

A COMPARATIVE STUDY ON SOME THERMODYNAMIC APPROACHES FOR PREDICTING THE CATION EXCHANGE ISOTHERMS IN BINARY SYSTEMS

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ABSTRACT: The current study aimed to assess the applicability of some exchange isotherm approaches, i. e., Gains-Thomas (equivalent fraction) and Argersinger-Vanselow (mole fraction) for describing the cation adsorption in soil system. To achieve this target, an experiment was carried out on the exchange isotherms for binary systems of Na-Ca and K-Ca in an aggregated sandy clay loam soil using batch and miscible-displacement techniques.

The obtained results revealed that the selectivity coefficient of Na-Ca exchange isotherm, as calculated using Gains-Thomas (K_{GT}^{Na}), approximately constant at all the studied solution concentrations, except that those of low Na:Ca ratios, which showed slightly high values. Whereas, K_v^{Na} of Argersinger-Vanselow exhibited gradually decrease with increasing the Na:Ca ratios.

As for the calculated true exchange constant, using the integral equation of the conventional thermodynamic approaches or Rothmund-Kornfeld formulation, that take into consideration the activity of adsorbed phase, appeared approximately constant values for the two conventions at all the studied solution concentrations.

The previous data indicated that the suitability of both approaches to describe the Na-Ca exchange isotherm. ΔG_{ex}^0 values of the previous system were positive and ranged 3.38-3.66 kJ mol^{-1} , which mean that the studied soil, which dominated by 2:1 clay minerals, prefer Ca^{2+} more than Na^+ .

Data of binary K-Ca exchange isotherm showed that the selectivity coefficients (K_{Gt}^K and K_v^K) differed clearly in the two conventions and their values tended to decrease gradually with increasing K:Ca ratios or the mole fraction of K^+ on the exchange phase. That means K_{Gt}^K and K_v^K are mainly depend on K^+ solution

activity and there are many sites for K-adsorbed on the soil colloids. Values of K-true exchange constant (K_{ex}^K), as calculated from the integral equations or using Rothmund-Kornfeld formulation, were approximately constant, except at the low solution concentration of 20 m mole L^{-1} . Negative values of ΔG_{ex}^0 for K-Ca isotherm denoted that the exchange phase prefer K^+ over Ca^{2+} .

Mathematical comparing of unsteady miscible-displacement data for both Na-Ca and K-Ca isotherms at $V_0 = 0.9$ and 1.9 ms^{-1} , as well as, with batch experiment data showed that there were no significant differences between them. This finding insure achieving the equilibrium state, and in turn the miscible-displacement can describe both Ca-Na and K-Ca exchange isotherms. The aforementioned result was confirmed by calculated Peclet number.

Key words: Cation exchange isotherm, batch and miscible-displacement techniques and selectivity coefficients.

INTRODUCTION

The equilibrium between the specific ions occurred in the soil solution and adsorbed phases through soil salinization process is more related to the chemical composition of shallow saline water table, nature of the irrigation water quality and intensive use of mineral fertilizers. Thus, the nature of the reactions in soil media pointed out attention to study the transport and adsorption behaviour of the inorganic ion species.

Several conventions have been proposed for defining the

exchange-phase coefficients. Argersinger (1950) and Gains & Thomas (1953) considered the most common conventions, which described the exchange isotherm phenomenon. The main difference between these two conventions is the definition of exchange cations activity. Argersinger applied the approach of Vanselow (1932) and defined the activity as mole fraction, whereas Gains and Thomas (1953) defined the activity in terms of equivalent fraction. In spite of the wide spare of defining activity in terms as

equivalent fraction, Sposito (1981) mentioned that it is a thermodynamically incorrect.

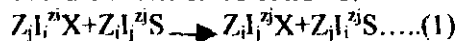
In general, results of Gains and Thomas approach produce thermodynamic data similar to that obtained by Vanselow convention (Ogwada and Sparks, 1986).

The main objective of the current work is to study the validity of the two conventions to describe the exchange isotherm of both Na-Ca and K-Ca systems in soil, which gives a more understanding about the processes of Na-salinity, K-fertilization and Ca-amelioration, with special reference to compare between the two used techniques of batch and miscible displacement for studying the exchange isotherm of the ions under investigation.

MATERIALS AND METHODS

1. Theory:

The general binary exchange could be written as follows:



where Z is the valence of cation I_j or I_i and X and S refer to the exchanger and solution phases, respectively. The thermodynamic equilibrium constant, K_{ex} defined as:

$$K_{ex} = a_i^{z_i} \Lambda_i^{z_i} / a_i^{z_j} \Lambda_j^{z_j} \dots (2)$$

where a_i the activity of cation I_i in the exchanger and A_i is the activity is the activity of cation I_i in the solution phase. The solution-phase activity is calculated from the measured solution concentration in mol L^{-1} and activity coefficient using Davies equation (Sposito, 1981). It should be noted that equilibrium constant coefficient (K_{ex}) is constant for a same cation pairs, specific exchanger and over the whole solution concentration ranges, but depends only on temperature.

Because the exchange phase activity coefficient could not be estimated directly from the exchange data, it is not possible to calculate K_{ex} from equation (1). Thus the resulting coefficient is named selectivity or conditional equilibrium coefficient.

If the exchange ions expressed in term of equivalent fractions, it can be obtained Gains-Thomas selectivity coefficient and equation (1) become as follows:

$$K_{GT} = N_j^{z_i} / N_i^{z_j} \cdot (\partial_i C_i)^{z_j} / (\partial_j C_j)^{z_i} \dots (3)$$

where $N_i^{z_j}$ and $N_j^{z_i}$ = equivalent fraction of the ions on the exchanger (CEC), ∂ = activity coefficient in the solution phase and C = concentration in mol L^{-1} .

When the exchange ions

expressed as mol kg⁻¹ on the exchanger, the coefficient named Vanselow-Argersinger and equation (1) become:

$$K_v = \chi_i^{z_i} / \chi_j^{z_j} \cdot (\partial C_i)^{z_j} / (\partial C_j)^{z_i} \dots \dots \dots (4)$$

where $\chi_i^{z_i}$ and $\chi_j^{z_j}$ = mol kg⁻¹ on the exchanger.

