ZESZYTY PROBLEMOWE POSTĘPÓW NAUK ROLNICZYCH 1992 z. 398, 91-96

EXCHANGEABLE ALUMINIUM AND HYDROGEN IONS IN ACIDIC SOIL - DEPENDENCE ON pH

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A b s t r a c t. The behaviour of exchangeable aluminium and hydrogen in the broad range of pH was studied at model conditions on clays taken from acidic soils of different origin. Sodium and aluminium forms of clays were used and ion exchange experiments were performed. On the basis of the results obtained and data previously reported, it was calculated that exchangeable aluminium below pH 4 is trivalent and in the pH range between 4 to 6 its average charge decreases. Measurable, exchangeable hydrogen quantities occur only at very low pH values.

INTRODUCTION

The acidic character of soils is connected mainly to the presence of exchangeable aluminium and hydrogen ions in soil exchange complex.

Exchangeable aluminium occurs in soils in the pH range below 5.5-6 [7]. Trivalent aluminium ions dominate in soils at low pH values. When pH increases, they hydrolyse according to the reaction [3]:

$$Al(H_2O)_6^{3+} \rightarrow Al(H_2O)_5(OH)^{2+} \rightarrow Al(H_2O)_4(OH)^{+} \rightarrow Al(OH)_3 \rightarrow Al(OH)_4^{-}$$

Divalent and monovalent hydrolysis products can be exchangeably adsorbed; however, they can polymerize giving a variety of different species e.g., $Al_2(OH)_2(H_2O)_4^{4+}$, $Al_3(OH)_7^{2+}$, $Al_4(OH)_{10}^{2+}$, $Al_8(OH)_{20}^{4+}$, $Al_{13}(OH)_{32}^{7+}$, $Al_{13}(OH)_{30}^{9+}$, and many others [1,2,5,6]. These species may be weakly exchangeable or non-exchangeable [10].

Controversies still exist in the literature concerning the status of exchangeable hydrogen [14,9]. However, from the physicochemical point of view, exchangeable protons behave the same as any other monovalent cation, as it has been experimentaly proven [8].

The purpose of the present work was to observe the behaviour of exchangeable aluminium and hydrogen in the broad range of soil pH.

MATERIALS AND METHODS

Sodium and aluminium forms of clay fractions separated from six acidic soils of different origin were used. The characteristics of the materials used was given in a previous paper [11].

Clay fractions were consecutively depleted from organic matter, iron oxides and aluminium oxides and then converted into homoionic sodium and aluminium forms according to the procedures presented in [12] and [13]. Samples obtained were equilibrated with 0.01 N NaCl (sodium forms) and with 0.005 N $NaCl_3$/0.005 N NaCl (aluminium forms). They were adjusted to different pH values with a N NaOH/0.01 N NaCl solution. Finally, the suspensions of 1 % w/w were prepared; and, after two weeks, exchangeable ions were extracted from the sediments (centrifuged) by double equilibration with N $LaCl_3$. Sodium was measured with flame photometry and aluminium with AAS.

RESULTS AND DISCUSSION

Measured quantities of exchangeable sodium and aluminium ions for clays in sodium forms (NaJW and AlJW) and for clays in aluminium forms (NaJW' and AlJW') at different pH values are presented in Table 1.

By comparing these values to the values of negative surface charge (see [12] for sodium forms and [13] for aluminium forms) it can be stated that the quantity of exchangeable sodium for sodium clays increases from about 90 % of the CEC (surface charge) at pH 3 to 100 % at pH 4.5 and higher. For sodium clays, the quantities of exchangeable aluminIum are very low even at low pH values (0.1-0.3 cmol $n^{-1}kg^{-1}$). This can be attributed to low kinetics of mineral components dissolution at pH 3 at the 0.01 N salt level (maximum concentration of Al in equilibrium solution was 50 μmol dm^{-3} for No. 6 clay). For aluminium clays, AlJW' values are practically equal to CEC up to pH 4. With further pH increases AlJW' decreased reaching zero at pH 6.0.

