

A COMPARISON OF SOME OF THE ION EXCHANGE EQUATIONS

by K. V. PALIWAL, *Agricultural Experiment Station, University of Udaipur, Udaipur*

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Ionic equilibrium studies were conducted on fifteen soils representing all the important soil groups of India using potassium, calcium and magnesium in various proportions and some of the ion exchange equations were statistically examined for their suitability. These were of Kerr, Vanselow, Gapon, Krishnamoorthy and Overstreet and one based on Donnan membrane equilibria. Equilibrium constants of all the equations generally decrease with the increase of potassium ion activity ratio (K.A.R.). Of these Gapon's equation showed the least coefficient of variation in the equilibrium constant followed by Donnan's and others. A new empirical equation, $D.K.S. = c_1 K.A.R.^{m_1}$, was found better even than Gapon's or its logarithmic form. Thus Gapon's equation seems to be more satisfactory than others. It was also observed that the coefficient of variation in equilibrium constant of Gapon's equation or its proportionality constant in the logarithmic form is related with the cation exchange capacity of the soil. Both proportionality constant and power index of the equation, $D.K.S = c_1 K.A.R.^{m_1}$ are significantly related with the C.E.C. Charge of the colloidal particle and variation in the activity coefficient of exchangeable cations seem to be responsible for the variation of the equilibrium constant.

INTRODUCTION

Various attempts have been made both theoretically and empirically to find out a quantitative expression (Bolt 1955; Davis 1945; Eriksson 1952; Gapon 1933; Krishnamoorthy and Overstreet 1950; Vanselow 1932) for explaining satisfactorily the distribution of ions in systems especially in those which contain unequivalent ions. Such an expression will be of considerable value for predicting the exchangeable cation status from the analysis of their equilibrium solution. The suitability of an equation is generally judged from the least variation in its equilibrium constant under varying degrees of concentration and ionic proportion in the solutions used.

Although a comparison of the various equations (Abrol 1962; Krishnamoorthy and Overstreet 1950; Magistad, Fireman and Mabry 1944) had been made under different conditions with different conclusions, a statistical examination of these results has not been made so far for finding out their comparative suitability. Recently Paliwal (1961) made such an examination for

some common clay minerals and oxides involving both mono- and di-valent cations. The present investigation was taken up to determine the suitability of some ion exchange equations containing the following three ions: calcium, magnesium and potassium which are predominantly present in soil systems. The common equations, viz. of Kerr, Vanselow, Gapon, Krishnamoorthy and Overstreet and the one based on Donnan membrane equilibria, were taken for the purpose. The equations for systems containing Ca, Mg and K can be written as below assuming identically the same activity coefficient for both calcium and magnesium. Several workers had done like this, as the U.S. Salinity Laboratory staff (1954) for calculating the S.A.R., Schofield and Taylor (1955) for calculating the lime potential, and Gething (1962), Abrol (1962) and Beckett (1964) for determining the activity ratio of potassium.

$$\frac{K_{\text{ex}}^2}{(\text{Ca} + \text{Mg})_{\text{ex}}} \cdot \frac{(\text{Ca}^{++} + \text{Mg}^{++})}{(\text{K}^+)^2} = K_1 \text{ (Kerr)} \quad \dots \quad (1)$$

$$\frac{K_{\text{ex}}^2}{(\text{Ca} + \text{Mg})_{\text{ex}} (\text{Ca} + \text{Mg} + \text{K})_{\text{ex}}} \cdot \frac{(\text{Ca}^{++} + \text{Mg}^{++})}{(\text{K}^+)^2} = K_2 \text{ (Vanselow)} \quad \dots \quad (2)$$

$$\frac{K_{\text{ex}}^2}{(\text{Ca} + \text{Mg})_{\text{ex}} [1.5(\text{Ca} + \text{Mg}) + \text{K}]_{\text{ex}}} \cdot \frac{\text{Ca}^{++} + \text{Mg}^{++}}{(\text{K}^+)^2} = K_3 \text{ (Krishnamoorthy and Overstreet)} \quad (3)$$

$$\frac{K_{\text{ex}}}{(\text{Ca} + \text{Mg})_{\text{ex}}} \cdot \frac{(\text{Ca}^{++} + \text{Mg}^{++})^{\frac{1}{2}}}{\text{K}^+} = K_4 \text{ (Gapon)} \quad \dots \quad (4)$$

$$\frac{K_{\text{ex}}}{(\text{Ca}^{\frac{1}{2}} + \text{Mg}^{\frac{1}{2}})_{\text{ex}}} \cdot \frac{\text{Ca}^{++\frac{1}{2}} + \text{Mg}^{++\frac{1}{2}}}{(\text{K}^+)} = K_5 \text{ (Donnan)} \quad \dots \quad (5)$$

Here 'ex' stands for exchangeable phase and

$$(\text{Ca} + \text{Mg})_{\text{ex}} = \frac{(\text{C.E.C.} - \text{K})}{2} \text{ for calculating } K_1 \text{ to } K_4.$$

MATERIALS AND METHODS

Fifteen samples (Table I) of the important soil groups of India were selected which varied widely in colour, texture, pH, cation exchange capacity and other physico-chemical properties. These comprised of four black soils, three red and yellow soils, one laterite, four alluvial soils including one calcareous, two of peaty and one brown forest soil. On the textural basis these comprised of three loams including one of calcareous soil, five of clayey soil, five clay-loams and two silty-clay-loams. The pH value of the soils ranged widely from 3 to 8.50 and the cation exchange capacity from 2.8 to 57.9 me/100 g of soil.

