Does Sodicity in Vertisols Affect the Layer Charge of Smectites?

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Abstract : Sodicity in smectite dominant shrink-swell soils (Vertisols and vertic intergrade) is common in the semi-arid region. It is not known whether long-term sodicity in soils changes the layer charge of smectites as layer charge is an important fundamental property of smectite-dominated soils and most of the soil properties depends upon the layer charge. Understanding the importance of layer charge of soil clay smectites, two benchmark Vertisols, one Paral soils (sodic) and the other Boripani soils (non-sodic) from Akola and Nagpur districts of Maharashtra were chosen for the study. The study intended to show whether long-term sodicity causes hydroxy-interlayering in smectites which result in an increase in layer charge. The soils had high clay and smectite content and the smectite charge was distributed in both tetrahedral and octahedral layers. The layer charge of both the soil fine clays are the lowest reported till date for Indian smectites and varied from 0.307 to 0.353 and 0.328 to 0.360 mol(-)/$\{Si, Al\}_4O_{10}(OH)_2\}$ in a soil profile for Paral and Boripani soils respectively. Hydroxy-interlayering in smectites was also negligible. The study discussed that sodicity may not be responsible for the formation of hydroxy-interlayering in smectites and thus not likely to increase the layer charge.

Shrink-swell soils of the Upper Peninsular India are mainly formed from the weathering of Deccan basalt, rich in plagioclase feldspars and yield dioctahedral smectite as the first weathering product (Pal and Deshpande, 1987; Bhattacharyya *et al*., 1993). These smectites are dominated by beidellite-nontronite type of minerals (Ghosh and Kapoor, 1982). It was later confirmed by diagnostic methods that smectites of Indian shrink-swell soils are nearer to montmorillonite of the montmorillonite-nontronite series (Pal and Deshpande, 1987).

To characterize the shrink-swell soils which contain dominant proportions of smectites, determination of their layer charge is fundamental to all physical and chemical properties of soils. The properties include soil structure, drainage, aeration, water retention (Laird *et al*., 1987), cation exchange reactions, specific surface area and degree of hydration (Bailey, 1980; Wilding and Tessier, 1988). The layer

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charge also determines the properties of soil clay minerals and indicates a mineral's capacity to retain cations and adsorb water and other polar organic molecules (Lagaly and Weiss, 1969; Malla and Douglas, 1987). It is also known that different swelling properties of clays with identical interlayer cations are mainly due to differences in layer charge densities (Weiss *et al.*, 1955).

Shrink-swell soils (Vertisols and vertic intergrades) of India contain smectites which are quite often hydroxy-interlayered (HI). It is reported that HI in smectites occurred due to the intrusion of positively charged HI materials into the smectite interlayers at much lower pH than the present day conditions (Deshmukh, 2009; Pal *et al*., 2012) and presence of HI indicated their formation in humid climate (Pal *et al*., 2012). Earlier studies indicated that in soils that have pH higher than 7, HI formation could be a possibility . Therefore, sodic shrink-swell soils in the semi-arid tract of Peninsular India may also be prone to form hydroxy-interlayering in smectites and may result increase in layer charge of smectites (Ray *et al*., 2008; Deshmukh, 2009; Bhople, 2010). The Peninsular India, particularly Maharashtra state has large tract of sodic soils. One such area is the Purna valley in Maharashtra (Pal *et al.,* 2000). Therefore, the present work was formulated based on the hypothesis whether long-term sodic environment in Vertisols would increase their layer charge as such increase is likely to reflect in the bulk soil properties.

Materials and Methods

Two benchmark soil series were selected for present study. One of these is Paral (P1) (Sodic Haplusterts) in Akola district which is a sodic soil, agriculturally important, widely distributed and intensively cultivated soils grown for cotton, sorghum, pigeonpea, etc. The other one is Boripani (P2) (Leptic Haplusterts) which is non-sodic supporting reserve forest in Nagpur district of Maharashtra was taken for comparison. Horizon-wise soil samples were collected for laboratory characterization. Some characteristics of the soils are shown in table 1. Silt varies from 21.8 to 37.6% and clay values ranged from 61.2 to 75.8%. Fine clay values are quite high which ranged from 42.6 to 59.4%. Fine clays being the dominant fraction in these soils were used for the determination of layer charge of fine clay smectites. High COLE values (> 0.10) are almost similar in both the soils. Available water capacity (AWC) is higher in Paral soils due to higher pH and exchangeable Na^+ content. Paral soils are strongly alkaline whereas Boripani soils are neutral to mildly alkaline. Organic carbon, CEC and base saturation are higher in Boripani soils, whereas $CaCO_3$ and ESP are higher in Paral soils.