It was observed that, for aluminium clays in the 4.5-6 pH range, the sum of exchangeable sodium and exchangeable aluminium is higher then the value of the surface charge (CEC). Because of this, it was assumed that the charge per exchangeable aluminium atom must be lower then three. The average charge per Al atom was calculated, assuming that the negative surface charge (q_-) is actually balanced by the sum of exchangeable sodium, exchangeable aluminium of n_{av} average valency, and exchangeable hydrogen (HJW'):

$$q_- = \text{AlJW'}\, n_{av} + \text{HJW'} + \text{NaJW'} \quad (1)$$

where HJW' was assumed to be equal to the difference between the surface charge and the sum of exchangeable Na and Al. Above pH 4, HJW' was zero (the above difference was negative) and

$$n_{av} = (q_- - \text{HJW'} - \text{NaJW'}) / \text{AlJW'}. \quad (2)$$

The values of the exchangeable aluminium atom average charge, calculated using the surface charge values from ref. [13], depend on the pH of the equilibrium solution. For every sample in the test these values are almost the same at a given pH. Below pH values of about 4, the average charge per Al atom is 3. At about pH 4.5, n_{av} is in the range between 2.3 to 2.6; and, at pH 5 it decreases to 1.6-2.0.

The quantities of exchangeable hydrogen can be evaluated from experimental data as a difference between surface charge and the sum of other exchangeable ions (Na and Al).

Assuming that exchangeable hydrogen behaves like any other monovalent cation, the ratio of hydrogen to e.g., sodium in equilibrium solution is approximately equal to the ratio of these ions on the surface. So, the following rough equations were used to perform some additional calculations of exchangeable hydrogen values:

$$\text{HJW} = 10^{-\text{pH}}\ \text{NaJW}/c\text{Na}_e \quad (3)$$

for sodium clay forms, and

$$\text{HJW'} = 10^{-\text{pH}}\ \text{NaJW'}/c\text{Na}_e \quad (4)$$

for aluminium clay forms, where $c\text{Na}_e$ is sodium concentration in equilibrium solution for a given case. Calculated exchangeable hydrogen values were (only!) about 100 % different from exchangeable hydrogen quantities evaluated from experimental data (of course, the last values for aluminium forms were evaluated only for pH 4 and lower). It certifies the opinion that exchangeable protons behave not different that any other exchangeable ion. For sodium clays, agreement between two exchangeable hydrogen values is closer than for aluminium clays.

Table 1. Quantities of exchangeable sodium and exchangeable aluminium (cmol n^{-1} kg^{-1}) for sodium forms (NaJW and AlJW) and aluminium forms (NaJW' and AlJW') of the clays investigated

pH	1A*		1B		1C		1D	
	NaJW	AlJW	NaJW	AlJW	NaJW	AlJW	NaJW	AlJW
3.0	22.2	0.2	22.4	0.1	22.3	0.1	22.9	0.1
3.5	25.8	0.1	24.3	0.1	25.9	0.1	27.2	0.1
4.0	29.7	-	27.4	-	28.4	-	29.6	-
4.5	37.7	-	29.0	-	30.5	-	30.7	-
5.0	41.6	-	30.3	-	31.5	-	32.4	-
6.0	49.2	-	31.5	-	32.3	-	32.9	-
7.0	62.4	-	33.1	-	33.0	-	33.4	-
8.0	75.5	-	34.8	-	33.8	-	34.0	-
8.5	81.2	-	35.6	-	34.4	-	34.5	-
pH	NaJW'	AlJW'	NaJW'	AlJW'	NaJW'	AlJW'	NaJW'	AlJW'
3.0	1.0	20.3	1.2	22.5	1.4	23.0	1.6	24.1
3.5	1.2	23.7	1.3	23.6	1.3	24.6	1.6	25.9
4.0	1.8	25.6	1.6	25.9	1.7	26.7	1.8	27.5
4.5	22.1	12.6	18.1	9.0	19.3	9.8	20.5	10.1
5.0	31.0	6.8	21.4	4.4	23.0	4.7	23.9	5.8
6.0	47.2	0.1	32.9	-	32.2	-	32.6	-
7.0	59.5	-	33.8	-	33.5	-	34.0	-
8.0	72.3	-	35.5	-	35.0	-	35.4	-
8.5	79.8	-	36.1	-	35.7	-	35.9	-
pH	2A		2B ·		2C		2D	
	NaJW	AlJW	NaJW	AlJW	NaJW	AlJW	NaJW	AlJW
3.0	20.2	0.2	18.4	0.1	20.3	0.1	22.2	0.1
3.5	23.0	0.1	19.7	0.1	21.9	0.1	24.7	0.1
4.0	23.9	-	20.6	-	22.9	-	25.6	-
4.5	26.7	-	22.0	-	23.5	-	26.1	-
5.0	30.3	-	22.4	-	23.8	-	26.7	-
6.0	38.2	-	22.5	-	24.1	-	27.1	-
7.0	44.6	-	23.6	-	24.5	-	27.5	-
8.0	50.6	-	25.8	-	25.2	-	27.9	-
8.5	54.3	-	27.6	-	26.0	-	28.3	-
pH	NaJW'	AlJW'	NaJW'	AlJW	NaJW'	AlJW'	NaJW'	AlJW'
3.0	1.0	20.3	1.2	18.1	1.4	20.4	1.6	22.5
3.5	1.2	20.5	1.3	18.4	1.3	21.3	1.6	23.3
4.0	1.8	21.6	1.6	19.2	1.7	21.2	1.8	24.0
4.5	17.1	10.4	14.1	7.6	15.1	8.5	17.0	9.1
5.0	24.7	6.0	17.3	3.6	19.0	4.1	21.3	3.3
6.0	36.6	0.1	22.5	-	24.4	-	26.7	-
7.0	43.2	-	23.8	-	25.0	-	27.9	-
8.0	49.1	-	26.5	-	25.9	-	28.5	-
8.5	53.2	-	28.4	-	26.8	-	29.1	-

