THE INFLUENCE OF VARIOUS CATIONS UPON THE RATE OF ABSORPTION OF AMMONIUM ION BY SOIL¹

By

K. MIYAKE, *Assistant Professor of Agricultural Chemistry, College of Agriculture, Tohoku Imperial University, Sapporo, Japan*

The mechanism of absorption has recently been carefully studied. Way's (8, 9) purely chemical hypothesis held the field for many years, and while his "double silicates" were never actually shown to exist in the soil, it was assumed that the reactive substances of similar constitution known as zeolites, and found naturally in volcanic districts, were normal soil constituents and responsible for the absorption. Some justification for this view was obtained when Hall and Gimingham (4) found that the interaction between ammonium sulphate and clay followed the ordinary law of mass action. But the old experiments of Weinhold (10) and more recent ones of Cameron and Patten (3) showed that this law is not obeyed over a wider range of concentration, and another hypothesis has therefore been developed.

Van Bemmelen (7) has demonstrated a close parallelism between the various interchanges and absorptions shown by the soil and those shown by colloids; and there is considerable evidence in other directions that some of the soil constituents, especially the clay, possess all the properties of colloids. Now the time relation of rate of the absorption by colloids is generally expressed by the equation

$$x = Kt^m$$

where x is the amount absorbed, t is the time, K and m are constants which depend upon the concentration and kind of colloid and solution used.

The relation $x = Kt^m$ was found first by Cameron and Bell (1, 2) and later confirmed by Ostwald (5) from the investigations of Goppels-roeder, to hold for the relation between the amount of fluid absorbed by a column of sand or of a strip of filter-paper and the time during which the fluid remained in contact with a portion of its surface. Robertson (6) has also found that this relation for the rate of solution of casein by sodium hydroxide is primarily determined by the rate at which the casein particles absorb the solvent.

¹ Received for publication September 21, 1916.

If we grant that absorption by a soil is mainly a colloidal phenomenon, it is of interest to study the influence of various cations upon the rate of absorption of the ammonium ion by the soil, since cations have a great influence upon the properties of colloidal substances. It is also important and interesting from the standpoint of agricultural practice to know the characteristic effects of one cation upon the absorption of another, since it is very seldom that single nutrient salts are used as fertilizer. Accordingly, the following experiments were undertaken.

The soil employed was Hagerstown loam. The solution to be absorbed was 0.1N. ammonium chloride solution. The salts employed were chlorides of sodium, potassium, magnesium, calcium and aluminium in the concentrations of 0.01N, 0.05N, and 0.1N. Fifty gm. of the soil were placed in 300-c.c. Erlenmeyer flasks: to these were added 100 c.c. of the solutions to be examined. The flasks were shaken frequently at room temperature and at stated intervals the supernatant fluid was filtered and analyzed according to the ordinary distillation method, using magnesium oxide and distilling the ammonia into standard acid. The results obtained are shown in Table I.

In the column headed "calculated" are given the value of x calculated from the above formula, the constants K and m being determined from the results of the all observations, employing for this purpose the form

$$\log x = \log K + m \log t.$$

It will be seen from the results given that the observed and calculated values of x agree very closely. It is, therefore, evident that the relation between the time during which the fluid has remained in contact with the soil and the amount of ammonia absorbed is expressed by $x = Kt^m$ when the chloride of another base is present with the ammonium chloride solution. In such an instance, however, the presence of the salt caused retardation of the rate of absorption of ammonia, and the greater the concentration of the salt, the greater was the retardation.

In regard to their power to cause retardation of the rate of absorption, there is a difference in the cations used. The retarding effect of the cations employed increases in the following order:

$$\text{Na} < \text{Mg} < \text{Ca} < \text{Al} < \text{K},$$

instead of the usual order in colloid chemistry:

$$\text{Na} < \text{K} < \text{Mg} < \text{Ca} < \text{Al},$$

potassium, in the former case, being the strongest, whereas in the latter it is the weakest of all except sodium.

The magnitudes of the constants K and m are affected by the salt. In the case of all salts tested except potassium chloride, the values of K and m decrease as the concentration of salt increases. In the case of potassium chloride the value of K decreases as the concentration of salt increases, while that of m increases.

