

Binary and Ternary Exchange of Potassium on Calcareous Montmorillonitic Soils

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ABSTRACT

Simultaneous K exchange with Ca, Mg, and Na occurs in soils, but most of the published information is obtained from binary systems. The theoretical question of whether selectivity coefficients obtained in binary systems are valid for ternary systems has not yet been clarified; however, no significant difference has been found between selectivity coefficients in binary and ternary systems. Potassium exchange with Mg plus Ca was studied in two calcareous soils with variable concentrations of Na, using batch and miscible-displacement methods. Preference for K over the divalent cations was found in both soils, regardless of Na concentration and the experimental methods. Modified Gapon (k_G) and Vanselow (k_v) selectivity coefficients were calculated for each cation pair in binary and ternary systems. In both soils, the k_v and the k_G decreased with increasing K fraction in the solution, but the k_G value was less affected than the k_v . A simple mathematical solution of the Gapon binary equations, $K - (Mg + Ca)$ and $Na - (Mg + Ca)$, in combination with an assumption of constant cation-exchange capacity (CEC), was used to predict the amount of exchangeable K as a function of solution composition in a ternary system. The high correlation of predicted exchangeable K with the directly measured values shows that binary selectivity coefficients can be used in multicationic systems on calcareous montmorillonitic soils.

POTASSIUM EXCHANGE REACTIONS with each of the cations Ca, Mg, or Na on clay minerals and soils have been investigated intensively (Bolt, 1979; Sparks and Huang, 1985). Irrigation water, especially sewage effluents and brackish waters, may contain considerable quantities of Na, K, Ca, and Mg. These cations undergo simultaneous exchange reactions with each other on soil surfaces. The possible reactions involving K-Ca-Mg, K-Na-Ca, and K-Na-Mg in soils and the study of their effect on K distribution between the solution and the solid phases is extremely important in plant nutrition.

Theoretical understanding of the relationship between ternary and binary exchange systems in clays and soils has been enhanced in the last decade. Chemical and geochemical models were adapted to soils for predicting cation exchange in a ternary system using binary-exchange data (Elprince and Babcock, 1975; Elprince et al., 1980). Chu and Sposito (1981), using data obtained from experiments with pure clays and with careful analytical methods, found that the effect of ternary systems on binary-exchange coefficients was not greater than experimental error. In subsequent studies on ternary cation exchange on clay minerals and soils, Sposito and others (Fletcher et al., 1984; Sposito et al., 1983; Sposito and Fletcher, 1985) found no effect of the ternary system on binary-exchange selectivity on

montmorillonite and montmorillonitic soils. However, the amount of adsorbed Na did affect the exchange selectivity of Ca over Mg on illite and illitic soils due to variable sorption sites (Sposito and LeVesque, 1985; Sposito et al., 1986).

Unfortunately, most reports that have appeared in the soil-chemistry literature on exchange phenomena involving binary and, particularly, ternary systems, do not involve K (Chu and Sposito, 1981; Elprince and Babcock, 1975; Elprince et al., 1980; Levy et al., 1983). Information on ternary systems involving K is meager, and the few studies that involve K used only quaternary data (Robbins, 1984; Robbins and Carter, 1983; Robbins et al., 1980; Thellier and Sposito, 1988). Accordingly, the objective of this work was to test the validity of exchange selectivity coefficients obtained in binary systems for prediction of ternary or quaternary exchange of K with other cations.

MATERIALS AND METHODS

The two soils used in this study were: Nordiya, a Rhodoxeralf, and Gilat, a Haploxeralf; selected physicochemical properties of the soils determined using standard methods are given in Table 1. The Nordiya soil is a sandy soil with low CEC, while the Gilat is a loam soil with a higher CEC. The CEC value was determined by saturation with NaCl followed by displacement with LiCl, rather than NH_4 , to avoid release of fixed K. In both soils, the predominant clay mineral in the $<2\text{-}\mu\text{m}$ fraction is smectite (Dan et al., 1975), but the content of the clay fraction in the Gilat soil is higher than that of the Nordiya soil. The pH of these soils is greatly influenced by carbonates, which are especially high in the Gilat soil.

Exchange isotherms for binary and ternary systems of K, Na, Ca, and Mg were conducted at room temperature, $23 \pm 2.0^\circ\text{C}$, to obtain a complete description of the exchange reactions on the two soils.

Binary-Exchange Experiments Using a Batch Technique

The whole soils were equilibrated with three sets of solutions with a constant ClO_4 concentration of 20 ± 0.5 mol m^{-3} , the first set with a range of Ca-Mg, K-Mg, and Na-Mg mixtures. The initial Mg equivalent fraction in the solution of the three sets increased from 0 to 1 while the equivalent fraction of the counter cation decreased from 1 to 0, using two replicates. Four and 6 g of Gilat and Nordiya soil, respectively, were equilibrated with 30 mL of solution. The soil suspensions were shaken for 30 min, centrifuged, and the supernatant was discarded. This process was repeated three times and, in the last supernatant, K, Na, Ca, and Mg concentrations were determined. The soil was then washed repeatedly with 80% (v/v) ethanol until free of electrolytes. Exchangeable cations were extracted from the soil by shaking with 30 mL of a 0.5 M LiCl solution, centrifuging, and collecting the supernatant. This process was repeated three times.