Table 1. Continued

pH	3A		3B		3C		3D	
	NaJW	AlJW	NaJW	AlJW	NaJW	AlJW	NaJW	AlJW
3.0	45.3	0.2	39.9	0.1	44.1	0.1	56.7	0.1
3.5	52.5	0.1	46.4	0.1	49.9	0.1	62.9	0.1
4.0	58.5	-	48.5	-	53.1	-	66.5	-
4.5	64.4	-	49.5	-	54.2	-	68.4	-
5.0	71.2	-	51.8	-	56.6	-	70.7	-
6.0	82.7	-	54.2	-	60.3	-	71.0	-
7.0	93.4	-	59.2	-	63.6	-	71.1	-
8.0	102.7	-	62.5	-	65.9	-	72.0	-
8.5	108.5	-	63.5	-	66.8	-	72.7	-

pH	NaJW'	AlJW'	NaJW'	AlJW'	NaJW'	AlJW'	NaJW'	AlJW'
3.0	1.0	44.7	1.2	43.0	1.4	46.6	1.6	50.8
3.5	1.2	47.7	1.3	45.4	1.3	49.1	1.6	53.8
4.0	1.8	53.9	1.6	47.2	1.7	51.7	1.8	55.9
4.5	41.4	21.2	32.0	17.3	35.6	17.4	37.7	20.5
5.0	56.1	11.6	40.1	7.8	44.0	7.7	47.5	8.3
6.0	80.1	0.1	53.9	-	60.3	-	64.6	-
7.0	91.4	-	59.4	-	64.5	-	66.7	-
8.0	101.8	-	63.2	-	66.8	-	68.5	-
8.5	107.5	-	64.9	-	68.1	-	695	-

pH	4A		4B		4C		4D	
	NaJW	AlJW	NaJW	AlJW	NaJW	AlJW	NaJW	AlJW
3.0	21.5	0.2	19.4	0.1	20.0	0.1	21.9	0.1
3.5	25.5	0.1	21.6	0.1	21.9	0.1	22.9	0.1
4.0	31.0	-	22.4	-	24.1	-	24.6	-
4.5	36.2	-	23.6	-	24.9	-	25.5	-
5.0	39.3	-	24.9	-	25.9	-	26.4	-
6.0	46.2	-	25.1	-	26.4	-	27.1	-
7.0	60.1	-	27.0	-	27.2	-	27.7	-
8.0	73.0	-	28.6	-	28.6	-	28.8	-
8.5	82.2	-	29.2	-	29.1	-	29.2	-

pH	NaJW'	AlJW'	NaJW'	AlJW'	NaJW'	AlJW'	NaJW'	AlJW'
3.0	1.0	20.8	1.2	19.9	1.4	20.8	1.6	21.4
3.5	1.2	22.1	1.3	20.4	1.3	21.6	1.6	22.5
4.0	1.8	26.6	1.6	20.9	1.7	22.6	1.8	23.2
4.5	21.8	12.2	15.3	7.2	16.0	8.3	16.5	8.5
5.0	30.2	5.6	18.2	3.5	20.0	5.1	20.1	4.4
6.0	44.2	0.1	25.2	-	26.8	-	26.6	-
7.0	57.5	-	27.5	-	28.2	-	28.9	-
8.0	71.3	-	29.7	-	29.4	-	30.2	-
8.5	80.9	-	36.5	-	30.7	-	30.5	-