Fine clays were separated from soil by size segregation method of Jackson (1979) following the removal of cementing agents. The fine clay (<0.2 μm) fractions of each horizon of the two pedons were analyzed for qualitative mineralogy by X-ray

Table 1. *Some properties of the soils given in ranges as they vary in a soil profile*

Sl. No.	Soil property	Paral (P1)	Boripani (P2)
1.	Sand (%)	0.6 – 1.1	1.3 – 2.2
2.	Silt (%)	31.1 – 37.6	21.8 – 32.5
3.	Clay (%)	61.2 – 68.2	65.5 – 75.8
4.	Fine clay (%)	42.6 – 51.7	47.8 – 59.4
5.	COLE[1]	0.17 – 0.25	0.17 – 0.26
6.	AWC[2] (%)	16.8 – 27.0	16.9 – 20.2
7.	pH	8.5 – 8.9	7.4 – 7.7
8.	Organic carbon (%)	0.51 – 0.65	0.14 – 1.00
9.	$CaCO_3$ equivalent (%)	9.5 – 11.2	3.8 – 7.9
10.	CEC {cmol(p+)kg^{-1}}	50.4 – 61.0	59.8 – 74.8
11.	Clay CEC {cmol(p+)kg^{-1}}	75.6 – 94.1	88.4 – 99.0
12.	Base saturation (%)	80.0 – 83.0	94.0 – 99.0
13.	ESP[3]	2.3 – 16.3	0.5 – 2.0

[1] COLE – coefficient of linear extensibility, [2] AWC – available water capacity, [3] ESP – exchangeable sodium percentage

diffraction (XRD) techniques. For identification of clay minerals, the fine clay fractions were subjected to XRD of the parallel oriented samples using a Philips X' Pert Pro diffractometer with Ni filtered Cu-Kα radiation at a scanning speed of 2°2θ/min. Different thermal pre-treatments of the K-saturated samples were given to distinguish and confirm the type of mineral present. Greene-Kelley (1953) test was also performed on these fine clays to distinguish between montmorillonite and beidellite / nontronite.

Characterization of layer charge

Alkylamines with carbon atoms 6, 7, 8, 9, 10, 11, 12, 13, 14, 16 and 18 were taken and their chloride salts were made (Lagaly, 1994; Ray *et al*., 2003, 2008) by first dissolving the required amount of respective amines in small amount of ethanol and then titrating it with HCl up to a pH of about 6.5 to 7. After preparing the various alkylammonium hydrochlorides, concentrations of various alkylamines were made as follows : 2M for chain lengths 6 and 7, 0.5 M for chain lengths 8, 9 and 10, 0.1 M for chain lengths 12, 13 and 14 and 0.05 M for chain lengths 16 and 18. Clay suspensions were pipetted containing 25-30 mg of Na-saturated clay. 10 ml of each alkylamine was added and kept at 65°C for 24 h. Another 10 ml of alkylamine was added after decanting the previously added amine and again kept at 65°C for 24 h. The excess alkylamine was washed first with 1:1 ethanol: water mixture and then with pure ethanol to remove excess salt. The alkylammonium-clay complexes formed were subsequently prepared as

oriented aggregates on glass slides. The alkylammonium treated samples were dried under vacuum in a dessicator at 65°C for 24 h before XRD analysis.