Ternary-Exchange Experiments Using the Miscible-Displacement Technique

In a preliminary test, no significant difference was found between the batch and miscible-displacement techniques for

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K-Mg or Na-Mg exchange systems. The latter method was preferred for the ternary exchange study because it enables one to control the soil-solution composition. The soils were equilibrated with solutions with a varied K/Na/(Ca + Mg) ratio in a constant Cl background concentration of 20 ± 0.5 mol m^{-3} . Each treatment was repeated at least twice and up to four times. The Cl anion was used in this study instead of ClO_4 since a large quantity of leaching solution is required in the miscible-displacement method, and the ClO_4 salts are much more expensive than the Cl salts. The use of Cl was justified by conducting a preliminary test in which no detectable difference was found in exchange isotherms between Cl and ClO_4 salts. One gram of soil, as a suspension with deionized water, was incorporated onto 0.47- μ m Gelman filter pads in a polycarbonate in-line filter-holder chamber, using low-pressure suction. The mixed solutions were pumped into the chamber using a peristaltic pump. They were passed through the saturated soil layer at a constant flow rate of 10 mL h^{-1} over an effective filtration surface area of 9.62 cm^2 , using a low-pressure suction and maintaining approximately 0.5-cm solution head above the soil layer. This leaching process continued until steady state in solution composition was established and not less than 250 mL of solution were used per sample. When steady state was achieved, an additional 50 mL of solution was leached and collected as the equilibrium solution. Then, 50 mL of 80% ethanol were leached through the adsorbent to remove entrained salts. Exchangeable cations were then displaced by leaching with 250 mL of 0.5 M LiCl.

Potassium and Na concentrations in the equilibrium and displaced solutions were determined by flame photometry, while Ca and Mg concentrations in the equilibrium solutions were determined by atomic absorption. Calcareous soils pose difficulties in the determination of adsorbed Ca and Mg. Consequently, the adsorbed Ca plus Mg in each treatment was calculated from the difference between the total CEC (Table 1) and the displaced Na and K, assuming a constant CEC. This assumption is based on published data showing constant CEC of montmorillonite and montmorillonitic soils (Elprince et al., 1980; Fletcher et al., 1984; Jensen, 1973; Levy et al., 1972; Shainberg et al., 1987; Sposito and Fletcher, 1985; Sposito et al., 1983; Suarez and Zahow, 1989). From the above batch and miscible-displacement experiments, K - (Ca + Mg) isotherms were determined and k_v and k_G were calculated.

Determination of Selectivity Coefficients

Two types of models, the Vanselow and the Gapon, were used to determine cation-exchange selectivities. For both models, activities of cations in the solutions were calculated using the Davies equation. Using GEOCHEM software (Sposito and Mattigod, 1980), the free cations were found to make up more than 99% of the total, and therefore no corrections were made for ion pairs and ligands in the solutions. Modified Vanselow and Gapon models (U.S. Salinity Laboratory Staff, 1954) were used that treat Ca and Mg identically. Vanselow selectivity coefficients were calculated using the following equations:

$$k_{V (Ca + Mg)}^K = \frac{f(C_{Ca} + C_{Mg})N_K^2}{a_K^2 (N_{Ca} + N_{Mg})} \quad [1]$$

$$k_{V (Ca + Mg)}^{Na} = \frac{f(C_{Ca} + C_{Mg})N_{Na}^2}{a_{Na}^2 (N_{Ca} + N_{Mg})} \quad [2]$$

where N is the mol fraction of the exchangeable phase, a is the solution ion activity in mol L^{-1} , C is the solution ion concentration in mol L^{-1} , and f is the activity coefficient of Ca and Mg assuming that these divalent cations have similar activity coefficients. Gapon selectivity coefficients were calculated using the following equations:

$$k_{G (Ca + Mg)}^K = \frac{EPR}{PAR_i} \quad [3]$$

where

$$PAR_i = \frac{a_K}{f(C_{Ca} + C_{Mg})^{1/2}} \quad [3a]$$

and

$$EPR = \frac{q_K}{(2q_{Ca} + 2q_{Mg})} \quad [3b]$$

$$k_{G (Ca + Mg)}^{Na} = \frac{ESR}{SAR_i} \quad [4]$$

where

$$SAR_i = \frac{a_{Na}}{f(C_{Ca} + C_{Mg})^{1/2}} \quad [4a]$$

and

$$ESR = \frac{q_{Na}}{(2q_{Ca} + 2q_{Mg})} \quad [4]$$

and where PAR and SAR are the K and Na molar ion ratios, respectively, EPR and ESR are the exchangeable K and Na ratios, respectively, and q is the quantity of sorbed cation (mol kg^{-1}).

For K-adsorption isotherms, renormalized equivalent fractions in solution (E'_K) and sorbed phases (\hat{E}'_K) were calculated according to Thellier and Sposito (1988), and the concentration of Na was excluded in both phases:

$$E'_K = \frac{C_K}{C_K + 2(C_{Ca} + C_{Mg})} \quad [5]$$

$$\hat{E}'_K = \frac{q_K}{q_K + 2(q_{Ca} + q_{Mg})} \quad [6]$$

RESULTS AND DISCUSSION

Binary Exchange

Nonpreference of Ca over Mg was found for a wide range of Mg fractions in solution for the Gilat soil (Fig. 1); this was also previously obtained for the Nordiya

Table 1. Selected chemical and physical properties of the studied soils.

