solid phases, respectively. In Eq. 2, $K_{\mathrm{M}^{n+}}^{\mathrm{Cs}^+}$ is written in terms of the thermodynamic equilibrium constant (K_c) and ionic activity coefficients as follows: $K_{\mathrm{M}^{n+}}^{\mathrm{Cs}^+} = K_\mathrm{c}\gamma_{\mathrm{Cs}^+}^n \bar{f}_{\mathrm{M}^{n+}} / (\gamma_{\mathrm{M}^{n+}} \bar{f}_{\mathrm{Cs}^+}^n)$. The ionic activity coefficients, γ_{Cs^+} and $\gamma_{\mathrm{M}^{n+}}$, refer to the individual cations in the solution phase. They are defined so as to approach unity as $[\mathrm{Cs}^+]_\mathrm{s}$ and the equilibrium concentration of M^{n+} in the solution, $[\mathrm{M}^{n+}]_\mathrm{s}$, approach zero. The ionic activity coefficients, $\bar{f}_{\mathrm{Cs}^+}$ and $\bar{f}_{\mathrm{M}^{n+}}$ refer to the individual cations in the solid phase and are defined so as to be equal to unity for pure homo ionic exchangers in equilibrium with an infinitely dilute solution of the same ion.[10] When the exchange equilibrium is attained in a solution which is sufficiently dilute so that the imbibition of anions by the exchanger can be neglected, the ratio $\bar{f}_{\mathrm{M}^{n+}}/\bar{f}^{n}_{\mathrm{Cs}^+}$ depends only on Q, irrespective of β, since both the ionic activity coefficients, $\bar{f}_{\mathrm{Cs}^+}$ and $\bar{f}_{\mathrm{M}^{n+}}$ vary with the mole fraction of Cs^+ (Q/C_{CEC}) in the solid solution of two homo-ionic exchangers. It then follows that by substituting $K_{\mathrm{d}}=Q/[\mathrm{Cs}^+]_{\mathrm{s}}$ in Eq. 2, the distribution coefficient of Cs^+, K_{d}, can be expressed in the form

$$K_{\mathrm{d}}=F(Q)\,\xi\sqrt[n]{\beta}\,, \tag{3}$$

where ξ denotes $\gamma_{\mathrm{Cs}^+}/\gamma^{1/n}_{\mathrm{M}^{n+}}$, which can be written in terms of the mean activity coefficients, $\gamma_{\pm\mathrm{CsCl}}$ and $\gamma_{\pm\mathrm{MCl}_n}$, of CsCl and MCl_n, respectively, as

$$\ln\xi=\ln\left(\gamma_{\mathrm{Cs}^+}/\gamma^{1/n}_{\mathrm{M}^{n+}}\right)=2\ln\gamma_{\pm\mathrm{CsCl}}-(n+1)/n\ln\gamma_{\pm\mathrm{MCl}_n}\,. \tag{4}$$

On the basis of Guggenheim's theory,[11] $\gamma_{\pm\mathrm{CsCl}}$ and $\gamma_{\pm\mathrm{MCl}_n}$ are given by

$$\begin{aligned}\ln\gamma_{\pm\mathrm{CsCl}}=-\frac{a\sqrt{I}}{1+\sqrt{I}}&+2\,\alpha_{\mathrm{Cs,Cl}}[\mathrm{Cs}^+]_{\mathrm{s}}\\&+(n\,\alpha_{\mathrm{Cs,Cl}}+\alpha_{\mathrm{M,Cl}})[\mathrm{M}^{n+}]_{\mathrm{s}},\end{aligned} \tag{5}$$

and

$$\begin{aligned}\ln\gamma_{\pm\mathrm{MCl}_n}=-\frac{an\sqrt{I}}{1+\sqrt{I}}+\frac{2}{1+n}&\Big\{2n\,\alpha_{\mathrm{M,Cl}}[\mathrm{M}^{n+}]_{\mathrm{s}}\\&+(\alpha_{\mathrm{M,Cl}}+n\,\alpha_{\mathrm{Cs,Cl}})[\mathrm{Cs}^+]_{\mathrm{s}}\Big\},\end{aligned} \tag{6}$$

where a is a constant in the Debye-Hückel formula (equal to 1.178 at 25 °C), and I the ionic strength, $\alpha_{\mathrm{M,Cl}}$ and $\alpha_{\mathrm{Cs,Cl}}$ the specific interaction coefficients of M^{n+} and Cs^+, respectively with Cl^-.

