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ABSTRACT

A thermodynamic treatment of cation exchange equilibria was used to interpret K-Al exchange equilibria in 0.01N chloride solutions for 9 common acid soils of Malaya. In 7 of the 9 soils, K was adsorbed more strongly than Al while for the remaining 2, the reverse was the case. The standard free energy for formation of K-soil from Al-soil varied from −2550 to 900 calories/mole.

In all soils, the activity coefficient of the adsorbed K ions, f_K*, first increased and then decreased with decreasing K-saturation, while* f_{Al}*, the activity coefficient of the adsorbed Al ions, decreased continuously with decreasing Al-saturation. Between soils, changes in* f_K *with K saturation varied much more than changes in* f_{Al}*. Excess free energy functions for* $Al \rightarrow K$ *exchange calculated from* (f_K, f_{Al}) *values for the soils showed distinct differences between all soils. For soils containing micaceous minerals, these differences in the surface chemistry of the soils were related to the release of initially non-exchangeable potassium in the soil to Pueraria phaseoloides in glass-house experiments.*

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K-Al exchange was studied by many workers in clays (Nye *et al.*, 1961 ; Clark & Turner 1965 ; Coulter 1969 ; Foscolos 1968) and some British soils (Nye *et al.* 1961 ; Coulter 1969) using the Law of Mass Action or the statistical approach (Krishnamoorthy & Overstreet 1949) on a thermodynamic basis. In this work, a rigorous thermodynamic approach (Gaines & Thomas 1953) is applied for the first time to K-Al exchange equilibria in acid soils of Malaya (Singh 1970).

EXPERIMENTAL

Tables 1 and 2 describe the soils used which were dried (55°C) and ground to 72 mesh. The soils differ widely in their physical and chemical properties and in their clay mineralogical composition. The

TABLE 1

Description of Soils

Series	Soil Group[a] (Parent Material)	Less than 2μ Clay %	Org. C[b] %	pH[c]	Surface area[d] 2—1 mg	Clay Minerals[e] % of clay content 1 : 1	2 : 1 Chl/Verm	2 : 1 Mont/Ill[f]
Rengam	Latosal (Granite)	49	2.0	4.0	111	80	1-5	0
Serdang	Latosol (Sandstone)	36	1.1	4.1	62	50-65	5-10	35-50
Selangor	Gley (Recent marine Alluvium)	45	2.0	3.8	188	50-65	0	30-50
Kuantan	Latosol (Basalt)	79	2.4	4.5	248	65-80	0	0
Prang	Laterite (Iron-rich shale)	34	1.4	4.4	76	65-80	5-10	0
Segmat	Latosol (Andesite)	82	2.1	4.9	149	65-80	0	0
Batu Anam	Latosol (Iron-poor Shale and Mudstone)	85	1.6	4.2	66	20-30	0	50-65
Chemor	Latosol (Riverine Alluvium)	18	1.2	4.2	44	80	10-20	0
Ulu Tiram	Latosol (Riverine Alluvium)	20	0.9	4.5	62	80	1-5	0

a : Guha (1965)
b : Walkley & Black's Method (Piper, 1950)
c : 1 : 10, 0.1N KCl
d : Courtesy of A.G. Rawson & O. Talibudeen, Rothamsted Experimental Station, U.K.
e : Courtesy of J.G. Pickering & K. Norrish, C.S.I.R.O., Adelaide.
f : Chl = Chlorite, Verm = Vermiculite, Mont = Montmorillonite, Ill = Illite.

TABLE 2

Description of Soils and K-uptake in Exhaustive Cropping with Pueraria.

