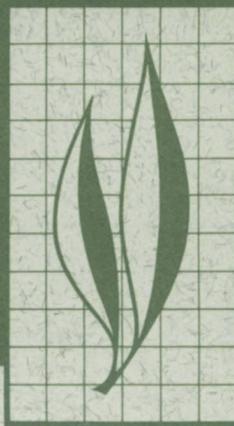


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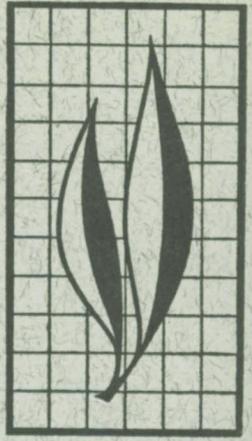


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Cation-Exchange Equilibria on a Yolo Loam

H. E. Jensen and K. L. Babcock

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An experimental study was made of several cation-exchange reactions on a Yolo loam soil by means of a leaching procedure. Adsorption isotherms for the K-Na, K-Mg, K-Ca, and Mg-Ca ion pairs were obtained. An application of thermodynamic equations was used to find the equilibrium constants and free-energy changes for the reactions. Activity coefficients of the adsorbed ions were also calculated. A comparison of various selectivity coefficients was included.

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Cation-Exchange Equilibria on a Yolo Loam¹

INTRODUCTION

IN THE PROCESS of cation-exchange, exchangeable cations adsorbed in the exchanger phase (i.e., the soil particles) are exchanged with cations in the solution phase. When no net transfer of cations between the two phases occurs the system is in a state of equilibrium and the distribution of cations between the two phases may then be described by a cation-exchange equation. Depending on the model assumption, the interface between the two phases may be considered as discrete or diffuse (Babcock, 1963). Many exchange equations and theories based on different assumptions have been proposed, e.g., Kerr (1928), Matson (1929), Vanselow (1932), Gapon (1933), Davis (1950), Eriksson (1952).

Recently, Bolt (1967) gave a review of cation-exchange equations used in soil science. With the exception of the equation derived from double-layer theory (Eriksson, 1952) all of the equations contain an empirical selectivity coefficient which is expected to be constant. However as the models underlying the different equations are still rather simple, there appears to be no reason to expect that any one of the selectivity coefficients will be truly constant over a wide range of conditions. For predictions for practical purposes over a limited range of compositions, one may select the coefficient which best

fulfills the condition of constancy under these circumstances.

Argersinger *et al.* (1950) introduced a thermodynamic approach which was further developed by Gaines and Thomas (1953). Although this approach provides no information about mechanisms and forces of adsorption, it is thermodynamically exact. The Gaines and Thomas theory reduces to that of Argersinger *et al.* when the activity of water is constant. The theory provides equations from which the thermodynamic equilibrium constant, the standard free-energy change for the exchange reaction, and individual activity coefficients of adsorbed cations can be calculated on the basis of an experimentally determined exchange isotherm, using the extra-thermodynamic assumption that the standard chemical potential of adsorbed cations is completely specified by assigning a mole fraction of unity as the standard state (Babcock, 1963).

In our study particular attention was paid to the Argersinger thermodynamic approach, and the present paper presents results of experiments designed to provide data in order to verify the assumption inherent in the theory. Furthermore, experimental data are used to test and compare several of the other models referred to above.

MATERIALS AND EXPERIMENTAL METHODS

The soil used in this study was a Yolo loam from which, in order to avoid possible interference, organic matter had

been removed by treating the soil with 10 per cent hydrogen-peroxide solution in a steam-bath. The soil was air-dried,

¹Submitted for publication February 17, 1972.

TABLE 1
 IONIC STRENGTH AND CATIONIC COMPOSITION OF MIXED SALT SOLUTIONS
 USED IN THE CATION-EXCHANGE EXPERIMENTS

Equivalent fraction	Solution concentrations (meq/l)				Equivalent fraction	Solution concentrations (meq/l)				
	I = 0.100*		I = 0.010*			Mg-Ca z _{Mg}	I = 0.010*		I = 0.001*	
	K ⁺	Na ⁺	K ⁺	Na ⁺			Mg ⁺⁺	Ca ⁺⁺	Mg ⁺⁺	Ca ⁺⁺
K-Na z _K					Mg-Ca z _{Mg}					
0.000.....	0	100	0	10.0	0.000	0.00	6.66	0.00	6.66	
0.050.....	5	95	0.5	9.5	0.100	0.66	6.00	0.06	6.00	
0.100.....	10	90	1.0	9.0	0.300	2.00	4.66	0.20	4.46	
0.200.....	20	80	2.0	8.0	0.500	3.33	3.33	0.33	3.33	
0.300.....	30	70	3.0	7.0	0.700	4.66	2.00	0.46	2.00	
0.500.....	50	50	5.0	5.0	0.900	6.00	0.66	0.60	0.66	
0.700.....	70	30	7.0	3.0	0.950	6.33	0.33	0.63	0.33	
1.000.....	100	0	10.0	0	1.000	6.66	0.00	0.66	0.00	
K-Ca z _K					K-Mg z _K					
	I = 0.001*		I = 0.01*			I = 0.01*		I = 0.001*		
	K ⁺	Ca ⁺⁺	K ⁺	Ca ⁺⁺		K ⁺	Mg ⁺⁺	K ⁺	Mg ⁺⁺	
0.000.....	0.00	6.66	0.00	0.66	0.000	0.00	6.66	0.00	0.66	
0.143.....	1.00	6.00	0.10	0.60	0.143	1.00	6.00	0.10	0.60	
0.333.....	2.50	5.00	0.25	0.50	0.333	2.50	5.00	0.25	0.50	
0.500.....	4.00	4.00	0.40	0.40	0.500	4.00	4.00	0.40	0.40	
0.778.....	7.00	2.00	0.70	0.20	0.778	7.00	2.00	0.70	0.20	
0.895.....	8.50	1.00	0.85	0.10	0.895	8.50	1.00	0.85	0.10	
0.931.....	9.00	0.66	0.90	0.06	0.931	9.00	0.66	0.90	0.06	
1.000.....	10.00	0.00	1.00	0.00	1.000	10.00	0.00	1.00	0.00	

*I = Ionic strength.

crushed to pass a 1-mm sieve, and mixed before subsampling. Eight series of these mixtures, each consisting of eight mixed chloride-salt solutions, were prepared. Table 1 lists the ionic strength of each solution series and the cationic composition of the individual solutions.