TABLE I
General Characteristics of the Soils

Soil	pH	C.E.C. me/100 g	Clay %	Silt %	Coarse and fine sand %	Textural classi- fication	Soil type
Raipur	6.0	19.70	35.5	21.7	41.1	Clay-loam	Red yellow
Raneshwar	6.1	13.20	28.8	14.9	53.3	Clay-loam	Red yellow
Chalkudi	6.0	5.60	30.1	24.2	44.5	Clay-loam	Mixed laterite
Agartala	5.1	12.10	35.1	32.2	31.3	Silty clay	Alluvial
Aryadu	5.3	10.10	38.1	10.2	50.2	Clay	Khari
Kuttanad	3.0	38.00	40.3	3.1	49.1	Clay	Peaty
Hagri	8.4	40.30	51.8	10.2	34.4	Clay	Black
Bangalore	6.9	12.80	29.2	18.4	50.3	Clay-loam	Red laterite
Mansong	5.2	10.80	33.4	28.6	32.9	Silty clay- loam	Brown forest acid soil
Bagwai	8.0	28.80	44.5	21.5	31.8	Clay	Black
Bichpuri	8.3	6.00	18.2	14.5	68.3	Loam	Alluvial
Reura	7.6	28.30	50.3	20.1	30.8	Clay	Mixed red and black
Powerkhara	8.1	28.50	37.5	23.8	38.9	Clay-loam	Black
Pusa	8.5	2.50	11.2	16.8	48.7	Calcareous loam	Grey and brown
Delhi	7.9	7.90	15.5	12.4	70.3	Loam	Alluvial

Suitable quantities of the soils from the samples were equilibrated in identical solutions whose concentration varied from 12.50 to 200 me/l. This was done by repeatedly shaking with the solution in the ratio of 1:5 of soil to solution and by decanting off the solution by centrifuging and by shaking with a fresh portion of the solution. This process was repeated till equilibrium was obtained between the soil and the solution phases. After equilibration the soil sample was made free of soluble salts with 90 per cent alcohol, air-dried and passed through a 60-mesh sieve. The activities of the ions in solutions were calculated by Debye-Hückel's formula and of 50 and 200 me/l solutions by their modified equation. Potassium adsorption ratios (K.A.R.) were expressed by the relations:

$$\text{K.A.R.} = \frac{K^+}{(Ca^{++} + Mg^{++})^{\frac{1}{2}}}; \text{K.A.R.}_D = \frac{K^+}{(Ca^{++\frac{1}{2}} + Mg^{++\frac{1}{2}})}$$

where K.A.R. is based on Gapon's equation and K.A.R._D on the Donnan membrane conditions. The equilibrium constants were calculated by considering the activities of the ions in mols/l and of the exchangeable ions in mols/100 g, except for Gapon's equation where it was in equivalents. The cation exchange capacity and the exchangeable cations, i.e. K, Ca and Mg, were

determined by normal ammonium acetate (pH 7.0) as given in Piper (1950). Potassium was estimated by Flame photometer and Ca and Mg by titrating against standard Versenate solution. The coefficient of variation (C.V.) was analysed according to the method of Panse and Sukhatme (1957).

TABLE II
Activities of ions and K.A.R. of equilibrating solutions (activities expressed in mols/l. $\times 10^3$)

Ions	Solution numbers									
	1	2	3	4A	4B	5	6	7	8	9
K ⁺	.. 0.171	0.256	0.427	0.854	1.277	1.279	2.134	3.430	33.10	18.345
Ca ⁺⁺	.. 2.921	2.784	2.921	2.523	1.920	2.597	2.134	1.975	6.70	2.901
Mg ⁺⁺	.. 0.212	0.318	0.133	0.398	0.842	0.188	2.389	0.189	6.70	0.725
K.A.R. $\times 10^2$.. 0.304	0.459	0.772	1.579	2.432	2.423	4.250	7.376	28.60	30.470
K.A.R.D $\times 10^2$.. 0.245	0.362	0.508	1.210	1.751	1.977	3.510	5.880	20.20	22.700

Note: 4A solution was used for the soils of Bagwai, Bichpuri, Reura, Powerkhara, Fusa and Delhi.

Total concentration of solutions from 1 to 6 was 12 me/l and those of 8 and 9 were 200 and 50 me/l. Anions used were Cl⁻, NO₃⁻ and SO₄²⁻.