Series	% K_2O in Clay fraction	CEC of Clay fraction me/100g	Exchangeable K	K-uptake[g] by Pueraria	Non-exchangeable[h] K uptake
			me/100g soil		
Rengam	0.1	11	0.14	0.19	0.05
Serdang	2.4	21	0.11	0.47	0.36
Selengor	2.0	30	0.40	0.76	0.36
Kuantan	0.05	12	0.10	0.08	—0.02
Prang	0.06	13	0.10	0.13	0.03
Segamat	0.06	11	0.16	0.09	—0.07
Batu Anam	4.04	10	0.18	0.33	0.15
Chemor	0.22	18	0.06	0.04	—0.02
Ulu Tiram	0.49	14	0.06	0.05	—0.01

g : Singh & Talibudeen (1969). These figures are slightly different from those in the quoted reference since subsequent croppings to exhaustion and corrections for root and seed contents have been introduced since the referred publication.

h : Non-exchangeable K uptake = K-uptake by *Pueraria* minus exchangeable K.

pHs of the soils is between 3.8 to 4.9. At this pH, the clays are predominantly Al-clays, the exchangeable K contents of the soils being about 1.7 to 7.8% only (Singh & Talibudeen 1969).

Exchange equilibria at 22°C were achieved as follows: 2g soil in a 100 ml pre-weighed centrifuge tube was wetted overnight at 40 per cent moisture content. 20 ml of the respective K-Al solutions whose pH had been adjusted to a pre-selected value (3.0 — 4.0), were added to the different tubes, shaken for 1 hour, and centrifuged at 40,000 g. The supernatant solution was decanted and a fresh lot of the chloride solutions added. The procedure was repeated until the original chloride solution came through unchanged. Five equilibrations were found to be sufficient. The final filtrate was collected and analysed for K in a Unicam SP 900 Flame spectrophotometer and for Al by the Aluminon method (Chenery 1948).

The entrained solution was determined by weighing the tube after the final decantation. The soil was then extracted (overnight shaking) 4 times with fresh lots of 50 ml N NH_4Cl at pH 4.0. The combined extract was analysed for K and Al. The amounts of K and Al extracted were corrected for the amounts of K and Al in the entrained solution and for the non-exchangeable Al solubilised during the extraction, to obtain the contents of exchangeable K and Al.

RESULTS AND DISCUSSION

Conventional K : Al adsorption isotherms

Conventional K : Al adsorption isotherms for the 9 soils at a electrolyte concentration of 0.01N and initial pH of equilibrating solutions at 4.0 are shown in Fig. 1. Adsorption isotherms of two soils (Selangor and Batu Anam) obtained at two pHs, 3.0 and 4.0, were identical, indicating that differences inH^+ did not affect the K : Al adsorption isotherms.

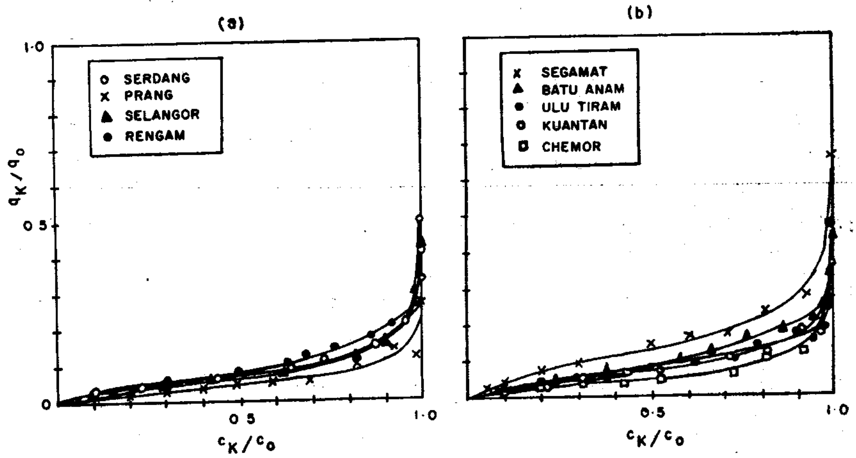

Fig. 1 Conventional K : Al adsorption isotherms for Malayan soils at an electrolyte concentration of 0.01N and pH of equilibrating solutions at 4.0

The exchange isotherms were all sigmoidal and showed a strong preference for Al to K in all the soils. The Al-preference decreased with decrease in electrolyte concentration and with increase in K-saturation. The exchange isotherms did not exhibit any selectivity reversal.

