CATION SELECTIVITY OF VERTISOLS

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ABSTRACT

The effect of salinity and SAR on Gapon selectivity coefficient of two Vertisols , collected from Duhok Governorate in northern Iraq(Summel and Zakho) classified taxonomically as (fine clay-smectitic-calcareous-cracked soils), were studied in a laboratory experiment. Twenty solutions , including five TEC levels (5,10, 20, 50 and 100 $mmol_c.l^{-1}$ and four SAR levels 2.5, 5.0 ,10 and 25($mmol.l)^{0.5}$ were synthesized to equilibrate the soil samples using chloride salts of sodium and calcium, magnesium . SAR of equilibrium solution decreased compared to equilibrating solution especially at high SAR and low electrolyte solutions . At low salt concentrations , the dissolution of $CaCO_3$ and Ca bearing minerals causes a decrease in SAR of the equilibrium solution but their effect becomes less at high electrolyte concentrations . Exchangeable sodium increased with increase in SAR and TEC . Irrecpective of TEC , NaX increased by about 2.8-fold and 0.8-fold and irrecpective of SAR , the increase was about 1.3-fold and 2.1-fold for Summel and Zakho sites respectively. An increase in ESP was observed when correction for anion exclusion was calculated especially at higher TEC level. All relationships between ESR and SAR were significant for each salinity level and when the treatments were handled as a composite data . The values of Gapon constant were in the range of (0.0057- 0.0259) and (0.0155- 0.0425)($mmol.l)^{-0.5}$ and   Correction for anion exclusion caused an increase by about 18% and 11% for Summel and Zakho sites respectively compared to not corrected samples .
Keywords: Selectivity, Vertisols, Gapon coefficient, Anion repulsion, TEC.

INTRODUCTION

Cation selectivity is the measurement of the relative affinity of surfaces for different cations . Theoretically , it depends on both the properties of surface functional groups and the adsorbed cations , with water playing an intermediary role (Xu and Harsh ,1990). Knowledge of the factors influencing cation selectivity is fundamental to an understanding of processes such as cation leaching , fertilizer-soil interactions , nutrient supply to plants and reclamation of salt-affected soils (Curtin etal. 1998) . Many theoretical exchange equations have been developed and reported in the literature to describe the equilibrium distribution between exchangeable and soluble cations . Accordingly, numerous cation exchange selectivity coefficients have been determined for different soils to predict cation composition at exchange sites (Sharma etal.1988).The Gapon equation is most often used to describe Na-Ca exchange in soil systems (Gapon,1933) . A modification of Gapon's equation (U.S. Salinity Laboratory Staff, 1954) permitted its extension to three cation systems by assuming that the divalent cations Ca^{2+} and Mg^{2+} have equivalent cation exchange

properties. Vertisols occur in almost every major climatic zone of the world with their distinctive properties such as shrinking and cracking when dry and swelling when wet are some of the main features affecting their use and management (Ahmad and Mermut,1996). Therefore, mismanagement of irrigation on poorly drained Vertisols under semi-arid conditions could lead to waterlogging and soil Salinization (Jutzi etal. 1988) . Prevention of soil Salinization is of strategic importance , since a salinized Vertisols by faulty irrigation present an extremely difficult prospect to ameliorate because uniform leaching will not take place due to the water transmitting characteristic of the soil (Hashim,2011). To the irrigation planner , the understanding of exchange equilibria is important in predicting changes in exchangeable cation properties caused by the use of a given water for irrigation . The present study was carried out on selected Vertisols from Duhok Governorate in northern Iraq to establish the nature of equilibria involving Na^+ with Ca^{2+} and Mg^{2+} and obtain Gapon constants to predict cation exchange properties of these soils .