RESULTS AND DISCUSSION

The chemical composition of the solutions used for equilibrating the soil samples (Table II) showed that though the total concentration of the solutions (1 to 6) was the same as 12 me/l, the activities of the ions varied to a great

TABLE III
Exchangeable cations and degree of potassium saturation of equilibrated soils (exch. cations expressed in me/100 g of soil)

Exchangeable cations	Solution Nos.		Equilibrated Soils								
	1	2	3	4	5	6	7	8	9		
	K.A.R. $\times 10^2$	0.304	0.459	2.432	2.423	4.250	7.376	23.600	30.470		
i	ii	iii	iv	v	vi	vii	viii	ix	x		
	<i>Raipur</i>										
Ca	17.820	17.550	18.000	13.950	17.100	15.750	15.500	6.500	9.000		
Mg	1.580	1.350	0.900	4.500	1.350	1.350	1.350	6.350	3.480		
K	0.350	0.670	0.938	1.570	1.600	2.144	2.680	7.320	7.460		
D.K.S.	1.680	3.230	4.530	7.580	7.730	10.360	12.940	35.360	36.040		
	<i>Raneshwar</i>										
Ca	11.300	11.250	11.700	9.900	11.040	9.900	9.600	5.400	6.480		
Mg	2.060	1.800	1.350	2.250	1.350	1.350	1.350	3.800	1.900		
K	0.291	0.402	0.504	1.072	1.100	1.510	2.116	4.430	4.650		
D.K.S.	2.080	2.870	3.600	7.650	7.850	10.780	15.110	31.640	33.210		
	<i>Chalchakudi</i>										
Ca	5.000	4.950	5.400	4.050	4.550	4.500	4.050	1.656	1.800		
Mg	0.800	0.670	0.310	1.200	0.450	0.310	0.360	1.035	1.150		
K	0.199	0.252	0.335	0.772	0.803	1.233	1.670	2.880	3.037		
D.K.S.	3.200	4.100	5.460	12.600	13.100	20.100	27.230	46.970	49.530		

extent. These variations were in an order of increasing values of K.A.R. For examining the effect of higher concentration and K.A.R., the solutions of concentrations 50 and 200 me/l were also included.

The data in Table III show that the amount of exchangeable K and the degree of potassium saturation increase with the K.A.R. of the equilibrium

TABLE III—(contd.)
Exchangeable cations and degree of potassium saturation of equilibrated soils (each, cations expressed in me/100 g of soil)

Exchangeable cations	Equilibrated Soils									
	Solution Nos.	1	2	3	4	5	6	7	8	9
K.A.R. $\times 10^2$	0.304	0.459	0.772	2.432	2.423	4.250	7.376	28.600	30.470	
i	ii	iii	iv	v	vi	vii	viii	ix	x	
<i>Agartala</i>										
Ca	11.900	11.700	12.150	9.800	11.250	10.350	9.550	6.480	4.460	
Mg	2.100	1.800	1.350	3.150	1.570	1.350	1.350	0.980	3.080	
K	0.220	0.335	0.469	1.088	1.106	1.742	2.513	6.030	6.264	
D.K.S.	1.500	2.280	3.200	7.430	7.560	11.800	17.160	41.180	42.780	
<i>Aryach</i>										
Ca	8.800	9.600	10.130	8.100	9.000	8.550	8.100	4.950	4.950	
Mg	1.360	0.900	0.450	1.800	0.670	0.450	0.585	2.480	1.360	
K	0.264	0.335	0.469	1.060	1.100	1.635	2.110	3.140	3.425	
D.K.S.	2.350	2.990	4.180	9.460	9.820	14.590	18.840	28.030	30.580	
<i>Kattamad</i>										
Ca	18.200	17.550	18.000	13.500	15.750	15.300	14.450	12.430	13.800	
Mg	1.600	1.350	0.930	2.250	0.900	1.350	1.350	6.620	5.400	
K	0.350	0.504	0.804	1.164	1.187	1.511	1.843	5.800	5.960	
D.K.S.	0.640	0.860	1.380	2.010	2.050	2.600	3.180	10.010	10.300	
<i>Hagari</i>										
Ca	38.600	38.880	40.680	35.790	38.360	38.190	36.040			
Mg	5.600	5.020	2.980	6.760	3.840	3.050	3.200			
K	0.723	1.072	1.340	2.420	2.500	3.680	5.896			
D.K.S.	1.600	2.370	2.970	5.350	5.530	8.000	13.040			

solution and that the exchangeable calcium and magnesium contents decrease. It was also noted that these soils followed Mattson's (1948) inverse relation between cation exchange capacity and degree of potassium saturation of the soils obtained on equilibrating them with one and the same solution, only in a

TABLE III—(contd.)
Exchangeable cations and degree of potassium saturation of equilibrated soils (Exch. cations expressed in me/100 g of soil)