Selectivity coefficients

Selectivity coefficients (K_C) were calculated for the reaction

$$\text{Al-soil} + 3K^+ \rightleftarrows 3\text{K-soil} + Al^{+++}$$

from the relation

$$K_C = \frac{(q_K/q_O)^3\ (1-c_K/c_O)}{(1-q_K/q_O)\ (c_K/c_O)^3 c_O^2}\ \frac{\gamma_{Al}}{(\gamma K)^3}$$

where o_K/q_O and c_K/c_O are equivalent ion fractions of K in soil and solution phases respectively ; q_O is the sum of the exchangeable ions, K and Al, on the exchanger ; c_O is the total electrolyte concentration in eq./l and γ_{Al} and γ_K are activity coefficients of Al and K respectively in the equilibrium solution.

The variation of the selectivity coefficient with q_K/q_O are shown in Fig. 2 for c_o = 0.01N. Due to the difficulty in attaining high K-saturation values were obtained by linear extrapolation. The ln K_C : qK/q_O relationship is sigmoidal for Rengam and Chemor series indicating the presence of possibly 3 types of adsorption sites : K-specific sites at small K-saturations, non-specific sites at medium K-saturations and Al-specific sites at larger K-saturations. For the other soils, the curves indicate the first two types of sites only.

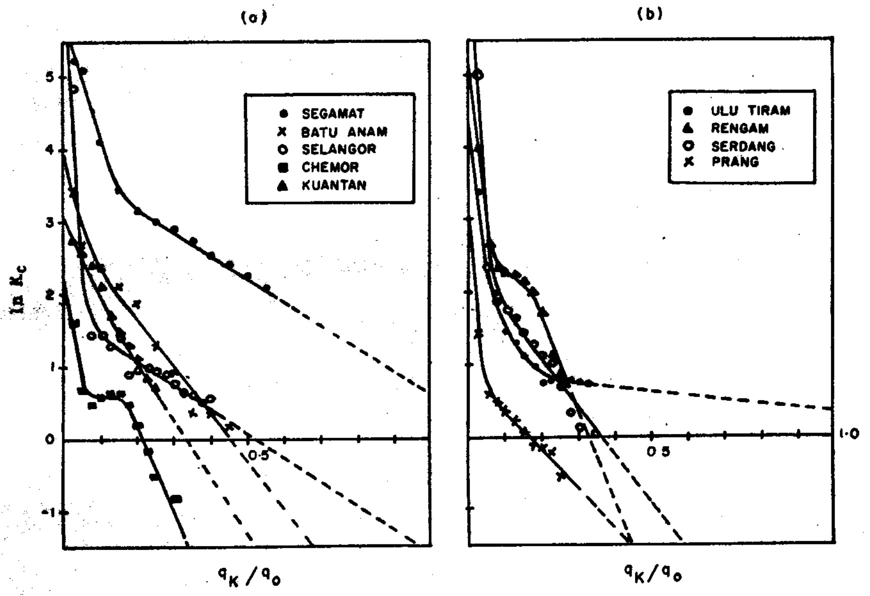

Fig. 2. Selectivity coefficients for K : Al exchange in Malayan soils in 0.01N electrolyte solution.

Standard free energies of exchange

The thermodynamic equilibrium constant K was obtained by graphically integrating the relationship between ln K_C and q_K/q_O given by

$$\ln K = 2 + \int_0^1 \ln K_C \, d(q_K/q_O)$$

using Simpson's quadrature formula (Scarborough 1958). From the values of K, standard free energies of exchange were calculated from

$$\Delta G_0 = -RT \ln K$$

Values of ΔG_0 are given in Table 3.