TABLE I

AMMONIA ABSORBED: AMOUNT FOUND COMPARED WITH AMOUNT CALCULATED

Mg. of Ammonia Absorbed by 50 gm. of Soil from 100 c.c. of Solution					
1. Solution: 0.1 N. NH_4Cl $K = 1.622$ $m = 0.4046$			9. Solution: 0.1 N. NH_4Cl + 0.05 N. MgCl_2 $K = 1.660$ $m = 0.2874$		
Time, Hours	Found	Calculated	Time, Hours	Found	Calculated
24	5.95	5.97	24	4.15	4.19
48	8.08	7.91	48	5.20	5.12
72	9.35	9.53	72	5.80	5.83
2. Solution: 0.1 N. NH_4Cl + 0.01 N. NaCl $K = 1.698$ $m = 0.3763$			10. Solution: 0.1 N. NH_4Cl + 0.1 N. MgCl_2 $K = 1.216$ $m = 0.2393$		
24	5.78	5.72	24	2.65	2.63
48	7.68	7.41	48	3.10	3.11
72	8.50	8.81	72	3.45	3.43
3. Solution: 0.1 N. NH_4Cl + 0.05 N. NaCl $K = 1.318$ $m = 0.3736$			11. Solution: 0.1 N. NH_4Cl + 0.01 N. CaCl_2 $K = 1.738$ $m = 0.3571$		
24	4.42	4.40	24	5.53	5.50
48	5.95	5.69	48	7.14	7.03
72	6.38	6.74	72	8.08	8.27
4. Solution: 0.1 N. NH_4Cl + 0.1 N. NaCl $K = 1.072$ $m = 0.3589$			12. Solution: 0.1 N. NH_4Cl + 0.05 N. CaCl_2 $K = 1.514$ $m = 0.3062$		
24	3.40	3.41	24	4.08	4.06
48	4.40	4.37	48	5.19	5.00
72	5.10	5.15	72	5.53	5.78
5. Solution: 0.1 N. NH_4Cl + 0.01 N. KCl $K = 2.399$ $m = 0.235$			13. Solution: 0.1 N. NH_4Cl + 0.1 N. CaCl_2 $K = 1.122$ $m = 0.2521$		
24	5.10	5.12	24	2.55	2.53
48	5.95	6.01	48	2.98	3.01
72	6.80	6.71	72	3.40	3.38
6. Solution: 0.1 N. NH_4Cl + 0.05 N. KCl $K = 0.7943$ $m = 0.364$			14. Solution: 0.1 N. NH_4Cl + 0.01 N. AlCl_3 $K = 1.799$ $m = 0.3316$		
24	2.55	2.57	24	5.27	5.24
48	3.40	3.30	48	6.60	6.59
72	3.83	3.91	72	7.60	7.67
7. Solution: 0.1 N. NH_4Cl + 0.1 N. KCl $K = 0.05623$ $m = 0.629$			15. Solution: 0.1 N. NH_4Cl + 0.05 N. AlCl_3 $K = 1.084$ $m = 0.3211$		
24	0.43	0.43	24	3.00	3.06
48	0.68	0.68	48	3.90	3.81
72	0.85	0.85	72	4.40	4.42
8. Solution: 0.1 N. NH_4Cl + 0.01 N. MgCl_2 $K = 1.778$ $m = 0.3541$			16. Solution: 0.1 N. NH_4Cl + 0.1 N. AlCl_3 $K = 0.3508$ $m = 0.435$		
24	5.60	5.59	24	1.40	1.43
48	7.15	7.11	48	2.00	1.93
72	8.25	8.36	72	2.33	2.36

Differentiating the equation

$$x = Kt^m$$

we find

$$\frac{dx}{dt} = Km t^{m-1}$$

in other words, the product Km , which we may term the coefficient of absorption in this case expresses the constant proportionality between the velocity of absorption and the exponent of the time during which the soil has been contacted with the fluid.

