

IDEAL BEHAVIOR IN Na⁺-TRACE METAL CATION EXCHANGE ON CAMP BERTEAU MONTMORILLONITE

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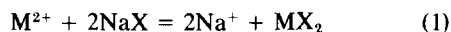
Abstract—The conditions under which an exchanger phase will behave as an ideal mixture are established from thermodynamic principles. It is shown that, if a stoichiometric cation-exchange reaction is reversible, the exchanger phase will exhibit ideal behavior if the Vanselow selectivity coefficient is independent of the exchanger composition. This criterion is applied to some recently published data for Na⁺-trace metal cation exchange on Camp Berteau montmorillonite. An analysis of the data suggests that, so long as the exchange process is reversible, Na⁺-trace metal cation exchange produces an exchanger phase that behaves as an ideal mixture.

Key Words—Cation Exchange, Heterovalent Exchange, Montmorillonite, Trace Metals

INTRODUCTION

Cation-exchange reactions that involve trace metals, such as Cd, Cu, Ni, and Zn, have taken on an added importance in recent years because of the current interest in the potentially harmful effects on plants and animals that result from the accumulation of these metals in soils. The thermodynamic properties of exchangeable trace-metal cations on clay minerals have been studied by Bittel and Miller (1974), El-Sayed *et al.* (1970), Maes *et al.* (1976), and McBride (1978). These investigations have given some indication of the relative exchange selectivities of the common clay minerals for trace-metal cations as well as the degree to which exchanger phases behave as ideal mixtures when trace metals are adsorbed.

In their comprehensive study of Na⁺-exchange with Cd²⁺, Co²⁺, Cu²⁺, Ni²⁺, and Zn²⁺ at pH 5.5 on Camp Berteau montmorillonite, Maes *et al.* (1976) found that adsorption isotherms (i.e., plots of the equivalent fraction of the metal in the exchanger phase vs. the equivalent fraction of the metal in the aqueous solution phase) corresponding to the reaction



were virtually identical for all the trace-metal cations studied. In Eq. (1), M refers to either Cd, Co, Cu, Ni, or Zn, and X refers to one equivalent of the anionic portion of the exchanger. The exchange reactions were found to be stoichiometric and reversible so long as the equivalent fraction of the trace metal in the exchanger phase, E_M , was <0.7. Under this condition, the selectivity coefficient, K_c , could be fit to the linear regression equations

$$\ln K_c = 1.205 + 0.47E_M \quad (t = 22^\circ\text{C}) \quad (2)$$

$$\ln K_c = 1.072 + 0.52E_M \quad (t = 4^\circ\text{C}) \quad (3)$$

in the cases of M = Co, Cu, Ni, and Zn. In Eq. (2) and (3),

$$K_c = \frac{E_M a_{Na}^2}{E_{Na}^2 a_M} \quad (4)$$

and a is a single-ion activity in the aqueous solution phase. Maes *et al.* (1976) also calculated "activity coefficients" for the components of the exchanger phase and found that these quantities varied with either E_M or E_{Na} in a manner consistent with Eq. (2) and (3). These results led them to conclude that Camp Berteau montmorillonite behaved as a nonideal exchanger phase, with respect to the reaction (1). In particular, they ascribed the linear forms of Eq. (2) and (3) to "the analog of a regular solution behavior" in the exchanger phase.

The conclusions of Maes *et al.* (1976) were based on the tacit assumption that nonideality in an exchanger, considered as a binary mixture, is indicated whenever the selectivity coefficient K_c varies in any manner with the equivalent fraction. This fundamental assumption is examined critically in the present paper and is shown to be incorrect. The proper criterion for ideal behavior in an exchanger phase is established and is employed to reanalyze the data of Maes *et al.* (1976). The results suggest that Na⁺-trace metal cation exchange is, in fact, *ideal* on Camp Berteau montmorillonite for $E_M < 0.7$.