MATERIALS AND METHODS

Two sites representing different locations in the north of Iraq (Summel, Soil-1 and Zakho, Soil-2 of Duhok Governorate) were selected depending in changes in width and depth of cracks (Fayadh,2007). They were classified taxonomically as (Fin Clay, Smectitic, Superactive, Calcareous, thermic, Cracked, Chromic Haploxerert) (Soil Survey Staff, 2006). Soil samples were collected at each site from 0-10cm depth, dried in air, passed through a sieve of 2mm. Basic physico-chemical properties are presented in Table (1). Dry soil samples were equilibrated with different quality waters encompassing four levels of sodium adsorption ratio (SAR) viz. 2.5, 5, 10 and 25 $(mmol.l)^{0.5}$ and five levels of total electrolyte concentrations (TEC) viz.5,10, 20, 50 and 100 $mmol_c.l$. Pure chloride salts of calcium , magnesium and sodium were used to prepare different water quality.

Table (1): Some chemical and physical properties of the studied soils

Soil properties		Summel	Zakho
pH		7.79	7.74
EC(dS.m^{-1})		0.56	0.57
CaCO$_3$ equivalent		156.4	225.5
Organic matter		14.93	12.95
Sand	gm.kg^{-1}	25.0	125.0
Silt		310.0	255.0
Clay		665.0	620.0
Texture		Clayey	Clayey
CEC (cmol$_c$.kg^{-1})		37.01	31.58

Procedure outlined by Jurinak et al . (1984) was followed for soil sample equilibration . In 50 ml centrifuge tubes , 4 g of sieved soil was taken and 30ml of a given quality water was added , shaken for 15 min. and centrifuged . This procedure was repeated three times and only the final equilibrium solution was analyzed for Na^+, Ca^{2+}, Mg^{2+} and CI^- by methods outlined by Tandon (1999) with three replicates for

each soil and water quality . After decanting , the tubes plus samples were weighed . The solution weight was determined by differences and the solution volume by dividing the density of the solution which was calculated by weighing a known volume of the solution . From these data , the final solution SAR and ionic concentration values were calculated for each water quality . The samples were then extracted three times with 30ml solution of 1N NH_4OAC of pH 8.6 and volume was made up to 100ml and extracts were analyzed for the total Na^+ and CI^- ions. The method used to calculate the exchangeable sodium Na$\mathbf{X}$ and exchangeable calcium and magnesium $(Ca+Mg)_{0.5}X$ was based on the ion excess concept applied to the charged interface which takes into account the negative adsorption of anions at the interface as outlined by Chaudhari and Somawanshi (2002) . The NaX was calculated as : $NaX = T_{Na} - \theta C_{ONa}$

Where T_{Na} is the total Na^+ content ($cmol.kg^{-1}$) obtained by extracting the sample with 1N NH_4OAC solution of pH 8.6 and θCo_{Na} in $cmol.kg^{-1}$ is the soluble sodium content where θ stands for water content in $cm^3/100g$ and Co_{Na} is the equilibrium concentration of Na^+ in $mmol_c.cm^3$. The term $(Ca+Mg)_{0.5}X$ was calculated as :

$$(Ca + Mg)_{0.5}X = CEC - NaX - V_{an}$$

where CEC is the cation exchange capacity in $cmolc.kg^{-1}$ and V_{an} is the anion exclusion term that account for the anions being repelled from the region adjacent to the negatively charged clay surface , it is a positive number and is calculated using the chloride ion as : $V_{Cl} = \theta C_{OCl} - T_{Cl}$

where terms were previously described . The ESR and ESP were computed as

$$ESR \frac{NaX}{(Ca + Mg)_{0.5}X} = \frac{NaX}{CEC - NaX - V_{an}} \qquad ESP \frac{ESR}{1 + ESR} \times 100$$

