Thermodynamics of the Ion Exchange Reaction Between Na and Mn

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The importance of manganese in plant nutrition is well established. Manganese may cause poor growth in acid soils and in neutral or alkaline soils. Toxicity may occur in the former but manganese deficiency may be encountered in the latter. The main factors influencing the availability of manganese in soils can be classified under three general headings: the pH, the organic matter content and the biological activity. Ion exchange reactions, however, appear to play an important role in controlling the concentrations of Mn in the soil solution but there have been few quantitative studies of the ion exchange behaviour of the Mn ion in soils. A systematic study of the Na—Mn exchange reaction was undertaken on three acid soils before and after the removal of organic matter. The main objectives of this investigation were: 1. to study the selectivity coefficients for manganese-sodium exchange in soils, 2. to examine the effect of organic matter on the selectivity coefficients, 3. to investigate the possible formation of organic matter-manganese complexes, 4. to ascertain the influence of the pH of the soil on manganese adsorption.

Experimental

The description of the soils selected for investigation is given in Table 1 As can be seen, the soils were acid and had a wide range of cation exchange capacity and organic matter content. The bulk samples were air-dried and passed through a 2 mm sieve. Subsamples of the 2 mm soil were ground to pass a 70 mesh sieve. The soils were washed with *N* sodium chloride several times over a period of five days. The soils were then washed with water till chloride free after which they were washed once with 95% ethanol and air-dried. Organic matter was destroyed from the sieved samples by the hypochlorite procedure based on ANDERSON's [1] method. After this treatment, the soils were brought to their initial pH with dilute HCl and excess chloride was removed with water and alcohol as before.

The exchange isotherms were determined using the equilibrium dialysis technique (MARTIN and LAUDELOUT [5]). The exchange reaction between Na and Mn was studied at either three or four total normalities (5, 10, 25, 50 meq/l) and at three temperatures (5, 25, 37 °C). The pH of the solution phases was adjuested to 4. A few trials were carried out at pH 7.

The concentrations quoted above refer to the final normalities of the solutions after the two salts have diffused into the dialysis bag. Na was measured by flame photometry on a Beckman spectrophotometer, for Mn

Table 1

Description of the soils

Site	Soil type	pH	% clay $< 2\,\mu$	Organic carbon of soils, %	
				untreated	treated by NaOCl
Deerpark	Glacial drift derived from solifluction and loess	5.2	18	2.90	0.09
Carlow	Gley derived from coal measure shale	5.5	17	6.18	0.08
Meath	Grey brown podzolic derived from limestone drift	5.4	19	3.80	0.09

an atomic adsorption spectrophotometer Techtron, model AA 100 was used. The adsorbed ions were removed from the colloidal phase with neutral *N* ammonium acetate for the Deerpark soil. For the two other soils the radioisotope technique was used to measure the exchangeable cations, ^{54}Mn and ^{22}Na labelling the mixed electrolyte solutions.

Theoretical considerations

For the exchange reaction

$$2\,\mathrm{Na} - \mathrm{soil} + \mathrm{MnCl}_2 \rightleftarrows \mathrm{Mn} - \mathrm{soil} + 2\,\mathrm{NaCl} \tag{1}$$

the uncorrected selectivity coefficient, K'_c is:

$$K'_c = \frac{N_{Mn} \cdot (m_{NaCl})^2}{(N_{Na})^2 \cdot m_{MnCl2}}\,, \tag{2}$$

where N and m refer to the equivalent ion fractions in the surface phase and the molalities in the solution respectively.

The selectivity coefficient K_c and the equilibrium constant K are expressed by:

$$K = K_c \frac{\gamma_{Mn}}{\gamma^2_{Na}} = K'_c \frac{f^2_{NaCl}}{f_{MnCl_2}} \cdot \frac{\gamma_{Mn}}{\gamma^2_{Na}} \tag{3}$$

γ and f being the activity coefficients in the surface phase and in the solution.

According to Gaines' and Thomas' [3] theory the equilibrium constant is approximated by averaging the selectivity coefficient over the entire range of saturation of the exchanger

$$\ln K = -1 + \int_0^1 \ln K_c \, d\, N_{Na}\,, \tag{4}$$

It must be noted that K_c and K_c are dimensionless numbers. Ion activities are expressed in terms of mole fraction rather than in molarity in order to avoid concealed terms in RT ln (mole per liter). Therefore, the results presented here will be greater in absolute value of RT ln 55.51 for free energy and smaller by R ln 55.51 for entropy if compared to other authors' results using the usual scale concentration.