Exchangeable cations	Solution Nos.										
	1	2	3	4	5	6	7	8	9		
	Equilibrated Soils										
	K.A.R. × 10 ²	0.804	0.459	0.772	2.432	2.423	4.250	7.376	28.600	30.470	
j	ii	iii	iv	v	vi	vii	viii	ix	x		
	<i>Bangalore</i>										
Ca	10.800	10.040	10.270	9.200	10.280	9.060	8.040				
Mg	1.800	1.680	0.520	2.100	0.770	0.550	0.800				
K	0.313	0.536	0.870	1.659	1.740	2.679	3.618				
D.K.S.	2.300	3.940	6.400	12.200	12.800	19.700	26.600				
	<i>Mansong</i>										
Ca	8.200	8.070	8.250	6.150	7.950	7.140	6.230				
Mg	1.680	1.540	0.450	2.490	0.960	1.000	1.980				
K	0.263	0.426	0.627	1.288	1.322	1.622	2.028				
D.K.S.	2.300	3.800	5.600	11.500	11.800	14.480	18.110				
	<i>Ragwal</i>										
Ca	25.800	25.730	27.100	23.130	23.420	22.630	22.700				
Mg	3.440	3.270	1.970	4.300	3.400	2.180	3.400				
K	0.457	0.790	0.983	1.511	1.995	2.762	3.837				
D.K.S.	1.490	2.410	3.000	4.950	6.550	9.050	12.580				
	<i>Bichpuri</i>										
Ca	4.620	4.600	5.100	4.200	4.020	4.200	3.400				
Mg	1.100	0.720	0.320	0.980	0.220	0.210	0.270				
K	0.307	0.628	0.796	0.961	1.173	1.340	1.675				
D.K.S.	4.800	9.890	12.520	15.130	18.460	21.100	26.370				

broad sense, as there were some exceptions in the case of the Hageri, the Powerkhera and the Bangalore soils.

The equilibrium constants calculated by the ion exchange equations of Kerr, Vanselow, Krishnamoorthy and Overstreet, and Gapon and Domnan

TABLE III—(concl'd.)
Exchangeable cations and degree of potassium saturation of equilibrated soils (Exch. cations expressed in me/100 g of soil)

Exchangeable cations	Equilibrated Soils									
	Solution Nos.	1	2	3	4	5	6	7	8	9
	K.A.R. × 10 ²	0.304	0.459	0.772	2.432	2.423	4.250	7.376	28.600	30.470
i	ii	iii	iv	v	vi	vii	viii	ix	x	
	<i>Reura</i>									
Ca	..	24.780	24.730	25.100	23.130	22.420	21.950	22.020		
Mg	..	2.680	2.500	1.250	3.700	3.200	2.900	2.100		
K	..	0.640	0.793	0.946	1.514	1.965	2.635	3.964		
D.K.S.	..	2.200	2.730	3.260	5.200	6.770	9.080	12.700		
	<i>Powerkhera</i>									
Ca	..	24.800	24.700	26.300	23.200	22.600	22.100	22.200		
Mg	..	3.600	2.500	1.300	3.200	3.100	2.600	1.010		
K	..	0.557	1.038	1.356	2.090	2.790	3.430	4.520		
D.K.S.	..	1.880	3.510	4.590	7.090	9.080	11.630	15.320		
	<i>Pusa</i>									
K	..	0.070	0.106	0.175	0.300	0.412	0.673	0.837		
D.K.S.	..	2.500	3.800	6.300	10.800	14.800	24.200	30.100		
	<i>Delhi</i>									
Ca	..	6.620	6.560	7.020	6.100	6.050	5.920	5.400		
Mg	..	0.870	0.835	0.340	1.100	0.280	0.230	0.290		
K	..	0.246	0.348	0.460	0.583	0.818	1.100	1.637		
D.K.S.	..	3.030	4.290	5.670	7.190	10.090	13.500	20.200		

(Table IV) generally decreased with the increase of potassium ion activity or K.A.R. of the equilibrium solution. The variation is much more in the last two solutions of high concentration and K.A.R. values. The coefficient of variation expressed as a percentage is an index of the suitability of the ion exchange equation which determines how best the distribution of ions between the solution and the exchange phases can be expressed, especially in

TABLE IV
Equilibrium constants obtained by various ion exchange equations

Solution No.	Total conc. in me/l	K.A.R. $\times 10^2$	Equations of				
			Kerr	Vanselow	K. and O.	Gapon	Donnan
i	ii	iii	iv	v	vi	vii	viii
<i>Raipur</i>							
1	12	0.304	1.289	122.00	79.80	5.62	0.939
2	12	0.459	2.120	198.00	135.00	7.27	1.540
3	12	0.772	1.490	137.00	94.50	6.13	1.230
4	12	2.432	0.402	36.20	25.20	3.22	0.650
5	12	2.423	0.466	40.80	28.20	3.44	0.680
6	12	4.250	0.274	24.00	17.00	2.71	0.530
7	12	7.376	0.154	13.13	9.50	2.01	0.400
8	200	28.600	0.100	6.98	5.64	1.91	0.317
9	50	30.470	0.091	6.43	5.20	1.84	0.305
<i>Rameshwar</i>							
1	12	0.304	1.330	186.00	120.00	6.95	0.894
2	12	0.459	1.120	155.00	105.00	6.45	1.050
3	12	0.772	0.630	86.80	59.20	4.81	0.753
4	12	2.432	0.301	39.90	27.90	3.38	0.580
5	12	2.423	0.319	42.20	29.60	3.48	0.553
6	12	4.250	0.202	26.00	18.50	2.84	0.495
7	12	7.376	0.138	17.10	12.50	2.41	0.385
8	200	28.600	0.051	5.43	4.31	1.62	0.230
9	50	30.470	0.050	5.34	4.22	1.63	0.218
<i>Chalakudi</i>							
1	12	0.304	1.433	452.00	289.00	11.00	0.935
2	12	0.459	1.020	319.00	218.00	9.30	1.020
3	12	0.772	0.658	200.40	138.00	7.46	0.796
4	12	2.432	0.377	109.00	78.80	5.91	0.655
5	12	2.423	0.412	118.00	85.80	6.20	0.647
6	12	4.250	0.343	93.10	69.90	5.91	0.605
7	12	7.376	0.231	59.10	46.00	5.06	0.486
8	200	28.600	0.062	13.80	11.70	3.10	0.250
9	50	30.470	0.064	14.00	11.90	3.19	0.252

TABLE IV—(contd.)