RESULTS AND DISCUSSION

1. SAR of equilibrium solution : The data presented in table 3 and 4 showed that the SAR of equilibrium solution (SAR_{eq}) decreased compared to the equilibrating solution (SAR_{iw}) especially at low electrolyte concentration and high SAR. The difference between the two parameters widened with increasing SAR_{iw} . The maximum differences was observed with maximum SAR_{iw}, i.e. 25($mmol.l)^{0.5}$ at all TEC levels and soils being 75.2 , 60.7, 49.4 ,43.6 and 37% for Soil-1 and 88.0 , 83.0 , 78.0 , 69.6 and 62.7% for Soil-2 at 5, 10 , 20 , 50 and 100 $mmol_c.l^{-1}$ respectively . Among the studied soils , differences were perceptible at all TEC levels in the order : Soil-1 > Soil-2. At low electrolyte concentration , high final SAR values were not attained because the dissolution of $CaCO_3$ and Ca primary minerals added sufficient calcium and magnesium to lower the initial SAR and more at Soil-2 due to the higher percentage of calcium carbonate (table1) , but at higher levels, the difference between SAR_{eq} and SAR_{iw} decreased especially at Soil-1 , because the salinity treatment retard the impact of mineral dissolution because of common ion effect . Jurinak etal., (1984) , Chaudhari and Somawanshi (2002) and Frenkel and Alperovitch (1984) reported similar results.

Table (2): Cation exchange characteristics of soil at Summel site.

TEC mmol$_c$/l	SAR$_{iw}$	SAR$_{eq}$	NaX	ESR	ESP[1]	ESP	K[1]$_G$	K$_G$
	(mmol.l)$^{0.5}$		cmol$_c$.kg^{-1}		%		(mmol/l)$^{-0.5}$	
5	2.5	0.67	0.631	0.0174	1.710	1.701	0.0259	0.0259
	5.0	2.53	1.124	0.0313	3.035	3.035	0.0124	0.0124
	10	4.13	1.528	0.0431	4.132	4.131	0.0105	0.0105
	25	6.19	1.639	0.0463	4.425	4.425	0.0075	0.0075
10	2.5	0.95	0.842	0.0233	2.277	2.277	0.0245	0.0245
	5.0	3.28	1.107	0.0310	3.010	2.988	0.0095	0.0094
	10	6.81	1.782	0.0510	4.853	4.816	0.0075	0.0074
	25	9.83	2.033	0.0598	5.643	4.816	0.0061	0.0059
20	2.5	2.44	0.892	0.0252	2.458	2.410	0.0103	0.0101
	5.0	3.61	1.185	0.0338	3.269	3.204	0.0094	0.0092
	10	6.91	2.069	0.0597	5.634	5.589	0.0086	0.0085
	25	12.65	2.361	0.0744	6.925	6.376	0.0059	0.0054
50	2.5	2.87	0.631	0.0186	1.826	1.701	0.0065	0.0060
	5.0	3.54	1.139	0.0342	3.307	3.082	0.0096	0.0089
	10	8.27	2.353	0.0690	6.455	6.358	0.0083	0.0082
	25	14.11	2.568	0.0807	7.467	6.942	0.0057	0.0053
100	2.5	3.34	0.852	0.0282	2.743	2.306	0.0087	0.0073
	5.0	5.28	1.096	0.0372	3.587	2.959	0.0072	0.0059
	10	8.98	2.085	0.0726	6.769	5.634	0.0081	0.0067
	25	15.76	2.607	0.0924	8.458	7.046	0.0058	0.0048

SAR$_{iw}$ = SAR of equilibrating solution (mmol.l)$^{0.5}$. SAR$_{eq}$ of equilibrium solution . NaX = exchangeable sodium cmol$_+$.kg^{-1}. ESP[1] = ESP corrected for anion exclusion .K[1]$_G$ = Gapon constant corrected for anion exclusion in (mmol/l) $^{-0.5}$.

2. Exchangeable sodium (ESR): The data obtained for exchangeable sodium presented in tables 3 and 4 showed that for the same level of TEC , exchangeable sodium values increased with increase in SAR from 2.5-25(mmol.l)$^{0.5}$ for all the soils with an average of 45 and 65% for Soil-2 and Soil-2 respectively. Increase in TEC also increased the NaX . In order to assess the individual contribution of TEC and SAR , NaX was calculated irrespective of these variables separately . Irrespective of TEC , NaX increased by about 2.8-fold and 0.8-fold when SAR was increased from 2.5(mmol.l)$^{0.5}$ to 25 and irrespective of SAR , the increase was about 1.3-fold and about 2.1-fold when TEC was increased from 5 to 100 mmol$_c$l^{-1} for Soil-1 and Soil-2 respectively , though the SAR and TEC of equilibrating solution were increased by 10 and 20-fold , respectively .The results indicated that SAR$_{iw}$ had more of an effect on NaX than TEC at Soil-1 and their interaction was positive in increasing the sodicity hazard of soils . These results are in agreement with Paliwal and Gandhi(1976) , Ponnia etal.(1984) and Chaudhari and Somawanshi(2002) . In Soil-2 , increasing ionic strength at a fixed SAR caused an increase in Na-saturation of soil exchange complex . These results are apparently in contradiction to the theory of diffuse double layer which predicts a decrease in the fractional saturation of NaX with increase in TEC at a fixed SAR . The studied soils are calcareous with small amounts of gypsum and