Always equations 3 and 4 yield a slope of one in a log-log plot of the amount adsorbed versus activity in solution (Vulava, 2000) and Voegelin *et al.* (2000). However, the experimental slope in most cases is often close, but not equal unity. In Rothmund-Kornfeld formulation (Bond, 1995 and Sposito, 1981) of Gains - Thomas and Vanselow - Argersinger exchange conventions, the activity of the equivalent or mole fraction of the exchanger species raised to the power n^{-1} , which give the flexibility to adjust the slope and vertical displacement of the adsorption isotherms, Voegelin *et al.* (2000). Then, equations 3 and 4 become:

$$K_{GT} = N_j^{z_j} / N_i^{z_i} \cdot [(\partial C_i)^{z_j} / (\partial C_j)^{z_i}]^n \dots \dots \dots (5)$$

and

$$K_v = \chi_i^{z_i} / \chi_j^{z_j} \cdot [(\partial C_i)^{z_j} / (\partial C_j)^{z_i}]^n \dots \dots \dots (6)$$

The true equilibrium constant could be calculated as a mean value with the extended Deby Huckel equation (Gains and Thomas, 1953, Sposito, 1981, Leij & Dane, 1990 and Bond, 1995). As for Vanselow-Argersinger

convention, the appropriate expression is:

$$\ln K_{ex} = \int_0^1 \ln K_v d N_j \dots \dots \dots (7)$$

and for Gains & Thomas is:

$$\ln K_{ex} = \int_0^1 \ln K_{GT} d N_j \dots \dots \dots (8)$$

The standard free energy:

$\Delta G [K_j \text{ mol}^{-1}]$ is given by:

$$\Delta G_{ex} = - RT \ln K_{ex} \dots \dots \dots (9)$$

2. Soil:

The current work was carried out using a soil sample collected from the Experimental Farm of the Agricultural Research Center at Giza. Some physical and chemical properties of the studied soil are presented in Table (1).

Table 1: Some physical and chemical properties of the studied soil.

Soil properties	Value
Particle size distribution %:	
Clay	39.40
Silt	23.00
Sand	37.60
CaCO ₃ %	2.34
Organic matter %	1.47
Soil pH (1:2.5 soil suspension)	7.95
ECe (dS m ⁻¹)	1.96
CEC (mol kg ⁻¹)	34.29

The clay minerals of the studied soil are dominated by smectites followed by illite and kaolinite (Noaman and Khalil, 1980).

The soil was Ca-saturated using concentrated CaCl₂ solution,

and then washed with distilled water to remove the excess of salts. The soil was air dried, ground and passed through a 0.35 mm sieve.

3. Exchange isotherm techniques:

i) Batch technique:

Batch exchange isotherm of Ca-saturated soil was determined in solution concentrations of 20, 100, 200 & 500 m mol L⁻¹ for Na-Ca exchange, and 20, 200 & 500 m mol L⁻¹ for K-Ca exchange.

Five or four different ratios for each of Na or K to Ca ranging from 0:1 to 1:0, and Cl-constant concentrations were used. Two replicates of 5 g Ca-saturated soil were shaken with 25 ml of each of the previous solutions for 4 hours for reaching the equilibrium (Bond *et al.*, 1982). Then, the supernatant solution analyzed for Ca and Na or K (Jackson, 1973). The differences between concentrations of the monovalent cations in the initial solutions and after equilibrium were used to determine the exchangeable Na or K.

b) Miscible displacement experiment:

The unsteady miscible displacement was carried out using the method described by Bond *et al.* (1982). Ca-saturated soil was

packed in polyvinyl chloride column of inner diameter of 17.5 mm and composed of 10 mm sections.

Solutions of NaCl or KCl (200 m mol L⁻¹) were applied to the surface of horizontal soil column at flux velocity (V₀) equal 1.9 and 0.9 x 10⁻⁶ m s⁻¹ using Mariotte reservoir (Conzanz and Marphy, 1987). The two different constant surface fluxes, terminated at different times (t_f), but having the same value of scaled termination time: T_f = V₀² t_f, as represented in the following:

T _f	V ₀ m s ⁻¹	t _f (sec.)
5.4 x 10 ⁻⁸	1.9 x 10 ⁻⁶	14958
	0.9 x 10 ⁻⁶	66666

After the end of each experiment, the soil column was rapidly sectioned. The content of each section transferred to pre-weighted centrifuge tube and weight of the tube and moist recorded. Soluble cations were extracted with 70 % (v/v) ethanol. Then, soil and centrifuge tube were oven dried to enable determination of the oven dried soil in each column section. Soluble and exchangeable Ca, Na and K were determined according to Jackson (1973).

RESULTS AND DISCUSSION

I. Sodium-calcium exchange isotherm:

Data in Table (2) represent the measured Na-Ca binary exchange isotherms, using batch technique with different charge concentration of 20, 100, 200 and

500 m mol L⁻¹ for Na-Ca exchange isotherm. The activities at equilibrium were calculated from the measured concentration of solution and activity coefficients using Davis equation, (Sposito, 1981).

Table (2): Sodium-calcium exchange isotherm of the studied soil.

