Potassium-exchange behaviour of an illite

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Summary

The specifity of the K-adsorption on illite with respect to divalent cations can be explained by accepting the existence of three different types of exchange sites. Each of these types shows a normal exchange process which may be described very well with the Gapon exchange equation, each type having its specific exchange constant. The K-exchange on an illite can therefore be mathematically described as the sum of these three processes. Proof of the validity of this mathematical expression is presented.

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1. Introduction

The distribution of mono- and divalent cations between an exchanger and its equilibrium solution is described by ERIKSSON (1952) using the Gouy-Chapman theory of the double layer. This expression has been simplified by LAGERWERFF and BOLT (1959) and in this way became identical to the one derived by Gapon (MAGISTED *et al.*, 1944) on the basis of kinetic considerations.

This exchange equation is represented by $\frac{\gamma^{+}}{\gamma^{++}} = G . \frac{C_o^{+}}{\sqrt{C_o^{++}}}$ in which γ^{+} and γ^{++} are the amounts of mono-, respectively divalent cations adsorbed (in m.e.); C_o^{+} and C_o^{++} are the concentrations of these cations in the equilibrium solution (mol/liter) and G is the Gapon exchange constant.

With the clay mineral illite as exchanger G stays at about the same level (G = ± 0,4, *c.f.* FIG. 1, which is remarkably close to the predicted theoretical value, ref. LAGERWERFF and BOLT, 1959) for various amounts of adsorbed cations and various electrolyte levels in the equilibrium solution in Ca-Na or Mg-Na systems as long as the monovalent cation adsorbed does not exceed more than about 40 % of the exchange capacity. If however K is introduced as the monovalent cation G increases gradually with diminishing amounts of K adsorbed. For the clay investigated G increases from about 2 to more than 30. FIG. 1 illustrates this phenomenon for Na or K containing systems in a 0,03 N equilibrium solution. Results at other electrolyte levels substantiate these findings.

This phenomenon of increasing G with decreasing K in the system may be explained either by assuming the existence of exchange sites with continuously increasing bonding energy for K or by assuming the existence of several types of exchange positions each having an exchange constant specific for this type of site.

The latter approach might be advantageous if the geometry of the illite mineral is taken into consideration. Roughly three different types of exchange sites may be

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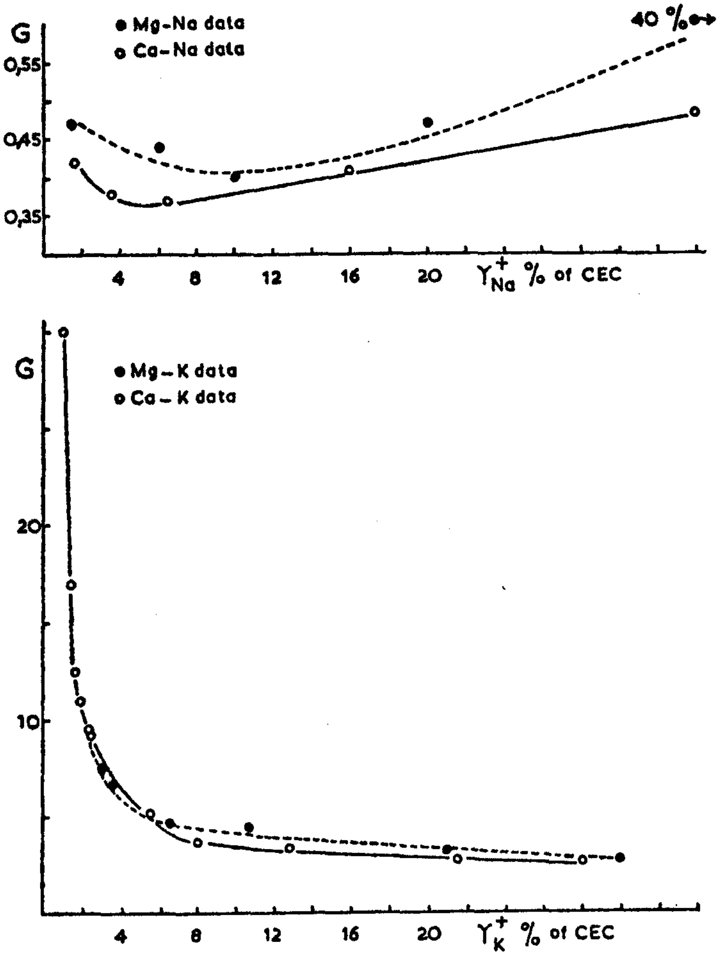
FIG. 1. Exchange constant G in relation to Na or K adsorption in 0,03 N equilibrium solutions



