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II. CHEMISTRY

Soil Chemistry

QUANTITY-INTENSITY (*Q/I*) RELATIONSHIP OF SOME SOIL CLAYS OF WEST BENGAL IN RELATION TO THEIR CLAY MINERALOGY

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The Quantity-Intensity (*Q/I*) relationship for potassium and some of its parameters were determined for some soil clays of West Bengal. The *Q/I* curves and their parameters bring out the characteristic feature of the dominant clay mineral in the composition of the clay fractions. The differences in the nature of the *Q/I* curves and also their parameters within the same group of soil clays have been attributed to the other associated minerals as well as sesquioxide contents on the colloid complex.

Keywords: Q/I Relationship; Equilibrium Activity Ratio; Free Energy; Buffering Capacities (LBC^k & TBC^k)

INTRODUCTION

CONSIDERABLE amount of work has been done on K-potential and *Q/I* relationship of Soils (Beckett, 1964, 1971; Acquaye & Maclean, 1965; and Acquaye *et al.*, 1967). All these studies indicate that the nature and mineralogy of soil clays influence the *Q/I* relationship of soils and related parameters. But detailed study of the *Q/I* relationship of soil clays are meagre (Beckett & Nafady, 1967*a,b,c*; Le Roux & Summner, 1968; and Maclean & Brydon, 1971). However, it is apparent from these studies that this information is insufficient to make any conclusion and a more detailed study of the mineralogy of the clays is still needed to explain the *Q/I* relationship of soils. The present study has been taken up to this end to fill up the above lacuna.

MATERIALS AND METHODS

Eleven surface soil samples were collected from different districts of West Bengal. A brief description of these soils has been summarised in Table I. The soil samples were treated with H_2O_2 and separation of the clay was carried out by the International method using dil. NH_4OH as the dispersing agent. Hydrogen clay system was prepared by repeated washing with 0.05 N HCl.

Mineralogical identification of the soil clays was done by X-ray analysis of Mg and K-saturated clays. The total Fe_2O_3, Al_2O_3, K_2O contents and the CEC of

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TABLE I

Description and locations of soil

Soil	Soil Group	Geology	Mean Ann. Rainfal (mm)	Soil Characteristic
Chinsurah (Hooghly)	Alluvial Soil (Entisol)	Gangetic Alluvium	1964	*p*H 7.1, Colour when dry 2.5*y* 7/2 light grey, clay loam.
Kakdwip (24-Parganas)	—do—	—do—	1670	*p*H 6.9, Colour when dry 2.5 *y* 7/2 light grey, clay loam, soluble salt content is high.
Muratipur (Nadia)	—do—	—do—	1624	*p*H 8.3, 2.5*y* 7/2 light grey, clay loam, $CaCo_3$ present.
Totpara (Burdwan)	—do—	Vindhya-Alluvium	1268	*p*H 5.2, 5*y*8/3 pale yellow, silty loam.
Raydak (Jalpaiguri)	Himalayan Submontane Soil	A thick gneiss of foliated type, frequently passing into mica schist, deposits brought down by hilly rivers, sandy and raw humas type.	3200	*p*H 5.5, 10*y*R 5/3 brown sandy loam, organic matter content is high.
Ging (Darjeeling)	—do—	—do—	3464	*p*H 4.7, 10*y*R 5/3 brown sandy loam, organic matter content is high.
Hatadah (Purulia)	Laterite soil (Oxisol)	Hill deposits from Chhota Nagpur plateau contain large amount of coarse sand and gravels.	1307	*p*H 5.2, 2.5*y* 7/4 pale yellow, low in soluble matter and humus, high Fe_2O_3 and Al_2O_3 contents.
Nalhati (Birbhum)	—do—	—do—	1491	*p*H 5.4, 10*y*R 7/3 very pale Brown, Loamy.
Mohammad Bazar (Birbhum)	—do—	—do—	1791	*p*H 6.9, Sandy loam.
Taldanga (Bankura)	—do—	Laterite interspersed with sand gravel	1272	*p*H 5.1, 2.5*y* 8/4 pale yellow sandy loam.
Jhargram Midnapur)	Red Soil (Oxisol)	Gravelly pisolitic and nodular, Laterite contains coarse gritty and stone of red colour.		*p*H 5.2, 5*y*R 5/6 yellowish red, sandy loam.

the soil clays were determined according to the standard procedure (Jackson, 1958; and Black, 1965).