Initial solution concentration (m mol L ⁻¹)	Na/Ca ratio	Solution concentration (mol L ⁻¹)		Sodium activity ratio (AR _{Na})	Exchange concentration (mol kg ⁻¹)	
		Na ⁺	Ca ²⁺		Na ⁺	Ca ²⁺
20	0.00	0.0000	0.0000	0.000	0.0000	0.1715
	0.25	0.0038	0.0081	0.050	0.0058	0.1685
	0.50	0.0077	0.0061	0.116	0.0112	0.1658
	0.75	0.0114	0.0043	0.203	0.0180	0.1625
	1.00	0.0145	0.0028	0.320	0.0275	0.1577
100	0.00	0.0000	0.0000	0.000	0.0000	0.1715
	0.20	0.0171	0.0415	0.110	0.0145	0.1640
	0.40	0.0348	0.0326	0.252	0.0260	0.1580
	0.60	0.0512	0.0241	0.429	0.0440	0.1490
	0.80	0.0670	0.0165	0.676	0.0650	0.1390
1.00	0.0810	0.0095	1.072	0.0950	0.1240	
200	0.00	0.0000	0.0000	0.000	0.0000	0.1715
	0.25	0.0457	0.0771	0.224	0.0214	0.1607
	0.50	0.0906	0.0547	0.526	0.0470	0.1481
	0.75	0.1323	0.0338	0.972	0.0880	0.1272
	1.00	0.1710	0.0145	1.902	0.1450	0.0989
500	0.00	0.0000	0.0000	0.000	0.0000	0.1715
	0.20	0.918	0.2036	0.274	0.0361	0.1534
	0.40	0.1884	0.1556	0.642	0.0578	0.1426
	0.60	0.2810	0.1095	1.147	0.0950	0.1239
	0.80	0.3707	0.0647	1.978	0.1465	0.0982
1.00	0.4542	0.0229	4.103	0.2290	0.0569	

Solution activity ratio (AR) of the monovalent cations defined as follows:

$$AR_{Na} = (Na^+) / (Ca)^{1/2}$$

() express the activity of ion.

Data in Table (2) indicated that the adsorption of Na^+ increased with increasing the Na:Ca ratio and solution concentration. At the solution concentration of 500 m mol L^{-1} , the adsorbed Na increased from 0.036 to $0.229 \text{ mol kg}^{-1}$ by increasing Na:Ca ratio from 0.2 to 1.0 . Whereas, at a ratio equal 1 , adsorbed Na increased from 0.0275 to $0.229 \text{ mol kg}^{-1}$ soil as solution concentration increased from 20 to 500 m mol L^{-1} .

Data in Table (3) showed that values of selectivity coefficient of Na-Ca isotherm as calculated using Gains-Thomas convention (equation, 3) are approximately constant through out all solution concentrations and different Na:Ca ratios, except that calculated at a low Na:Ca ratio, where it shows somewhat high value.

Values obtained from Argersinger equation showed a gradual decrease in the selectivity coefficient (K_v^{Na}), with increasing Na:Ca ratio of the solution phase at all the used concentrations.

Also, data indicated that the values of K_v^{Na} did not show any specific trend with changing solution concentration. Decreasing K_v^{Na} with increasing Na:Ca ratio, suggested that the K_v values are mainly depend on the Na:Ca ratio, even at a constant solution concentration. The same finding was observed by Voegelin *et al.* (2000) and Vulava *et al.* (2000).

Data in Table (3) illustrated that values of K_v^{Na} were higher than that of K_k^{GT} . Values of K_{GT}^{Na} ranged between 0.068 and 0.165 , whereas that of K_v^{Na} ranged between 0.19 and 0.595 . Goulding (1983) mentioned that in heterovalent exchange reaction, where $\chi \neq N$, values of selectivity coefficients defined by equivalent fractions (K_{GT}) will defer from those defined by mol fraction.

Statistical comparison of the combined data was carried out fitting $\log N^2_{Na} / N_{Ca}$ or χ^2_{Na} / χ_{Ca} against $AR^2_{Na} \{ (\partial_{Na} C_{Na})^2 / (\partial_{Ca} C_{Ca}) \}^1$. Values of R^2 (0.990 and 0.986) indicated that good fit was obtained for all data set for the both conventions at level of 0.01 . This also, confirmed by the residual mean square, which was less than 0.02 . Consequently, all data can be accurately represented by single line fitted them.

Table (3): Values of selectivity coefficients of Na-Ca and K-Ca isotherms using Gains-Thomas and Argersinger-Vanselow equations.

Initial solution concentration (m mol l. ⁻¹)	Na/Ca or K/Ca ratios	K_{GT}^{Na}	K_v^{Na}	K_{GT}^K	K_v^K
20	0.00	---	---	---	---
	0.25	0.116	0.455	5.280	12.577
	0.50	0.082	0.318	1.914	7.097
	0.75	0.071	0.268	1.720	6.133
	1.00	0.068	0.258	1.185	4.12
100	0.00	---	---	---	---
	0.20	0.153	0.588	---	---
	0.40	0.098	0.365	---	---
	0.60	0.102	0.362	---	---
	0.80	0.097	0.326	---	---
	1.00	0.092	0.289	---	---
200	0.00	---	---	---	---
	0.25	0.083	0.312	2.304	7.550
	0.50	0.078	0.274	2.134	6.005
	0.75	0.095	0.302	1.378	3.534
	1.00	0.086	0.241	1.214	2.814
500	0.00	---	---	---	---
	0.20	0.165	0.595	2.426	12.516
	0.40	0.083	0.284	2.330	6.028
	0.60	0.081	0.253	1.340	3.239
	0.80	0.081	0.228	1.260	2.783
	1.00	0.079	0.191	1.249	2.594

Fitting line, Fig. (1), of Gains and Thomas convention gives the following linear equation:

$$\text{LogAR}_{Na}^2 = -1.06 + 0.9604 \log N_{Na}^2 / N_{Ca}$$

and the following equation for Argersinger-Vanselow fitting line (Fig., 2):

$$\text{LogAR}_{Na}^2 = -0.5764 + 0.911 \log X_{Na}^2 / X_{Ca}$$

The intercept of the equations represent $\log K_{GT}^{Na}$ and $\log K_v^{Na}$ of the whole measured data. While, the slope represent n^{-1} power of the charge fraction in Rothmund-Kornfeld formulation of both Gains-Thomas and Argersinger-Vanselow (equations, 5 & 6).

As mentioned before, it is

Fig(1). Sodium-calcium isotherm data (scattered points) and Gains-Thomas line fit.