A knowledge of the activity coefficients in the mixed solution of electrolytes (Na + $MnCl_2$) is necessary to compute K_c from K'_c. The necessity of calculating activity coefficients can be avoided by extrapolating the values of K'_c obtained at different total normalities to infinitely small ionic strength. This method (Van Bladel and Laudelout [8]) provides the true values of equilibrium and applied to the reverse reaction it determines whether the irreversibility shown by isotherm hysteresis of the exchange is true or only apparent.

Results and discussion

Influence of pH on the adsorption of manganese

An excess adsorption of a metal ion with respect to the CEC measured with NH_4Ac has often been reported when exchange reactions were carried out between soil colloids and polyvalent electrolytes. The excess amounts have been explained by precipitation of the metal hydroxyde or adsorption of monovalent ions of the type XOH^+ (Bower and Truog [2]). Attempting to avoid extracting the exchangeable cations or the use of isotopes by estimating the amounts of ions adsorbed from measures of concentration changes in the liquid phase may also be misleading if precipitation occurs.

In a preliminary study, the CEC value obtained with a montmorillonite sample saturated with manganese was 103.53 meq/100 g which compared well with the values found for the same clay saturated with NH_4^+ (103.20 meq/100 g), Ca^{2+} (104.50 meq/100 g), Mg^{2+} (106.60 meq/100 g). The pH of the external solutions were adjusted to 4 for the exchange reactions reported in this study. A few experiments were carried out at pH 7. The isotherms of the experiments carried out after adjusting the pH of the external solutions to 7 were similar to those obtained when the pH of the liquid phase was adjusted to 4 (Fig. 1). The pH values of the external solutions read from 5.0 to 5.8, which is not surprising because the pH's of the soils were between 5.0 and 5.5 (Table 1). Clearly, the buffer capacity of the soils determined the pH's of the solutions.

Even though the formation and adsorption of monovalent hydroxy-ions of the type XOH^+ might occur at higher pH, it was unlikely that this ion ($MnOH^+$) was present to any significant extent at the final pH existing in the systems studied, because at pH 5.0 the ionic ratio of $Mn^{2+}/MnOH^+$ is $10^{5.7}$. Obviously, too, there was no precipitation of $Mn(OH)_2$ or other insoluble Mn solid phases. These results are in good agreement with those presented by Mehlich [6] and Rivenbark [7].

Cation exchange capacity of the soils

For the reaction Na—Mn carried out on the Deerpark soil, full recoveries are given for the surface (i) and the solution (o) phases. All the cations originally present as exchangeable cations or added as soluble salts could be accounted for when exchangeable cations were extracted with NH_4Ac indicating that this method was satisfactory for the extraction of exchangeable cations (Table 2).

Although quantitative recovery of the Mn and Na added in soluble and exchangeable form was obtained also when adsorbed ions were determined by isotopic exchange, the isotopic exchange capacity values (IEC) were consistently lower than the values obtained by extraction of the homoionic soil with NH_4Ac (CEC) (Table 3).

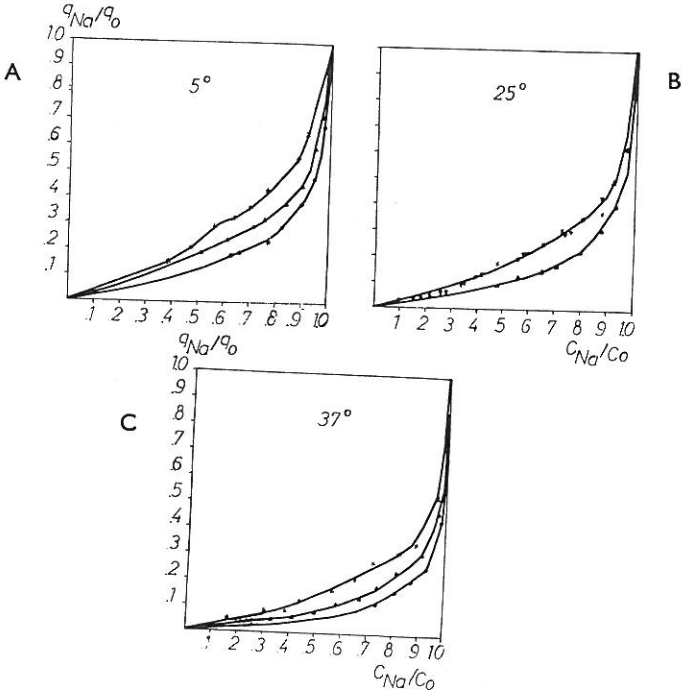

Fig. 1.