THEORY OF IDEAL CATION EXCHANGERS

An exchanger phase is a macroscopically homogeneous mixture with a variable composition. It is, therefore, a solution (see, e.g., Lewis and Randall, 1961, p. 8). The chemical potential of any component in a solution at equilibrium is well defined and, accordingly, the activity of any component is also well defined. In an exchanger phase appropriate to reaction (1), the

Table 1. Comparison of two conventions for expressing selectivity coefficients in cation-exchange reactions.

$vA + uBX_v = uB + vAX_u$	
$E_A = \frac{uN_A}{v + (u-v)N_A}$	$N_A = \frac{vE_A}{u + (v-u)E_A}$
$E_B = \frac{vN_B}{u + (v-u)N_B}$	$N_B = \frac{uE_B}{v + (u-v)E_B}$
$E = \text{Equivalent fraction}$	$N = \text{Mole fraction}$
$K_c = K_{\frac{u}{v}}^{\frac{v}{u}}(uN_A + vN_B)^{u-v}$	$K_v = K_c \frac{v^v}{u^u} (vE_A + uE_B)^{v-u}$
$g_A = \frac{f_A}{u}[v + (u-v)N_A]$	$f_A = \frac{g_A}{v}[u + (v-u)E_A]$
$g_B = \frac{f_B}{v}[u + (v-u)N_B]$	$f_B = \frac{g_B}{u}[v + (u-v)E_B]$

components are MX_2 , NaX , and H_2O . It may be noted that each of these chemical species is a thermodynamically meaningful entity and that its activity is, in principle, measurable without recourse to extrathermodynamic assumptions such as are required, e.g., when dealing with ions in aqueous solutions. Furthermore, activity coefficients for the species MX_2 and NaX may be defined in the usual way for components of mixtures, i.e., as the ratio of the actual activity to its numerical value under those limiting conditions when the mixture obeys Raoult's law (see, e.g., Guggenheim, 1952, p. 33). Therefore

$$f_{Na} = \frac{(NaX)}{N_{Na}} \quad f_M = \frac{(MX_2)}{N_M} \quad (5)$$

express the activity coefficients of NaX and MX_2 , respectively, where () refers to an activity in the exchanger phase, and N is a mole fraction in the exchanger phase. The criterion for ideality in a solution may be defined simply in terms of the activity coefficients in Eq. (5)—a solution is ideal if the activity coefficients are each equal to 1 (Lewis and Randall, 1961, Ch. 18).

The definition of ideality just cited may be applied at once to reaction (1). The thermodynamic equilibrium constant for Eq. (1) is

$$K_{ex} = \frac{(MX_2)a_{Na}^2}{(NaX)^2a_M} = \frac{f_M N_M a_{Na}^2}{f_{Na}^2 N_{Na}^2 a_M} = \frac{f_M K_v}{f_{Na}^2} \quad (6)$$

where

$$K_v = \frac{N_M a_{Na}^2}{N_{Na}^2 a_M} \quad (7)$$

is the Vanselow selectivity coefficient (Vanselow, 1932). It is evident that the exchanger phase will show ideal solution behavior if K_v is observed to be constant as the composition of the exchanger is varied. Thus, it is the constancy of the selectivity coefficient K_v , not K_c , that determines whether an exchanger phase is ideal.

The relationship between the selectivity coefficients K_v and K_c for a general, stoichiometric cation-ex-

change reaction is illustrated in Table 1. The left-hand column of the table gives expressions for calculating quantities related to K_c if K_v and the mole fractions in the exchanger phase are known. The right-hand column gives comparable expressions for K_v and related quantities if K_c and the equivalent fractions in the exchanger phase are known instead. The "activity coefficients" g_A and g_B are defined by (Gaines and Thomas, 1953)

$$g_A = \frac{(AX_u)}{E_A} \quad g_B = \frac{(BX_v)}{E_B} \quad (8)$$

and connect K_c to K_{ex} through the expression

$$K_{ex} = g_A^v (K_c) / g_B^u \quad (9)$$

The coefficients g_A and g_B are not true activity coefficients because the activity of a component of a mixture does not become equal to its equivalent fraction in the limiting case where Raoult's law is obeyed. Essentially this same point has been made previously by Gaines and Thomas (1953) and by Sposito (1977).