Equilibrium constants obtained by various ion exchange equations

Solution No.	Total conc. in me/l	K.A.R. $\times 10^2$	Equations of				
			Kerr	Vanselow	K. and O.	Gapon	Donnan
i	ii	iii	iv	v	vi	vii	viii
<i>Agartala</i>							
1	12	0.304	0.719	96.70	63.20	4.99	0.660
2	12	0.459	0.743	99.00	67.80	5.09	0.868
3	12	0.772	0.520	68.80	46.80	4.27	0.694
4	12	2.432	0.295	37.50	26.20	3.29	0.581
5	12	2.423	0.307	38.90	27.20	3.35	0.543
6	12	4.250	0.260	31.70	22.70	3.18	0.506
7	12	7.376	0.186	21.60	16.00	2.81	0.451
8	200	28.600	0.103	9.96	8.24	2.45	0.323
9	50	30.470	0.101	9.66	8.05	2.45	0.348
<i>Aryadu</i>							
1	12	0.304	1.257	202.00	130.00	7.27	0.941
2	12	0.459	0.978	169.00	115.00	6.70	1.055
3	12	0.772	0.686	117.00	80.50	5.63	0.835
4	12	2.432	0.375	61.80	43.20	4.30	0.644
5	12	2.423	0.407	66.00	46.90	4.46	0.651
6	12	4.250	0.309	48.10	35.00	4.01	0.579
7	12	7.376	0.179	26.80	20.00	3.15	0.444
8	200	28.600	0.030	4.17	3.25	1.36	0.181
9	50	30.470	0.032	4.44	3.51	1.45	0.199
<i>Kuttanad</i>							
1	12	0.304	0.252	8.660	5.740	1.950	0.691
2	12	0.459	0.418	14.300	9.590	1.910	1.160
3	12	0.772	0.379	12.900	8.680	1.820	1.060
4	12	2.432	0.081	2.730	1.840	0.840	0.574
5	12	2.423	0.085	2.860	1.930	0.860	0.545
6	12	4.250	0.045	1.510	1.020	0.636	0.379
7	12	7.376	0.022	0.723	0.492	0.443	0.282
8	200	28.600	0.016	0.490	0.357	0.386	0.238
9	50	30.470	0.015	0.450	0.328	0.373	0.233
<i>Hagri</i>							
1	12	0.304	2.526	110.0	74.1	5.31	1.241
2	12	0.459	2.467	106.0	72.1	5.28	1.232
3	12	0.772	1.372	58.0	40.0	3.92	0.954
4	12	2.432	0.463	19.4	13.4	2.32	0.518
5	12	2.423	0.498	20.8	14.4	2.41	0.565
6	12	4.250	0.348	14.2	10.0	2.05	0.489
7	12	7.376	0.325	12.7	9.2	2.03	0.431

TABLE IV—(contd.)
Equilibrium constants obtained by various ion exchange equations

Solution No.	Total conc. in me/l	K.A.R. $\times 10^2$	Equations of				
			Kerr	Vanselow	K. and O.	Gapon	Donnan
i	ii	iii	iv	v	vi	vii	viii
<i>Bangalore</i>							
1	12	0.304	1.582	227.0	147.0	7.71	0.995
2	12	0.459	2.083	294.0	201.0	8.93	1.539
3	12	0.772	1.993	275.0	191.0	8.83	1.520
4	12	2.432	0.783	102.0	73.7	5.71	0.944
5	12	2.423	0.870	113.0	81.0	6.05	0.969
6	12	5.250	0.729	89.5	67.0	5.77	0.909
7	12	7.376	0.483	56.0	43.0	4.76	0.738
<i>Mansong</i>							
1	12	0.304	1.188	207.0	134.5	7.37	0.871
2	12	0.459	1.592	273.0	187.0	8.60	1.288
3	12	0.772	1.240	209.0	144.0	7.63	1.217
4	12	2.432	0.566	90.6	64.8	5.34	0.812
5	12	2.423	0.602	96.1	68.9	5.52	0.784
6	12	4.250	0.304	47.4	34.5	3.97	0.563
7	12	7.376	0.165	24.9	18.5	2.99	0.396
<i>Bagwai</i>							
1	12	0.304	1.491	96.3	62.9	4.99	0.970
2	12	0.459	1.990	12.7	86.4	5.75	1.119
3	12	0.772	1.097	69.7	47.4	4.30	0.861
4	12	1.579	0.631	39.4	27.1	3.29	0.621
5	12	2.423	0.475	29.2	20.3	2.88	0.557
6	12	4.250	0.305	18.2	12.9	2.34	0.443
7	12	7.376	0.203	11.8	8.5	1.95	0.352
<i>Bichpuri</i>							
1	12	0.304	3.350	1006.0	632.0	16.70	1.413
2	12	0.459	6.530	1870.0	1320.0	23.90	2.002
3	12	0.772	3.820	1069.0	771.0	18.53	1.629
4	12	1.579	1.370	374.0	274.0	11.29	0.895
5	12	2.423	0.904	240.0	178.0	9.36	0.874
6	12	4.250	0.396	102.0	77.0	6.26	0.562
7	12	7.376	0.221	55.0	42.6	4.84	0.430
<i>Reura</i>							
1	12	0.304	3.099	209.0	135.0	7.40	1.455
2	12	0.459	2.110	141.0	96.0	6.10	1.180
3	12	0.772	1.070	71.4	48.6	4.36	0.974
4	12	1.579	0.670	43.9	30.2	3.57	0.637
5	12	2.423	0.486	31.3	21.8	3.00	0.540
6	12	4.250	0.291	18.4	12.9	2.37	0.434
7	12	7.376	0.191	11.3	8.1	1.90	0.391