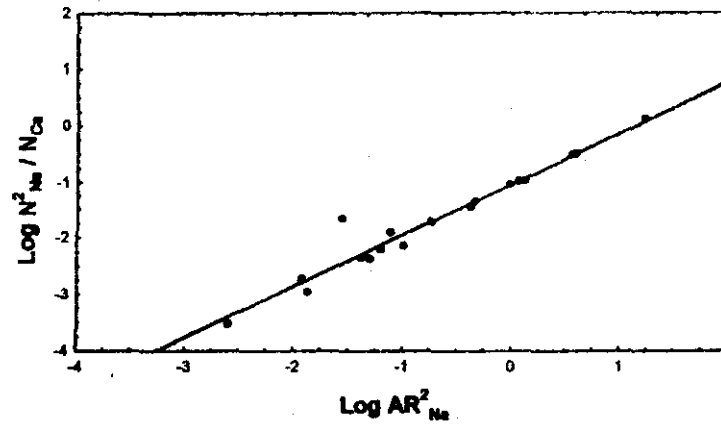
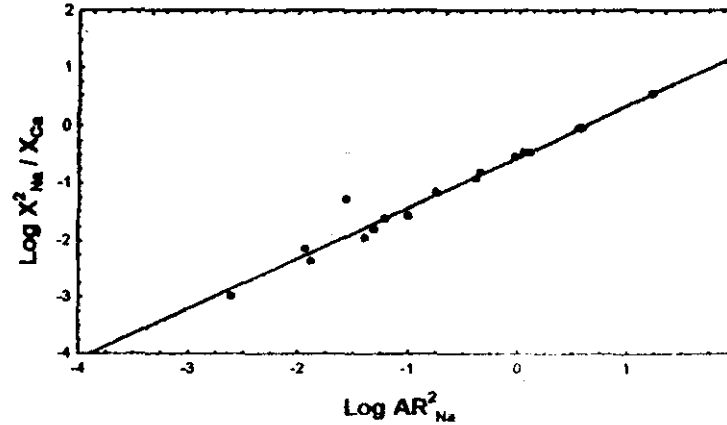


Fig (2). Sodium-calcium exchange isotherm data (scattered points) and Argersinger-Vanselow line fit.



not possible to estimate the exchange phase activity directly from isotherm data, thus true equilibrium constant can be obtained from the exchange measurements and applying the integral equations 7 and 8 (Sposito, 1981 and Bond, 1995). The calculated data of Table (4) illustrated that the true equilibrium constant (K_{ex}) was approximately constant in all solution concentration. Also, its value was approximately constant when

calculated using the previous two used approaches, this finding approved by Bond (1995).

Also, it is possible to calculate the true equilibrium constant using Rothmund-Kornfeld formulation, which account activity of the adsorbed cation under consideration (Bond, 1995) and using the following equations:

$$K_{ex}^{GT} = 1/n_{Gt} (Z_{Ca} - Z_{Na}) + \ln K_{Gt}^{Na} \dots (10)$$

and

$$K_{ex}^v = (K_v^{Na})^{1/nv} \dots \dots \dots (11)$$

Table (4): Thermodynamic equilibrium constant (K_{ex}) as calculated from integration of conditional equilibrium constant and Rothmund-Kornfeld (K_{RK}) equations.

Exchange isotherm system	Solution concentration (m mol L ⁻¹)	Gains-Thomas			Argersinger-Vanselow		
		Equ. (3) using K_{GT}	n_{GT}	Equ. (5) K_{RK}^{GT}	Equ. (4) using K_v	N_v	Equ. (6) K_{RK}^v
Na-Ca	20	0.222	0.854	0.169	0.228	0.876	0.148
	100	0.230	0.899	0.204	0.256	0.835	0.218
	200	0.227	1.020	0.243	0.240	0.974	0.238
	500	0.237	0.881	0.216	0.249	0.804	0.219
K-Ca	20	3.530	0.735	1.310	4.350	0.707	1.680
	200	4.490	0.828	4.710	4.490	0.744	4.780
	500	4.970	0.869	5.340	5.000	0.779	5.703

Calculated values of K_{ex}^{GT} and K_{ex}^v for the measured data at different solution concentrations of Na-Ca exchange isotherm (Table, 5) were very close to that obtained from the integral equation. Stability of K_{ex} values, calculated from the different conventions,

confirms its suitability to describe Na-Ca exchange isotherms.

Values of ΔG_{ex} presented in Table (5) illustrated that ΔG_{ex} of Na-Ca isotherm ranged 3.3-3.6 kJ mol⁻¹. The positive value of ΔG_{ex} indicated that the exchanger phase prefer Ca than Na (Sparks, 1995).

Table (5): Standard Gibbs free energy of exchange (ΔG_{ex}°).

Solution concentration (m mol L ⁻¹)	ΔG_{ex}° (kJ mol ⁻¹)			
	Na-Ca		K-Ca	
	Using K_{ex}^{GT}	Using K_{ex}^v	Using K_{ex}^{GT}	Using K_{ex}^v
20	+3.666	+3.601	-3.073	-3.581
100	+3.580	+3.319	---	---
200	+3.612	+3.476	-3.658	-3.658
500	+3.507	+3.386	-3.906	-3.921

II. Potassium- calcium exchange isotherm:

Data of K-Ca exchange isotherm (Table, 6) showed an increase in K activity (AR_K) in the solution accompanied with the increase in the adsorbed K.

Also, increasing the K:Ca ratio in the solution led to a gradually decrease in both selectivity coefficients of K_{GT}^K and K_v^K (Table, 3). Sparks (1995) and Ogwada & Sparks (1986b) mentioned that K_v values decreased as the mole fraction of K^+ on the exchanger phase increased. They also described the decrease in K_v with increasing mole fraction to the heterogeneous exchange sites and a specific decreasing of the surface for K^+ ions.

Jardine and Sparks (1984a&b) had shown earlier that there were different sites for K^+ exchange on soils. Also, Dufey and Delaux (1989) reported that soil exchanger contains various types of sites with

different affinities for K^+ ions, thus the exchange reaction is governed by single values of K_v for each type of sites.