Calculation of Layer Charge

It has been observed by Lagaly and Weiss (1969, 1976) that short chain alkylammonium-smectite derivatives have basal spacings of about 13.6 Å, reflecting a monolayer of interlayer alkylammonium cations. Long chain alkylammonium-smectite derivatives have basal spacings of about 17.6 Å indicating a bilayer of interlayer alkylammonium cations and also at about 22 Å indicating a pseudotrimolecular layer of alkylammonium cations. The layer charge density was calculated by using the following equation:

$\xi = 23.25/ (5.67n_c + 14)$ for dioctahedral clays, where ξ is the layer charge density and n_c is the number of carbon atoms in the alkylammonium chain

Results and Discussion

Mineralogy of the fine clay fractions (<0.2 µm)

The fine clay fractions are mostly composed of smectite with small amounts of vermiculite and traces of chloritized smectites, mica, kaolin, quartz and feldspar (Table 2, Fig. 1). On glycolation the 1.4 nm peak expanded to about 1.7 nm indicating the presence of smectites. On K-saturation at 25°C the smectite peak shifted from 1.1 to 1.2 nm, which is characteristic of smectite (Pal and Deshpande, 1987). The shifting of the 1.0 nm peak of K-saturated and heated (300°C)

Table 2. *Semi-quantitative estimates of minerals in fine clay fraction of soils*

Horizon	Depth (cm)	Clay Minerals (%)						
		Smectite	Vermiculite	Chlorite	Kaolin*	Mica	Quartz	Feldspar
Paral soils								
Ap	0-9	76	12	2	2	3	2	3
Bw1	9-35	75	13	1	1	3	3	4
Bssk1	35-69	81	10	2	1	3	1	2
Bssk2	69-105	78	10	1	1	3	3	4
Bssk3	105-132	80	7	3	1	3	2	4
Bssk4	132-150+	80	5	5	1	3	2	4
Boripani soils								
A1	0-16	77	7	7	1	3	3	2
Bw1	16-44	86	4	5	2	1	1	1
Bss1	44-57	88	4	4	1	1	1	1
Ck1	57-94+	91	3	2	1	1	1	1

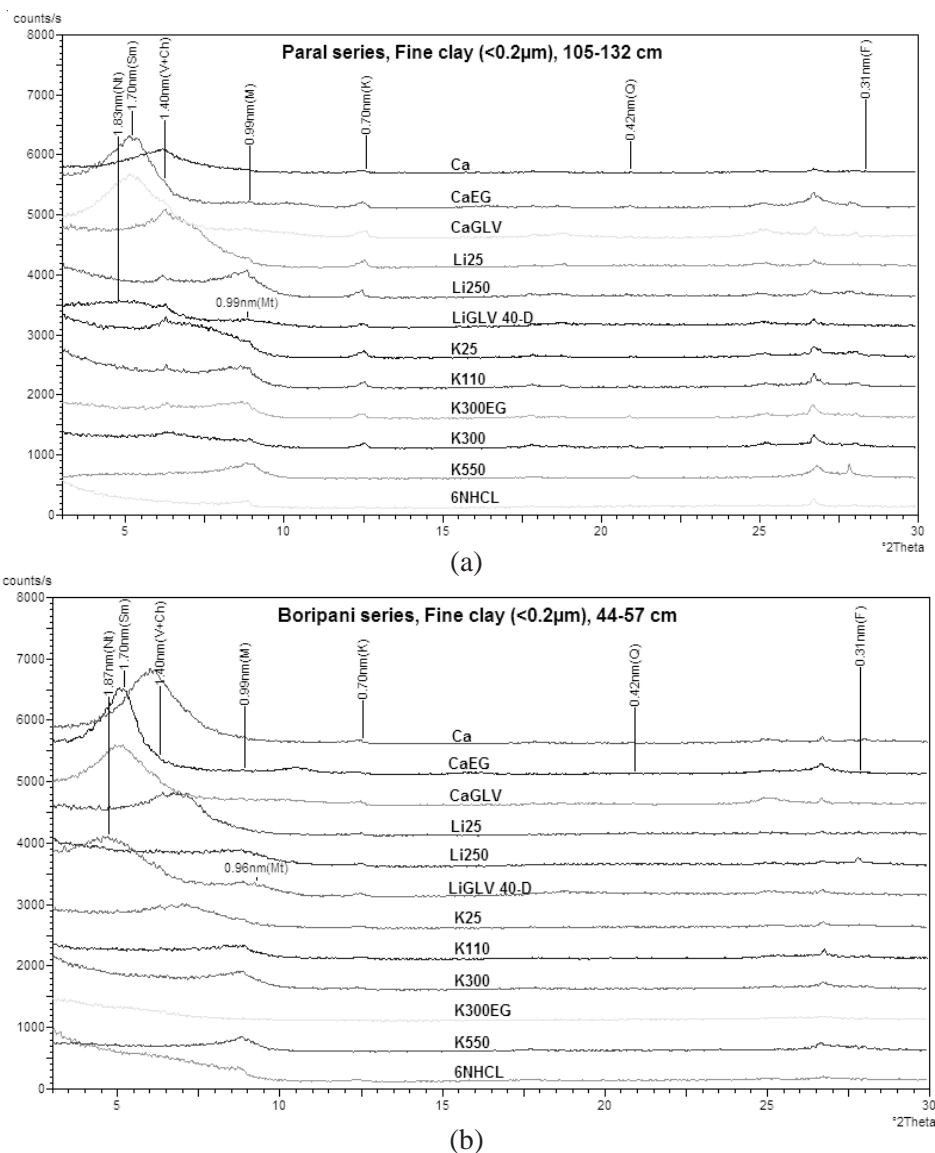*Interstratified smectite – Kaolinite mineral.