Eqs. 4—6 reduce to

$$\begin{aligned}\xi=\exp\Bigg[&\frac{a(n-1)\sqrt{I}}{1+\sqrt{I}}\\&+\frac{2(n\,\alpha_{\mathrm{Cs,Cl}}-\alpha_{\mathrm{M,Cl}})}{n(n+1)}\Big\{2+\theta(n-1)\Big\}I\Bigg],\end{aligned} \tag{7}$$

where θ is the ionic strength fraction of CsCl.

By substituting $[\mathrm{M}^{n+}]_{\mathrm{s}}=Q/n\beta$ and $[\mathrm{Cs}^+]_{\mathrm{s}}=Q/K_{\mathrm{d}}$ in the respective definition formulas, I and θ are given as

$$I=0.5\,n(n+1)[\mathrm{M}^{n+}]_{\mathrm{s}}+[\mathrm{Cs}^+]_{\mathrm{s}}=0.5\,Q\{(n+1)/\beta+2/K_{\mathrm{d}}\}, \tag{8}$$

and

$$\theta=[\mathrm{Cs}^+]_{\mathrm{s}}/I=2\beta/\{2\beta+(n+1)K_{\mathrm{d}}\}. \tag{9}$$

The substitution of Eqs. 7—9 in Eq. 3 indicates that K_{d} (also $[\mathrm{Cs}^+]_{\mathrm{s}}$) can be regarded as a function of Q and β. It is then concluded that plots of K_{d}/ξ vs. $\sqrt[n]{\beta}$ or $\log(K_{\mathrm{d}}/\xi)$ vs. $\log\beta$ at a given Q should be a straight line passing through the origin or with a slope of $1/n$, respectively.

Experimental

Materials. As a typical organic or inorganic cation exchanger, a sulfonated polystyrene-type resin (Dowex 50W-X8, Dow Chemical Co.) and a synthetic mordenite (Zeolon 100Na, Norton Co.) were used, respectively. The Dowex 50W resin was converted to the homo ionic forms by an exhaustive treatment with the corresponding metal chloride solutions. The synthetic mordenite (Na^+ form) was used without further treatment.

Measurements and Procedures. The experimental procedures were similar to that described previously.[7] The value of $[\mathrm{Cs}^+]_{\mathrm{s}}$ for the La^{3+} form resin was determined based on the concentration of displaced La, which was measured using radiofrequency inductively coupled plasma atomic-emission spectrometry. The observed values of K_{d} and Q for a given β were obtained according to

$$Q=([\mathrm{Cs}^+]_0-[\mathrm{Cs}^+]_{\mathrm{s}})\beta \quad (\mathrm{mequiv\,g^{-1}})$$

and

$$K_{\mathrm{d}}=Q/[\mathrm{Cs}^+]_{\mathrm{s}} \qquad (\mathrm{cm^3\,g^{-1}})$$

where $[\mathrm{Cs}^+]_0$ is the initial concentration ($\mathrm{mol\,dm^{-3}}$) of Cs^+.

Calculation of ξ. The value of ξ at the observed point (Q, K_{d}) for a given β was calculated from Eqs. 7—9 where the specific interaction coefficient, that is, $\alpha_{\mathrm{Cs,Cl}}$, $\alpha_{\mathrm{Na,Cl}}$, $\alpha_{\mathrm{Ca,Cl}}$, or $\alpha_{\mathrm{La,Cl}}$ was estimated to be 0, 0.16, 1.01, or 3.88, respectively, on the basis of Eq. 5 ($[\mathrm{M}^{n+}]_{\mathrm{s}}=0$) or Eq. 6 ($[\mathrm{Cs}^+]_{\mathrm{s}}=0$), using the published values of mean activity coefficient for a single chloride solution.