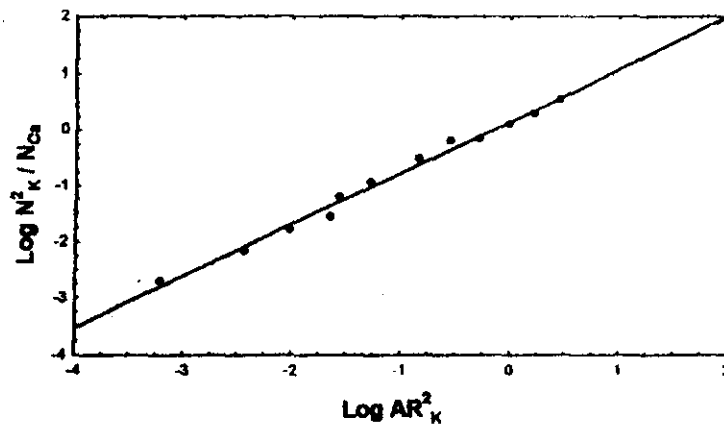
As for Na-Ca exchange data, it is helpful to fit a mathematical relationship for the data to facilitate statistical comparison (Figs. 3 and 4). There were no visible differences between the data of the three concentrations (i. e., 20, 200 and 500 m mole L⁻¹ and the fitting of both Gains-Thomas and Argersinger approaches, where there was no significant difference between them at the level of 0.01. R^2 value was 0.992 for the two approaches, and individual residual showed no trends.

The linear equation resulted from fitting parameters of the two approaches are as follows:

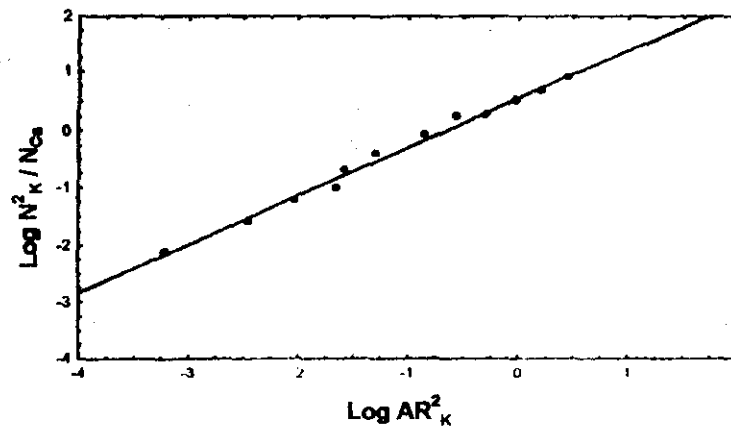
$\text{Log}AR^2=0.162+0.921\text{log}N_K^2/N_{Ca}$ for Gains-Thomas approach, and $\text{Log}AR^2=0.552+0.846\text{log}X_K^2/X_{Ca}$ for Argersinger-Vanselow equations.

The intercept of the previous linear equations represents the mean

Fig(3). Potassium- calcium exchange isotherm data(scattered points) and Gains-Thomas line fit.



Fig(4). Potassium-calcium exchange isotherm data (scattered points) and Argersinger -Vanselow line fit.



values of $\log K_{Gt}^K$ and K_v^K , where the slope of the fitted line equal the power of the solution phase activity $\{(\partial_{Ca}C_{Ca})^1/(\partial_{Na}C_{Na})^2\}$, which introduced by Rothmund-Kornfeld formulation (1919).

Table (6): Potassium-calcium exchange isotherm of the studied soil.

Initial solution concentration (m mol L ⁻¹)	K/Ca ratio	Solution concentration (mol L ⁻¹)		Potassium activity ratio (AR _K)	Exchange concentration (mol kg ⁻¹)	
		K ⁺	Ca ²⁺		K ⁺	Ca ²⁺
20	0.00	0.0000	0.0000	0.0000	0.0000	0.1715
	0.25	0.0020	0.0090	0.0247	0.0150	0.1639
	0.50	0.0045	0.0077	0.0602	0.0274	0.1577
	0.75	0.0068	0.0066	0.0975	0.0411	0.1509
	1.00	0.0095	0.0053	0.1528	0.0525	0.1452
200	0.00	0.0000	0.0000	0.0000	0.0000	0.1715
	0.25	0.0348	0.0826	0.1650	0.0758	0.1335
	0.50	0.0710	0.0644	0.3810	0.1450	0.0989
	0.75	0.1116	0.0441	0.7190	0.1920	0.0755
	1.00	0.1499	0.0251	1.2770	0.2510	0.0462
500	0.00	0.0000	0.0000	0.0000	0.0000	0.1715
	0.20	0.0794	0.2103	0.2300	0.1028	0.1201
	0.40	0.1625	0.1688	0.5320	0.1875	0.0777
	0.60	0.2546	0.1228	0.9820	0.2270	0.0579
	0.80	0.3442	0.0779	1.6780	0.2790	0.0319
	1.00	0.4358	0.0321	3.3140	0.3210	0.0109

If calculating the true constant of the equilibrium coefficient, depending on the integral equations of 7 and 8, it can be seen that calculation of K_{ex} require values of selectivity coefficients at $N_K = 0$ and $N_K = 1$, but these coefficients are undefined at these points and must be obtained by extrapolation calculated at other values of N_K . Thus, any change in \tilde{N}_x will be accompanied with change in the selectivity coefficient and its extrapolation values and integration result.

Data in Table (4) showed that values of K_{ex}^K were not constant as in the case of Na-Ca isotherm, where it increased somewhat with increasing solution concentration. The changes in the constant of equilibrium coefficients with changing ionic strength were also observed by Bond (1995). Ogwada and Sparks (1986) attributed the change in K_{ex} to the small changes in X_K at the end of isotherm.