The soil was brought to equilibrium with these salt solutions by leaching a soil pad with the solution under study. The leaching runs were carried out in a specially constructed filter funnel which consisted of a cellulose membrane mounted on a coarse glass frit. The inside diameter of the funnel was 36 mm and the cellulose membrane had a maximum porosity of less than 1 μ m. The procedure was to transfer 0.5 to 1.0 g of soil to the funnel containing 25 ml of the solution under study. The suspension was carefully stirred by means of a plunger after which soil particles were allowed to settle and form a pad, which was then leached under vacuum filtra-

tion with 4 liters of the salt solution being studied. When this was accomplished the vacuum was automatically removed by an electronic device, thus preventing drying and subsequent destruction of the soil pad. Preliminary studies showed that ion-exchange equilibrium was reached between soil and solutions by the time that less than 2 liters of the solutions were used.

After leaching was completed the soil was extracted with 200 ml neutral 1 N NH₄OAc. The chloride and the cations resulting in the extract were determined and then, using a correction for soluble salts according to the composition of the mixed salt solution, the exchangeable cations were calculated. Calcium, magnesium, and potassium analyses were carried out using atomic-absorption spectrophotometry, whereas sodium was determined by using emission-flame photometry. Chloride was determined by potentiometric titration

with AgNO_3 as described by Johnson and White (1958). All leaching was done in duplicate at room temperature. The activity coefficients in the mixed

chloride solutions were estimated from data given by Harned and Owen (1958) using the principle of ionic strength in the usual manner (Babcock, 1963).

RESULTS AND DISCUSSION

Cation-adsorption isotherms

Table 2 gives results of the eight series of leaching experiments and the two series of different ionic strength for each of the four pairs of cations under study; in this table x_i and \bar{x}_i are equivalent fractions of the cation i in the solution and exchanger phase, respectively. I is the ionic strength and CEC the cation exchange capacity, which is taken as the sum of the exchangeable metal ions. The absolute amounts of exchangeable cations can be obtained by multiplying the value of CEC by the respective equivalent fractions of cations in the exchanger phase.

For K-Na and K-Mg exchange equilibria the values of CEC are fairly independent of ionic strength and exchanger composition, whereas for equilibria involving calcium ions (i.e., Mg-Ca and K-Ca exchange equilibria) the values of CEC increase with ionic strength and with increasing fraction of calcium ions in the exchanger phase. Adsorption of complex cations such as $\text{Ca}(\text{OH})^+$ and $\text{Mg}(\text{OH})^+$ would lead to an overestimation of CEC (Bower and Truog, 1940; Babcock *et al.*, 1959). This may explain some of the observed variation in CEC. However, such an effect should also be expected in the K-Mg system, which was not observed.

In the case of homovalent exchange equilibria, the K-Na and Mg-Ca systems, the equivalent fraction of cations in the exchanger phase is independent of ionic strength. This is not the case for the monovalent exchange equilibria. For the K-Mg and K-Ca systems, the equivalent fraction of the monovalent cation in the exchanger phase in-

creases with increasing ionic strength in the equilibrium solution.

By plotting equivalent fraction of cations in the exchanger phase as a function of the corresponding fraction in solution and drawing smoothed curves, the adsorption isotherms shown in figure 1 were obtained. For the homovalent exchange equilibria which were not influenced by valence effects or by the effects of ionic strength in the concentration range employed, the broken diagonal lines (fig. 1) can be used as non-preference adsorption isotherms. Thus from figure 1 it can be concluded that K is adsorbed in preference relative to Na, and that Ca is adsorbed in preference relative to Mg.

Isotherms for the K-Mg and K-Ca systems lie below the diagonal lines. However, this does not necessarily indicate that Ca and Mg are adsorbed in preference relative to K. Ionic strength, which cannot appreciably affect the binding energy of the cations (Deist and Talibudeen, 1967), greatly affects the course of the isotherms (Jensen, 1972a), which in the case of heterovalent exchange equilibria cannot therefore be directly interpreted regarding adsorption preference. For monovalent exchange equilibria the diagonal line is therefore not considered as a non-preference adsorption isotherm and therefore it is not plotted.

By using an equation derived by Jensen (1972a) non-preference adsorption isotherms ($\Delta G^\circ = 0$) at ionic strengths corresponding to those used in the experiments have been calculated. Figure 1 shows these isotherms plotted as broken lines. Since the experimental

exchange isotherms for both the K-Mg and K-Ca systems lie above the corresponding non-preference adsorption isotherms, potassium is adsorbed in preference to both Mg and Ca according to free energy considerations.