despite their equilibration with chloride salts of Na^+, Ca^{+2} and Mg^{+2}, it seems that with the increase in TEC at a fixed SAR , the concentration of Ca^{+2} was also increased which resulted in an increase in the amounts of ion pairs mostly with HCO_3 in the equilibrium solution .This ultimately would have lead to an increase in Na-saturation of soil exchange complex (Kachoui et al., 1994 and Kopittke et al., 2006).

Table (3): Cation exchange characteristics of soil at Zakho site.

TEC $mmol_c/l$	SAR_{iw}	SAR_{eq}	NaX	ESR	ESP	ESP^1	K^1_G	K_G
	$(mmol.l)^{0.5}$		$cmol_c.kg^{-1}$		%		$(mmol/l)^{-0.5}$	
5	2.5	0.49	0.766	0.0249	2.429	2.429	0.0508	0.0508
	5.0	2.03	1.214	0.0399	3.844	3.844	0.0197	0.0197
	10	2.34	1.267	0.0418	4.012	4.012	0.0179	0.0179
	25	3.04	1.413	0.0468	4.471	4.471	0.0154	0.0154
10	2.5	0.95	1.016	0.0335	3.217	3.241	0.0425	0.0353
	5.0	2.17	1.587	0.0534	5.027	5.069	0.0246	0.0244
	10	2.61	1.673	0.0568	5.294	5.375	0.0218	0.0214
	25	4.35	2.006	0.0679	6.349	6.358	0.0156	0.0156
20	2.5	1.32	1.307	0.0442	4.141	4.233	0.0336	0.0327
	5.0	2.53	1.811	0.0629	5.732	5.918	0.0249	0.0240
	10	4.42	2.275	0.0806	7.201	7.459	0.0183	0.0176
	25	5.51	2.302	0.0813	7.287	7.519	0.0148	0.0143
50	2.5	1.63	1.589	0.0582	5.029	5.499	0.0436	0.0325
	5.0	2.45	1.913	0.0710	6.059	6.629	0.0289	0.0263
	10	4.32	2.375	0.0909	7.519	8.333	0.0211	0.0188
	25	7.59	3.072	0.1180	9.731	10.55	0.0155	0.0142
100	2.5	1.76	1.865	0.0769	5.851	7.141	0.0437	0.0353
	5.0	3.03	2.326	0.0981	7.365	8.934	0.0324	0.0263
	10	5.65	2.461	0.1038	7.792	9.404	0.0184	0.0149
	25	9.33	3.236	0.1478	10.25	12.88	0.0158	0.0122

SAR_{iw} = SAR of equilibrating solution $(mmol.l)^{0.5}$. SAR_{eq} of equilibrium solution . NaX = exchangeable sodium $cmol_+.kg^{-1}$. ESP^1 = ESP corrected for anion exclusion . K^1_G = Gapon constant corrected for anion exclusion in $(mmol/l)^{-0.5}$.