The *Q/I* relationship and its parameters for the above Soil clays (H-system) were determined as per the standard procedures (Beckett, 1964; Acquaye & Maclean, 1969; and Moss & Beckett, 1971).

Results and Discussion

The general physico-chemical properties of the soils and the clay mineralogical compositions as determined by X-ray analysis are tabulated in Tables II and III respectively. The soil clays are grouped into classes according to their clay mineralogical composition and the Q/I relationship has been discussed accordingly.

TABLE II

Some physico-chemical properties of the soils

Soils	(pH : 2.5 soil : water)	C.E.C. me/100g soil	O.M (%)	Exchangeable cations (me/100g soil)			Clay (%)	Silt (%)	Sand (%)
				K	Ca	Mg			
Chinsurah (Hooghly)	7.1	29.74	0.81	0.46	22.05	2.50	44.0	38.20	15.5
Kakdwip (24-Parganas)	6.9	18.4	1.90	0.35	12.30	8.55	22.0	49.0	26.3
Muratipur (Nadia)	8.3	20.6	2.40	0.34	16.1	1.85	26.3	45.0	28.2
Burdwan	5.2	9.78	0.62	0.25	1.40	0.50	12.9	48.0	38.2
Purulia	5.2	7.0	0.97	0.70	4.20	0.21	11.0	35.9	50.2
Darjeeling	4.7	12.48	5.90	1.50	0.70	0.50	13.6	8.45	76.98
Jalpaiguri	5.5	11.25	6.40	0.50	0.50	0.20	12.0	31.95	53.5
Nalhati (Birbhum)	5.4	13.29	0.80	0.38	5.10	1.50	24.2	36.9	37.95
Bankura	5.1	4.9	0.61	0.11	0.40	0.11	22.2	9.82	66.96
Mohammad Bazar (Birbhum)	6.9	11.2	0.40	0.24	4.10	0.49	19.6	32.0	48.18
Midnapur	5.2	8.6	0.70	0.18	1.50	0.09	10.0	32.19	55.95

The Quantity-Intensity (Q/I) relationship of smectitic soil clays (H-system)

The Q/I curves for these soil clays are characterised by an upper linear portion at moderate values of activity ratio and a curved lower region at low values of activity ratio. Kakdwip soil clay shows maximum curvature upto 0.006 $M/L^{1/2}$ in Q/I curve followed by Muratipur, Burdwan and Chinsurah H-clays upto the activity ratios of 0.005, 0.003, and 0.0025 $M/L^{1/2}$ respectively. Chinsurah soil clay shows steep linear Q/I curve compared to those of Burdwan, Muratipur and Kakdwip H-clays indicating higher amount of potassium adsorption at the same values of activity ratio in the Chinsurah soil clay. Some points below the base line ($\triangle K = 0$) denote the release of potassium from the clays on shaking with $CaCl_2$ solution alone without any addition of KCl. The amounts of released potassium are high in Kakdwip and Muratipur soil clays than those of Burdwan and Chinsurah H-clays (Fig. 1). The nature of the Q/I curves of the above soil clays which are dominant in smectite, reveals the effect of large external and internal surface areas of the expanding lattice type of structure of smectite. Thus the Q/I curves indicate a slight curvature at low 'I' values indicating a small number of specific sites for potassium