Results and Discussion

Fig. 1 shows the variation of the distribution coeffi-

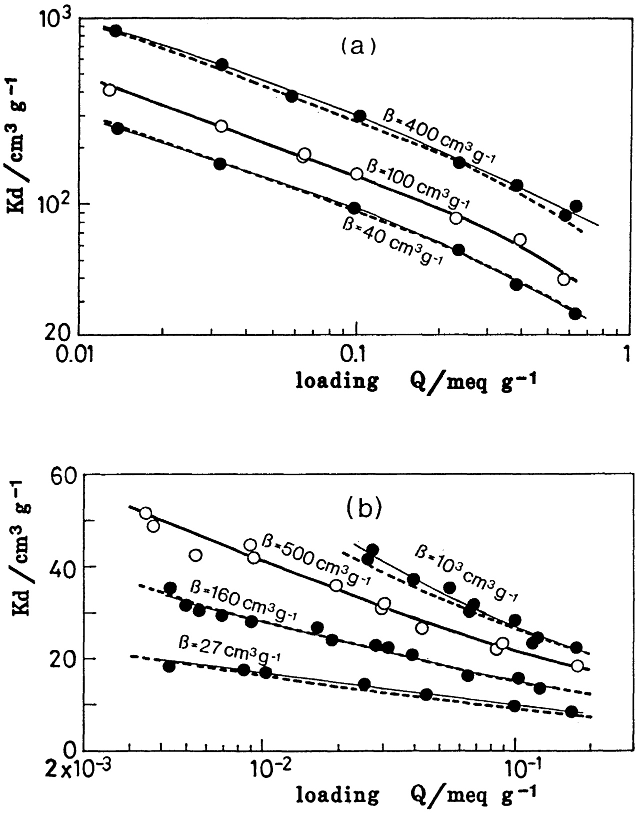

Fig. 1. Variations of K_{d} with Cs loading, Q, at different batch factors for Dowex 50W resin of Ca^{2+} or La^{3+} form. (a) Ca^{2+}-form, (b) La^{3+}-form. The experimental data point is indicated by a open or closed circle. The dashed curves represent the calculated curves obtained from a reference curve (denoted by a bold solid line among the open circles) at a given batch factor.

cient of cesium, K_d, with its loading, Q, at given values of the batch factor, β, for the Dowex 50W of Ca^{2+} and La^{3+} forms when Ca^{2+} and La^{3+} ions, respectively, are initially absent in the solution. In these experiments K_d and Q at equilibrium were measured by changing the initial concentrations of Cs^+ at different fixed values of β in the ionic strength range $I<0.1$. Plots of the ξ value at each point of K_d vs. Q data in Fig. 1 and in previous paper[7] for Na^+ form reveal that the effects of Q and β on ξ greatly differ with the n values of the Dowex resin, as can be seen in Fig. 2.

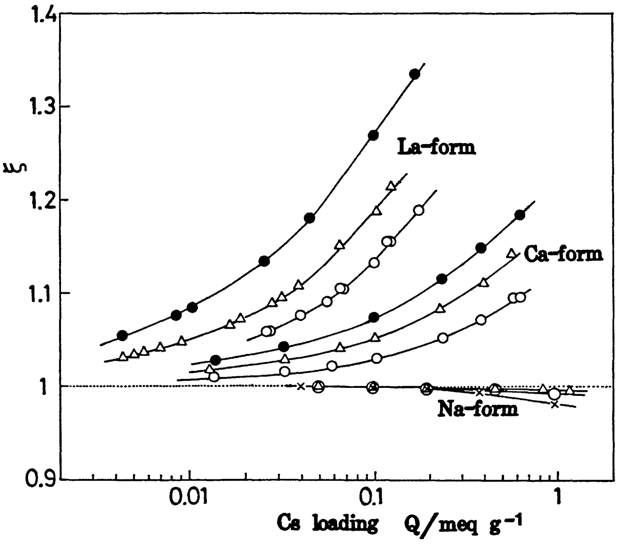

Fig. 2. Variations of ξ with the Cs loading, Q, at different batch factors for Dowex 50W resin of various ionic form: Na^+ form (β(cm^{3}g^{-1}): 20 (×); 50 (○); 100 (△)), Ca^{2+} form (β(cm^{3}g^{-1}): 40 (●); 100 (△); 400 (○)), La^{3+} form (β(cm^{3}g^{-1}): 27 (●); 160 (△); 1000 (○)).

The proportional expression, $K_d/\xi \propto \sqrt[n]{\beta}$, derived from Eq. 3, was verified, as shown in Fig. 3, by good linear relationships with slope of $1/n$ between $\log(K_d/\xi)$ and $\log\beta$, where K_d and β were read for an arbitrarily specified Q ranging from small to relatively large values on the basis of the graphs in Fig. 1 and those drawn in a previous paper[7] for other exchangers. These results indicate that the underlying assumptions in Eq. 3, based on a theory by Gaines and Thomas,[10] are not only valid for an exchanger of non-swelling type, such as Zeolon 100Na, but also for that of the swelling type, such as Dowex 50W, as long as the ionic strengths in the solutions are in a range less

Based on the above results, $K_d(=K_{d_i})$ vs. Q curves at different $\beta(=\beta_i)$ can be drawn from one reference curve of the K_{d_0} curve constructed at a given $\beta(=\beta_0)$, as described below.