TABLE 3

Standard free energies of exchange, ΔG_0, for the reaction Al-soil → 3K-soil in 0.01N chloride solution

Soil					ΔG_0 cal/mole
Rengam	...	...	...	...	146
Serdang	...	...	...	...	— 713
Selangor	...	...	...	...	—1293
Kuantan	...	...	...	...	— 429
Prang	...	...	...	...	— 111
Segamat	...	...	...	...	—2541
Batu Anam	...	...	...	...	— 999
Chemor	...	...	...	...	900
Ulu Tiram	...	...	...	...	—1653

The values ΔG_0 are negative for 7 of the 9 soils investigated, indicating that formation of K-soil is preferred to Al-soil in these soils at $c_0 = 0.01N$. (Measurements with 0.1N chloride solution showed that increasing the electrolyte concentration reduces this K-preference). The small K-ion (diameter 4A°) is therefore bound more strongly than $[Al(H_2O)_6]^{3+}$ (diameter 8A°) in these soils since it presumably can approach the surface more closely resulting in a stronger electrostatic force of attraction. On the other hand, the positive ΔG_0 values for the Rengam and Chemor series soils indicate that in these soils, the Al-soil is preferentially formed.

Activity coefficients of adsorbed ions

The activity coefficients of adsorbed K and Al ions were calculated using the equations by Gaines and Thomas (1953).

$$\ln f_K^3 = (1 - q_K/q_O)\,(2 - \ln K_C) + \int_{q_K/q_O}^{1} \ln K_C \, d(q_K/q_O)$$

$$\ln f_{Al} = -(q_K/q_O)\,(2 - \ln K_C) + \int_{0}^{q_K/q_O} \ln K_C \, d(q_K/q_O)$$

The activity coefficients f_K and f_{Al} are shown in Fig. 3

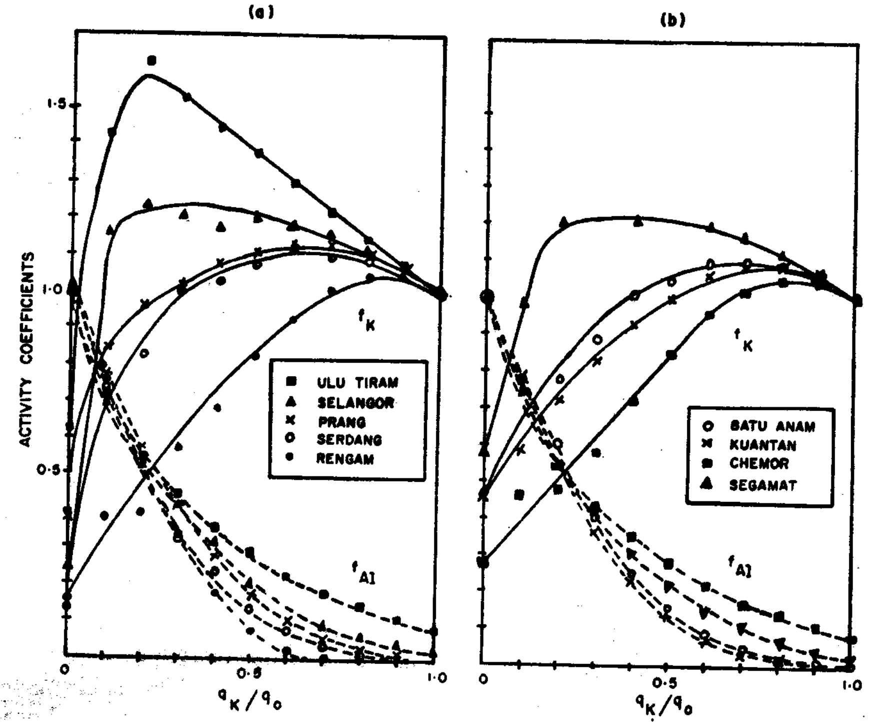

Fig. 3. Activity coefficients of adsorbed K^+ and Al^{3+} in Malayan soils in 0.01N electrolyte solution.

for c_o = 0.01N. For all soils, f_K increased gradually with decreasing K-saturation to a maximum value and then decreased sharply with further decreases in the saturation. The f_{Al} values on the other hand, decreased continuously with decrease in Al-saturation. Differences in f_K values for the various soils are fairly large whereas differences in f_{Al} values are less marked indicating that the differences in clay mineralogy between the soils affected f_K more than f_{Al}.