Using mean values of K_{GT} and K_v resulted from fitting the obtained data at different solution concentrations and applying the equations of 5 and 6 derived from Rothmund-Kornfeld formulation, values of K_{ex} are in close agreement with each other (Table, 4) and similar to those calculated from equations 5 and 6, except for 20 mmolL⁻¹ solution concentration. Whereas, values of Rothmund-Kornfeld formulation are less than those calculated from integral equations.

Values of ΔG_{ex} , which calculated using equation (9) and K_{ex}^{GT} and K_{ex}^v (Table, 5), ranged from -3.07 to -3.90 kJ mol⁻¹. The negative value denote, when K⁺ displace Ca²⁺, the reaction given by Eq (1) tends to move the right and the exchanger complex favors K⁺ over Ca²⁺ ($\Delta G_{ex}^0 < 0$). The same finding is observed by Goulding and Talibudeen (1984), Leij and Dane (1990) and Spark (1995).

Unsteady miscible-displacement:

Batch technique is considered one of the most popular method for studying the exchange isotherms. Limitations of this method could be summarized into the following:

i) Break-down of small aggregates resulting from a mechanical action of shaking.

ii) Solubility of some constituents of soil and probably the excess of water cause some physicochemical changes in the exchanging materials.

iii) The fact that solution and composition can be changed during equilibrium period, which is very important for kinetic studied (Schweich and Sardin, 1981 and Bond & Phillip, 1990).

Conversely, these changes seem to be negligible in column or miscible displacement. It is probably due to the fact that flow does not destroy the small aggregates and the contact between the soil and water in the column is more relevant to the natural situation.

Data of exchange isotherm obtained from the unsteady miscible displacement experiments at flux flow 0.9 and 1.9X10⁻⁶ ms⁻¹ presented in Tables (7 and 8) for Na-Ca exchange isotherm and Tables (9 and 10) for K-Ca exchange isotherm.

By fitting the mathematical relationship of the Na-Ca isotherm data to facilitate the statistical comparison, it was found that there was no visible difference between the combined data of the two applied water fluxes (V_0) of 200 m mol L⁻¹ NaCl and fitting of Gains-Thomas equation at 0.01 level, where R² equal 0.993 (Fig., 5).

Fig (5). Sodium -calcium exchange isotherm data (scattered points)
of miscible-displacement ($V_0=0.9$ and $1.9 \cdot 10^{-4} \text{ms}^{-1}$)
with Gaines -Thomas line fit.

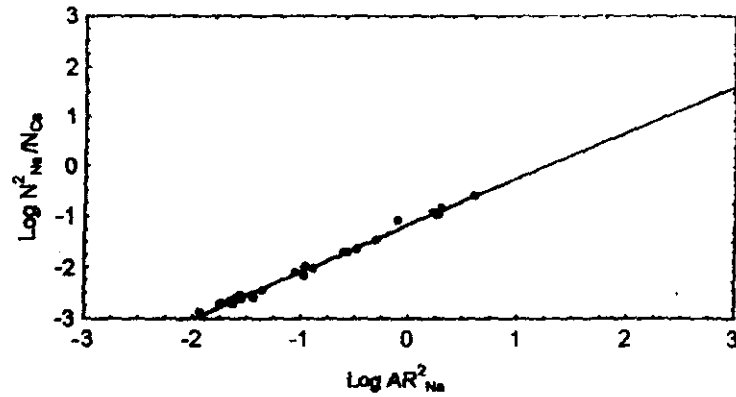


Fig (6). Potassium -calcium exchange isotherm data (scattered points)
of miscible-displacement ($V_0=0.9$ and $1.9 \cdot 10^{-4} \text{ms}^{-1}$)
with Gaines -Thomas line fit.

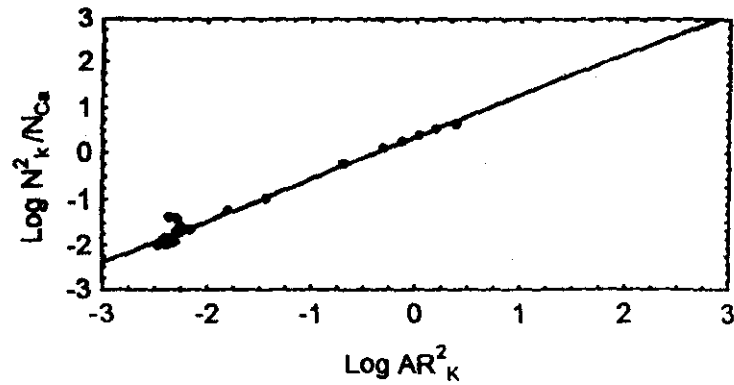


Table (7): Sodium-calcium exchange isotherm data and K_{GT}^{Na} by miscible displacement at water flux ($V_o = 0.9 \times 10^{-6} \text{ m sec}^{-1}$).

Depth (cm)	Solution concentration (mol L ⁻¹)		Exchange concentration (mol kg ⁻¹)		K_{GT}^{Na}
	Na ⁺	Ca ²⁺	Na ⁺	Ca ²⁺	
1	0.2398	0.0264	0.1349	0.1040	0.062
2	0.1825	0.0300	0.1082	0.1174	0.072
3	0.1016	0.0227	0.0755	0.1337	0.077
4	0.0932	0.0306	0.0613	0.1408	0.077
5	0.0805	0.0338	0.0488	0.1471	0.069
6	0.0696	0.0336	0.0457	0.1486	0.080
7	0.0599	0.0505	0.0320	0.1555	0.073
8	0.0567	0.0551	0.0272	0.1576	0.062
9	0.0300	0.0578	0.0169	0.1630	0.091
10	0.0309	0.0767	0.0167	0.1631	0.067
11	0.0319	0.0721	0.0166	0.1632	0.095
12	0.0326	0.0884	0.0149	0.1640	0.088
13	0.0343	0.0934	0.0157	0.1636	0.093
14	0.0420	0.1167	0.0162	0.1634	0.083
15	0.0392	0.1209	0.0148	0.1641	0.082

Table (8): Sodium-calcium exchange isotherm data and K_{GT}^{Na} by miscible displacement at water flux ($V_o = 1.9 \times 10^{-6} \text{ m sec}^{-1}$).