identified with an illite mineral, *viz. planar* sites on the outer surfaces of the lattice, *edge* sites and *interlattice* sites situated between the layers of the mineral. Especially the interlattice positions will show preferent K-adsorbing characteristics. For an extensive review about the subject readers are referred to AGARWAL (1960), SCHUFFELEN and VAN DER MAREL (1955) and WIKLANDER (1954). This assumption leads to the following three exchange equations for:

planar sites $\gamma_p^+/\gamma_p^{++} = G_p \cdot R$ (1)

edge sites $\gamma_e^+/\gamma_e^{++} = G_e \cdot R$ (2)

interlattice sites $\gamma_i^+/\gamma_i^{++} = G_i \cdot R$ (3)

R representing $C_o^+/\sqrt{C_o^{++}}$

The three processes should take place simultaneously; and R, representing the reduced ratio of mono- and divalent molar concentration in the equilibrium solution, is then identical for all three cases.

Combination of equations (1) and (2) renders:

$$\frac{\gamma_p^+}{\gamma_p^{++}} = \frac{G_p}{G_e} \cdot \frac{\gamma_e^+}{\gamma_e^{++}} \text{ and } \frac{\gamma_p^+ + G_p/G_e \cdot \gamma_e^+}{\gamma_p^{++} + \gamma_e^{++}} = \frac{\gamma_p^+}{\gamma_p^{++}} G_p \, . \, R$$

Introduction of (3) leads to:

$$\frac{\gamma_p^+ + G_p/G_e \cdot \gamma_e^+}{\gamma_p^{++} + \gamma_e^{++}} = \frac{G_p}{G_i} \cdot \frac{\gamma_i^+}{\gamma_i^{++}} \text{ and } \frac{\gamma_p^+ + G_p/G_e \cdot \gamma_e^+ + G_p/G_i \cdot \gamma_i^+}{\gamma_p^{++} + \gamma_e^{++} + \gamma_i^{++}} = G_p \, . \, R$$

which may be rewritten as:

$$\frac{\gamma_p^+ + \gamma_e^+ + \gamma_i^+}{\gamma_p^{++} + \gamma_e^{++} + \gamma_i^{++}} = G_p \, . \, R - \frac{(\gamma_e^+ \, . \, G_p/G_e - \gamma_e^+) + (\gamma_i^+ \, . \, G_p/G_i - \gamma_i^+)}{\gamma_p^{++} + \gamma_e^{++} + \gamma_i^{++}}$$

In case $G_i >> G_e >> G_p$ the above expression may be simplified to:

$$\frac{\gamma_p^+ + \gamma_e^+ + \gamma_i^+}{\gamma_p^{++} + \gamma_e^{++} + \gamma_i^{++}} = G_p \, . \, R + \frac{\gamma_e^+ + \gamma_i^+}{\gamma_p^{++} + \gamma_e^{++} + \gamma_i^{++}}$$

Introducing

$$\gamma_t^+ = \gamma_p^+ + \gamma_e^+ + \gamma_i^+ \text{ and } \gamma_t^{++} = \gamma_p^{++} + \gamma_e^{++} + \gamma_i^{++}$$

$$\gamma_t^+ = G_p \, . \, R \, . \, \gamma_t^{++} + \gamma_e^+ + \gamma_i^+ \qquad (4)$$

If the amount of ions adsorbed on edge- and interlattice sites is treated the same way this leads to

$$\gamma_e^+ + \gamma_i^+ = G_e \, . \, R \, (\gamma_e^{++} + \gamma_i^{++}) + \gamma_i^+ \qquad (5)$$