Soil	Soil subgroup	CaCO ₃	Organic matter	Particle size			Textural class	pH paste	CEC†
				Sand	Silt	Clay			
				g kg^{-1}					cmol _c kg^{-1}
Gilat	Calcic Haploxeralf	203.0	9.0	436	368	196	1	7.8	9.6 ± 0.80
Nordiya	Typic Rhodoxeralf	1.4	14.0	854	48	98	s	7.5	5.3 ± 0.50

† Cation-exchange capacity.

soil (Seyfried et al., 1989). These results are in good agreement with published data for other soils from the same geographical areas (Levy et al., 1972), and with reported data for clay minerals and for soils with low organic-matter contents (Salmon, 1964; Sposito et al., 1983). Fletcher et al. (1984) and Haghnia and Pratt (1988) found that, when Ca was preferred over Mg, this was often correlated with the organic-matter content of the soils. Consequently, the lack of preference of Ca over Mg in soils from semiarid regions that are low in organic matter is reasonable. Therefore, the approach of the U.S. Salinity Laboratory Staff (1954), Salmon (1964), and Lai et al. (1978) in treating Mg and Ca as one divalent ion in exchange with other cations was used in this study, reducing the ternary system to a binary one and the quaternary system to a ternary system.

Data for K exchange with Mg and Ca on the Nordiya and Gilat soils from the batch experiment are given in Table 2. Sodium concentrations in solution and on the exchange complex were negligible. Potassium concentration in the soil solutions increased from 1.7 or 1.8 to 17.2 mol m⁻³, but adsorbed K did not exceed 0.6 of the CEC in either soil. To determine which cation is preferred over the other in mono-divalent exchange systems, we followed the method of Thellier and Sposito (1988), using E'_K , \bar{E}'_K (Eq. [5] and [6]). The isotherms of \bar{E}'_K vs. E'_K for the Nordiya and Gilat soils are presented with calculated lines (after Jensen, 1973) for nonpreference and ideal solution conditions for the liquid and solid phases (Fig. 2a, 2b). The experimentally observed points for the two soils lie well above the theoretical curve, indicating a preference for K over Mg plus Ca. Moreover, this high K selectivity

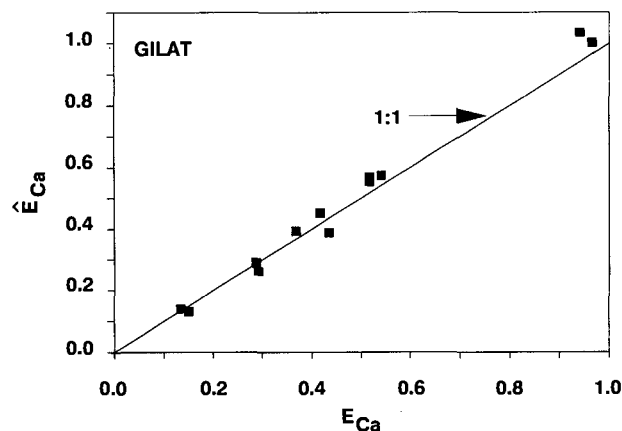


Fig. 1. Isotherm for Ca-Mg exchange (equivalent fractions in solution [E_{Ca}] vs. sorbed [\bar{E}_{Ca}]) on a Gilat soil using a batch method.

over Ca + Mg was observed over a wide range of K equivalent fractions. Similar results have been observed for kaolinite, illite, and montmorillonite, and for soils (Jensen, 1973; Levy et al., 1988; Salmon, 1964; Schwertmann, 1962; Udo, 1978).

The k_v values for K exchange with Ca plus Mg in the Nordiya soil decreased from 70.9 to 6.4 L mol⁻¹ and, in the Gilat soil, from 95.1 to 8.5 L mol⁻¹ (Table 2) as C_K increased from 1.8 to 17.2 mol m⁻³. Thus, the k_v values are higher when K concentration is lower, as has been found for soils and clays in numerous studies (Jensen, 1973; Ogwada and Sparks, 1986; Shainberg et al., 1987; Talibudeen, 1972; Udo, 1978). Increasing the PAR_i in solution from 0.02 to 0.5 (L mol⁻¹)^{1/2}, reduced the k_G from 4.6 to 2.3 (mol⁻¹L)^{1/2},

Table 2. Batch experimental data for K exchange with Mg + Ca in a 20 mol m⁻³ ClO₄ background (solution concentration, C_{Na} , and quantity sorbed, q_{Na} , values were below 0.02 mol m⁻³ and 0.05 cmol kg⁻¹, respectively, for all treatments of both soils).

C_K †	C_{Ca} ‡	C_{Mg}	K ion ratio	q_K	$q_{Ca} + q_{Mg}$ §	EPR¶	k_v K (Ca + Mg)*	k_G K (Ca + Mg)††
mol m ⁻³			(L/mol) ^{1/2}	cmol kg ⁻¹			L mol ⁻¹	(mol/L) ^{1/2}
Nordiya								
1.8	2.07 ± 0.15	7.19 ± 0.09	0.019	0.42	2.42	0.09	70.9	4.6
3.3	1.91 ± 0.00	6.06 ± 0.03	0.037	0.68	2.29	0.14	48.8	4.0
4.9	1.96 ± 0.02	5.29 ± 0.18	0.057	0.88	2.17	0.20	35.2	3.5
6.8	1.93 ± 0.03	4.31 ± 0.20	0.086	1.17	2.05	0.28	28.1	3.3
8.5	1.88 ± 0.03	3.96 ± 0.29	0.111	1.32	1.97	0.33	21.9	3.0
10.2	1.74 ± 0.06	2.91 ± 0.00	0.150	1.58	1.84	0.43	17.6	2.9
11.5	1.72 ± 0.06	1.93 ± 0.03	0.191	1.79	1.74	0.52	14.5	2.7
13.5	1.57 ± 0.05	1.16 ± 0.00	0.257	2.07	1.60	0.65	11.2	2.5
15.8	1.45 ± 0.07	0.54 ± 0.00	0.353	2.37	1.45	0.82	8.2	2.3
17.2	1.17 ± 0.04	0.00 ± 0.00	0.500	2.80	1.23	1.15	6.4	2.3
Gilat								
1.7	1.61 ± 0.05	7.73 ± 0.14	0.018	0.83	4.29	0.09	95.1	5.3
3.2	1.52 ± 0.04	6.29 ± 0.47	0.036	1.28	4.06	0.15	55.5	4.3
5.1	1.47 ± 0.07	5.54 ± 0.12	0.061	1.92	3.74	0.25	44.8	4.1
7.0	1.37 ± 0.04	4.60 ± 0.03	0.091	2.30	3.55	0.32	29.4	3.5
8.7	1.46 ± 0.12	3.50 ± 0.30	0.124	2.69	3.86	0.39	22.4	3.2
10.2	1.30 ± 0.01	2.62 ± 0.06	0.164	3.04	3.18	0.46	16.7	2.8
11.9	1.16 ± 0.12	1.96 ± 0.06	0.213	3.65	2.88	0.62	14.9	2.9
13.5	1.23 ± 0.06	1.14 ± 0.03	0.276	4.29	2.56	0.81	13.2	2.9
15.8	1.18 ± 0.00	0.52 ± 0.03	0.382	5.03	2.19	1.11	10.4	2.9
17.2	1.11 ± 0.14	0.00 ± 0.00	0.518	5.76	1.82	1.51	8.5	2.9