TABLE III

Clay mineralogy and different oxides content of soil clays of West Bengal

Location	Smectite	Vermiculite	Chlorite or Pro-chlorite	Illite	Interstratified minerals	Kaolinite	Al_2O_3 (%)	Fe_2O_3 (%)	K_2O (%)	CEC me/100g
Chinsurah (Hooghly)	D	—	(++)	(++)	—	(+)	22.20	9.9	2.78	52.0
Kakdwip (24-Parganas)	D	—	(++)	(++)	—	(+)	25.28	7.20	3.20	44.2
Muratipur (Nadia)	D	—	(++)	(++)	—	(+)	24.10	8.90	2.67	46.7
Totpara (Burdwan)	D	—	(++)	(+)	(+) (Ill. Mont)	(+)	25.0	9.25	1.73	39.0
Hatadah (Purulia)	(+)	—	—	D	(+++) (Ill. Mont) (+) (Ill. Ch. Mont)	(++)	29.5	11.01	2.10	24.5
Rydak (Jalpaiguri)	Tr.	—	(+++)	D	—	(+)	25.0	8.79	2.83	32.0
Ging (Darjeeling)	(+)	(+)	(+)	D	(+) (Ill. Ver)	(+)	23.7	9.35	3.25	27.5
Nalhati (Birbhum)	(+)	(+)	Tr.	(++)	—	D	31.5	8.60	1.10	27.0
Bankura	—	—	—	(++)	(+) (Ill. Mont) (++) (Deg. Ill)	D	30.82	9.12	2.25	23.5
Mohammad Bazar (Birbhum)	(+)	—	—	(+)	(+) (Ch. Mont)	D	29.19	11.06	0.97	25.0
Midnapur	—	—	—	(++)	(+) (Ch. Mont)	D	34.21	13.15	0.82	20.5

Legend : D = Dominant; (+) = Relative abundance; Tr. = Trace; Mont. = Montmorillonite; Ch. Mont. = Chloritised montmorillonite; Ill. = Illite; Ver. = Vermiculite; Ch. = Chlorite/Pro-chlorite.

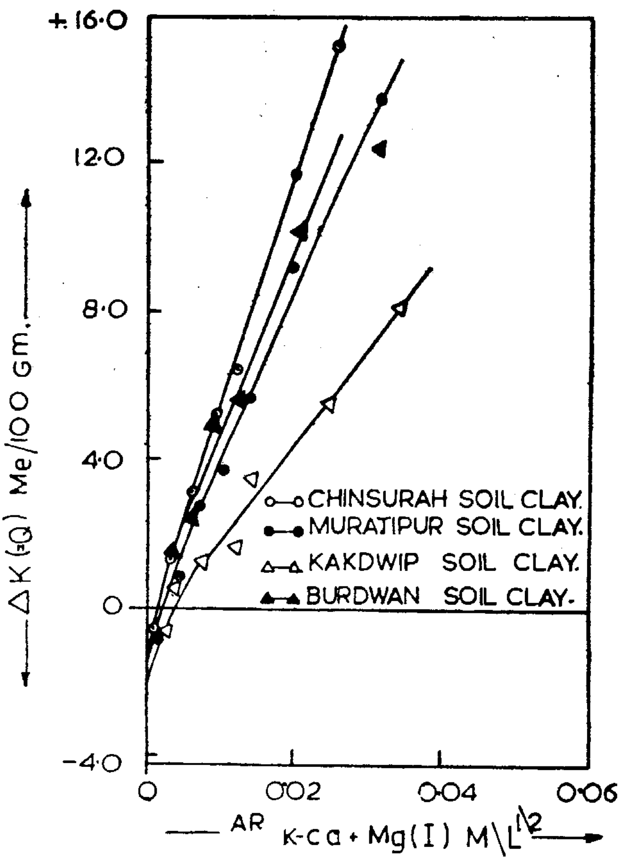

FIG. 1. The *Q/I* relation of soil clays dominant in smectite.

ion adsorption, while the upper straight portion of the curve indicate a larger planar surface of adsorption. The larger surface area of the mineral and its larger C.E.C. determine the *Q/I* isotherm, adsorbing larger amount of potassium at low activity ratios, compared to other minerals. Amongst the smectite group, there are difference between themselves. These differences, to a great extent, are due to the associated minerals as illite and chlorite in Chinsurah, Muratipur and Kakdwip soil clays (Table III) having lower specific surfaces. The amount of free sesquioxides as is reflected from the total sesquioxides contents also contribute to the different behaviour of the soil clays. Further, interstratified mineral illite-montmorillonite in Burdwan H-clay appears to have an effect on the *Q/I* curve, as they can offer some interlattice specific edge spots for stronger bonding of potassium ion.