3. Exchangeable sodium percentage (ESP) : Data presented in tables 2 and 3 revealed that the ESP increased with increasing SAR and TEC of equilibrating solutions . Irrespective of TEC , the ESP increased from 2.1 to 5.9 and from 4.1 to 7.6 in Soil-1 and Soil-2 respectively when SAR was increased from 2.5 to 25. $(mmol.l)^{0.5}$ Similarly , increase in TEC from 5 to 100 $mmol_c l^{-1}$ increased ESP from 3.3 to 4.5 and 3.69 to 7.8 for the same sequence above when considered irrespective of SAR . It seems that the lowered CEC and higher exchangeable sodium of Soil-2 are the main reasons for higher ESP.. Additive effects of 100 $mmol_c l^{-1}$ total electrolyte concentration and 25 $mmol/l^{0.5}$ sodium adsorption ratio recorded the highest level of ESP (12.88) in Soil-2 compared with 7.05 in Soil-2 . An increase in ESP was observed when correction for anion exclusion was calculated especially at higher TEC level and more so in Soil-2 (from 4.5 to 8.4 when SAR was increased from 2.5 to 25

$(mmol.l)^{0.5}$ and from 3.7 to 9.6 when TEC was increased from 5 to 100 $mmol_c l^{-1}$. However, at lower TEC level (5 $mmol_c l^{-1}$) , such effect was not noticed at both sites. It is clear that for chloride rich waters anion exclusion play a significant role and should be corrected for a precise assessment of soil sodicity as was emphasized by Jurinak etal.(1984), Amrhein and Suarez (1991) and Chaudhari and Somaawanshi (2002) .

4- ESR–SAR relationship and Gapon constant (KG) : The regression of ESR on SAR presented in table 4 showed a significant regression coefficient when each level of salinity is statistically analyzed and when the treatments were handled as a composite data set and which indicate that the Gapon relationship is valid . The data revealed that correcting for anion exclusion increased R^2 values . Data obtained on Gapon selectivity coefficient are presented in tables 1 and 2. The values of Gapon constant were in the range of (0.0057- 0.0259) and (0.0155- 0.0425)(mmol/l) $^{-0.5}$ in Soil-1 and 2 respectively.   They decreased with increasing salinity (TEC) and SAR at soil-1 which suggests an apparent increasing preference for Ca^{2+} and Mg^{2+} by the exchange phase(lower KG values) . The values of Soil-2 showed the same trend with increasing SAR but there mean were almost constant with increasing salinity and a comparison of data on KG revealed that Soil-2 showed higher values compared to Soil-1 at all interaction of TEC x SAR and could be caused by higher effect of calicum and magnesium ions causing a decrease in SAR of the equilibrating solutions as outlined in table 3 , the decrease in SAR has the effect of causing an apparent increase in KG . Under the studied TEC and SAR range of equilibrating solution , these soils exhibited differential affinity for Ca^{2+} and Mg^{2+} or Na^+ ions . A cursory survey of the literature reveals published KG values ranging from as low as 0.005 (Jurinak etal.1984) to > 0.03(mmol/l) $^{-0.5}$ (Miller etal.1990; Chaudhari and Somawanshi 2002) . Such variability of KG makes an accurate prediction of the NaX from the SAR measurement difficult unless supporting data are available . This investigation showed that among soil factors influencing the ESR-SAR relationship are . (1) organic matter content which has a high affinity for divalent cations and correspondingly lowering the KG (Haghina and Pratt,1988). (2) Cation exchange capacity where selectivity for Na^+ decreased as CEC increases (Miller etal.1990). The values of KG obtained in this study especially at Soil-1 are much lower than the value of (0.0154 mmol/l) $^{-0.5}$ (U.S. Salinity Laboratory Staff 1954) and could , in part , be due to the use of the Polemio and Rhoades(1977) method for determining CEC . As outlined in table 1 Soil-1 has higher values of organic matter and cation exchange capacity and accordingly showed lower values for selectivity .(3) the interaction of salinity and clay mineral type is considered a prime factor and may influence CEC and cation preference of the exchanger . The mineralogical analysis results outlined by Fayadh(2007) on selected soils of this study showed that the dominant minerals were Smectite , Illite , Kaolinite , Vermiculite , Palygorkite and the stratified minerals . Despite the fact that the Smectitic minerals were dominant in the studied area , Kaolinite content increased in Soil-2 in addition to Palygorkite which was rare in Soil-1 and common in Soil-2 on the account of Smectite and associated with high calcium carbonate . Kopittke etal.(2006) indicated that for the expanding 2:1 clay minerals , their preference for Ca^{2+} increased with increasing ionic strength unlike the minerals in which external exchange sites dominated where they show an increase preference for Na^+. Correction

for anion exclusion caused an increase in the values of KG by about 18% in Soil-1 and 11% in Soil-2 compared to not corrected samples .