TABLE 2
FRACTIONS OF CATIONS IN SOIL AS A FUNCTION OF THE CORRESPONDING FRACTIONS IN SOLUTION FOR SEVERAL CATION-EXCHANGE SYSTEMS

Solution equivalent fraction	Soil composition			
	I = 0.010*		I = 0.100*	
K-Na $\bar{x}_K \uparrow$	$\bar{x}_K \uparrow$	CEC ‡ meq/100 g	$\bar{x}_K \uparrow$	CEC ‡ meq/100 g
1.000	1.000	18.04	1.000	18.41
0.700	0.890	18.35	0.878	18.88
0.500	0.790	18.01	0.771	17.93
0.300	0.648	17.55	0.657	18.49
0.200	0.550	17.97	0.574	18.49
0.100	0.409	17.44	0.388	18.12
0.050	0.271	17.43	0.254	18.44
0.000	0.000	18.88	0.000	19.18
K-Mg $\bar{x}_K \uparrow$	I = 0.001*		I = 0.01*	
1.000	1.000	18.00	1.000	18.04
0.931	0.363	17.90	0.670	18.11
0.895	0.323	17.60	0.584	18.19
0.778	0.242	18.47	0.447	18.29
0.500	0.125	18.26	0.251	18.49
0.333	0.093	18.47	0.203	18.52
0.143	0.053	18.38	0.099	18.99
0.000	0.000	18.64	0.000	18.60
Mg-Ca $\bar{x}_{Mg} \uparrow$	$\bar{x}_{Mg} \uparrow$		$\bar{x}_{Mg} \uparrow$	
1.000	1.000	18.64	1.000	18.60
0.950	0.907	18.08	0.912	19.35
0.900	0.831	18.29	0.843	19.28
0.700	0.594	17.98	0.602	19.18
0.500	0.378	17.85	0.374	20.21
0.300	0.210	17.85	0.194	21.23
0.100	0.066	18.80	0.060	21.68
0.000	0.000	19.00	0.000	21.20
K-Ca $\bar{x}_K \uparrow$	$\bar{x}_K \uparrow$		$\bar{x}_K \uparrow$	
1.000	1.000	18.00	1.000	18.60
0.931	0.302	17.80	0.587	18.76
0.895	0.255	17.90	0.500	18.20
0.778	0.200	18.17	0.341	19.40
0.500	0.120	18.65	0.162	20.45
0.333	0.084	18.79	0.128	20.64
0.143	0.054	18.89	0.054	20.82
0.000	0.000	19.00	0.000	21.20

* Ionic strength.
 † Equivalent fraction.
 ‡ Cation-exchange capacity.

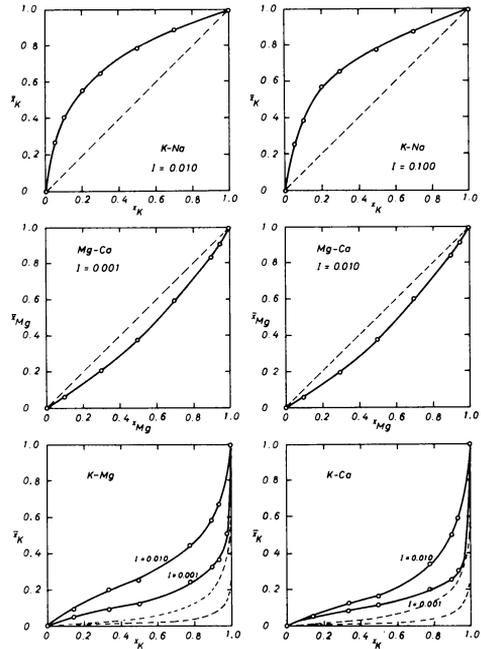
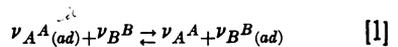


Fig. 1. Cation-adsorption isotherms for several cation-exchange systems. x = equivalent fraction in solution. \bar{x} = equivalent fraction in soil. Broken lines represent nonpreference adsorption isotherms.

Application of 2-phase models

Assuming the system to consist of two discrete phases (i.e., an exchanger phase and a solution phase) the law of mass-action can be applied. The process of cation exchange may be represented as an interchange of ions between the exchanger phase and the solution phase as follows:



The ν with subscripts A and B represent numbers of reacting ions A and B , respectively, (ad) denotes ions in the exchanger phase, while absence of suffix denotes ions in solutions. Assuming the activity of water to be constant, the standard free-energy change, $\Delta G^\circ_{(B-A)}$, the thermodynamic equilibrium con-

stant, $K_{(B-A)}$, and the activity of cations, a_i , are related by the following equation:

$$\frac{a_{B(ad)}^{\nu} a_A^{\nu}}{a_{A(ad)}^{\nu} a_B^{\nu}} = \exp\left(-\frac{\Delta G_{(B-A)}^{\circ}}{RT}\right) = K_{(B-A)} \quad [2]$$

in which R and T are the gas constant and the absolute temperature, respectively.

In order to obtain a cation-exchange equation a theory must be found for the activity of ions in the exchanger phase. Vanselow (1932) assumed that the exchanger phase could be treated in analogy with an ideal solid solution, according to which activities of adsorbed ions are set equal to their mole fraction, N_i ,

in the exchanger phase. Argersinger *et al.* (1950) extended Vanselow's theory to non-ideal exchangers and introduced activity coefficients, f_i , for adsorbed ions defined as

$$f_i = \frac{a_i}{N_i} \quad [3]$$

Substituting equation [3] into equation [2] the following equation is obtained:

$$\frac{f_B^{\nu} N_B^{\nu} a_A^{\nu}}{f_A^{\nu} N_A^{\nu} a_B^{\nu}} = \frac{f_B^{\nu}}{f_A^{\nu}} K_{v(B-A)} = K_{(B-A)} \quad [4]$$

The $k_{v(B-A)}$ defined by equation [4] may be called a selectivity coefficient. Applying the Gibbs-Duhem equation to the exchanger phase and combining with equation [4], the following equations are obtained using a mole fraction of unity as the standard state for adsorbed ions, Argersinger *et al.* (1950):

$$\nu_A \ln f_A = \bar{x}_B \ln k_{v(B-A)} - \int_0^{\bar{x}_B} \ln k_{v(B-A)} d\bar{x}_B \quad [5]$$

$$\nu_B \ln f_B = (\bar{x}_B - 1) \ln k_{v(B-A)} - \int_0^1 \ln k_{v(B-A)} d\bar{x}_B \quad [6]$$

$$\ln K_{(B-A)} = \int_0^1 \ln k_{v(B-A)} d\bar{x}_B \quad [7]$$

In these equations \bar{x}_B is the equivalent fraction of B in the exchanger phase. Thus, if $K_{v(B-A)}$ is known as a function of \bar{x}_B , individual activity coefficients of the adsorbed cations and the thermodynamic equilibrium constant can be calculated by integration of equations [5], [6], and [7], respectively.