The adjacent table (Table IV) illustrates different *Q/I* parameters of the soil clays. The AR_e^{ok} value for Kakdwip, Muratipur, Burdwan and Chinsurah H-clays are 0.003, 0.002, 0.0018 and 0.0015 $M/L^{1/2}$ respectively. The high AR_e^{ok} values indicate a larger proportion of potassium ion in equilibrium solution. This is in conformity with

TABLE IV

Q/I parameters of the soil clays (H-system)

Soil Clays	AR_e^{ok} $M/L^{1/2}$	ΔG_{k-Ca} Kcal mole^{-1}	LBC^k	TBC^k
	Soil clays dominated by Smectite			
Chinsurah	0.0015	− 3.806	500	800
Muratipur	0.0020	− 3.679	461	600
Kakdwip	0.0030	− 3.400	400	500
Burdwan	0.0018	− 3.698	300	475
	Soil clays dominated by Illite			
Purulia	0.0010	− 4.049	312	500
Darjeeling	0.0015	− 3.806	250	333
Jalpaiguri	0.0020	− 3.679	300	450
	Soil clays dominated by Kaolinite			
Bankura	0.0022	− 3.589	200	400
Nalhati (Birbhum)	0.0018	− 3.698	350	444
Mohammad Bazar (Birbhum)	0.0015	− 3.806	285	400
Midnapur	0.0025	− 3.558	150	272

the ΔG_{k-Ca} value in the same table. High K^+ activity in equilibrium solution is associated with less negative value of free energy which indicates less strong binding of K^+. For the above soil clays, the exchange reaction at the surface of the smectitic clays and their variations follow their *Q/I* curve as discussed above. The higher negative values of $-\Delta G_{k-Ca}$ i.e. ΔG_{Ca-k} which indicates 'Ca' replacing 'K', can be expressed as $-\Delta G_{k-Ca} = \Delta G_{Ca-k}$. Thus Ca^{+2} in equilibrium solution has a higher free energy with respect to K^+ or from this equilibrium solution if K^+ is removed then more K^+ will be released being displaced by Ca^{+2}. Hence, more negative value of ΔG_{k-Ca} would result in more release of K^+. The values of linear buffering capacity (LBC^k) and tangential buffering capacity (TBC^k) for Chinsurah, Muratipur, Kakdwip and Burdwan H-clays are 500, 461, 400 and 315 and 800, 600, 500 and 475 respectively (Table IV). The Chinsurah soil clay indicates highest LBC^k and TBC^k values which correspond to low AR_e^{ok} and high negative values of ΔG_{k-Ca} which suggest that the K-release will be higher in Chinsurah soil as compared to the other soil clays as potassium is removed from the system. So all the above *Q/I* parameters are characteristics of *Q/I* curve and also follow the mineralogical composition of the soil clays as described above.

The Quantity-Intensity (Q/I) relationship of illitic soil clays (H-system)

The nature of the *Q/I* curves of Purulia, Jalpaiguri and Darjeeling soil clays (H-system) in which the clay fractions are dominantly illitic are also characterised by the lower curved region at low values of activity ratio and linear portion at high values of activity ratio. The slight curved region of Purulia H-clay is observed at low activity ratio upto 0.003 $M/L^{1/2}$ beyond which the curve is linear. Without doubt this indicates the similarity of the exchange spots on the clay surface with fewer specific sites or lattice holes (interlayer or broken bond edge holes) on the clay surface (Beckett, 1971). Further as has been assumed previously that most of the specific sites for strong bonding of K^+ are covered by free sesquioxide and hence it appears as linear. The pronounced curvature is observed in Jalpaiguri H-clay compared to that of Darjeeling H-clay at low values of activity ratio. The linear part in the *Q/I* curve of these H-clays are less steeper than that of the Purulia soil clay. The curvature in these *Q/I* curves are undoubtedly due to illite as well as associated minerals (Table III) which offer sufficient number of specific sites for strong bonding of potassium ion. In Darjeeling, soil clay the vermiculite illite-vermiculite interstratified minerals also have an appreciable potassium holding capacity (Fig. 2).