The behaviour of f_K is similar to that of K-Ca exchange reported by Deist and Talibudeen (1967) for British soils. No values of f_{Al} are available in the literature for comparison.

The values of f_K are relative to a standard state which is taken as the mono-ion solid and assigned an f_K value of 1. A value greater than 1 indicates that the freedom of movement of the ions increases while a value less than 1 shows the reverse. The initial increase in f_K, from the standard state value of 1, as the K-saturation decreased, indicated that as more of the larger Al^{3+} replaced K^+ the freedom of movement of K ions increased which may be due to an increase in inter-layer space. After the maximum increase in inter-layer space, further replacement of K by Al would not increase the freedom of movement of K ions. At low K-saturations, the smaller activity coefficients of the K ions in the Stern layer and other 'specifically' adsorbed K ions would contribute increasingly to f_K causing the observed decrease in f_K as K-saturation fell to low levels. Replacing Al^{3+} by the smaller K^+ would cause a decrease in inter-layer space and therefore in f_{Al}. At lower Al-saturations, the smaller activity coefficients of Al ions in the Stern layer will further reduce f_{Al}. This would account for the observed continuous decrease in f_{Al} with decreasing Al-saturation, unlike f_K which initially increased and then decreased with decrease in K-saturation.

Use of thermodynamic functions to predict release of non-exchangeable K in soil to plants

Values of "non-exchangeable" K uptake by *Pueraria* in glasshouse cropping experiments are given in Table 2. These are calculated as the difference between total K uptake and exchangeable K. 3 soils (Serdang, Selangor and Batu Anam) released appreciable amounts of non-exchangeable K to the crop while Rengam and Prang soils released only small amounts. In the case of 4 soils however (Segamat, Kuantan, Chemor and Ulu Tiram) K uptake was less than exchangeable K (negative values of non-exchangeable K uptake). In 3 of these soils, the exchangeable K not taken up is $\leqslant$ 0.22 me/100g. This small amount may be considered within experimental error suggesting that all the exchangeable K is taken up. Also, *Pueraria* appears unable to extract some of the exchangeable K held at sites at very small K potentials in the soil. This seems especially true of the Segamat soil from which 0.07 me/100g of exchangeable K is not taken up by the crop. Conventional adsorption isotherms and ΔG_0 values both support a greater presence of highly specific sites for K in this soil than in the other soils.

The minerals in the soil, particularly in the clay fraction, influence mainly the changes in f_K with the K-saturation of the adsorbed ions (Talibudeen 1971). 2 of the 9 soils, Kuantan and Segamat, described in this paper contain varying amounts of 1 : 1 type minerals and sesquioxides—these should not and do not release any "non-exchangeable K" in exhaustive cropping by *Pueraria*, although the $f_K : q_K/q_O$ relationship of the exchangeable cations is similar to those of soils containing 2 : 1 minerals that do release "non-exchangeable" K. Soils containing only chloritic-vermiculitic forms of the 2 : 1 minerals as well—Prang, Rengam, Chemor and

Ulu Tiram—release little or no "non-exchangeable" K on cropping. Of these, the last three have ($f_K : q_K/q_O$) relationships similar in shape, i.e. f_K rises sharply and linearly with q_K/q_O from small initial values to maxima at $q_K/q_O = 0.8$, 0.8 and 0.2 respectively, and then decreases linearly to the standard state value at $q_K/q_O = 1.0$. This indicates clearly that only one mineral phase is involved in $Al \rightarrow K$ exchange at small values of q_K/q_O, that this phase prefers K very strongly and is, therefore, likely to release little, if any, "non-exchangeable" K.