From the smoothed curves for the isotherms (fig. 1) values of the equivalent fractions of B in solution x_B were read off for selected values of equivalent fraction of B in the exchanger phase, \bar{x}_B , of 0.1, 0.2, . . . , 0.9. Then the selectivity coefficients, $k_{v(B-A)}$, for the four pairs of cations considered were calculated from equation [4]. The results are given in table 3, except for the K-Ca system at the smallest ionic strength for

which values were not calculated because of difficulties in reading the correct values of \bar{x}_K , especially at high values of x_K . From table 3 it appears that for all systems, save the one in which potassium is absent, the values of $k_{v(B-A)}$ are not constant but always decrease with increasing degree of potassium saturation. For the Mg-Ca system, however, the selectivity coefficient is constant and independent of exchanger composition. Thus, the concept of non-ideality is associated not only with the nature of the exchanger itself but also with the nature of the cations involved. For the present soil the exchanger would be regarded as an ideal exchanger when the Mg-Ca systems are considered, but as a non-ideal exchanger when the K-Na, K-Mg, and K-Ca systems are con-

TABLE 3
SELECTIVITY COEFFICIENTS, ACTIVITY COEFFICIENTS OF ADSORBED CATIONS, AND THERMODYNAMIC EQUILIBRIUM CONSTANTS FOR SEVERAL CATION-EXCHANGE SYSTEMS

Equivalent fraction in soil	Characteristics of adsorbed ions							
	I = 0.010*				I = 0.100*			
	$k_v(K-Na)†$	$f_{Na}‡$	$f_K‡$	$K_{(K-Na)}§$	$k_v(K-Na)†$	$f_{Na}‡$	$f_K‡$	$K_{(K-Na)}§$
0.00.....	7.39	1.000	0.693	5.121	7.39	1.000	0.687	5.077
0.10.....	7.29	0.999	0.703	5.130	7.30	0.999	0.696	5.085
0.20.....	7.10	0.995	0.719	5.130	6.89	0.991	0.730	5.075
0.30.....	6.72	0.982	0.749	5.126	6.48	0.975	0.765	5.084
0.40.....	6.21	0.955	0.788	5.124	6.00	0.950	0.804	5.078
0.50.....	5.37	0.895	0.854	5.124	5.68	0.919	0.837	5.082
0.60.....	4.75	0.837	0.902	5.119	4.88	0.854	0.889	5.080
0.70.....	4.01	0.748	0.958	5.136	4.11	0.764	0.944	5.078
0.80.....	3.62	0.693	0.982	5.130	3.54	0.683	0.980	5.079
0.90.....	3.33	0.645	0.995	5.137	3.16	0.620	0.996	5.076
1.00.....	3.01	0.586	1.000	5.137	2.95	0.580	1.000	5.086
	I = 0.01*				I = 0.001*			
K-Mg x_K	$k_v(K-Mg)†$	$f_{Mg}‡$	$f_K‡$	$K_{(K-Mg)}§$	$k_v(K-Mg)†$	$f_{Mg}‡$	$f_K‡$	$K_{(K-Mg)}§$
0.00.....	142.0	1.000	0.400	22.72	149.0	1.000	0.393	23.01
0.10.....	107.6	0.985	0.460	23.11	113.2	0.986	0.446	22.84
0.20.....	51.8	0.886	0.624	22.76	54.6	0.884	0.609	22.91
0.30.....	28.3	0.760	0.785	22.95	31.2	0.769	0.752	22.94
0.40.....	20.4	0.677	0.873	22.97	20.8	0.666	0.859	23.04
0.50.....	15.7	0.603	0.938	22.91	15.6	0.584	0.931	23.15
0.60.....	13.1	0.543	0.979	23.12	13.4	0.538	0.962	23.05
0.70.....	11.9	0.512	0.995	23.01	11.3	0.482	0.992	23.07
0.80.....	11.3	0.496	0.999	22.74	10.3	0.450	1.000	22.89
0.90.....	11.4	0.496	0.999	22.94	10.7	0.465	0.999	22.96
1.00.....	11.2	0.493	1.000	22.72	10.3	0.448	1.000	22.99
K-Ca x_K	I = 0.01*				Mg-Ca x_{Mg}	I = 0.010*	I = 0.001*	
	$k_v(K-Ca)†$	$f_{Ca}‡$	$f_K‡$	$K_{(K-Ca)}§$		$k_v(Mg-Ca)†$	$k_v(Mg-Ca)†$	
0.00.....	99.5	1.000	0.348	12.05	0.00	0.612	0.611	
0.10.....	39.3	0.955	0.541	12.04	0.10	0.606	0.617	
0.20.....	15.0	0.825	0.817	12.14	0.20	0.618	0.615	
0.30.....	12.1	0.781	0.887	12.19	0.30	0.606	0.604	
0.40.....	10.5	0.746	0.926	12.07	0.40	0.604	0.603	
0.50.....	9.0	0.698	0.966	12.03	0.50	0.615	0.613	
0.60.....	8.2	0.660	0.986	12.08	0.60	0.618	0.615	
0.70.....	7.8	0.636	0.995	12.14	0.70	0.615	0.608	
0.80.....	7.5	0.620	0.996	12.00	0.80	0.626	0.612	
0.90.....	7.6	0.619	0.999	12.25	0.90	0.602	0.613	
1.00.....	7.5	0.614	1.000	12.21	1.00	0.612	0.611	