Table IV also includes the AR_e^{ok} and $\triangle G_{k-Ca}$ values for Jalpaiguri, Darjeeling

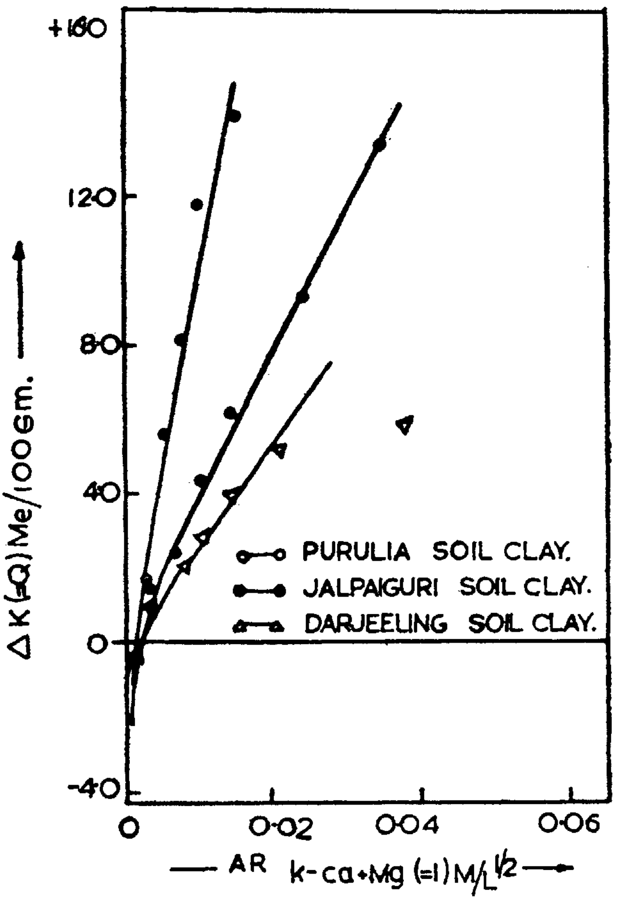

FIG. 2. The *Q/I* relation of soil clays dominant in illite.

and Purulia H-clays being 0.002, 0.0015, 0.001 $M/L^{1/2}$ and −3.679, −3.806 and −4.049 kcal mole^{-1} respectively. The same table also shows that LBC^k values of the same clays follows the reverse order of AR_e^{ok} and ΔG_{k-Ca} values. The LBC^k and TBC^k values of Purulia, Jalpaiguri and Darjeeling soil clays are 312, 300, 250 and 500, 450, 333 respectively. According to Table III these soil clays are dominantly illite and follow the same trend with respect to the aforesaid *Q/I* parameters as the soil clays of the smectitic group. The nature of the *Q/I* curve for Purulia soil clay indicates that most of the potassium ions are adsorbed on non-specific sites than that on the specific sites and gives the high LBC^k value. Very high values of TBC^k of this soil clay suggests that some specific spots are still open due to the presence of illite and illite-montmorillonite inspite of it being lateritic in nature. The mineralogy of Darjeeling and Jalpaiguri soil clays (Table II) are consistent with their *Q/I* parameters.

The Q/I relationship of Kaolinitic soil clays (H-system)

The *Q/I* curves of the soil clays of this group are similar to the other soil clays described earlier. The *Q/I* curves of Mohammad Bazar and Nalhati H-clays show less curvature upto the activity ratio of 0.002 and 0.003 $M/L^{1/2}$ beyond which these curves show steep linear rise (Fig. 3).