The proportionality constant, $F(Q)$, of K_d/ξ to $\sqrt[n]{\beta}$ at an arbitrarily given Q in Eq. 3 can be determined from a point, (Q, K_{d_0}), on the reference curve for β_0 as $K_{d_0}/(\xi_0\sqrt[n]{\beta_0})$, where ξ_0 can be calculated according to

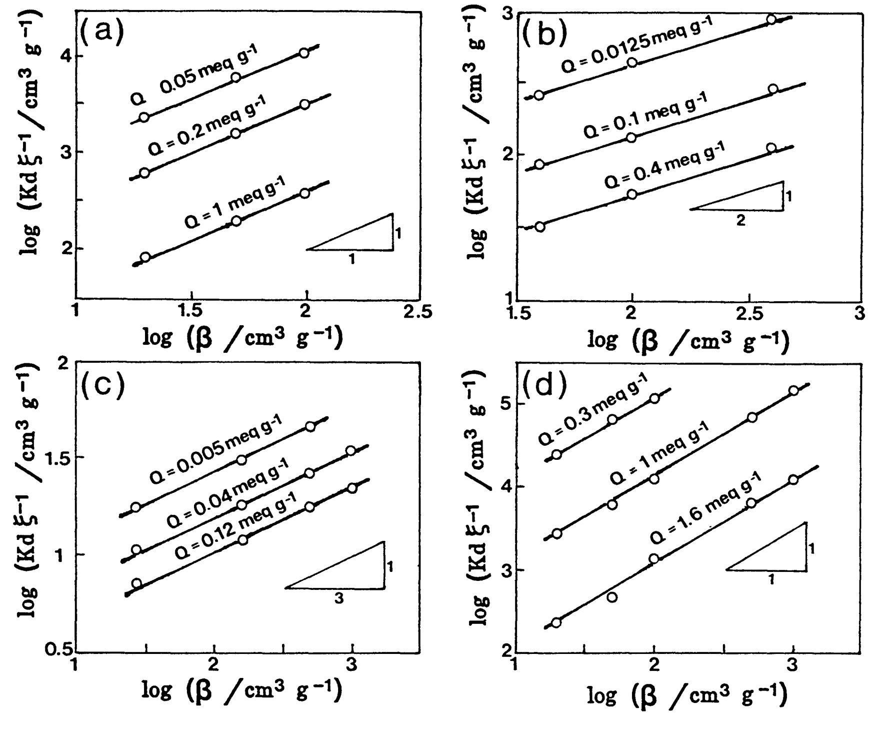

Fig. 3. Linear relationships with slope $1/n$ between $\log(K_d/\xi)$ and $\log\beta$ at different values of Q.
(a) Dowex 50W (Na^+ form), (b) Dowex 50W (Ca^{2+} form), (c) Dowex 50W (La^{3+} form), (d) Zeolon 100Na.

Eqs. 7—9 by substituting $\beta=\beta_0$ and $K_d=K_{d_0}$ into Eqs. 8 and 9. In order to calculate K_{d_i} corresponding to β_i at the given Q using Eq. 3, $\xi(=\xi_i)$ at β_i must be determined. Since the value of $K_{d_i}/\xi_i(=D_i)$ at Q and β_i can be calculated as $K_{d_0}\sqrt[n]{\beta_i}/(\xi_0\sqrt[n]{\beta_0})$ by substituting $F(Q)=K_{d_0}/(\xi_0\sqrt[n]{\beta_0})$ in Eq. 3, a transcendental equation for ξ_i is obtained when $K_d=\xi_i D_i$ and $\beta=\beta_i$ are substituted in Eqs. 8 and 9, followed by the substitutions of I and θ in Eq. 7. This equation can be readily solved by applying a numerical analysis with the aid of a personal computer when Q and β_i are given. Accordingly, K_{d_i} can be calculated as $\xi_i D_i$. As can be seen in Fig. 1, the dashed lines, which represent K_d vs. Q curves predicted from a reference curve (bold solid line) measured for a fixed β, are found to closely agree with the observed values. Similar results were obtained for the Dowex 50W of Na^+ form and Zeolon 100Na. From the K_d vs. Q curves, thus obtained, for different values of β, the corresponding Q vs. $[Cs^+]_s$ curves, that is, "adsorption isotherms" which may be distinguished from the usual "ion exchange isotherm at a constant total solution normality"[9] (independent of the batch factor), can be easily calculated for each β value using the relation $K_d=Q/[Cs^+]_s$.

As demonstrated above, K_d vs. Q curves or "adsorption isotherms" at different β can be calculated without requiring any knowledge concerning the properties of the exchanger, other than one measured K_d vs. Q curve for one value of β.

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