Table (4): The regression equation between ESR corrected for anion exclusion and SAR at various electrolyte concentrations and when the data were handled as a composite.

TEC(mmol$_c$l^{-1})	Regression equation	R^2
Soil -1		
5	Y = 0.0156 + 0.0066X	0.998
10	Y = 0.0209 + 0.004X	0.978
20	Y = 0.0199 + 0.0046X	0.935
50	Y = 0.0128 + 0.0053X	0.884
100	Y = 0.0131 + 0.0053X	0.935
Composite data	Y = 0.0178 + 0.0048X (corrected)	0.919
	Y = 0.0192 + 0.0041X(not corrected)	0.863
Soil-2		
5	Y = 0.0161 +0.0106 X	0.962
10	Y =0.0294 + 0.0095 X	0.939
20	Y = 0.0363 + 0.009 X	0.922
50	Y = 0.0454 + 0.0098 X	0.987
100	Y = 0.064 + 0.0086 X	0.939
Composite data	Y = 0.0284 + 0.0123X(corrected)	0.842
	Y = 0.031 + 0.0096X (not corrected)	0.796

التفضيل الكاتيوني لترب الفرتيسول

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الخلاصة

لدراسة تأثير نوعية المياه في معامل التفضيل الكاتيوني لگابون تم اختيار موقعين في محافظة دهوك الواقعة شمال العراق (سميل وزاخو) لتمثل هذة الرتبة حسب الدراسات السابقة التي اجريت عليها وصنفت بانها: طينية ناعمة سمكتاتية كلسية متشققة. تم تحضير عشرين محلول وبواقع خمسة تراكيز الكتروليتية (5,20,50,100ملليمولشحنة/لتر) واربعة مستويات من الصوديوم الممتز (2.5,5,10,25 ملليمول/لتر)$^{1/2}$. نسبة امتزاز الصـوديوم لمحلول الاتـزان انخفضـت بشـدة مقارنـة مـع مثيلاتهـا لميـاه الـري خاصـة عند التراكيـز الالكتروليتية المنخفضة بسبب الاضافات لكل من الكالسيوم والمغنيسيوم والناتجة من تحلل معادن الكاربونات ومن أسطح التبـادل. الصـوديوم المتبـادل زاد مـع زيـادة كـل مـن التركيـز الالكتروليتـي ونسبة امتزاز الصـوديوم وبصـرف النظر عن التركيز الالكتروليتـي فان نسبة الصـوديوم المتبـادل ازدادت بمقدار 2.8 و0.8 مرة وعند عدم أخذ نسبة امتزاز الصـوديوم بنظر الاعتبار فان الصـوديوم المتبـادل ازداد بمقدار 1.3 و 2.1 مرة ولترب سـميل وزاخـو عـلى التوالي. النسبة المئوية للصـوديوم المتبـادل ازدادت مـع زيـادة التركيز الالكتروليتي ونسبة الصـوديوم وكذلك عند التصحيح للاستبعاد الانيوني وخاصـة عند التراكيز الالكتروليتيـة العاليـة . أظهرت الدراسة علاقة إحصائية قوية بين نسبة الصوديوم المتبـادل ونسبة امتزاز الصـوديوم عند كل تركيز الكتروليتـي وعنـد أخـذ البيانـات ككـل. قـيم ثابـت گـابون تراوحـت بـين (0.0259-0.0057) و (0.0425-0.0155)

مللیمول /لتر $^{-1/2}$ والتصحيح للاستبعاد الانيوني سبب زيادة في قيم معامل التفضيل بمقدار 18 و 11% ولكل من تربتي سيميل وزاخو على التوالي مقارنة مع الغير مصححة.

الكلمات الدالة: التفضيل، الفيرتيسول، معامل گابون، الاستبعاد الانيوني، التركيز الالكتروليتي الكلي.

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