† No differences in K concentration in solution and exchangeable phases were found between duplicates under the analytical limitations of K determination.

‡ The ± value represents the standard deviation of Ca and Mg concentrations in solution.

§ Calculated as the difference between total cation-exchange capacity (Table 1) and $q_K + q_{Na}$.

¶ Exchangeable K ratios.

* Vanselow selectivity coefficients for K exchange with Ca + Mg.

†† Gapon selectivity coefficients for K exchange with Ca + Mg.

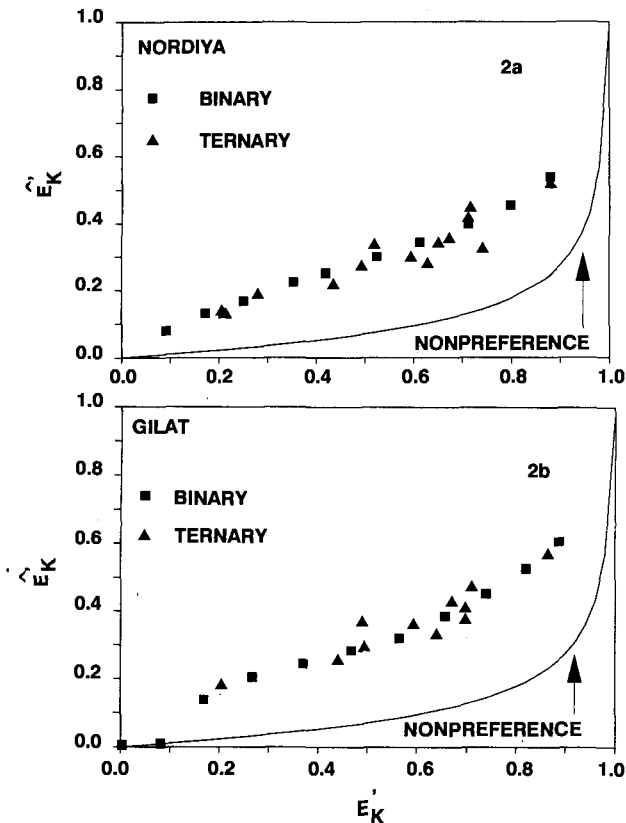


Fig. 2. Renormalized exchange isotherms for K exchange (equivalent fractions in solution [E_K] vs. sorbed [\bar{E}_K]) with (Ca + Mg) on (a) Nordiya and (b) Gilat soils without and with Na in the system, using batch (binary) and miscible-displacement (ternary) methods.

and from 5.3 to 2.9 ($\text{mol}^{-1} \text{L}$)^{1/2} in the Nordiya and Gilat soils, respectively (Table 2). The value of k_G in the Gilat soil sharply decreased from 5.3 to 3.2 ($\text{mol}^{-1} \text{L}$)^{1/2} when EPR increased from 0.09 to 0.39, and then leveled off to approximately 2.9 ($\text{mol}^{-1} \text{L}$)^{1/2}, a phenomenon that is well documented in the literature (Goulding, 1983; Shaviv et al., 1985). In the Nordiya soil, k_G monotonously decreased from 4.6 to 2.3 ($\text{mol}^{-1} \text{L}$)^{1/2} as EPR increased from 0.09 to 0.82. However, the change in k_G vs. C_K was much smaller than what was found for the change in k_V vs. C_K for both soils, which is in agreement with other published data (Levy et al., 1988; Shainberg et al., 1987). The k_G values (the slope of EPR vs. PAR_i) for the studied range in the Nordiya and Gilat soils were estimated from Table 2 data, by the SAS Institute (1985) GLM procedure as 2.4 ± 0.05 and 2.9 ± 0.04 ($\text{mol}^{-1} \text{L}$)^{1/2}, respectively. These values of k_G for both soils are in the same magnitude as published values for montmorillonite and montmorillonitic soils (Bolt, 1979). The corresponding values of the correlation coefficients (r^2) were 0.989 for the Nordiya soil and 0.996 for the Gilat soil, indicating the success of the Gapon model in describing K - (Ca + Mg) exchange in both soils. To improve the predictions of EPR as a function of PAR_i , empirical functions relating k_G values to corresponding EPR and their power values were fitted to the exchange data, using the SAS Institute (1985) STEPWISE procedure. The EPR power values were added to the mod-

el until the level of significance did not exceed 0.15. The following equations were obtained:

Nordiya soil

$$k_{G(\text{Ca}+\text{Mg})}^{\text{K}} = 5.668 - 15.673\text{EPR} + 33.278\text{EPR}^2 - 33.353\text{EPR}^3 + 12.222\text{EPR}^4 \quad 0 < \text{EPR} < 1.12$$

$$k_{G(\text{Ca}+\text{Mg})}^{\text{K}} = 2.23 \quad \text{EPR} \geq 1.12 \quad [7]$$

Gilat soil

$$k_{G(\text{Ca}+\text{Mg})}^{\text{K}} = 6.577 - 16.755\text{EPR} + 27.153\text{EPR}^2 - 18.656\text{EPR}^3 + 4.609\text{EPR}^4 \quad 0 < \text{EPR} < 1.5$$

$$k_{G(\text{Ca}+\text{Mg})}^{\text{K}} = 2.89 \quad \text{EPR} \geq 1.5 \quad [8]$$

Sodium exchange with Mg plus Ca data for Na concentrations ranging from 2.0 to 17.4 on the Nordiya soil and from 1.6 to 15.6 mol m^{-3} on the Gilat soil is shown in Table 3. Although not shown, preference of Ca plus Mg over Na was found using renormalized Na equivalent fractions, according to the method of Thellier and Sposito (1988). These findings are in agreement with the considerable amount of research that indicates a preference of Ca and Mg over Na (Bolt, 1979; Fletcher et al., 1984; Robbins and Carter, 1983; Sposito and LeVesque, 1985; Thellier and Sposito, 1988).

The calculated k_G values for Na exchange with (Ca + Mg) for each C_{Na} level in the Nordiya and Gilat soils were less affected by the solution composition than the calculated k_V values were (Table 3). The k_G values (the slope of ESR vs. SAR_i) for the studied range in the Nordiya and Gilat soils were estimated from Table 3 data, by the SAS Institute (1985) GLM procedure as 0.28 ± 0.01 and 0.42 ± 0.02 ($\text{mol}^{-1} \text{L}$)^{1/2}, respectively. These values are in good agreement with published data (Bolt, 1979; U.S. Salinity Laboratory Staff, 1954). The correlation coefficients (R^2) for the Gapon model were 0.98 with the Nordiya soil and 0.99 with the Gilat soil. The low standard deviations of k_G and the high R^2 values make the Gapon model a useful tool for predictive purposes. To improve the prediction of ESR as a function of the ion ratio in the solution, however, empirical equations for k_G as a function of ESR were derived using the STEPWISE subroutine (SAS Institute, 1985). The following equations were obtained

Nordiya soil

$$k_{G(\text{Ca}+\text{Mg})}^{\text{Na}} = 0.185 + 0.639\text{ESR} \quad 0 < \text{ESR} < 0.22 \quad [9]$$

$$k_{G(\text{Ca}+\text{Mg})}^{\text{Na}} = 0.33 \quad \text{ESR} \geq 0.22$$

Gilat soil

$$k_{G(\text{Ca}+\text{Mg})}^{\text{Na}} = 0.267 + 0.795\text{ESR} \quad 0 < \text{ESR} < 0.27 \quad [10]$$

$$k_{G(\text{Ca}+\text{Mg})}^{\text{Na}} = 0.484 \quad \text{ESR} \geq 0.27$$

Ternary Exchange

The data for K exchange with Na and Ca plus Mg on both soils, using the miscible-displacement method, are given in Table 4. To examine whether C_{Na} affected K exchange with Ca plus Mg, isotherms of the E_K vs. the \bar{E}_K obtained from the ternary system were compared with the binary isotherms. The presence of Na in the ternary system did not alter the curve of

\hat{E}'_K vs. E'_K in either the Nordiya or Gilat soils (Fig. 2a and 2b, respectively).

The k_V values for K exchange with Ca plus Mg dras-

tically decreased for both soils as C_K increased, due to an increase in the PAR_i value. The k_V values decreased in the Nordiya soil from 67.3 to 6.8 ($L \text{ mol}^{-1}$), in the

Table 3. Batch experimental data for Na exchange with Mg + Ca in a $20 \text{ mol m}^{-3} \text{ ClO}_4$ background (solution concentration, C_K , values were below 0.04 mol m^{-3} for all treatments of both soils, and quantity sorbed, q_K , values in the Nordiya and Gilat soils ranged from 0.02–0.04 and 0.10–0.15 cmol kg^{-1} , respectively).