The 'Prang' soil gives an anomalous ($f_K : q_K/q_O$) relationship that is similar to those of the remaining soils—Serdang, Selangor and Batu Anam. These 3 soils also contain appreciable amounts of montmorillonite and/or hydrous micas, release moderate amounts of non-exchangeable K and their f_K values decrease sharply only below $q_K/q_O = 0.1$. Above $q_K/q_O = 0.1$., f_K rises slowly to a maximum and back to the standard state value at $q_K/q_O = 1.0$ in a broad smooth curve. This pattern is not too dissimilar to that shown in K : Ca exchange by soils releasing much non-exchangeable K except for the sharp decrease in f_K below $q_K/q_O = 0.1$ in K : Al exchange (Talibudeen, this conference).

This latter anomaly seems to be resolved by considering the relative change in the values of f_K and f_{Al} with q_K/q_O. In contrast with the f_{Ca} values in K : Ca exchange, f_{Al} values decrease much more sharply in K : Al exchange in these acid soils. The excess free energy of mixing, ΔG_E, (calculated analogously to that in K : Ca exchange, Talibudeen, this conference, using the equation of Barrer *et al*, 1963) which takes into account this relative change, shows that this function changes much less with q_K/q_O for soils with large proportions of montmorillonitic-illitic 2 : 1 minerals (Serdang, Selangor and Batu Anam) than for soils containing chloritic/vermiculitic components only (Rengam, Chemor and Prang) (Figure 4), predicting, therefore, the release of "non-exchangeable" K from their sub-surface layers if the K concentration in the soil solution was vanishingly small. The anomalous Ulu Tiram soil, containing <5% of chloritic/vermiculitic 2 :1 minerals, gives a similar pattern but does not release any "non-exchangeable" K; this suggests that its 2 : 1 mineral content differs greatly in quantity and K-fixing ability than that in Rengam soil. The clay mineralogy of the two soils is very similar but their total K contents are very different (see Table 2).

Thus, from a knowledge of the C.E.Cs. of the soil and its clay fraction and thermodynamic functions derived from the K : Al exchange isotherms of an acid soil, it should be possible to predict whether it would release "non-exchangeable" k · to a demanding crop.

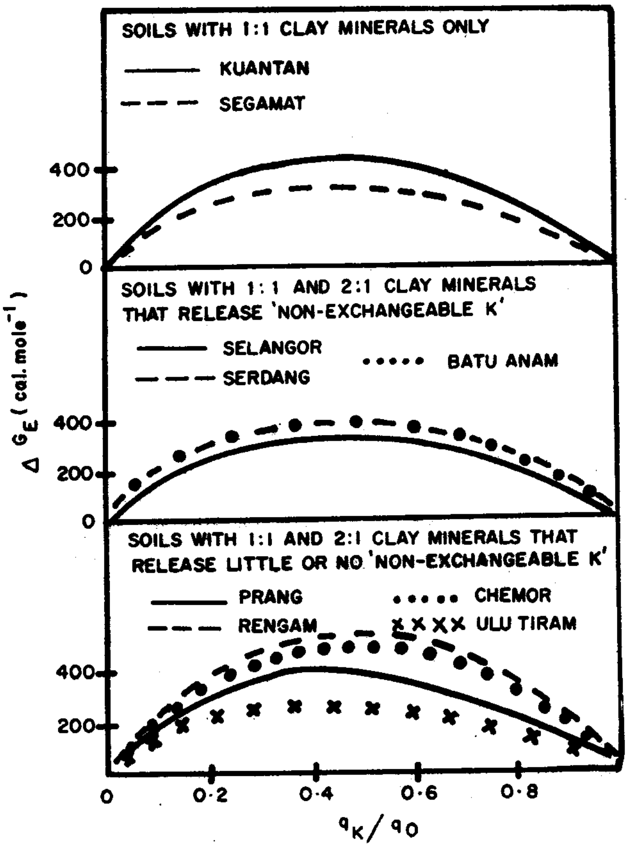

Fig. 4. Excess free energy of mixing, ΔG_E, for K : Al exchange in Malayan soils.

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