*Ionic strength.
†Selectivity coefficient.
‡Activity coefficient.
§Equilibrium constant.

sidered. The non-ideality in the present case therefore seems to be associated with the nature of the potassium ion, as it appears only in the systems where potassium ions are present. Such behavior could be associated with the presence of an illitic type of clay minerals, but X-ray diffraction pattern of clays from the Yolo series shows it to be predominantly montmorillonitic (Krishnamoorthy and Overstreet, 1950). Due to the variation in $k_{v(B-A)}$ with exchanger composition it is difficult to compare with results in literature for which the exchanger composition is not given. Values of $k_{v(Mg-Ca)}$ of 0.61, 0.76, and 0.92 for Wyoming bentonite, Yolo clay, and Utah bentonite, respectively, have been reported (Krishnamoorthy and Overstreet, 1950, and Tabik *et al.*, 1962), which are comparable to the value of 0.61 obtained in the present study. For Yolo clay, Krishnamoorthy and Overstreet (1950) obtained results from which a value of $k_{v(K-Na)}$ of 3.33 can be derived. According to results obtained in the present study such a value corresponds to an exchanger composition of 10 per cent Na and 90 per cent K (table 3).

From table 3 it also appears that the selectivity coefficients are fairly independent of ionic strength. This is also evident from figure 2 where the logarithm of the selectivity coefficients for the K-Na and K-Mg systems, respectively, are plotted as a function of the degree of potassium saturation. The thermodynamic equilibrium constants, $K_{(B-A)}$, for the different systems were obtained from plots of $\ln k_{v(B-A)}$ against \bar{x}_B , using graphical integration of equation [7], applying the trapezoidal rule. Then from equation [2] the standard free energy change, $\Delta G^\circ_{(B-A)}$, was calculated. The results are shown in table 4; it is evident that the experimental values of $\Delta G^\circ_{(B-A)}$ and $K_{(B-A)}$ for the various systems considered are determined independently of ionic strength. The negative value of $\Delta G^\circ_{(B-A)}$ for the

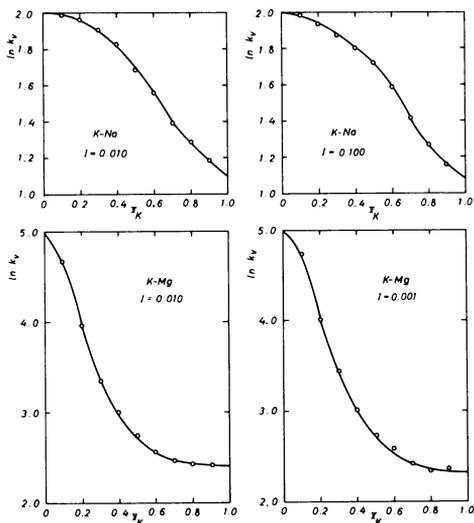


Fig. 2. The Vanselow selectivity coefficient k_v plotted against the mole fraction in the exchanger phase \bar{x} for several cation-exchange systems.

K-Na, K-Mg, and K-Ca systems implies that reaction [1] would proceed to the right from the standard states, thus forming K-soil from Na-soil, Mg-soil, and Ca-soil, respectively. It is generally believed that calcium and magnesium as divalent ions are adsorbed in preference relative to the monovalent potassium ion, but this is not the case in several soils according to the free-energy changes. Values of $\Delta G^\circ_{(K-Ca)}$ for soils and clays of the same order of magnitude as the value obtained in the present study have been reported by Deist and Talibudeen (1967a, 1967b), Hutcheon (1966), and Jensen (1972b). The value of $\Delta G^\circ_{(Mg-Ca)}$ is positive which implies that reaction [1] could proceed to the left from the standard states, thus forming a Ca-soil from a Mg-soil.

Additivity is a necessary requirement for thermodynamic consistency. In order to satisfy this requirement the experimental data must satisfy the following relation:

$$\Delta G^\circ_{(K-Ca)} = \Delta G^\circ_{(Mg-Ca)} + \Delta G^\circ_{(K-Mg)} \quad [8]$$

TABLE 4
STANDARD FREE-ENERGY CHANGE AND THERMODYNAMIC EQUILIBRIUM
CONSTANTS FOR SEVERAL CATION-EXCHANGE SYSTEMS

Ionic strength I	Standard free-energy change				Equilibrium constants			
	$\Delta G^\circ_{(K-Na)}$	$\Delta G^\circ_{(Mg-Ca)}$	$\Delta G^\circ_{(K-Mg)}$	$\Delta G^\circ_{(K-Ca)}$	$K_{(K-Na)}$	$K_{(Mg-Ca)}$	$K_{(K-Mg)}$	$K_{(K-Ca)}$
0.001.....	—	291	-1856	—	—	0.61	22.93	—
0.010.....	-968	291	-1854	-1474	5.12	0.61	22.85	12.04
0.100.....	-963	—	—	—	5.08	—	—	—

Table 4 shows that the data satisfy this requirement within reasonable limits of experimental uncertainty. Using this triangular rule, values of $k_{v(Na-Ca)}$ and $k_{v(Na-Mg)}$ can be calculated from the results in table 3. The respective values calculated in this way appear to be fairly constant in a range of \bar{x}_{Na} from 0.2 to 0.8, which suggests ideal exchanger behavior also for (Na-Ca) and (Na-Mg) systems in contrast to the non-ideality of the corresponding potassium systems.