$C_{Na}\dagger$	$C_{Ca}\ddagger$	C_{Mg}	Na ion ratio	q_{Na}	$q_{Ca} + q_{Mg}\S$	ESR¶	k_V Na (Ca + Mg) [#]	k_G Na (Ca + Mg) ^{††}
mol m^{-3}			(L/mol) ^{1/2}	cmol kg^{-1}			L mol^{-1}	(mol/L) ^{1/2}
Nordiya								
2.0	1.25 ± 0.11	8.06 ± 0.03	0.021	0.04	2.61	0.007	0.46	0.34
3.9	1.14 ± 0.02	6.60 ± 0.09	0.044	0.04	2.62	0.007	0.10	0.16
5.2	1.21 ± 0.09	5.48 ± 0.68	0.064	0.05	2.61	0.010	0.09	0.15
7.2	1.26 ± 0.09	4.85 ± 0.15	0.092	0.07	2.61	0.013	0.07	0.14
8.7	1.34 ± 0.02	3.58 ± 0.06	0.124	0.12	2.58	0.022	0.13	0.18
10.0	1.27 ± 0.03	2.90 ± 0.03	0.155	0.15	2.57	0.029	0.13	0.19
12.0	1.21 ± 0.05	2.00 ± 0.00	0.211	0.21	2.54	0.041	0.14	0.20
13.5	1.02 ± 0.00	1.34 ± 0.12	0.277	0.38	2.45	0.077	0.27	0.28
15.2	0.99 ± 0.03	0.07 ± 0.02	0.466	0.51	2.30	0.106	0.17	0.23
17.4	0.63 ± 0.02	0.04 ± 0.00	0.674	0.96	2.16	0.223	0.30	0.33
Gilat								
1.6	1.54 ± 0.02	6.83 ± 0.12	0.018	0.05	4.72	0.006	0.40	0.32
3.8	1.60 ± 0.03	5.40 ± 0.15	0.045	0.09	4.70	0.009	0.16	0.20
4.6	1.60 ± 0.00	4.62 ± 0.11	0.058	0.16	4.67	0.017	0.36	0.30
5.4	1.46 ± 0.02	4.20 ± 0.18	0.072	0.22	4.64	0.023	0.40	0.33
7.6	1.52 ± 0.05	3.31 ± 0.03	0.109	0.27	4.61	0.029	0.27	0.27
8.7	1.47 ± 0.07	2.47 ± 0.03	0.138	0.36	4.57	0.039	0.30	0.28
10.9	1.35 ± 0.00	1.70 ± 0.06	0.196	0.51	4.49	0.057	0.30	0.29
12.2	1.26 ± 0.02	1.02 ± 0.03	0.254	0.81	4.34	0.094	0.46	0.37
13.9	1.07 ± 0.07	0.50 ± 0.00	0.351	1.09	4.21	0.129	0.43	0.37
15.6	0.74 ± 0.02	0.01 ± 0.00	0.572	2.06	3.72	0.278	0.60	0.49

† No differences in Na concentration in solution and exchangeable phases were found between duplicates under the analytical limitations of Na determination.

‡ The ± value represents the standard deviation of Ca and Mg concentrations in solution.

§ Calculated as the difference between total cation-exchange capacity (Table 1) and $q_K + q_{Na}$.

¶ Exchangeable Na ratios.

Vanselow selectivity coefficients for Na exchange with Ca + Mg.

†† Gapon selectivity coefficients for Na exchange with Ca + Mg.

Table 4. Miscible-displacement exchange data for K with Na, C, and Mg in a $20 \text{ mol m}^{-3} \text{ Cl}$ background, including solution concentration (c), quantity sorbed (q), and the Vanselow (k_V) and Gapon (k_G) selectivity coefficients for K exchange with Ca plus Mg.

C_K	C_{Na}	C_{Ca}	C_{Mg}	K ion ratio	Na ion ratio	q_K	q_{Na}	$q_{Ca} + q_{Mg}$	k_V K (Ca + Mg)	k_G K (Ca + Mg)
mol m^{-3}				(L mol^{-1}) ^{1/2}		cmol kg^{-1}			L mol^{-1}	(L mol^{-1}) ^{1/2}
Nordiya										
2.2	10.1	2.10 ± 0.03†	2.11 ± 0.06	0.033	0.156	0.69 ± 0.010	0.22 ± 0.010	2.19	67.3	4.7
2.2	10.3	3.95 ± 0.01	0.00 ± 0.00	0.035	0.164	0.64 ± 0.004	0.22 ± 0.000	2.22	54.2	4.2
4.3	4.9	3.14 ± 0.03	2.53 ± 0.05	0.058	0.066	0.95 ± 0.020	0.17 ± 0.000	1.09	42.8	4.0
4.3	9.8	2.81 ± 0.00	0.01 ± 0.00	0.082	0.185	1.12 ± 0.065	0.22 ± 0.009	1.98	30.5	3.5
4.2	12.0	2.13 ± 0.07	0.00 ± 0.00	0.090	0.259	1.35 ± 0.086	0.23 ± 0.034	1.86	37.8	4.0
6.1	9.8	2.08 ± 0.01	0.00 ± 0.00	0.134	0.214	1.53 ± 0.047	0.18 ± 0.021	1.79	21.7	3.2
7.1	3.9	4.55 ± 0.00	0.01 ± 0.00	0.147	0.058	1.76 ± 0.188	0.01 ± 0.009	1.77	23.0	3.4
7.3	9.2	2.15 ± 0.02	0.01 ± 0.00	0.157	0.199	1.41 ± 0.010	0.18 ± 0.010	1.86	30.3	2.4
7.7	8.7	2.06 ± 0.03	0.01 ± 0.00	0.169	0.191	1.66 ± 0.168	0.43 ± 0.038	1.61	18.5	3.1
5.4	12.6	0.94 ± 0.00	0.00 ± 0.00	0.177	0.410	1.60 ± 0.030	0.27 ± 0.010	1.71	14.4	2.6
8.6	7.9	2.08 ± 0.00	0.01 ± 0.00	0.187	0.174	1.81 ± 0.025	0.13 ± 0.00	1.68	15.9	2.9
9.8	7.0	1.94 ± 0.00	0.01 ± 0.00	0.223	0.158	2.24 ± 0.009	0.27 ± 0.010	1.39	19.9	3.6
10.5	6.0	2.13 ± 0.01	0.00 ± 0.00	0.227	0.129	2.12 ± 0.083	0.11 ± 0.028	1.53	15.6	3.0
14.3	5.0	0.97 ± 0.00	0.01 ± 0.00	0.459	0.160	2.65 ± 0.094	0.16 ± 0.009	1.24	6.8	2.3
Gilat										
2.2	10.3	2.09 ± 0.01	2.03 ± 0.05	0.034	0.161	1.28 ± 0.020	0.52 ± 0.020	3.90	71.0	4.9
2.2	10.1	4.00 ± 0.01	0.02 ± 0.00	0.034	0.159	1.64 ± 0.050	0.35 ± 0.025	3.81	110.7	6.3
4.3	5.0	3.15 ± 0.03	2.57 ± 0.05	0.057	0.066	1.97 ± 0.010	0.35 ± 0.010	3.64	57.7	4.7
4.3	9.8	3.19 ± 0.00	0.03 ± 0.00	0.077	0.173	2.30 ± 0.050	0.35 ± 0.000	3.47	44.9	4.3
4.2	12.1	2.13 ± 0.01	0.03 ± 0.00	0.091	0.259	2.65 ± 0.032	0.38 ± 0.054	3.28	43.7	4.4
6.1	10.2	2.08 ± 0.00	0.02 ± 0.00	0.134	0.223	3.31 ± 0.190	0.32 ± 0.052	2.98	32.4	4.1
5.4	12.6	1.18 ± 0.00	0.02 ± 0.00	0.157	0.366	3.32 ± 0.300	0.61 ± 0.010	2.83	25.2	3.7
7.2	9.2	2.08 ± 0.01	0.02 ± 0.00	0.158	0.202	3.32 ± 0.010	0.52 ± 0.010	2.88	24.8	3.6
7.7	8.7	2.13 ± 0.02	0.03 ± 0.00	0.165	0.187	3.02 ± 0.160	0.26 ± 0.010	3.16	17.1	2.9
8.6	7.9	2.08 ± 0.00	0.01 ± 0.00	0.187	0.174	3.92 ± 0.025	0.13 ± 0.00	2.71	24.6	3.9
9.6	7.1	2.08 ± 0.00	0.01 ± 0.00	0.210	0.154	3.78 ± 0.110	0.22 ± 0.010	2.81	17.7	3.2
10.5	6.0	2.13 ± 0.02	0.02 ± 0.00	0.226	0.129	4.38 ± 0.202	0.21 ± 0.054	2.51	21.7	3.9
14.7	5.4	1.12 ± 0.00	0.26 ± 0.00	0.434	0.160	5.00 ± 0.000	0.70 ± 0.040	1.95	9.8	2.9