For the interlattice positions one finds

$$\gamma_i^+ = G_i \, . \, R \, . \, \gamma_i^{++} \qquad (6)$$

Thus if γ_t^+ is plotted against $R \, . \, \gamma_t^{++}$ one should expect a straight line for high values of γ_t^+, the edge and interlattice positions being satured with K at this stage. The slope of this line then represents G_p, and its intercept with the γ_t^+-axis will equal the adsorption capacity of edge and interlattice sites, $\gamma_e + \gamma_i$. Subtraction of this value from the total exchange capacity, *i.e.* $\gamma_t^+ + \gamma_t^{++}$ then yields the exchange capacity of the planar sites. Employing equation (1) one then finds immediately γ_p^+ and γ_p^{++}, according to

$$\frac{\gamma_p^+}{\gamma_p^+ + \gamma_p^{++}} = \frac{G_p \, . \, R}{G_p \, . \, R + 1} \qquad (7)$$

Subtraction of the calculated amounts on the planar sites from the total amounts determined finally yields $(\gamma_e^+ + \gamma_i^+)$ and $(\gamma_e^{++} + \gamma_i^{++})$, which may then be used to evaluate G_e and γ_i (the adsorption capacity of the interlattice sites) from a plot of $(\gamma_e^+ + \gamma_i^+)$ against $R \, . \, (\gamma_e^{++} + \gamma_i^{++})$ according to equation (5).

Repeating the above procedure for the edge sites one finds γ_e^+ and γ_e^{++}, by subtracting γ_i^+ from $(\gamma_e^+ + \gamma_i^+)$ and using the equation:

$$\frac{\gamma_e{}^{+}}{\gamma_e{}^{+} + \gamma_e{}^{++}} = \frac{G_e \, . \, R}{G_e \, . \, R + 1} \tag{8}$$

In turn the amounts in the interlattice positions, found by subtraction of $\gamma_e{}^{+}$ from $(\gamma_e{}^{+} + \gamma_i{}^{+})$, can be plotted according to equation (6), yielding G_i .
Obviously the described procedure will yield reliable results only if the exchange behaviour of the different types of sites may be described by means of the Gapon equation and if $G_i >> G_e >> G_p$, *i.e.* if the types of sites are sufficiently different in behaviour.

2. Experimental procedure

For the experiments a Winsum illite was used containing about 50 % material smaller than 2 μ. After dispersion in water this fraction was syphoned off and repeatedly (at least 7 times) batch treated with either normal $MgCl_2$ or normal $CaCl_2$. It was assumed that the accessible exchange positions were now occupied by Mg or Ca. The suspensions of Mg- or Ca-illite were then each divided into three portions which were repeatedly diluted untill 12 % clay suspensions were obtained in equilibrium with solutions of 0,03; 0,01 or 0,003 normal electrolyte ($MgCl_2$ or $CaCl_2$). Fifty ml portions of these suspensions were pipetted into cellulose dialysis bags (A. H. Thomas Cy., Philadelphia) which were closed by knotting the ends. Before use the dialysis tubing had been cleaned thoroughly by repeated washing in demineralised water untill the conductivity of the water did not exceed 1,5 micromhos. cm^{-1}.
The bags, filled with the suspension, were immersed in glass cylinders already containing 100 ml of a solution with the same normality of $MgCl_2$ or $CaCl_2$ as the suspension. Next a calculated amount of K-resin (Dowex 2) was added (BOLT and FRISSEL, 1960) and the tubes were allowed to reach equilibrium by continuous end-overend shaking (2 rpm) during 10 days. Preliminary experiments had shown that a satisfactory degree of equilibration was attained in that period of time even with solutions 0,001 normal in electrolyte content.
The resin technique was used because in this way cations could be introduced without changing the electrolyte content in the equilibrium solution and comparison of results could be made at the same electrolyte level. After ten days of shaking the bags were opened and emptied into weighed centrifuge tubes. The clay content was then determined in a small aliquot. By weighing the centrifuge tubes the amount of clay in the tubes could be calculated. Next the suspension was concentrated by centrifugation, discarding the supernatant. By weighing the centrifuge tubes again the remaining quantity of equilibrium solution could be calculated. By five successive extractions with 50 ml of normal NH_4NO_3 the adsorbed cations were stripped from the clay together with the included equilibrium solution. The five extracts were combined and brought to volume in a 250 ml flask. Next the concentrations of the cations K, Mg and Ca were determined. The amounts stripped from the clay were then calculated by subtracting the amount in solution from the total amount. The latter was found as the product of the moisture content after decantation and the concentration in the equilibrium solution, as determined in the remainder of the solution left in the cylinders used for shaking, after removal of the resin.