Table 1. Continued

pH	5A		5B		5C		5D	
	NaJW	AlJW	NaJW	AlJW	NaJW	AlJW	NaJW	AlJW
3.0	36.7	0.2	36.4	0.1	39.5	0.1	44.3	0.1
3.5	40.8	0.1	40.3	0.1	43.7	0.1	49.7	0.1
4.0	43.2	-	42.1	-	45.4	-	50.7	-
5.5	46.0	-	42.8	-	46.0	-	52.4	-
5.0	51.2	-	43.7	-	46.3	-	52.8	-
6.0	58.3	-	44.5	-	47.2	-	52.9	-
7.0	63.7	-	46.9	-	49.0	-	53.4	-
8.0	70.2	-	47.5	-	51.1	-	54.0	-
8.5	73.2	-	49.1	-	51.8	-	54.6	-

pH	NaJW'	AlJW'	NaJW'	AlJW'	NaJW'	AlJW'	NaJW'	AlJW'
3.0	1.0	34.0	1.2	38.2	1.4	41.9	1.6	43.7
3.5	1.2	37.2	1.3	39.6	1.3	43.1	1.6	45.2
4.0	1.8	39.9	1.6	40.9	1.7	44.0	1.8	46.9
4.5	28.5	16.2	29.3	14.3	30.6	15.1	33.0	18.7
5.0	40.0	6.7	35.5	7.7	37.0	7.6	41.0	7.2
6.0	56.1	0.1	44.9	-	47.2	-	51.3	-
7.0	62.5	-	46.7	-	49.5	-	53.4	-
8.0	69.3	-	48.9	-	51.9	-	54.8	-
8.5	71.8	-	50.6	-	52.7	-	56.1	-

pH	6A		6B		6C		6D	
	NaJW	AlJW	NaJW	AlJW	NaJW	AlJW	NaJW	AlJW
3.0	15.9	0.1	13.4	0.1	15.7	0.1	19.1	0.1
3.5	17.9	0.1	14.7	-	17.2	0.1	21.1	0.1
4.0	19.0	-	15.8	-	18.3	-	22.8	-
4.5	20.4	-	16.1	-	18.8	-	23.5	-
5.0	22.6	-	16.5	-	19.1	-	23.9	-
6.0	28.8	-	17.0	-	20.4	-	24.5	-
7.0	32.5	-	17.7	-	21.3	-	24.8	-
8.0	35.2	-	20.6	-	22.8	-	25.0	-
8.5	37.1	-	21.2	-	23.3	-	25.6	-

pH	NaJW'	AlJW'	NaJW'	AlJW'	NaJW'	AlJW'	NaJW'	AlJW'
3.0	0.4	15.2	0.3	14.7	0.4	16.6	0.6	20.6
3.5	0.7	16.1	0.3	14.9	0.5	17.1	0.8	20.5
4.0	0.9	17.0	0.5	15.3	0.7	17.7	1.2	21.5
4.5	12.6	6.8	10.4	5.0	12.5	7.0	15.6	7.7
5.0	17.1	4.1	13.0	2.7	15.4	3.0	19.0	3.9
6.0	27.0	-	17.0	-	20.6	0.1	24.7	-
7.0	31.5	-	17.8	-	21.5	-	25.9	-
8.0	33.9	-	21.6	-	23.5	-	26.2	-
8.5	36.3	-	22.5	-	24.8	-	27.3	-

* 1-Mollic Gleysol; 2-and 3-Eutric Cambisols; 4-Stagnogleyic Phaeozem; 5-Orthic Luvisol; 6-Podzoluvisol. A-natural clays; B-after organic matter removal; C-after Fe removal; D-after Al removal.

It can be stated, then, that the quantity of exchangeable hydrogen is rather low in the samples investigated. In sodium clays, it reaches a maximum value of about 10 % of the CEC at pH 3 and becomes practically negligibile at pH 4-4.5. In aluminium clays, it is much lower and vanishes below pH about 3-3.5.

CONCLUSIONS

1. Exchangeable aluminium below pH 4 is trivalent and in the pH range between 4 to 6 its average charge decreases.

2. Measurable, exchangeable hydrogen quantities occur only at very low pH values.

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WYMIENNE JONY GLINU I WODORU W GLEBACH KWAŚNYCH - ZALEŻNOŚĆ OD pH

W warunkach modelowych badano zachowanie wymiennych jonów glinu i wodoru na frakcjach ilastych wydzielonych z kwaśnych gleb o zróżnicowanym pochodzeniu. Na podstawie wcześniejszych wyników oraz otrzymanych w niniejszej pracy obliczono, iż glin wymienny występuje w postaci jonu trójwartościowego przy pH poniżej 4, a w zakresie pomiędzy pH 4 do 6 jego średni ładunek maleje. Powyżej pH 6 glinu wymiennego nie stwierdzono. Mierzalne ilości wodoru wymiennego występowały jedynie przy bardzo niskich wartościach pH.