The activity coefficients for the adsorbed ions were obtained by integration of equations [5] and [6]; results are listed in table 3. For the K-Na and K-Mg systems the data are presented graphically in figure 3; in accordance with the theory activity coefficients are independent of ionic strength. By using the obtained activity coefficients for adsorbed ions and the corresponding selectivity coefficients, the values of the thermodynamic equilibrium constant were recalculated by using equation [4]. At each exchanger composition the value should agree with the value found by integrating over all points in equation [7] the values which are listed in table 4. In all cases the agreement is excellent. However, it should be realized that this agreement does not confirm the validity of the assumptions inherent in the theory; it confirms only the consistency in the calculations. Applicability of the

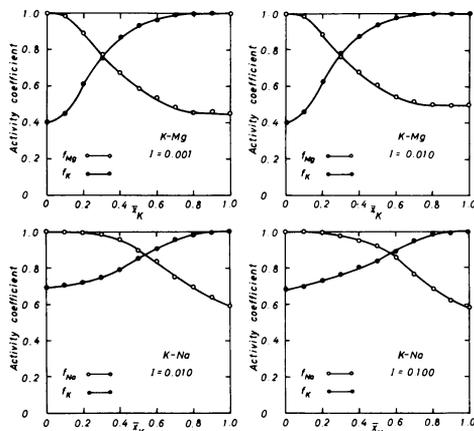


Fig. 3. Activity coefficients or adsorbed cations plotted against the mole fraction in the exchanger phase \bar{x} for several cation-exchange systems.

theory is demonstrated by the fact that the various parameters which can be obtained are independent of ionic strength. Even though the perspective for interpretative usage of individual activity coefficients as obtained by this method may be limited (El-Sayed *et al.*, 1970) it is appropriate to summarize experimental data in terms of a plot relating values of $k_{v(B-A)}$, f_B , and f_A to the exchanger composition.

Many equations have been proposed to describe monovalent exchange equilibria. Among these are the following four equations in which B and A are assumed to be monovalent and divalent cations, respectively:

$$\frac{N_B^2 a_A}{N_A a_B^2} = k_{v(B-A)} \quad [9]$$

$$\frac{\bar{x}_B \sqrt{a_A}}{\bar{x}_A a_B} = k_{g(B-A)} \quad [10]$$

$$\frac{n_B^2 a_A}{n_A a_B^2 (n_A + q n_B)} = k_{d(B-A)} \quad [11]$$

$$\frac{\bar{x}_B^2 a_A}{\bar{x}_A a_B^2} = k_{e(B-A)} \quad [12]$$

Equations [9], [10], and [11] have been introduced by Vanselow (1932), Gapon (1933), and Davis (1950), re-

spectively; equation [12] has been used by Gaines and Thomas (1955). In equation [11] n_i is moles of adsorbed ions and q is a function of the assumed number of nearest neighbors of adsorbed ions which are assumed to be localized. The different ion exchange equations rest on different model assumptions, and if the assumptions underlying a given equation are met by a particular cation exchanger, the respective exchange "constant" should yield a constant value independent of exchanger composition.

Comparing the exchange constants defined above, the following equation is found:

$$\begin{aligned} k_{v(B-A)} &= k_{e(B-A)} \frac{4}{1 + \bar{x}_B} = k_{g(B-A)}^2 \frac{4 - 4\bar{x}_B}{1 + \bar{x}_B} \\ &= k'_{d(B-A)} \frac{2 + 2\bar{x}_B}{3 + \bar{x}_B} = k''_{d(B-A)} \frac{3 + 3\bar{x}_B}{5 + \bar{x}_B} \end{aligned} \quad [13]$$

In this equation $k'_{d(B-A)}$ and $k''_{d(B-A)}$ are based on an assumed number of nearest neighbors of adsorbed ions of 4 and 6, respectively.

Table 5 lists relative values of the different exchange constants (assuming the Vanselow selectivity coefficient to be constant and unity). In the present study the Vanselow selectivity coefficients for K-Mg and K-Ca systems decrease with potassium saturation. Since the values of the various constants rela-

tive to those of the Vanselow selectivity coefficient increase with \bar{x}_B (table 3), each of them would give a more constant value for the systems considered than those of the Vanselow selectivity coefficient. Although its derivation seems to be a bit strained, it appears that $k_{g(B-A)}$ among the constants considered fulfills best the condition of constancy, and therefore it is possible that it may have practical applications in this particular Yolo soil.

TABLE 5
RELATIVE VALUES OF DIFFERENT SELECTIVITY COEFFICIENTS

Soil equivalent fraction	Selectivity coefficients				
	$k_{v(B-A)}$	$k_{e(B-A)}$	$k_{g(B-A)}$	$k'_{d(B-A)}$	$k''_{d(B-A)}$
0.1.....	1.0	0.275	0.553	0.709	0.647
0.2.....	1.0	0.300	0.612	0.750	0.692
0.3.....	1.0	0.325	0.681	0.789	0.736
0.4.....	1.0	0.350	0.764	0.824	0.778
0.5.....	1.0	0.375	0.866	0.857	0.818
0.6.....	1.0	0.400	1.000	0.889	0.857
0.7.....	1.0	0.425	1.190	0.919	0.895
0.8.....	1.0	0.450	1.500	0.947	0.931
0.9.....	1.0	0.475	2.179	0.974	0.966

Application of double-layer theory

Cation-exchange equations which contained an exchange constant to be determined experimentally were discussed in the previous section. The thermodynamic equilibrium constant $K_{(B-A)}$ and the standard free energy change $\Delta G^\circ_{(B-A)}$ are also to be experimentally determined. The cation-exchange equation derived from double-layer theory (Eriksson, 1952) offers a means of calculating the coulombic energy component of the total standard free energy change (Jensen, 1972c). From this an estimation of the relative contribution of coulombic and non-coulombic interaction to the total interaction between ions and colloid can be made. The equation derived by Eriksson is:

$$\bar{x}_B = \frac{r}{\delta\sqrt{\beta}} \operatorname{Sinh}^{-1} \left(\frac{\delta\sqrt{\beta}}{r + 4v\sqrt{c_A}} \right) \quad [14]$$

in which B and A are mono- and divalent cations, respectively, σ and β are surface charge density, meq/cm², and a constant equal to 10.8×10^{14} cm/mmole, respectively; c is concentration in moles/l; and v is related to the interaction between clay particles and is often conventionally taken as unity, which corresponds to infinite distance, whereas $r = c_B / \sqrt{c_A}$.