TABLE IV—(concl'd.)

Equilibrium constants obtained by various ion exchange equations

Solution No.	Total conc. in me/l	K.A.R. $\times 10^2$	Equations of				
			Kerr	Vanselow	K. and O.	Gapon	Donnan
i	ii	iii	iv	v	vi	vii	viii
<i>Powerkhara</i>							
1	12	0.304	2.304	153.0	103.0	6.32	1.217
2	12	0.459	3.585	234.0	160.0	7.90	1.540
3	12	0.772	2.189	142.0	97.4	6.20	1.180
4	12	1.579	1.284	81.2	56.6	4.80	0.896
5	12	2.423	0.985	61.0	43.1	4.27	0.787
6	12	4.250	0.501	30.4	21.8	3.10	0.571
7	12	7.376	0.301	17.6	12.9	2.45	0.478
<i>Pusa</i>							
1	12	0.304	0.516	480.0	318.0	11.35	
2	12	0.459	0.395	237.0	187.0	8.58	
3	12	0.772	0.393	266.0	184.0	8.70	
4	12	1.579	0.291	188.0	134.0	7.62	
5	12	2.423	0.243	152.0	111.0	7.15	
6	12	4.250	0.237	137.0	105.0	7.49	
7	12	7.376	0.132	73.0	57.5	5.82	
<i>Delhi</i>							
1	12	0.304	1.657	387.0	248.0	10.30	1.033
2	12	0.459	1.479	350.6	240.0	9.74	0.977
3	12	0.772	0.928	216.0	149.0	7.78	0.828
4	12	1.579	0.363	83.5	58.3	4.90	0.468
5	12	2.423	0.312	69.9	49.6	4.62	0.505
6	12	4.250	0.191	41.9	30.0	3.67	0.398
7	12	7.376	0.152	31.2	23.4	3.41	0.346

systems containing both mono- and di-valent cations. The coefficients of variation in equilibrium constants calculated by different ion exchange equations are given in Table V. These values are higher by about a factor of two for the equations of Kerr, Vanselow, and Krishnamoorthy and Overstreet, compared to those for the equations of Gapon and Donnan. There is, however, a slight tendency for the equilibrium constants of Vanselow to show a greater degree of variation than there is for the equilibrium constants of Kerr, Krishnamoorthy and Overstreet. Similarly there seems to be a general tendency of the equilibrium constants of Donnan to show a slightly larger variation than those of Gapon. Thus Gapon's equation seems to be more

satisfactory for explaining the ionic distribution in systems containing three ions involving Ca, Mg and K for the type of soils under investigation.

TABLE V
The coefficients of variation in equilibrium constants for soils obtained by various ion exchange equations (expressed as percentage)

Soil	Equations of				
	Kerr	Vanselow	K. and O.	Gapon	Donnan
Bagwai ..	75.4	69.7	76.0	38.7	40.6
Hagri ..	86.8	88.4	87.3	44.6	46.0
Reura ..	95.8	97.8	88.9	49.2	50.3
Powerkhera ..	73.1	75.8	73.5	38.5	40.3
Bangalore ..	53.8	59.0	55.5	24.2	28.8
Bichpuri ..	97.5	99.3	98.6	47.8	52.1
Delhi ..	86.9	89.2	85.9	45.0	44.2
Raipur ..	84.9	86.6	85.9	45.6	47.8
Raneshwar ..	68.7	74.3	67.8	41.8	35.1
Agartala ..	50.3	64.0	56.5	23.2	22.7
Chalakudi ..	86.7	74.3	67.8	27.6	25.6
Pusa ..	40.6	59.3	53.6	21.2	—
Mansong ..	66.1	69.6	67.2	34.5	38.1
Aryadu ..	65.8	67.6	66.3	23.9	29.4
Kuttanad ..	90.1	96.5	85.6	51.5	49.2
Raipur* ..	104.1	101.7	105.6	53.6	58.3
Raneshwar*	102.3	106.0	102.2	49.0	49.7
Agartala* ..	68.3	74.6	69.7	26.5	31.3
Chalakudi* ..	89.1	96.0	87.2	40.8	43.0
Aryadu* ..	89.4	91.1	86.9	48.7	49.6
Kuttanad* ..	108.9	109.1	107.3	62.0	57.6

* C.V. calculated including equilibrium constants for solutions of total higher salt concentrations.