Gilat soil from 110.7 to 9.8 (L mol⁻¹). In general, the k_V values for K exchange with Ca plus Mg decreased as the value of PAR_i increased, regardless of C_{Na} . The k_G for K exchange with Ca plus Mg in both soils varied less than the k_V values in the presence of Na (Table 4), as well as without Na (Tables 2 and 3). The range in the k_G values in the presence of Na was 2.3 to 4.7 (mol⁻¹ L)^{1/2} for the Nordiya soil and 2.9 to 6.3 (mol⁻¹ L)^{1/2} for the Gilat soil.

The ability of the modified Gapon model (Eq. [3]) to predict EPR in ternary systems as a function of the PAR_i and using the estimated k_G obtained from the binary systems is demonstrated in Fig. 3a and 3b. In the Gilat soil, most of the points from the binary system are above the line, thus EPR in the ternary system was slightly underestimated by the model, using k_G from the binary system. Moreover, it is not possible to calculate the amounts of exchangeable K directly from EPR and the CEC values in ternary systems, but all the cations participating in the exchange reactions have to be taken into account. Assuming a constant CEC composed of K, Ca, Mg, and Na, the following equation can be introduced:

$$q_K = CEC - [q_{Na} + 2(q_{Ca} + q_{Mg})] \quad [11]$$

If the Gapon selectivity coefficients that were obtained in the binary system hold in the ternary system, the unknown values q_{Na} and $q_{Ca} + q_{Mg}$ can be replaced by the known solution-composition values using Eq. [3] and [4] (the modified Gapon model), and the following equation is obtained:

$$q_K = CEC - \frac{q_K k_G (Ca^{Na} + Mg) SAR_i}{k_G (Ca^K + Mg) PAR_i} - \frac{q_K}{PAR_i k_G (Ca^K + Mg)} \quad [12]$$

where the k_G values are coefficients that are functions of EPR and ESR according to Eq. [7] to [10]. Equation [12] was rearranged to calculate q_K :

$$q_K = \frac{CEC k_G (Ca^K + Mg) PAR_i}{PAR_i k_G (Ca^K + Mg) + k_G (Ca^{Na} + Mg) SAR_i - 1} \quad [13]$$

The predicted values of q_K using Eq. [13] were compared with the measured q_K values and linear relationships were obtained for both soils (Fig. 4a and 4b).

Most of the predicted points for the Nordiya soil lie near the 1:1 line, but there is a slight underestimation of q_K by the prediction method. A regression analysis of predicted q_K as a function of actual q_K shows a high correlation, $R^2 = 0.926$. The slope of the regression line is 0.92 with a standard error of 0.065, while the intercept is 0.03 cmol_c kg⁻¹ with a standard error of 0.098. The regression parameters indicate that the underestimation of q_K by the model is small for low values of q_K , but it increases for higher values of q_K as shown in Fig. 4a. The difference between the actual q_K and the predicted q_K values for a q_K of 2.6 (half of the CEC) is 0.18 according to the regression line, an underestimation of 7.0%. The standard deviation in determining the CEC of the soil was 0.5, which is 9.5% of its value. The assumption of a constant CEC in the prediction model could be the main cause for the slight