Depth (cm)	Solution concentration (mol L ⁻¹)		Exchange concentration (mol kg ⁻¹)		K_{GT}^{Na}
	Na ⁺	Ca ²⁺	Na ⁺	Ca ²⁺	
1	0.1262	0.0147	0.0948	0.1241	0.055
2	0.0917	0.0084	0.0995	0.1222	0.061
3	0.0557	0.0189	0.0456	0.1486	0.074
4	0.0523	0.0455	0.0338	0.1546	0.098
5	0.0623	0.0801	0.0293	0.1518	0.091
6	0.0509	0.1091	0.0198	0.1616	0.079
7	0.0331	0.1115	0.0146	0.1640	0.103
8	0.0341	0.1171	0.0149	0.1635	0.106
9	0.0403	0.1276	0.0159	0.1653	0.094
10	0.0308	0.1466	0.0123	0.1648	0.112

Table (9): Potassium-calcium exchange isotherm data and K_{GT}^K by miscible displacement at water flux ($V_o = 0.9 \times 10^{-6}$ m sec $^{-1}$).

Depth (cm)	Solution concentration (mol L $^{-1}$)		Exchange concentration (mol kg $^{-1}$)		K_{GT}^K
	K $^+$	Ca $^{2+}$	K $^+$	Ca $^{2+}$	
1	0.0953	0.0097	0.2332	0.0548	0.908
2	0.0850	0.0110	0.2125	0.0652	0.945
3	0.0831	0.0152	0.1933	0.0748	0.945
4	0.0667	0.0381	0.1230	0.1099	0.968
5	0.0359	0.0620	0.0548	0.1441	0.807
6	0.0123	0.0608	0.0205	0.1612	0.849
7	0.0120	0.0649	0.0188	0.1621	0.792
8	0.0125	0.0714	0.0205	0.1612	0.954
9	0.0132	0.0744	0.0205	0.1612	0.892
10	0.0127	0.0655	0.0219	0.1605	0.978
11	0.0150	0.0774	0.0228	0.1601	0.884
12	0.0131	0.0654	0.180	0.1624	0.616
13	0.0142	0.0718	0.0188	0.1621	0.626
14	0.0163	0.0884	0.240	0.1595	0.444
15	0.0139	0.0706	0.0184	0.1623	0.623

Table (10): Potassium-calcium exchange isotherm data and K_{GT}^K by miscible displacement at water flux ($V_o = 1.9 \times 10^{-6}$ m sec $^{-1}$).

Depth (cm)	Solution concentration (mol L $^{-1}$)		Exchange concentration (mol kg $^{-1}$)		K_{GT}^K
	K $^+$	Ca $^{2+}$	K $^+$	Ca $^{2+}$	
1	0.1039	0.0163	0.2460	0.0485	1.572
2	0.0935	0.0309	0.1700	0.0864	0.988
3	0.0195	0.0419	0.0412	0.1508	1.038
4	0.0121	0.0625	0.175	0.1627	0.659
5	0.0110	0.0625	0.0170	0.1629	0.745
6	0.0139	0.0676	0.0240	0.1595	1.013
7	0.0154	0.0757	0.0274	0.1577	1.208
8	0.0177	0.0842	0.0257	0.1586	0.875

Also, data of K-Ca isotherms for 200 m mol L⁻¹ KCl and water fluxes 0.9 and 1.9X10⁻⁶ m sec⁻¹ are presented by line fitted to the data (Fig., 6). There was no visible difference between the obtained data and the fitting of Gains-Thomas equation.

The fit line (Figs., 7 and 8) of miscible displacement data in combination with batch experiments data for both Na-Ca and K-Ca isotherms, represent no significant differences between them at the level of 0.1.

In general, it could be concluded that the unsteady miscible displacement technique provides an accurate means to describe either Na-Ca or K-Ca exchange isotherms. Also, the good agreement between data of the exchange isotherms obtained using miscible displacement (at the two water fluxes) and the data obtained from batch experiments, indicate that the equilibrium was achieved during the column experiment. This may be due to the time scale for the diffusion of ion into the soil aggregates was less than that for their transport over similar distance by advection (Bond and Phillip, 1990).

This could be proved by the calculated Peclet number, which

represents the ratio of two scales:

$$Pe = \mu \delta / D_0$$

Pe = Microscopic Peclet number.

μ = Pore velocity (i. e., water flux / volumetric water content).

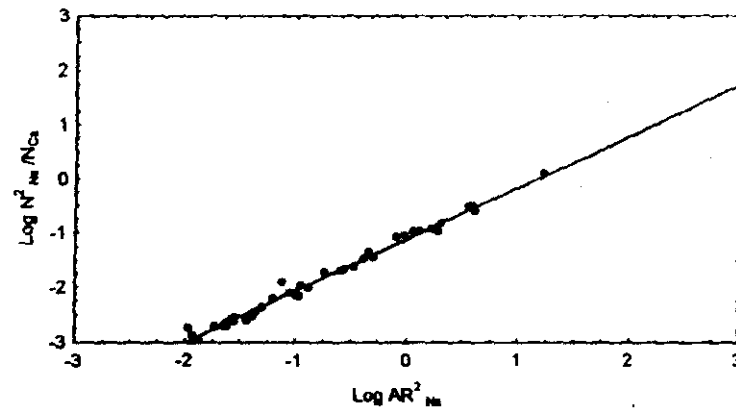
δ = Characteristic length scale of diffusion (i. e., radius of soil aggregates).

D_0 = Molecular - diffusion in free solution.