It is clear from Table 1 that K_c will not be constant when K_v is constant, and that g_A and g_B will not be equal to 1 when f_A and f_B are equal to 1, unless $u = v$ (homovalent exchange). In the case of reaction (1), in fact,

$$K_c = 2K_v(1 + N_M) = \frac{4K_v}{2 - E_M} \quad (10)$$

Eq. (10) may be rewritten in the form

$$\ln K_c = \ln(2K_v) - \ln(1 - \frac{1}{2}E_M) \quad (11)$$

If the exchanger phase is an ideal solution, the dependence of $\ln K_c$ on E_M is expressed entirely in the second term of Eq. (11). Under the condition that $E_M \ll 2$, this term may be expanded in a MacLaurin series to first order in E_M , and Eq. (11) becomes

$$\ln K_c = \ln(2K_v) + \frac{1}{2}E_M \quad (E_M \ll 2) \quad (12)$$

Eq. (12) is of the same form as Eq. (2) and (3) if $\ln K_v$ is taken to have the values 0.512 at 22°C and 0.379 at 4°C. It may be noted that the theory of ideal exchangers predicts that the coefficient of E_M will be 0.5, independent of the temperature. This prediction agrees with experiment as summarized in Eq. (2) and (3). Therefore, it may be concluded that the regression equations (2) and (3) are consistent with ideal behavior of Na^+ -trace metal cation exchange on Camp Berceau montmorillonite.

The values of K_v for $Na^+ - M^{2+}$ -exchange ($M = Cd, Co, Cu, Ni, Zn$) may be calculated directly using Eq. (10) and the values of K_c published in graphical form by Maes *et al.* (1976). Plots of the resulting values of $\ln K_v$ vs. E_M at 22°C are shown in Figure 1. For $E_M < 0.8$, despite the scatter in the data, which also was apparent in the plots of Maes *et al.* (1976), $\ln K_v$ is seen to be

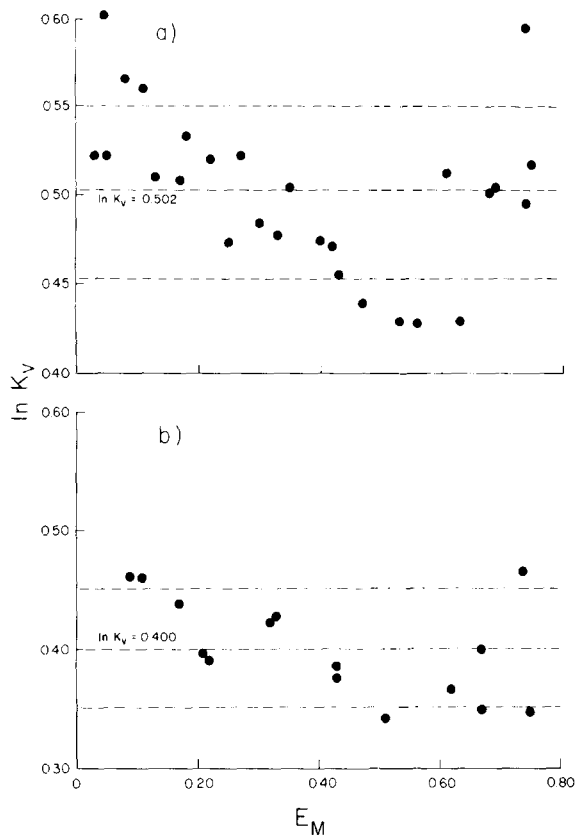


Figure 1. (a) Plot of $\ln K_V$ against the equivalent fraction of the bivalent trace-metal cation for Na⁺-exchange with Co²⁺, Cu²⁺, and Ni²⁺ on Camp Berteau montmorillonite at 22°C. (b) Plot of $\ln K_V$ against the equivalent fraction of the bivalent trace-metal cation for Na⁺-exchange with Cd²⁺ and Zn²⁺ on Camp Berteau montmorillonite at 22°C.

