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A Thermodynamic Treatment of
Anion-Exchange Absorption of Metals

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James S. Coleman

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A THERMODYNAMIC TREATMENT OF ANION-EXCHANGE ABSORPTION OF METALS

by

James S. Coleman

ABSTRACT

A thermodynamic description is given of the equilibrium distribution of a metal between an aqueous phase and an anion exchanger. The approach follows the lines established by Fronaeus, Marcus and Coryell, and Kraus and Nelson. Explicit account is taken of stepwise complex formation in each phase, Donnan invasion of the resin, and the formation of polymerized, hydrolyzed, and weakly acid complex ions.

Thermodynamic descriptions of the anion-exchange absorption of metals have been developed by Fronaeus,¹ Marcus and Coryell,² and Kraus and Nelson.³ A summary of this work is given in the standard text by Helfferich.⁴ The present work constitutes an elaboration on the same theme. In particular, the equations are extended for several cases not considered explicitly in earlier publications. The extension is laborious, though basically straightforward. The equations have seemed useful in the form given here, despite the rather opaque notation, and are presented here in the hope of saving other workers the labor of rederivation.

Measurements of anion-exchange absorption of metals are most conveniently reported in terms of the distribution coefficient, D , defined as the ratio of the stoichiometric concentration of the metal in the resin phase, P , to that in the surrounding aqueous phase, Q . In this paper, systems will be considered in which the general formula of the metal-containing species is $H_h M_m L_{\ell}^{+z}$; H^+ is the hydrogen ion, $M^{+\mu}$ is the metallic ion under study, and $L^{-\lambda}$ is the complex-forming anion

or ligand. Hydrolysis may be taken into account by allowing h to assume negative values.

The stoichiometric concentration of the metal in each phase is given by a sum over the species concentrations, $(H_h M_m L_{\ell}^{+z})$, so that the distribution coefficient is related to the species concentrations as shown in Equation (1).

$$D = \frac{P}{Q} = \frac{\sum_{hml} m(H_h M_m L_{\ell}^{+z})}{\sum_{hml} m(H_h M_m L_{\ell}^{+z})} \quad (1)$$

Underlines are used in Equation (1) and throughout this paper to distinguish the resin phase. If the thermodynamic constant and activity coefficient ratio appropriate to the exchange of λ moles of $H_h M_m L_{\ell}^{+z}$ for $-z$ moles of $L^{-\lambda}$ are denoted, respectively, by k_{hml}^{λ} and g_{hml}^{λ} , the ratio of concentrations of each species in the two phases will be given by Equation (2).

$$\frac{(H_h M_m L_{\ell}^{+z})}{(H_h M_m L_{\ell}^{+z})} = k_{hml}^{\lambda} g_{hml}^{\lambda} (L^{-\lambda})^{z/\lambda} / (\underline{L}^{-\lambda})^{z/\lambda} \quad (2)$$

The distribution coefficient may be seen to correspond to an average value of this ratio of species concentrations, in particular, to an average weighted according to the concentration of metal in each form in the aqueous phase. This type of average of any property of the species will be represented here by a superscript bar.

$$D = \frac{\sum_{hml} \left[\frac{(H_h M_m L_l^{+z})}{(H_h M_m L_l^{+z})} \right] m(H_h M_m L_l^{+z})}{\sum_{hml} m(H_h M_m L_l^{+z})}$$

$$= \overline{\left[\frac{(H_h M_m L_l^{+z})}{(H_h M_m L_l^{+z})} \right]}$$

$$= k_{hml} g_{hml} (L^{-\lambda})^{z/\lambda} / (\underline{L})^{z/\lambda} \quad (3)$$

The same sort of averages have been used by Rossotti⁵ in his discussion of the partition equilibria of indium halide complexes.

The relationship between the distribution coefficient and the species concentrations may also be expressed in terms of the fraction, f_{hml} , of the metal present as the particular species $H_h M_m L_l^{+z}$. In the notation used here, the corresponding fraction in the resin phase is $\underline{f}_{hml}$, and D is given by Equation (4).

$$D = k_{hml} g_{hml} \frac{f_{hml} (L^{-\lambda})^{z/\lambda}}{\underline{f}_{hml} (\underline{L})^{z/\lambda}} \quad (4)$$

Equations (3) and (4) do not indicate explicitly the effects to be expected with variation in the average charge on the complex ions, the extent of Donnan invasion of the resin, weak acid formation, etc. For this purpose, it is useful to consider the derivatives of the distribution coefficient with respect to ligand, acid, and total metal concentrations. In evaluating these derivatives, the independent variables must be chosen with care; e.g., partial derivatives taken with respect to the concentration of free metal ion or at constant concentration of free metal ion may be very difficult to relate to experimental measurements. The variables to be used here are the stoichiometric concentration of metal, the concentration of free ligand, $(L^{-\lambda})$, and the concentration of free hydro-

gen ion, (H^+) . Under conditions used for the study of anion-exchange absorption of metals, good estimates of the latter two concentrations may usually be made.