By using activities rather than concentrations, and the activity ratio, r' , rather than the concentration ratio, and assuming a surface charge density of 1.1×10^{-7} meq/cm², which corresponds to that of montmorillonite, the relation between \bar{x}_K and $r' = a_K / \sqrt{a_{Ca}}$ was obtained from equation [14]. The results are shown in figure 4 as a broken line. As the activity coefficients for Ca and Mg ions in solution are of similar magnitude, the theoretical relation applies equally well to the K-Mg systems. In figure 4 the experimental values of \bar{x}_K are plotted as a function of r' for both K-Ca and K-Mg systems. Even though the theoretical and experimental rela-

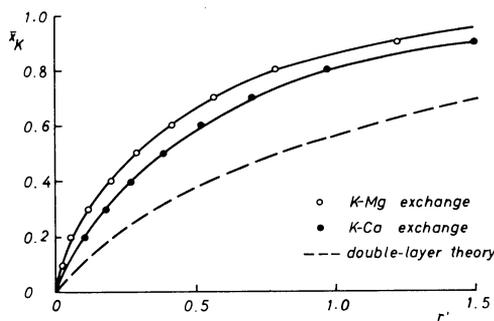


Fig. 4. Equivalent fraction of potassium in soil \bar{x}_K in relation to the activity ratio r' calculated from double-layer theory in comparison to corresponding experimentally determined relations

tions have a similar form, the discrepancies are obvious. In some cases the double-layer theory is reported to describe adequately cation equilibria—e.g., in systems of Na-Ca illite (Bolt, 1955); K-Ca montmorillonite (Lagerwerff and Bolt, 1958); and Na-Ca soils (Pratt and Bair, 1962)—but in many cases—e.g., in other systems of K-Ca illite (Lagerwerff and Bolt, 1958); K-Ca montmorillonite and kaolinite (Jensen, 1972c); and Na-Ca soils (Bower, 1959); Bower and Hatcher, 1962; Pratt *et al.*, 1962, Pratt and Grower, 1964)—the double-layer theory has failed to describe the equilibria if not corrected with a factor for surface-charge density.

Table 6 lists experimental values of the thermodynamic equilibrium con-

TABLE 6
STANDARD FREE-ENERGY CHANGE AND THERMODYNAMIC EQUILIBRIUM CONSTANTS CALCULATED FROM DOUBLE-LAYER THEORY IN COMPARISON TO CORRESPONDING EXPERIMENTALLY DETERMINED VALUES

System	Equilibrium constant	Free-energy change
	$K_{(B-A)}$	$\Delta G^\circ_{(B-A)}$
K-Ca.....	12.0	-1474
K-Mg.....	22.9	-1855
Double-layer theory.....	2.18	- 456

stant and the standard free-energy change for K-Mg and K-Ca systems together with corresponding values calculated from double-layer theory according to Jensen (1972c). According to these calculations the coulombic energy component of the standard free energy change is 25 and 30 per cent for K-Ca and K-Mg systems, respectively. The main part is therefore due to spe-

cific interactions and is probably associated with specific adsorption of potassium ions. The adsorption may take place at the edges of clay minerals (Becket and Nafady, 1967) as well as at the planar surfaces as the potassium ion is of the right size to establish a favorable 12-coordination with opposite hexagonal oxygen rings of adjoining unit layers (Olphen, 1963).

SUMMARY

For several pairs of cation exchange, the properties of a Yolo loam soil were investigated. Cation-exchange isotherms at two ionic strengths for K-Na, Mg-Ca, K-Ca, and K-Mg systems were obtained by using a leaching technique. For homo-valent exchange systems, the isotherms were independent of ionic strength whereas in the case of heterovalent exchange systems the well-known valence or dilution effect appeared and greatly affected the course of the isotherms.

For each cation pair the values of the Vanselow selectivity coefficient were calculated at different exchanger compositions. For the systems involving K ions the Vanselow selectivity coefficient was dependent on ionic strength and indicated a selectivity for K over Na, Mg, and Ca which decreased with increasing K-saturation. However, for the Mg-Ca system the Vanselow selectivity coefficient was independent of ionic strength and exchanger composition, and indicated a constant selectivity for Ca over Mg. Thus soil may be considered as an ideal exchanger with regard to Mg-Ca exchange, whereas for systems involving K the exchanger exhibits non-ideal exchanger behavior.

The respective values of the thermodynamic equilibrium constant, the standard free-energy change, and the individual activity coefficients of adsorbed cations were calculated by applying the Argersinger thermodynamic approach

to the isotherms for the various exchange systems; all of these parameters were found to be independent of ionic strength. It is therefore concluded that the theory is valid for the cation-exchange systems considered. By means of the Vanselow selectivity coefficients, and the individual activity coefficients for adsorbed cations, the thermodynamic equilibrium constant could be recalculated for each data point.