relatively constant as expected. For M = Co, Cu, and Ni, the average natural logarithm of K_V in the domain $0 \leq E_M \leq 0.8$ is 0.502 ± 0.046 . For M = Cd, Zn, the average $\ln K_V$ is 0.400 ± 0.051 . The first average value mentioned is not significantly different from 0.512, given the root mean square deviation of 0.057 for Eq. (2) reported by Maes *et al.* (1976). The average value of $\ln K_V$ found for Cd and Zn, however, would appear to be different from 0.512, although it must be remembered that the Cd data were not used by Maes *et al.* (1976) in obtaining Eq. (2). Regardless of the value of the average $\ln K_V$, Figure 1 is further statistical evidence that $\ln K_V$ is a constant for $E_M < 0.7$.

CONCLUSIONS

The principal conclusions to be drawn from the analysis presented here are that ideality in cation-exchanger phases must be studied in terms of the Vanselow selectivity coefficient, not the coefficient K_c , and that Na⁺-trace metal cation exchange on Camp Berteau montmorillonite is quite likely an ideal exchange at least at low equivalent fractions of the trace metal-montmorillonite component. This latter conclusion is of particular significance for the molecular theory of cation exchange, since heterovalent exchange ordinarily would be expected to involve a "configurational interaction" due to one M²⁺ replacing two Na⁺, that would preclude ideal behavior in the exchanger phase even if the exchange were an athermal process (cf. Guggenheim, 1952, Ch. X).

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Резюме—Исходя из термодинамических принципов, были установлены условия, при которых обменная фаза ведет себя как идеальная смесь. Показано, что если стехиометрическая реакция катионного обмена является обратимой, обменная фаза проявляет свойства идеальной смеси при условии, что коэффициент селективности Ванселоу является независимым от обменного состава. Этот критерий применим к некоторым недавно опубликованным данным, касающимся катионного обмена рассеянных металлов с Na^+ в монтмориллоните Кэмп Бертеау. Анализ Данных показал, что до тех пор пока процесс является обратимым, в результате катионного обмена Na^+ с рассеянными металлами образуется обменная фаза, которая ведет себя как идеальная смесь.

Resümee—Die Bedingungen, unter denen sich eine Austauschphase wie eine ideale Mischung verhält, werden aus thermodynamischen Prinzipien aufgestellt. Es wird gezeigt, daß, wenn eine stöchiometrische Kationenaustauschreaktion umkehrbar ist, die austauschphase ideales Verhalten zeigt, falls der Vanselow Selektivitätskoeffizient unabhängig von der Zusammensetzung der Austauschers ist. Dies Kriterium wird auf einige, vor kurzem veröffentlichte Daten für Na^+ -Spurenmetailkationenaustausch mit Camp Berteau Montmorillonit angewendet. Eine Analyse der Daten schlägt vor, daß solange wie der Austauschvorgang umkehrbar ist, Na^+ -Spurenmetailkationenaustausch eine Austauschphase produziert, die sich wie eine ideale Mischung verhält.

Résumé—Les conditions sous lesquelles une phase d'échange se comportera comme un mélange idéal sont établies à partir de principes thermodynamiques. Il peut être démontré que si une réaction stœchiométrique d'échange de cation est réversible, la phase d'échange montrera un comportement idéal si le coefficient de sélectivité Vanselow est indépendant de la composition de l'élément échangeur. Ce critère est appliqué à des données récemment publiées concernant l'échange de cation du métal traceur- Na^+ sur de la montmorillonite Camp Berteau. Une analyse des données suggère que, tant que la processus d'échange est réversible, l'échange de cation du métal traceur- Na^+ produit une phase d'échange se comportant comme un mélange idéal.