The derivatives of the distribution coefficient itself appear intractable, but the partial derivatives of $\ln D$ with respect to $\ln(L^{-\lambda})$, $\ln(H^+)$, and $\ln P$ or $\ln Q$ are readily simplified. Equation (5) relates the concentration of each metal-containing species to the activity, a_o , of the neutral species $ML_{\mu/\lambda}$. The charge on the metal ion is denoted by μ , the thermodynamic formation constant of the species $(H_h M_m L_l^{+z})$ by K_{hml} , and γ_L , γ_H , and γ_{hml} represent the activity coefficients of the free ligand, free hydrogen ion, and complex species, respectively.

$$(H_h M_m L_l^{+z}) =$$

$$K_{hml} a_o^m (H^+)^h (L^{-\lambda})^{\ell - m\mu/\lambda} \gamma_H^h \gamma_L^{\ell - m\mu/\lambda} / \gamma_{hml}$$

$$(H_h M_m L_l^{+z}) =$$

$$\underline{K}_{hml} a_o^m (\underline{H}^+)^h (\underline{L})^{\ell - m\mu/\lambda} \underline{\gamma}_H^h \underline{\gamma}_L^{\ell - m\mu/\lambda} / \underline{\gamma}_{hml} \quad (5)$$

The logarithm of the stoichiometric concentration of the metal in the aqueous phase, $\ln Q$, is given by Equation (6) and $\ln Q$ by Equation (7).

$$\ln Q = \ln \sum_{hml} m(H_h M_m L_l^{+z})$$

$$= \ln \sum_{hml} m K_{hml} a_o^m \gamma_H^h (H^+)^h \left[\gamma_L (L^{-\lambda}) \right]^{\ell - m\mu/\lambda} / \gamma_{hml}$$

$$(6)$$

$$\begin{aligned}
\left[\sum_{hml} m(H_h M_m L_l^z) \right] d \ln Q &= \sum_{hml} m(H_h M_m L_l^z) \left[m d \ln a_o + h d \ln \gamma_H(H^+) \right. \\
&\quad \left. + (\ell - m\mu/\lambda) d \ln \gamma_L(L^{-\lambda}) - d \ln \gamma_{hml} \right] \\
d \ln Q &= \bar{m} d \ln a_o + \bar{h} d \ln \gamma_H(H^+) + (\bar{\ell} - \mu\bar{m}/\lambda) d \ln \gamma_L(L^{-\lambda}) - \overline{d \ln \gamma_{hml}}
\end{aligned} \tag{7}$$

The differential $d \ln P$ may be expressed similarly in terms of $\bar{m}$, $d \ln a_o$, $\bar{h}$, etc. Since the chemical potentials of each neutral species must be the same in each phase at equilibrium, we may replace $d \ln a_o$ by $d \ln a_o$ and $d \ln \gamma_H^\lambda$ by $d \ln \gamma_H^\lambda \gamma_L^\lambda (H^+)^\lambda (L^{-\lambda}) / \gamma_L(L^{-\lambda})$ and obtain Equation (8).

$$\begin{aligned}
d \ln P &= \bar{m} d \ln a_o + \bar{h} d \ln \gamma_H \gamma_L^{1/\lambda} (H^+) (L^{-\lambda})^{1/\lambda} \\
&\quad - \bar{z} d \ln \gamma_L^{1/\lambda} (L^{-\lambda})^{1/\lambda} - \overline{d \ln \gamma_{hml}}
\end{aligned} \tag{8}$$

The average charge, $\bar{z}$, is equal to $\bar{h} + \mu\bar{m} - \lambda\bar{\ell}$. The several partial derivatives of $\ln a_o$ may be evaluated using Equation (7). The corresponding derivatives of $\ln P$, and, hence, of $\ln D$, may then be evaluated using Equation (8). The resulting equations are given below [see Equations (9), (10), and (11)]. The functions δ_L , δ_H , etc. involve the concentration derivatives of the activity coefficients γ_L , γ_H , etc., and become zero when the activity coefficients are constant; they are defined by Equations (12) through (19).