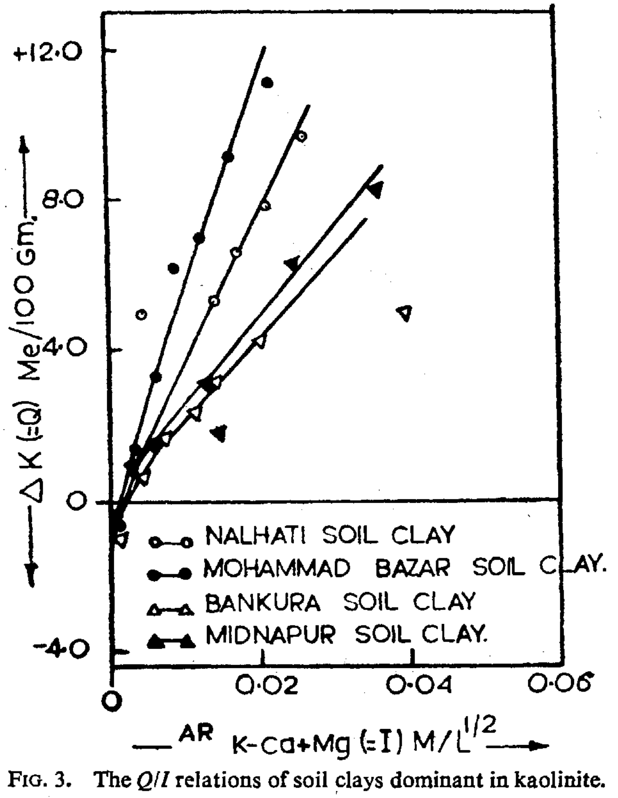

FIG. 3. The *Q/I* relations of soil clays dominant in kaolinite.

The Q/I curve of the kaolinitic soil clays with practically not much of inter-lattice specific edge surface and lower CEC, have practically little of the curvature. The plannar surfaces are characteristic of the kaolinite mineral which causes the steepness in the Q/I curves of the above two soil clays. Comparatively more marked curvatures are observed in the Q/I curves of Bankura and Midnapur H-clays upto the activity ratio of 0.005 and 0.007 $M/L^{1/2}$ respectively (Fig. 3). The small curvatures in these soil clays are mainly due to their associated minerals (Table III) with high specific region of absorption of potassium ions as referred to earlier in the case of smectitic soil clay. The buffering capacity values for these soil clays are also presented in the Table III. The LBC^k and TBC^k values of Nalhati, Mohammad Bazar, Bankura and Midnapur H-clays are 350, 285, 200, 150 and 444, 400, 400 and 272 respectively. These data indicated that the high values of AR_e^{ok} and low negative values of free energy ($\triangle G_{k-Ca}$) for Midnapur and Bankura soil clays are mainly due to the presence of illite which may provide some strong bonding sites for potassium ion not covered by sesquioxide (Table III). The LBC^k and TBC^k values are also well related to the mineralogy of these clays. The low AR_e^{ok} values and high LBC^k values of Nalhati and Mohammad Bazar H-clays compared to other soil clays in this group are characteristic of their Q/I curve. Nalhati and Mohammad Bazar soil clays have high negative values of free energy followed by the soil clays of Bankura and Midnapur. In this group of soil clays the free energy values are also well related to the LBC^k and TBC^k values as explained to the other soil clays of other group.

Conclusion

It may be concluded from the preceding discussion that smectitic soil clays with their expanded lattice offer both internal and external surfaces freely for exchange reaction. Consequently, the nature of the Q/I curves are influenced. Further the differences in the nature of the Q/I isotherms within the soil clays of the smectitic group are to a great extent determined by the associated minerals and by the presence of sesquioxides which cover the exchange spots. Similar conclusion also holds good in illitic and kaolinitic soil clays. No doubt, illites with their lower CEC and interlattice edge surfaces are responsible for the pronounced curvature of the Q/I curves of low K^+ activity ratio. On the contrary small curvatures in the same region to Q/I curves of kaolinitic soil clays having lower CEC may be due to the presence of very little interlattice specific edge surface or some broken bond edge holes of kaolinite as well as some specific spots contributed by the associated minerals mainly illite.

The study of the Q/I parameters for different groups of soil clays, namely equilibrium activity ratio (AR_e^{ok}) and buffering capacities (LBC^k and TBC^k) reveals that they are all related to their clay mineralogy. Since Q/I relation is mainly determined by the mineralogy of the soil clays, the above parameters are also dependent on clay mineralogy. The values of free energy ($\triangle G_{k-Ca}$) of K—Ca exchange is also very significant. A large value of free energy denotes a tendency for potassium ion to be released, but the rate of release per unit change in '*I*' values, depends on total Δ K or *Q* values which represent total potassium ion adsorbed on the clay. Thus the rate of release per unit change in '*I*' i.e., LBC^k (or TBC^k) is not directly related to the free energy of exchange, whereas the order of release of potassium ion per unit '*I*' value is smectitic soil clays > illitic soil clays > Kaolinitic soil clays.

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