A similar conclusion regarding the suitability, and a better fit, had been obtained with Gapon's equation, by earlier workers (Abrol 1962; Beckett 1964; Paliwal 1961; U.S. Salinity Staff 1954). The inclusion of solutions with a higher total salt concentration resulted in an increase in the values of the coefficients of variation in all the six types of soil studied for the purpose. There also, generally speaking, the relative differences in the coefficients of variation in equilibrium constants of various equations studied were nearly the same as those which were obtained with solutions of lower total salt concentration. Thus Gapon's equation is relatively more suitable even in solutions of higher concentration than the others.

It is interesting to note that the coefficients of variation in Gapon's constant are correlated statistically with the cation exchange capacity of different soils and also with the cation exchange capacity of soils calculated

for 100 g. of clay. The coefficient of correlation for the former is -0.56 which is significant at 5 per cent level whereas for the latter it is -0.68 and is significant at 1 per cent level. This shows that the disturbance in the Gapon's equilibrium constant is caused by the cation exchange capacity of the clay which is related to the charge of the colloidal particles. Thus it is the charged surface which is causing the variation in the activities of the exchangeable ions. It is, therefore, quite probable that the variation in Gapon's equilibrium constant is due either to incomplete or to excess correction for the variation in the activity coefficient of the ion with increasing amounts of saturation of the exchangeable ion concerned.

LOGARITHMIC EQUATIONS

In addition to the above empirical equations some logarithmic relations between the degree of potassium saturation (D.K.S.) or exchangeable potassium ratio (E.K.R.) and K.A.R. were also used to examine their suitability. These were of the type $D.K.S. = cK.A.R.^m$ or $E.K.R. = cK.A.R.^m$ where m occurs as a power of the K.A.R. of the equilibrium solution and c is the proportionality constant. The values of m and c for different equations were obtained by drawing the best fitting straight line connecting the logarithms of the two variables.

From the values of m and c for the best fitting straight lines shown in Table VI, it can be seen that, in general, there is no significant difference

TABLE VI

' c ' and ' m ' values of the best fitting straight line obtained by various equations for soils

Locality	$D.K.S. = c_1 K.A.R.^{m_1}$		$D.K.S. = c_2 K.A.R.^{m_2}$		$E.K.R. = c_3 K.A.R.^{m_3}$		$K.A.R._{Dex} = c_4 K.A.R.^{m_4}$	
	c_1	m_1	c_2	m_2	c_3	m_3	c_4	m_4
Bagwai	69.82	0.644	72.81	0.622	0.759	0.650	0.157	0.63
Hagri	52.48	0.600	63.10	0.600	0.670	0.633	0.267	0.74
Reura	50.70	0.545	54.33	0.533	0.752	0.633	0.148	0.60
Powerkhera	66.68	0.550	80.35	0.560	0.891	0.600	0.257	0.67
Bangalore	199.50	0.750	190.50	0.680	3.473	0.838	0.333	0.73
Bichpuri	62.52	0.340	88.33	0.433	0.997	0.400	0.141	0.53
Delhi	95.50	0.600	100.00	0.580	1.128	0.614	0.145	0.63
Raipur	47.86	0.500	53.09	0.500	0.562	0.520	0.104	0.53
Raneshwar	72.44	0.610	81.28	0.600	0.955	0.650	0.118	0.60
Agartala	127.40	0.766	136.20	0.735	1.660	0.810	0.219	0.76
Chalakudi	156.70	0.675	186.20	0.675	2.924	0.789	0.243	0.74
Pusa	239.90	0.760	260.00	0.740	3.802	0.833	—	—
Mansong	194.90	0.583	100.00	0.583	1.157	0.625	0.237	0.73
Aryadu	117.50	0.685	144.50	0.690	1.585	0.736	0.195	0.70
Kuttanad	13.57	0.500	14.79	0.520	0.134	0.510	0.066	0.47

between the values of m_1 , m_2 , m_3 and m_4 obtained by using different equations for the same soil.

However, the power index m_1 in the equation $D.K.S. = c_1(K.A.R.)^{m_1}$ is statistically correlated ($r = -0.635$) (Table VI) significantly at 2 per cent level with the C.E.C. of different soils used. It can be inferred from this that the adsorption of potassium by the soil is not inversely related to the C.E.C. in accordance with Mattson's inverse ratio law. The power indices m_2 , m_3 and m_4 of other logarithmic equations showed no statistically significant correlation with the C.E.C.'s either of the soils or of the clays (Table VII). In the case of the proportionality constants, i.e. c values, there exists a highest (0.83) and statistically significant correlation at 1 per cent level between c_1 and C.E.C. of the soils. The c_2 and c_3 values are also correlated with those of the soils but to a lesser extent. It can also be noted from the same table that the C.E.C. of clays correlate statistically significant at 1 per cent level with the c_1 , c_2 and c_3 values. Thus the proportionality constants (c_1 and c_2) of the equation $D.K.S. = cK.A.R.^m$ type, whether K.A.R. is expressed in Gapon or Donnan form, are more closely related with the C.E.C. of the exchange complex than the power index.