$$\begin{aligned}
\lambda [\partial \ln D / \partial \ln (L^{-\lambda})]_{(H), Q} &= \bar{z} (1 + \delta_L) \bar{m} / \bar{m} - \bar{z} (1 + \delta_L) [\partial \ln (L^{-\lambda}) / \partial \ln (L^{-\lambda})]_{(H), Q} \\
&\quad + (\bar{h} - \bar{h} \bar{m} / \bar{m}) (1 + \delta_{\pm L})
\end{aligned} \tag{9}$$

$$\begin{aligned}
[\partial \ln D / \partial \ln (H^+)]_{(L), Q} &= (\bar{h} - \bar{h} \bar{m} / \bar{m}) (1 + \delta_{\pm H}) \\
&\quad - \bar{z} (1 + \delta_H) [\partial \ln (L^{-\lambda}) / \partial \ln (H^+)]_{(L), Q} + \delta_H
\end{aligned} \tag{10}$$

$$(\partial \ln D / \partial \ln P)_{(H), (L)} = \frac{-\bar{z} [\partial \ln (L^{-\lambda}) / \partial \ln P]_{(H), (L)} + (\bar{m} - \bar{m}) / \bar{m} + \delta_Q - \delta_P}{1 + \delta_Q} \tag{11}$$

$$\delta_L = [\partial \ln \gamma_L / \partial \ln (L^{-\lambda})]_{(H), Q} + \lambda [\partial \ln \gamma_{hml} / \partial \ln (L^{-\lambda})]_{(H), Q} / \bar{z} \tag{12}$$

$$\delta_L = [\partial \ln \gamma_L / \partial \ln (L^{-\lambda})]_{(H), Q} + \lambda [\partial \ln \gamma_{hml} / \partial \ln (L^{-\lambda})]_{(H), Q} / \bar{z} \tag{13}$$

$$\delta_{\pm L} = [\partial \ln \gamma_H^\lambda \gamma_L^\lambda / \partial \ln (L^{-\lambda})]_{(H), Q} \tag{14}$$

$$\delta_{\pm H} = [\partial \ln \gamma_H^\lambda / \partial \ln (H^+)^\lambda]_{(L), Q} \quad (15)$$

$$\delta_H = [\partial \ln \gamma_L / \partial \ln (L^{-\lambda})]_{(L), Q} + [\partial \ln \gamma_{hmL} / \partial \ln (L^{-\lambda})]_{(L), Q} / \bar{z} \quad (16)$$

$$\delta_H = [\partial \ln \gamma_L / \partial \ln (H^+)]_{(L), Q} \bar{z} \bar{m} / \lambda \bar{m} + [\partial \ln \gamma_{hmL} / \partial \ln (H^+)]_{(L), Q} \bar{m} / \bar{m} \quad (17)$$

$$\begin{aligned} \delta_Q = & (\bar{h} \bar{m} / \lambda \bar{m} - \bar{h} / \lambda) (\partial \ln \gamma_H^\lambda / \partial \ln Q)_{(L), (H)} + \bar{z} (\partial \ln \gamma_L / \partial \ln Q)_{(L), (H)} \\ & + (\partial \ln \gamma_{hmL} / \partial \ln Q)_{(L), (H)} \end{aligned} \quad (18)$$

$$\delta_P = \bar{z} (\partial \ln \gamma_L / \partial \ln P)_{(L), (H)} + (\partial \ln \gamma_{hmL} / \partial \ln P)_{(L), (H)} \quad (19)$$

With the common assumptions of constant activity coefficients ($\delta_H = \delta_L = \dots = 0$), negligible Donnan invasion [$\partial \ln (L^{-\lambda}) / \partial \ln (L^{-\lambda}) = \partial \ln (L^{-\lambda}) / \partial \ln (H^+) = 0$], no polymerization ($\bar{m} = \bar{m} = 1$), and no hydrolysis or weak acid formation ($\bar{h} = \bar{h} = 0$), Equations (9), (10), and (11) reduce to Equations (20), (21), and (22) respectively.

$$[\partial \ln D / \partial \ln (L^{-\lambda})]_{(H), Q} = \bar{z} / \lambda \quad (20)$$

$$[\partial \ln D / \partial \ln (H^+)]_{(L), Q} = 0 \quad (21)$$

$$\begin{aligned} (\partial \ln D / \partial \ln P)_{(H), (L)} = \\ - \bar{z} [\partial \ln (L^{-\lambda}) / \partial \ln P]_{(H), (L)} \end{aligned} \quad (22)$$