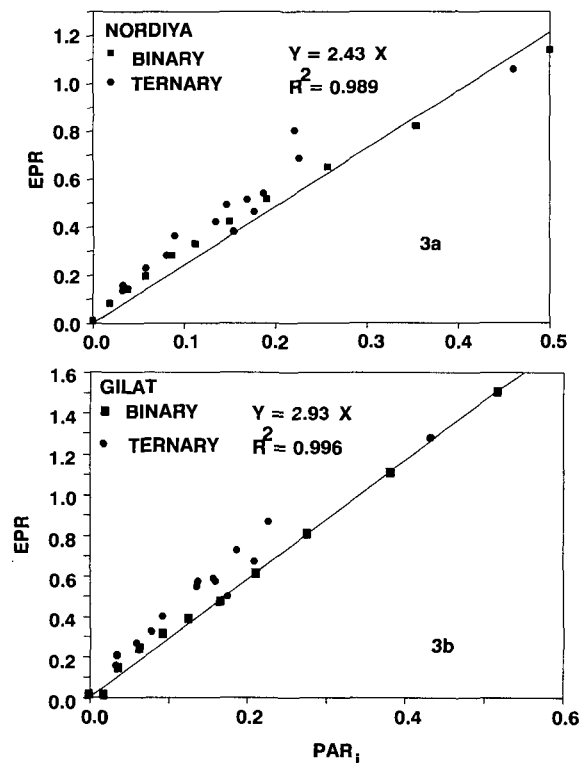


Fig. 3. Potassium exchangeable (EPR) as a function of solution-K ionic ratio (PAR_i) in (a) Nordiya and (b) Gilat soils, obtained without and with Na in the system, using batch (binary) and miscible-displacement (ternary) methods. The regression lines were fitted to the system without Na.

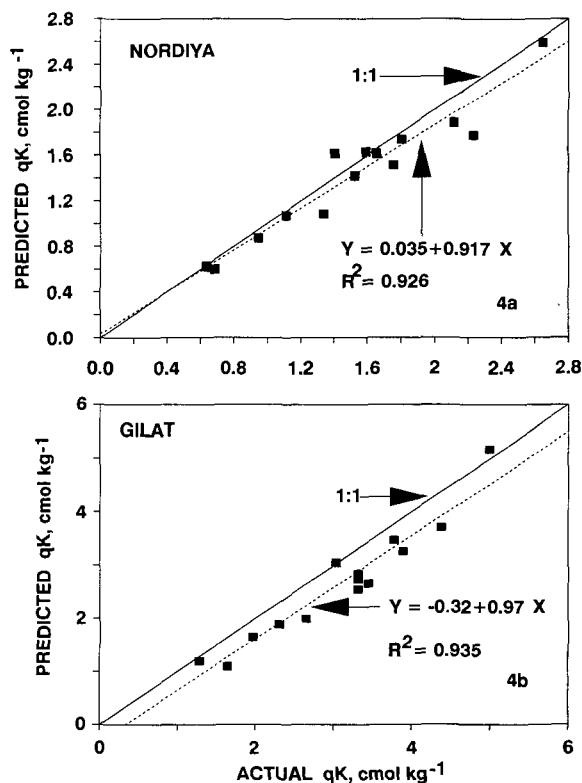


Fig. 4. Predicted adsorbed K (q_K) in the ternary system using the Gapon model and coefficients obtained from binary systems, vs. the measured q_K in the ternary system for the (a) Nordiya and (b) Gilat soils.

underestimation of q_K in the ternary system for the Nordiya soil using coefficients from the binary system.

Most of the predicted q_K points for the Gilat soil lie below the 1:1 line, indicating an underestimation of q_K by the prediction method. Regression analyses of predicted q_K as a function of actual q_K show a high correlation, $R^2 = 0.935$. The slope of the regression line is 0.976 with a standard error of 0.0636, while the intercept is $-0.322 \text{ cmol}_c \text{ kg}^{-1}$ with a standard error of 0.194. Hence, the difference in the slope from 1.0 is insignificant and the statistical significance of the intercept is low (probability of $T = 0.12$). The underestimation of q_K by the model is almost constant for the whole range of q_K studied, $0.32 \text{ cmol}_c \text{ kg}^{-1}$, unlike the situation in the Nordiya soil. Therefore, the relative difference decreases from 15 to 6.4% as q_K increases from 2 to $5 \text{ cmol}_c \text{ kg}^{-1}$. The underestimation of q_K by the model is due to the underestimation of EPR and probably to the assumption of a constant CEC. The standard deviation in determining the CEC was 0.8, which is 8.3% of its value. An overestimation of the CEC or a drop in the CEC value in the ternary system could have led to the underestimation of q_K by the model, since the model is based on an assumption of a constant CEC.

SUMMARY AND CONCLUSIONS

A preference for K over Ca plus Mg was shown for both soils, regardless of the experimental method, Na concentration, or anionic background. The k_G values were less affected by C_K than were the k_V values for both soils. Using a selectivity coefficient obtained from the binary batch system, the Gapon model was able to predict satisfactorily EPR in ternary flow systems in the Nordiya soil, but a slight underestimation of the prediction was found in the Gilat soil. Using a simple mathematical solution of the Gapon binary systems $K - (Mg + Ca)$ and $Na - (Mg + Ca)$ in combination with an assumption of a constant CEC, the predicted amount of exchangeable K as a function of solution composition was slightly smaller than the actual amount of exchangeable K for most data points in both soils. However, the difference was insignificant for a large range of q_K values in the Nordiya soil. By assuming a constant CEC and treating Mg and Ca as identical cations, we believe that binary coefficients can be used in ternary systems for predicting exchange phenomena on calcareous, montmorillonitic soils, poor in organic matter.

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