3. Analytical methods

K in the NH_4NO_3-extract of the clay was determined flame-photometrically (Eppendorf flame-photometer using propane as fuel) directly or in a 1 + 9 dilution taking care that the standard had the same NH_4NO_3-concentration. The determination of K in the equilibrium solution was also carried out in 0,1 normal NH_4NO_3. The determination of very low quantities of K was seriously affected by small contaminations with Na. This interference was taken care of by the addition of 100 ppm Na to objects as well as standards.

The determination of Ca was carried out flame-photometrically (using acetylene as fuel) after bringing objects and standards to the same K-level. Low concentrations of Ca were determined titrimetrically with EDTA (VAN SCHOUWENBURG, 1960). Cross checks between these two different methods were carried out regularly in the higher Ca-ranges.

The determination of Mg was carried out with titan yellow (SCHUFFELEN, MULLER and VAN SCHOUWENBURG, 1961) in the higher ranges or with oxine in the lower ranges (VAN SCHOUWENBURG, 1962). Cross checks between the two different methods were made regularly in the higher Mg-ranges.

4. Results

Only the results of the Mg-series are shown in TABLE 1. The data from the Ca-series were not exact enough in the low K-range to permit a separate and reliable treatment of the results.

TABLE 1. Composition of adsorption complex (in m.e. of K or Mg/g of clay) and equilibrium solution (in mmol/l) of the Mg-illite K-series

Nr.	Adsorption complex (me/gram)		Equilibrium solution (mmol/l)	
	γ_K	γ_{Mg}	K_o	Mg_o
1	0,0485	0,3952	3,23	13,6
2	0,0946	0,3515	8,36	10,7
3	0,1439	0,3272	14,1	7,68
4	0,2444	0,2104	24,4	2,55
5	0,0423	0,4088	1,49	4,07
6	0,0758	0,3705	3,44	3,25
7	0,1061	0,3520	5,28	2,33
8	0,1981	0,2351	8,72	0,65
9	0,0317	0,4152	0,59	1,36
10	0,0362	0,3783	0,795	1,33
11	0,0738	0,3947	1,74	0,81
12	0,1828	0,2670	2,98	0,14
13	0,0112	0,4458	0,32	14,6
14	0,0138	0,4366	0,506	14,4
15	0,0170	0,4433	0,69	14,8
16	0,0300	0,4240	1,82	13,9
17	0,0113	0,4440	0,211	4,79
18	0,0145	0,4440	0,333	4,63
19	0,0170	0,4341	0,425	4,72
20	0,0288	0,4171	0,998	4,47
21	0,0188	0,4423	0,135	1,44
22	0,0142	0,4346	0,195	1,56
23	0,0172	0,4300	0,246	1,48
24	0,0297	0,4170	0,578	1,35

Using equation (4) the data are presented in a graphical form in FIG. 2. The Ca data are also given in order to show that these substantiate the data from the Mg-series and that G_p and $\gamma_e + \gamma_i$ for he Ca-series are undoubtedly of the same order of magnitude although a different badge of clay was used.

FIG. 2 shows that for $\gamma_t^+ > 0{,}04$ m.e./g the experimental points are situated along a straight line whereas for $\gamma_t^+ < 0{,}04$ m.e./g the points deviate from this course. According to the theory developped in the introduction the tangent of the straight line is G_p and the intercept with the γ_t^+-axis represents $\gamma_e + \gamma_i$ which is that part of the total exchange capacity attributed to edge and interlattice positions. In this case, *i.e.* at high overall K-saturation, the edge and interlattice sites should be virtually completely satured with K-ions.

For the calculation of G_p those data were used where the influence of $\gamma_e^+ + \gamma_i^+$ is constant. As an arbitrary limit $\gamma_t^+ > 0{,}039$ m.e./g was assumed.