At low metal concentrations, the right-hand side of Equation (22) will approach zero and the approximation that $\delta_P = \delta_Q = 0$ will become increasingly good. Under these conditions, Equation (23) will apply, so that appreciable variation of $\ln D$ with $\ln P$ at low metal concentrations provides strong evidence for polymer formation. Similarly, at progressively lower hydrogen ion concentrations, the approximation that $\delta_{\pm H} = \delta_H = \delta_L = 0$

will become increasingly good, and there will ordinarily be negligible changes in Donnan invasion at constant ($L^{-\lambda}$) (i.e., $[\partial \ln (L^{-\lambda}) / \partial \ln (H)]_{(L), Q} = 0$). Equation (24) will then apply, and appreciable variation of $\ln D$ with $\ln (H^+)$ will imply hydrolysis ($\bar{h}$ and/or $\bar{h} < 0$) or weak acid formation ($\bar{h}$ and/or $\bar{h} > 0$). At high acid and metal concentrations, where the effects of polymerization and

$$(\partial \ln D / \partial \ln P)_{(H), (L)} = (\bar{m} - \bar{m}) / \bar{m} \quad (23)$$

$$[\partial \ln D / \partial \ln (H^+)]_{(L), Q} = \bar{h} - \bar{h} \bar{m} / \bar{m} \quad (24)$$

weak acid formation are most likely to be important, it will usually be necessary to consider other effects specified in Equations (10) and (11).

The influence of each of these effects must, of course, be assessed with particular care in any attempt to conduct a quantitative study of the formation of complex ions through use of anion-exchange absorption. Since it does not appear feasible to use added "inert" electrolytes, consideration of activity coefficient changes becomes particularly important. No generally useful discussion of the evaluation of the functions $\delta_{\pm L}$, δ_L , etc., which depend

on the changes of activity coefficients, will be given here. However, the function $\delta_{\pm L}$, for example, may be seen to represent the rate of change of $\ln \gamma_H^\lambda \gamma_L$, the logarithm of the activity coefficient of the acid $H_\lambda L$, with changes in concentration of a corresponding salt (e.g., $Na_\lambda L$). Similarly, $\bar{z} \delta_L$ represents an average rate of change of $\ln \gamma_L^z \gamma_{hm}^\lambda$ with ligand concentration. It remains to be established whether functions of the type of δ_L , which involve changes in activity coefficients of complex salts in the resin phase, behave similarly to the corresponding functions in the aqueous phase. It is noteworthy, in this regard, that Kraus and Moore⁶ have found that the changes in the mean activity coefficient of hydrochloric acid with respect to changes in the chloride ion molality are essentially the same in anion-exchanger and aqueous phases of the same molality.

The condition for a maximum in D as the ligand concentration is varied may be defined accurately by equating the right hand side of Equation (9) to zero. If the effects of polymerization, Donnan invasion, and hydrolysis or weak acid formation may be neglected, the maximum will occur near the ligand concentration at which $\bar{z} = 0$. At high ligand concentrations, the effects of Donnan invasion will become important and will tend to shift the maximum toward higher ligand concentrations. In particular, at concentrations sufficiently high that $\partial \ln (L^{-\lambda}) / \partial \ln (L^{-\lambda})$ approaches one, a maximum will occur near the ligand concentration at which $\bar{z} = \bar{z}$.

In conclusion, it seems appropriate to summarize the principal qualitative implications of the equations developed in this discussion. First, whether consideration of the effects of polymerization and hydrolysis or weak acid formation is necessary at moderately low metal and hydrogen ion concentrations may be established simply and quite rigorously by measurement of $[\partial \ln D / \partial \ln (H^+)]_{(L), Q}$ and $(\partial \ln D / \partial \ln P)_{(H), (L)}$. If these quantities are small, then increase of D with increasing $(L^{-\lambda})$ implies that the average charge on the complexes is positive (at low ligand concentrations), or, at least that $\bar{z} > \bar{z}$ (at high ligand concentrations). Conversely, an inverse dependence of D on the ligand concentration will, under these conditions, imply $\bar{z} < 0$ or $\bar{z} < \bar{z}$. The formation

of incompletely dissociated complex acids will lead to an inverse dependence of D on acidity if the average number of hydrogen ions bound to the complex ions in the aqueous phase, $\bar{h}$, is greater than the average number in the resin phase, $\bar{h}$, and vice versa. The variation of D with loading will similarly depend on whether $\bar{m}$ is greater or less than $\bar{m}$ at low metal concentrations; but at higher metal concentrations, changes with loading in the free ligand concentration of the anion exchanger will also become important.

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