TABLE VII

Coefficient of correlation of 'm' and 'c' with cation exchange capacity of soil and clay (calculated) (C.E.C. calculated for 100 g)

C.E.C.		c_1	c_2	c_3	c_4	m_1	m_2	m_3	m_4
Soil	..	0.830*	0.703*	0.621†	0.237	0.635†	0.344	0.368	0.340
Clay	..	0.797*	0.815*	0.673*	0.275	0.377	0.398	0.486	0.440

All correlations are negative and calculated for 15 soils.

* Significant at 1 per cent level.

† Significant at 2 per cent level.

In order to analyse statistically the extent of variation from this best fitting curve in each of the soils studied, the values of the constant c for each one of the points on the curve of the soils were calculated assuming the value of m for all the points to be the same as that of the best fitting straight line. The coefficients of variation are calculated from the values of c_1 , c_2 , c_3 and c_4 for each soil (Table VIII). When the solutions of the total salt concentration of 12 me per litre are only considered, the equation, $K.A.R._{Dex} = c_4 K.A.R._{Dex}^{m_4}$, connecting the exchangeable cations expressed in the Donnan form ($K.A.R._{Dex}$) with the $K.A.R._D$ of the equilibrium solutions, has given the largest variation and seems to be the least applicable in this case. On the other hand the equation $D.K.S. = cK.A.R.^{m_1}$ gives the least variation with

an average value of 9.5 per cent. Gapon type equation in the logarithmic form, i.e. $E.K.R. = c_3 K.A.R.^{m_3}$, is next to it in variation with an average value of 10 per cent. The variations obtained by the equation $D.K.S. = c_2 K.A.R.^{m_2}$ are of intermediate values. When the c values obtained from the solutions of higher total salt concentration are also included in those of lower ones, i.e. 12 me, there is a greater variation as expected. The coefficients of variation in the c values are by far the largest, 19.8 per cent in the equation connecting E.K.R. of soil with K.A.R. of equilibrium solution, while the other three equations show nearly the same extent of variation with a value of about 17.7 per cent.

TABLE VIII

The coefficients of variation in 'c' values obtained by various equations for soils (expressed as percentage)

Locality	c_1	c_2	c_3	c_4
Bagwai ..	6.39	6.12	6.85	11.39
Hagri ..	9.94	9.42	11.19	23.30
Reura ..	4.04	2.49	8.19	11.24
Powerkhera ..	13.30	11.46	13.03	16.58
Bangalore ..	11.97	15.10	10.42	20.30
Bichpuri ..	18.54	22.86	20.23	17.72
Delhi ..	8.06	10.70	11.20	11.31
Raipur ..	15.30	15.27	15.94	19.23
Raneshwar ..	4.48	4.16	3.90	14.97
Agartala ..	4.84	7.43	4.92	7.90
Chalakuadi ..	4.47	2.62	6.68	14.21
Pusa ..	9.40	12.93	9.35	—
Mansong ..	13.10	18.18	11.26	26.10
Aryadu ..	5.23	6.39	5.42	6.02
Kuttanad ..	13.70	23.80	12.60	24.07
Raipur*	22.90	26.84	44.60	27.89
Raneshwar*	4.90	3.60	6.40	17.14
Agartala*	9.33	6.98	9.31	8.07
Chalakuadi*	15.50	13.95	10.10	15.67
Aryadu*	21.70	21.50	18.06	20.01
Kuttanad*	32.28	33.40	30.30	16.45

* C.V. calculated including solutions of total higher salt concentrations.

It has been noted that on comparing the modified Gapon's equation with its logarithmic form the average coefficient of variation has been reduced from 37.2 to 10 per cent.

As pointed out earlier the equilibrium constant of Gapon shows a statistically negative correlation with the cation exchange capacity of the soil. This type of correlation has also been noted between the c values and the C.E.C. of soils when Gapon's equation is expressed in the logarithmic form.

It seems that the variation in Gapon's equilibrium constant is related to the cation exchange capacity of the soil. The charge density of the clay particles affects the distribution of both mono- and di-valent cations on the clay phase (3) and the variation in the activity coefficient of the ion concerned takes place in such a way that these common equations are unable to make necessary correction for this variation. Thus the complex behaviour of exchangeable cations under varying charge density of exchange complex and ionic strength of the solution is not fully understood.

However, Gapon's equation is more satisfactory and can be safely used for general purposes.

SUMMARY

Some of the ion exchange equations have been tried to find out their suitability for expressing the distribution of ions in Ca-Mg-K soil systems. Out of the equations of Kerr, Vanselow, Krishnamoorthy and Overstreet and Gapon and one based on Donnan membrane equilibria, Gapon's equation was found to be more satisfactory than others. A new logarithmic equation $D.K.S. = c_1 K.A.R.^{m_1}$ gave a slightly better fit with the experimental data on fifteen soils studied than simple Gapon or its logarithmic form.

Cation exchange capacity of the soils seems to be related to the equilibrium constant of Gapon or its proportionality constant in a logarithmic form. Both c_1 and m_1 values of the best fitting equation $D.K.S. = c_1 K.A.R.^{m_1}$ show statistically significant negative correlation with the C.E.C. of the soils.

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