After elimination of the influence of the adsorption on the planar positions the data where $\gamma_t^+ < 0{,}039$ m.e./g have been used for the calculation of G_e and γ_i according to the procedure described. These data are presented in FIG. 3 using equation (5).

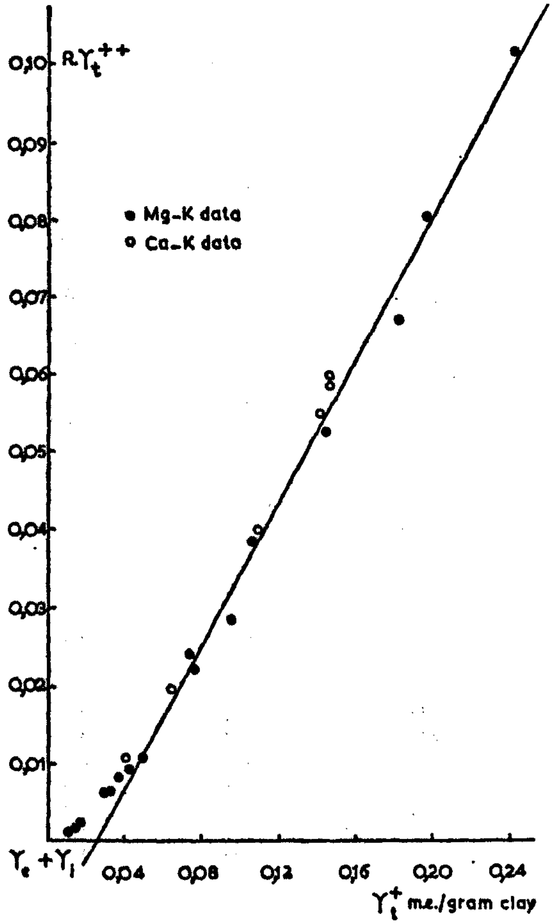


FIG. 2.
Relation of adsorbed γ_t^+ and R γ_t^{++} according to equation 4

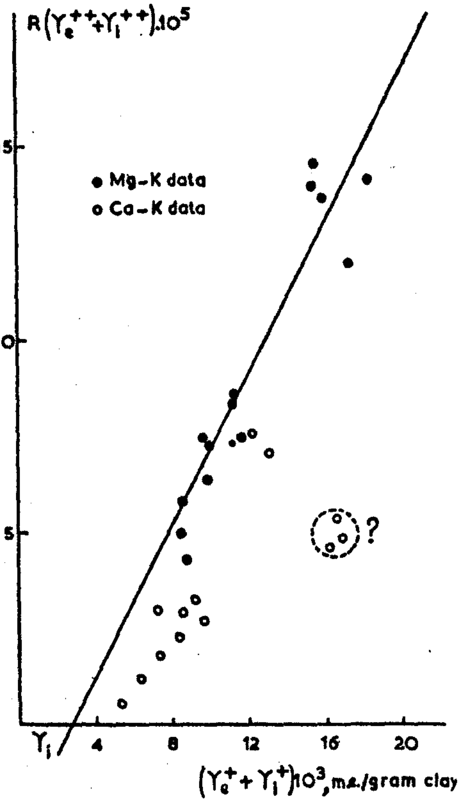


FIG. 3.
Relation of adsorbed $\gamma_e^+ + \gamma_i^+$ and R $(\gamma_e^{++} + \gamma_i^{++})$ according to equation 5

These same data have also been used for the calculation of G_i after elimination of the influence of the edge sites. The analytical data proved however not to be exact enough for this purpose. Nevertheless the data suggest that G_i is higher than 2000 and probably infinite meaning that interlattice K did not take part in the exchange with Mg or Ca.

The statistical analysis (VAN UVEN, 1935) of the data of the Mg-series produced the results as shown in TABLE 2.