The coulombic component of the standard free-energy change was calculated from double-layer theory. For K-Ca and K-Mg systems the coulombic energy component was 25 and 30 per cent, respectively, of the total standard free-energy change. Thus for these systems it is concluded that non-coulombic interactions between soil colloids and cations is predominant and is most likely to be specific adsorption of potassium ions.

For the heterovalent exchange systems studied, several exchange constants were compared to the Vanselow selectivity coefficient. It appeared that the Gapon exchange constant best fulfilled the condition of constancy and therefore may have practical application for this particular soil. However, the exchanger behavior may be better expressed by plotting the Vanselow selectivity coefficient and the individual activity coefficients for adsorbed cations against exchanger composition for the various ion pairs.

LITERATURE CITED

- ARGERSINGER, W. J., A. W. DAVIDSON, and O. D. BONNER
1950. Thermodynamics and ion exchange phenomena. *Kansas Acad. Sci. Trans.* 53:404-410.
- BABCOCK, K. L.
1963. Theory of the chemical properties of soil colloidal systems at equilibrium. *Hilgardia* 34:417-542.
- BABCOCK, K. L., R. M. CARLSON, R. M. SCHULZ, and R. OVERSTREET
1959. A study of the effect of irrigation water composition on soil properties. *Hilgardia* 29:155-70.
- BOLT, G. H.
1955. Ion adsorption by clays. *Soil Sci.* 79:267-276.
1967. Cation exchange equations used in soil science—a review. *Neth. J. Agric. Sci.* 15:81-103.
- BOWER, C. A.
1959. Cation-exchange equilibria in soils affected by sodium salts. *Soil Sci.* 88:32-35.
- BOWER, C. A., and E. TRUOG
1940. Base exchange capacity determination as influenced by nature of the cation employed and formation of basic exchange salts. *Soil Sci. Soc. Amer. Proc.* 5:86-89.
- BOWER, C. A., and J. T. HATCHER
1962. Characterization of salt-affected soils with respect to sodium. *Soil Sci.* 93:275-80.
- DAVIS, L. A.
1950. Ion exchange and statistical thermodynamics. *J. Colloid Sci.* 5:71-79.
- DEIST, J., and O. TALIBUDEEN
1967*a*. Ion exchange in soils from the ion pairs K-Ca, K-Rb and K-Na. *J. Soil Sci.* 18:125-37.
1967*b*. Thermodynamics of K-Ca ion exchange in soils. *J. Soil Sci.* 18:138-48.
- EL-SAYED, M. H., R. G. BURAU, and K. L. BABCOCK
1970. Thermodynamics of Copper (II)—Calcium exchange on bentonite clay. *Soil Sci. Soc. Amer. Proc.* 34:397-400.
- ERIKSSON, E.
1952. Cation exchange equilibria on clay minerals. *Soil Sci.* 74:103-13.
- GAINES, G. L., and H. C. THOMAS
1953. Adsorption studies on clay minerals. II. A formulation of the thermodynamics of exchange adsorption. *J. Chem. Phys.* 21:714-18.
1955. Adsorption studies on clay minerals. V. Montmorillonite-caesium-strontium at several temperatures. *J. Chem. Phys.* 23:2322-25.
- GAPON, E. N.
1933. On the theory of exchange adsorption in soils. *J. Gen. Chem. U.S.S.R.* 3:144-63.
- HARNED, H. S., and B. B. OWEN
1958. The physical chemistry of electrolytic solutions. Reinhold Pub. Corp. N.Y. Pp 645.
- HUCHEON, A. T.
1966. Thermodynamics of cation exchange on clay: Ca-K montmorillonite. *J. Soil Sci.* 17:339-55.
- JENSEN, H. E.
1972*a*. Cation adsorption isotherms derived from mass-action theory. *Royal Vet. Agric. Univ. Copenhagen. Yearbook*: 88-103.
1972*b*. Potassium-calcium exchange on a montmorillonite and a kaolinite clay. I. A test on the Argersinger thermodynamic approach. *Agrochimica* (in press).
1972*c*. Potassium-calcium exchange on a montmorillonite and a kaolinite clay. II. Application of double-layer theory. *Agrochimica* (in press).
- JOHNSON, C. M., and H. ULRICH
1959. Plant analysis and analytical methods. *Calif. Agric. Sta. Bul.* 766.
- KERR, H. W.
1928. The nature of base exchange and soil acidity. *J. Amer. Soc. Agron.* 20:309-35.
- KRISHNAMOORTHY, C., and R. OVERSTREET
1950. An experimental evaluation of ion exchange relationships. *Soil Sci.* 69:44-53.
- LAGERWERFF, J. V., and G. H. BOLT
1959. Theoretical and experimental analysis of Gapon's equation for ion exchange. *Soil Sci.* 87:217-22.
- MATSON, S.
1929. The laws of colloidal behaviour. I. *Soil Sci.* 23:179-220.

OLPHEN, H. VAN

1963. An introduction to colloid chemistry. Interscience Pub. N.Y. Pp 301.

PRATT, P. F., and F. L. BAIR

1962. Cation-exchange properties of some acid soils of California. *Hilgardia* 33:689-706.

PRATT, P. F., O. D. WHITTING, and B. L. GROVER

1962. Effect of pH on sodium-calcium exchange equilibria in soils. *Soil Sci. Soc. Amer. Proc.* 26:227-30.

PRATT, P. F., and B. L. GROVER

1964. Monovalent-divalent cation-exchange equilibria in soils in relation to organic matter and type of clay. *Soil Sci. Soc. Amer. Proc.* 28:32-35.

TABIKH, A. A., I. BARSHAD, and R. OVERSTREET

1960. Cation-exchange hysteresis in clay minerals. *Soil Sci.* 90:41-53.

VANSELOW, A. P.

1932. Equilibria of the base exchange reactions of bentonites, permutites, colloids and zeolites. *Soil Sci.* 33:95-113.

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