TABLE II
COEFFICIENT OF ABSORPTION: OBSERVED VALUES COMPARED WITH
CALCULATED VALUES

1. NaCl $K_1m_1 = 0.656$ $\alpha = 2.05$ $\beta = 19.21$				
Solution	K	m	$K \times m$	
			Found	Calculated
0.1 N. NH_4Cl	1.622	0.4046	0.656	0.656
0.1 N. NH_4Cl + 0.01 N. NaCl.....	1.698	0.3763	0.639	0.635
0.1 N. NH_4Cl + 0.05 N. NaCl.....	1.318	0.3736	0.492	0.505
0.1 N. NH_4Cl + 0.10 N. NaCl.....	1.072	0.3589	0.265	0.259
2. KCl $K_1m_1 = 0.656$ $\alpha = 9.234$ $\beta = -30.75$				
0.1 N. NH_4Cl	1.6220	0.4046	0.656	0.656
0.1 N. NH_4Cl + 0.01 N. KCl.....	2.3990	0.2350	0.564	0.567
0.1 N. NH_4Cl + 0.05 N. KCl.....	0.7943	0.3640	0.289	0.271
0.1 N. NH_4Cl + 0.10 N. KCl.....	0.0562	0.6290	0.035	0.040
3. MgCl_2 $K_1m_1 = 0.656$ $\alpha = 2.878$ $\beta = 8.452$				
0.1 N. NH_4Cl	1.622	0.4046	0.656	0.656
0.1 N. NH_4Cl + 0.01 N. MgCl_2	1.778	0.3541	0.630	0.626
0.1 N. NH_4Cl + 0.05 N. MgCl_2	1.660	0.2874	0.477	0.491
0.1 N. NH_4Cl + 0.10 N. MgCl_2	1.216	0.2393	0.291	0.284
4. CaCl_2 $K_1m_1 = 0.656$ $\alpha = 3.700$ $\beta = 0.635$				
0.1 N. NH_4Cl	1.622	0.4046	0.656	0.656
0.1 N. NH_4Cl + 0.01 N. CaCl_2	1.738	0.3571	0.621	0.619
0.1 N. NH_4Cl + 0.05 N. CaCl_2	1.514	0.3062	0.464	0.469
0.1 N. NH_4Cl + 0.10 N. CaCl_2	1.122	0.2521	0.283	0.280
5. AlCl_3 $K_1m_1 = 0.656$ $\alpha = 6.562$ $\beta = -14.28$				
0.1 N. NH_4Cl	1.622	0.4046	0.656	0.656
0.1 N. NH_4Cl + 0.01 N. AlCl_3	1.799	0.3316	0.597	0.592
0.1 N. NH_4Cl + 0.05 N. AlCl_3	1.084	0.3211	0.348	0.364
0.1 N. NH_4Cl + 0.10 N. AlCl_3	0.351	0.4350	0.153	0.143

Since the value of K decreases more rapidly than m increases, even in the case of potassium chloride, with increasing concentration of salt, the effect of all the salts is to cause a decrease in the value of the coefficient of absorption, a decrease which is a definite function of the concentration of salt employed.

The relationship between the value of the coefficient of absorption and the concentration of salt added to the fluid may be defined by the interpolation equation.

$$K_1m_1 - Km = \alpha c + \beta c^2$$

where K_1m_1 is the coefficient of absorption for the standard solution (in this case 0.1N. NH_4Cl), Km is its value when a given salt has been added in concentration c , α and β are constants dependent upon the nature of the salt added.

In Table II the observed values of the coefficient of absorption are compared with the values calculated from the equation; the values of the constants α and β being calculated by the method of least squares from all of the observations obtained with the given salt.

TABLE III
VALUES OF CONSTANTS

	K_1m_1	α	β
Na	0.656	2.050	19.210
Mg	0.656	2.878	8.452
Ca	0.656	3.700	0.635
Al	0.656	6.562	-14.280
K	0.656	9.234	-30.750

The observed and calculated values of Km are very close. These results reveal another striking difference between the effects of various cations upon the rate of absorption of ammonia by the soil, for whereas NaCl , MgCl_2 and CaCl_2 in increasing concentration decrease the rate of absorption with a positive acceleration, AlCl_3 and KCl decrease the rate of absorption with a negative acceleration.

SUMMARY

1. The relation between the time which a solution of ammonium chloride has remained in contact with soil and the amount of ammonia absorbed by the soil is expressed by the equation $x = Kt^m$ even in the presence of another chloride in solution.

2. The presence of other chlorides decreases the rate of absorption of ammonia from ammonium chloride solution by the soil. The retardation increases with the concentration of salt employed.

3. Salts differ in their power of causing retardation of the rate of absorption of ammonia. The retarding effect of the salts employed increases in the following order:

$$\text{Na} < \text{Mg} < \text{Ca} < \text{Al} < \text{K}.$$

4. The value of $K \times m$ which we term the coefficient of absorption in this case, decreases with increasing concentrations of the salts, the acceleration of the decrease being positive in the cases of NaCl , MgCl_2 and CaCl_2 , and negative in the cases of AlCl_3 and KCl .

In conclusion, the author wishes to express his thanks to Dr. Edmund C. Shorey for the kindness which he has shown during this experiment.

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