TABLE 2. Exchange constants and adsorption capacities of the different exchange sites with Winsum illite

K-Mg exchange		
G_p	2,21 ± 0,059	
G_p	102,3 ± 10,3	
G_p	probably infinite	
CEC planar	0,4258 ± 0,004	m.e./g of clay
CEC edge + interlattice	0,0248 ± 0,00026	m.e./g of clay
CEC interlattice	0,0028 ± 0,00025	m.e./g of clay
K-Ca exchange		
G_p	2,12 ± 0,071	
CEC planar	0,472 ± 0,005	m.e./g of clay
CEC edge + interlattice	0,0202 ± 0,00075	m.e./g of clay

5. Discussion of the results

The results shown in FIGURES 2 and 3 and mathematically evaluated in TABLE 2 lend a strong support to the hypothesis forwarded in the introduction: the specifity of the K-adsorption on illite can be explained by accepting the existence of three different types of exchange sites showing normal exchange processes which take place simultaneously, each site having however an exchange constant which differs widely in magnitude from the exchange constants of the other sites.

It is interesting to note that a somewhat different approach to the investigation of the exchange behaviour of this clay as presented by BOLT, SUMNER and KAMPHORST (1962) leads to essentially the same conclusions.

Of these three sites the interlattice sites show the highest exchange constant. Although the data are not exact enough for an evaluation of G_i the results however suggest that G_i in any case is larger than 2000 and probably is infinite with respect to K-Ca and K-Mg exchange. This means for all practical purposes, that Ca nor Mg are able to expel K from interlattice positions in a reasonable period of time. The fact that the interlattice positions could be established in these experiments is a consequence of the fact that NH_4-ions are capable of dislodging part of the K from these positions. A total analysis of the Ca- and Mg-illite revealed that 0,73 m.e. K/g of clay is still present although these clays were repeatedly batch-treated with large amounts of normal $MgCl_2$ or $CaCl_2$. This K can be attributed to interlattice positions inaccessible to Ca and Mg.

The edge sites show a very marked preference for K. An exchange constant of 102 has been established for the K-Mg exchange. The data from the Ca-series are to limited in number and restricted to the lowest part of the edge region only, the points being furthermore scattered too much to allow a reliable treatment of the results. FIG. 3 however shows that the Ca-data support the Mg-results reasonably well which means that the exchange constant for the K-Ca exchange on these sites will be of the same order of magnitude.

The batch treatment of the illite during the preparation of the clays resulted in Ca-clays with less K left in the edge positions than in the case of the Mg-illite. This is shown clearly in FIG. 3: all the experimental points in the low K-range have been obtained with the Ca-illite. This indicates that Ca is adsorbed somewhat stronger than Mg meaning that G_e for the K-Ca exchange will be smaller than 102.

This slight preference of the illite for Ca with respect to Mg is supported by the data about the exchange on planar sites. Although the difference is not significant the results seem to indicate that G_p in the Ca-series (TABLE 2) is somewhat smaller than in the Mg-series. This indication is also supported by work, not presented here, on the Na-Ca and Na-Mg exchange on the same illite (FIG. 1).

The experiments were carried out in equilibrium solutions with electrolyte contents of 0,003; 0,01 and 0,03 normal. The influence of this variation, if present, is negligible. Thus apparently as long as R ($= C_o^+/\sqrt{C_o^{++}}$) is constant there is little or no influence of the electrolyte content on the composition of the exchange complex. The full ratio of C_o^+ and C_o^{++} of the equilibrium solution has to change however in order to keep R constant with a changing normality of the equilibrium solution (for instance $R = 0{,}01$ in 0,01 normal solution means $C_o^+ = 0{,}005$; $C_o^{++} = 0{,}0025$ mol/liter, whereas in a 0,03 normal solution it means $C_o^+ = 0{,}01$ and $C_o^{++} = 0{,}01$ mol/l).