Na—Mn isotherms on Deerpark soil. Parts A&C. Total normality: (upper curve) 0,025N; (middle curve) 0,01N; (lower curve) 0,005N; Part B, (upper curve) 0,025N at 4 and 7 pH respectively; (lower curve) 0,01N

The reason for this difference is not known, particularly because with the Deerpark soil the amount of (Mn + Na) extracted with NH_4Ac after exchange equilibration were close to those obtained by extracting the homoionic Na saturated soil. The observations that complete recoveries were obtained and that the sum of exchangeable (Mn + Na) in both methods did not exceed the measured cation exchange capacity values is worthy of note because they indicate that no detectable amounts of organic matter-manganese complexes were formed and that all the manganese adsorbed was divalently charged under the acidity conditions prevailing in the systems studied. It should also be pointed out that the sum of (Na + Mn) adsorbed by the soils did not change with changing composition in the adsorbed phase. Because of this and the previous observations indicating that the adsorbed ions

Table 2

Recoveries at the normality: 10 meq/l at 5° and 25°C

$\Sigma(Mn_l{}^* + Mn_0{}^{**})$ meq/l		Mn added	$\Sigma(Na_0 + Mn_0)$ meq/l		$\Sigma(Na + Mn)_{ads}$ meq/100 g	
5°C	25°C		5°C	25°C	5°C	25°C
19.60	19.90	20	10.00	9.90		7.16
17.80	18.10	18	10.00	9.90	7.06	7.26
15.70	16.05	16	9.80	9.95	7.36	7.20
13.00	13.85	14	10.10	10.15	6.90	6.83
12.10	12.10	12	10.00	10.10	7.90	6.93
9.80	10.20	10	10.00	10.10	7.20	7.33
7.95	7.80	8	9.95	10.10	7.50	7.13
5.90	6.00	6	10.00	10.10	7.80	8.06
3.90	4.10	4	10.05	10.20	7.73	7.20
1.90	2.10	2	10.10	10.50		7.80
107.65	110.20	110	100.00	101.00		

* Surface phase.
** Solution phase.

determined by isotopic exchange or by extraction with NH_4Ac were apparently entirely in the exchange phase, the GAINES and THOMAS treatment [3] was applied to the experimental results.

Exchange isotherms and thermodynamic functions

The exchange isotherms for one soil (Deerpark) are presented in Fig. 1. They show that, as expected, dilution of the soil solution favoured the adsorption of manganese. The same preference was observed with increasing temperature at constant normality. The K_c' values at given surface composition were calculated from the smoothed best fit curves in Fig. 1 and were then plotted as a function of ionic strength (Fig. 2) so that log K_c at finite dilution could be obtained. The log K_c' values at infinite dilution represent, of course,

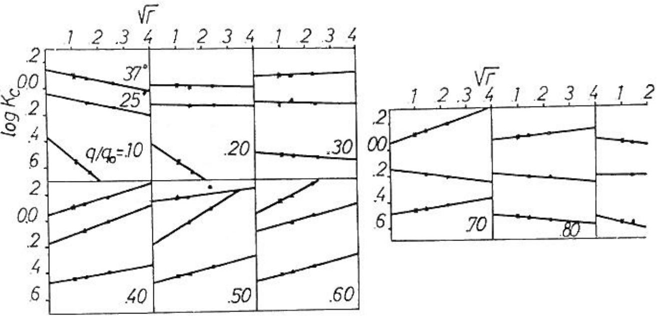

Fig. 2

Uncorrected selectivity coefficients vs. the square root of twice the ionic strength for different compositions of the surface phase and three temperatures. Total normality: 0.005 N, 0.01 N, & 0.025 N. Exchange: Na—Mn on Deerpark soil the selectivity coefficients and the plot of these against surface composition (Fig. 3) was used to calculate the equilibrium constants by graphical integration. From the values of the equilibrium constants obtained at different temperatures, the standard enthalpy change, ΔH_0 was obtained (Fig. 4). The values of ΔS_0 were then calculated and the values obtained are given in Table 4.

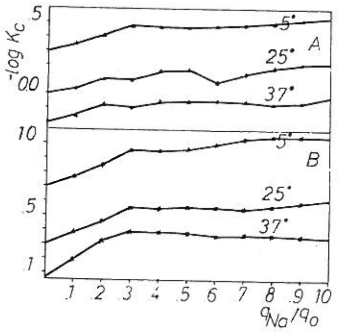

Fig. 3

Corrected selectivity coefficients as a function of the composition of the exchanger

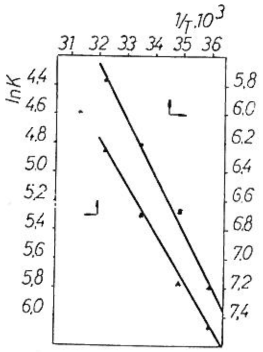

Fig. 4

Logarithm of the equilibrium constant as a function of the inverse of temperature.