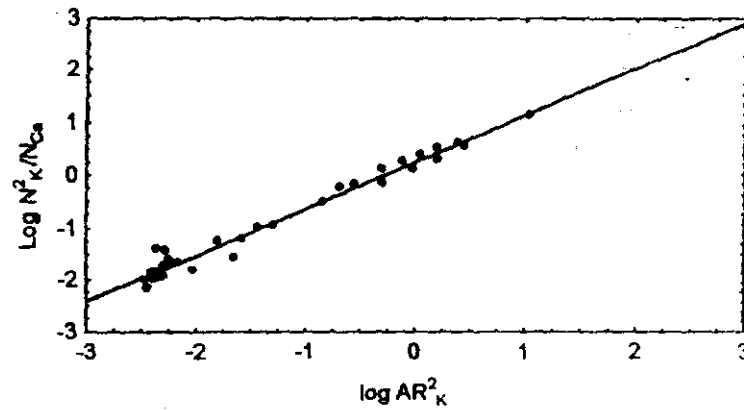
The mean values of volumetric water content ranged 44.1-44.5 % for Na-Ca isotherm and 48.2-49.1 % for K-Ca isotherm of miscible displacement experiments. Maximum radius of aggregates was 0.25 mm, whereas the molecular-diffusion coefficient of ion species involved was approximately 10⁻⁹ (Bond and Phillip, 1995). Then, the calculated Peclet number of the present work ranged 0.985-1.07 for water flux of 1.9X10⁻⁶ m sec⁻¹ and from 0.46-0.51 for the water flux of 0.9X10⁻⁶ m sec⁻¹.

If Peclet number is less than the unity, that indicate the time scale for diffusion is less than that for advection or sufficient time for diffusion of Na or K into aggregates was achieved. Also, it means that the first rate of water flux 0.9X10⁻⁶ m sec⁻¹ is very suitable to give the enough time to

Fig (7). Sodium-Calcium exchange isotherm combined data (scattered points) of miscible-displacement and batch experiments with Gains-Thomas line fit.



Fig(8) Potassium-calcium exchange isotherm combined data(scattered points) of miscible-displacement and batch experiments with Gains-Thomas line fit.



reach equilibrium, but water flux of 1.9×10^{-6} m sec⁻¹ is not suitable to reach the equilibrium state.

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دراسة مقارنة عن بعض فروض الديناميكا الحرارية للتنبؤ بسلوك خاصية التبادل الكاتيوني في النظم الثنائية (Na-Ca and K-Ca)

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تهدف هذه الدراسة إلى إستبيان مدى صلاحية بعض فروض الديناميكا الحرارية ممثلة في فرضى Gains-Thomas and Argersinger-Vanselow في وصف خاصية التبادل الكاتيوني في التربة . ولتحقيق هذا الهدف أجريت تجربة تبادل كاتيوني على نظامى إمصاص ثنائى (Na-Ca and K-Ca) لأرض طميية طينية رملية باستخدام طريقتى:

Batch and miscible displacement.

وتشير النتائج المتحصل عليها إلى أن قيم معامل الإمصاص الإختياري (K_{GT}^{Na}) لنظام Na-Ca - المقدره باستخدام معادلة Gains-Thomas تتصف بالثبات النسبى لقيمتها تحت ظروف إختلاف تركيز المحلول فيما عدا تلك المنخفضة في نسب Na:Ca والتي أظهرت إرتفاع قليل في قيمها ، بينما أظهرت قيم معامل الإمصاص الإختياري -Argersinger-Vanselow (K_V^{Na}) إخفاضاً تدريجياً مع زيادة نسبة Na:Ca . وبالنسبة لثابت الإمصاص الحقيقى (K_{ex}) - المحسوب بتفاضل معادلات الديناميكا الحرارية المستخدمة أو باستخدام تعديل Rothmund-Kornfeld أخذاً في الإعتبار نشاط الكاتيونات المدمجة على معقد الإمصاص - فقد وجد أن قيمه تشير إلى الثبات تحت ظروف جميع تركيزات المحاليل وتلك في كلا المعادلتين المستخدمتين ، وهذا يدل على صلاحية كلاهما في وصف نظام الإمصاص الثنائى Na-Ca .

كما تدل نتائج لدراسة على أن قيم حرارة إمصاص النظام الثنائى Na-Ca كانت موجبة ، تراوحت ما بين ٣,٢٨ - ٣,٦٦ كيلو جول / مول ، مما يدل على تفضيل معقد الإمصاص للكالسيوم على الصوديوم في التربة تحت ظروف سيادة معادن الطين السيليكاتية ١:٢ . أما بالنسبة لإمصاص البوتاسيوم على معقدات التربة الغروية المشبعة بالكالسيوم ، فإن قيم معاملى الإمصاص الإختياري (K_{GT}^K and K_V^K) قد أظهرت إختلافاً واضحاً ، وبصفة عامة فإن قيمهما تتناقص تدريجياً بزيادة قيم نسبة K-Ca أو بزيادة ال Mole fraction للبوتاسيوم الممنص ، وهذا يعنى أن كلا المعاملين يعتمداً أساساً على النشاط الأيوني للبوتاسيوم في المحلول ، وكذا لإختلاف مواضع إمصاص البوتاسيوم على معقد الإمصاص (معادن طين ١:٢) .

كما أظهرت قيم ثابت الإمصاص الحقيقى للبوتاسيوم - المحسوبة باستخدام المعادلات التفاضلية أو تعديل Rothmund-Kornfeld - ثبات تقريبى - فيما عدا تركيز ٢٠ ملليمول / لتر . وتشير القيم السالبة لحرارة التفاعل الإمصاص (ΔG_{ex}^0) للنظام الثنائى K-Ca أن معقد الإمصاص يفضل البوتاسيوم على الكالسيوم . وتدلل نتائج المقارنة الرياضية لنظامى Na-Ca ، K-Ca عند سرعتى سريان للمياه ٠,٩ ، ١,٠ ، ١,٩ ، ١٠ متر / ثانية - فى تجربة الأعمدة - عند مقارنتها مع نتائج تجربة ال Batch أنه ليس هناك فروق معنوية ، مما يؤكد الوصول إلى حالة الإتزان فى تجربة الأعمدة وأن هذه الطريقة يمكنها أن تصف السلوك التبادلى لكل من نظامى Na-Ca and K-Ca بدقة ، وقد تأكد هذا من حساب رقم Peclet .