Using the experimental values for G_i (infinite), G_e (102.3) and G_p (2,21) and taking the exchange capacities of the interlattice, edge and planar sites as 0,0028 m.e., 0,0220 m.e. and 0,4258 m.e./g of clay respectively, the total adsorption of mono- and divalent cations on the illite can now be described as the sum of the adsorption on each of the sites as a relation of R. These Mg-K adsorption curves are presented in FIG. 4. Each curve shows the percentage saturation with K of one of the different sites. The interlattice adsorption curve is not shown because all the interlattice exchange sites are, with our experiments, virtually completely occupied with K meaning that the percentage saturation is 100 for the whole range of R-values. For practical purposes the R-axis has been drawn as the logaritm of the R-values. The equations used for constructing these graphs were

$$\gamma_t{}^{+} = \underset{\text{(planar)}}{\frac{2{,}21 \,.\, R \,.\, 0{,}4258}{1 + 2{,}21\ R}} + \underset{\text{(edge)}}{\frac{102{,}3 \,.\, R \,.\, 0{,}0220}{1 + 102{,}3 \,.\, R}} + \underset{\text{(interlattice)}}{0{,}0028\ \text{m.e./g of clay}}$$

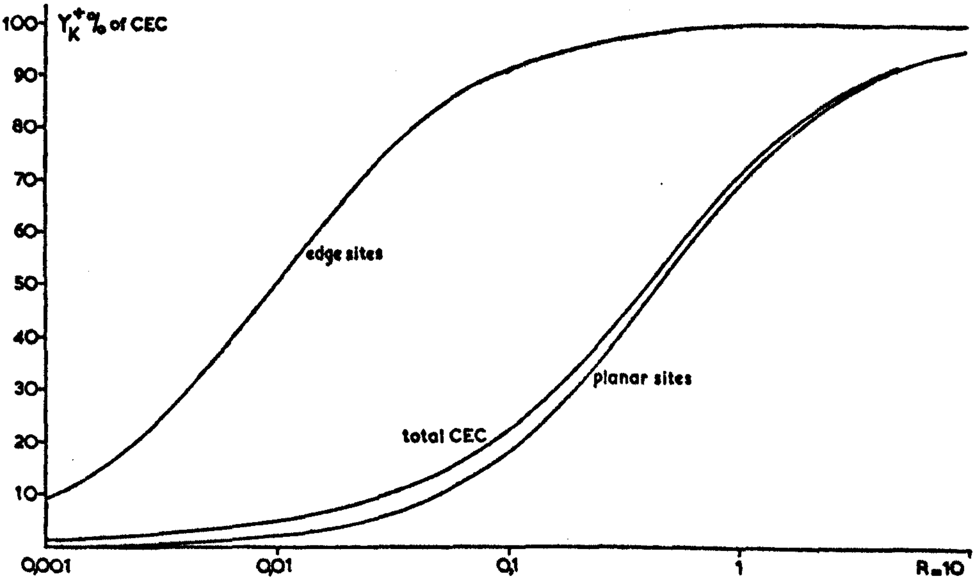
$$= \frac{0{,}941 \,.\, R}{1 + 2{,}21 \,.\, R} + \frac{2{,}2506 \,.\, R}{1 + 102{,}3 \,.\, R} + 0{,}0028\ \text{m.e./g of clay}$$

Furthermore:

$$\gamma_t{}^{++} = (0{,}4506 - 0{,}0028) - \frac{0{,}941 \,.\, R}{1 + 2{,}21 \,.\, R} - \frac{2{,}2506 \,.\, R}{1 + 102{,}3 \,.\, R}\ \text{m.e./g of clay.}$$

From the graphs it can be concluded that at R < 0,001 the bulk of the K adsorbed is in the interlattice positions. For 0,001 < R < 0,01 the main part of the K is in the edge positions whereas from R > 0,01 the planar adsorption dominates because of its far greater adsorption capacity.

FIG. 4. Composition of edge-, planar- and total exchange complex in relation to the composition of the equilibrium solution (R)



It should be remembered that the value of 0,0028 m.e. K adsorbed on the interlattice sites is arbitrary because normal NH_4NO_3 was used as the extractant. With another extractant this value would have changed (Bolt, Sumner and Kamphorst, 1962). Perhaps the best attitude would be to introduce 0,7300 m.e. instead, this being the total amount of K in interlattice positions, which as a whole would have an exchange constant of infinity towards Ca and Mg.

The statement that G_i is infinite should, however, not be taken too litterally. It only means that in our experiments NH_4-ions have exchanged K from positions which were not accessible to either Ca or Mg in a relatively short period of time. It is a well known fact, however, that Ca or Mg are able to exchange interlattice K if given enough time because it seems (Mortland and Ellis, 1959) to be a film-diffusion governed process.

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