A) Exchange: Na—Mn on Deerpark soil; B) Exchange: Na—Mn on treated Deerpark soil

Studying the exchange between ammonium and the alkali ions, Martin and Laudelout [5] found that replacement of ammonium by a less polarizable ion was accompanied by a positive change of free energy and enthalpy. Similarly the thermodynamic functions for the reaction Na : Mn (Table 4) show that the replacement of Na^+ (polarizability: 0.17 Å^3) by Mn^{2+} (polarizability: 0.11 Å^3) involves a positive change of free energy and enthalpy.

Since for all the soils studied, the sign of standard free energy changes is positive, the formation of a Na-soil is spontaneous although the isotherms indicate a preference for manganese. The selectivity of exchangers, i.e., the selection by the soil of one ion in preference to the other, is a function of the electrolyte concentration of the liquid phase. Changing that concentration

Table 3

Cation exchange capacities and isotopic exchange capacities of homo- and bi-ionic exchangers in meq/100 g

	CEC_{Na}	IEC_{Na}	CEC_{Na+Mn}	IEC_{Na+Mn}
Deerpark soil: untreated	7		7.10	
NaOCl treated	4.65		4.73	
Carlow soil: untreated	9.25	7.90		7.81
NaOCl treated	4.70	3.25		3.31
Meath soil: untreated	11.67	9.80		9.87
NaOCl treated	8.45	7.40		7.32

Table 4

Thermodynamic functions

Exchanger	T°C	$-\ln K$	K	ΔF_0	ΔH_0	ΔS_0 e.u. eq^{-1}
				kcal.eq^{-1}		
Deerpark	5°	6.059	$2.339\ 10^{-3}$	1.667	3.240	5.64
	25°	5.300	$4.497\ 10^{-3}$	1.563		
	37°	4.840	$7.914\ 10^{-3}$	1.485		
Treated D.	5°	7.190	$7.551\ 10^{-4}$	1.978	3.800	6.60
	25°	6.210	$2.014\ 10^{-3}$	1.832		
	37°	5.760	$3.154\ 10^{-3}$	1.767		
Carlow	5°	5.810	$3.005\ 10^{-3}$	1.599	2.687	3.88
	25°	5.190	$5.577\ 10^{-3}$	1.531		
	37°	4.800	$8.237\ 10^{-3}$	1.473		
Treated C.	5°	7.664	$4.710\ 10^{-4}$	2.109	4.690	9.30
	25°	6.506	$1.496\ 10^{-3}$	1.919		
	37°	5.900	$2.742\ 10^{-3}$	1.810		
Meath	5°	5.280	$5.098\ 10^{-3}$	1.450	1.870	1.51
	25°	4.820	$8.074\ 10^{-3}$	1.420		
	37°	4.576	$10.305\ 10^{-3}$	1.400		
Treated M.	5°	5.774	$3.111\ 10^{-3}$	1.580	1.993	1.48
	25°	5.278	$5.107\ 10^{-3}$	1.550		
	37°	5.025	$6.578\ 10^{-3}$	1.540		

can reverse the selectivity as shown by GILBERT and VAN BLADEL [4] for the exchange NH_4-Mn on montmorillonite. The normality of the soil solution has no effect on the equilibrium constant and, therefore, on the standard free energy of exchange.

It is interesting to note that the ΔF_0 values for the different soils vary in the reverse order of the CEC or IEC. The higher the CEC or IEC, the lower the free energy changes (Tables 2 and 4). Even if such a comparison between the three soils may not be entirely justified because two methods were used for the determination of exchangeable cations, it should be noted that the same trend was observed for the Carlow and Meath soils both before and after the removal of organic matter.

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Summary

The Na—Mn exchange reaction was studied on some acid soils and the isotherms indicated that dilution and increasing temperature favoured the adsorption of Mn ions. The equilibrium constants were influenced by the presence of organic matter which contributed in some cases as much as 50% to the CEC. The quantitative recoveries of the added Mn at the end of the reaction and the constancy of the CEC over the whole range of the iso-

therms ruled out the possibility of complex formation with organic matter and of significant adsorption of manganese in the form of $MnOH^+$. Under the pH conditions existing in the systems used in this investigation, adsorption characteristics of Mn were normal and similar to ordinary divalent cations.

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