Fig. 1. *X-ray diffractograms of representative fine clay fractions (<0.2μm) for (a) Paral series and (b) Boripani series; Ca = Ca saturated; Ca-EG = Ca saturated plus ethylene glycol vapour treated; CaGLV = Ca-saturated plus glycerol vapour treated; Li = Li-saturated and heated to 25°C, 250°C (16h), LiGLV 40-D = Li-saturated and heated at 250°C plus glycerol vapour treated and scanned after 40 days; K-saturated and heated to 25, 110, 300, 550°C. K300EG = K-saturated and heated to 300°C plus ethylene glycol vapour treated; 6NHCl = 6N HCl treated fine clays; Sm = Smectite, B/N = beidellite/nontronite; V+Ch = vermiculite plus chlorite; M = mica; Mt = montmorillonite; K = Kaolinite; F = Feldspars*

sample on glycolation to 1.4 nm indicates its low charge density (Bhattacharyya *et al.,* 1993).

The presence of 0.70 and 0.35 nm peaks in Ca-saturated and glycolated sample and 0.72 nm peak in K-saturated and heated (300°C) sample and its disappearance at 550°C and reappearance of the peak at 0.70 nm after treating with HCl indicates the presence of kaolin. The smectite was little chloritzed as evidenced by the broadening towards the low angle side of 1.0 nm peak in K-saturated sample after subsequent heating to 550°C. Such chloritization is common in black soils (Pal and Deshpande, 1987a; Pal and Durge, 1989; Balpande, 1993; Kadu, 1997; Pal *et al.,* 2000). On K-saturation and subsequent heating at 110°C, the 1.0 nm peak of mica was reinforced which indicates the presence of vermiculite. A weak peak of 0.97 nm followed by 0.48 nm peaks indicates the presence of small amount of mica in these fine clay fractions of the soils.

Ca-treated and glycerol solvated samples gave distinct peak at around 1.8 nm showing the presence of montmorillonite (Borchardt, 1989). The Li-treated samples at 25°C showed a broad peak around 1.4 nm. However, the Li-treated clays on heating at 250°C for 16 h (Lim and Jackson, 1986) gave a broad peak around 1.0 nm and another at about 1.4 nm. The same sample when glycerol solvated, gave a strong peak around 1.4 nm and another at around 0.95-1.0 nm.

There is only a small hump at around 1.8 nm. This hump developed into a mature peak after about 40 days of glycerol solvation. This indicates that the fine clays consist of both montmorillonite and beidellite/nontronite. As these samples are unstable in 6NHCl, they are closer to nontronite. Thus, charge of smectites is distributed in both octahedral and tetrahedral layers (Bhattacharyya *et al.,* 1993; Kapse, 2007; Ray *et al.,* 2008; Kapse *et al.*, 2010; Bhople *et al.*, 2011; Deshmukh *et al.,* 2012).

Alkylammonium treatment of clays

The X-ray diffraction patterns of the representative fine clay samples of Paral and Boripani soils treated with alkylammonium hydrochlorides are presented in figure 2. The alkylamines treated with lower chain lengths (containing carbon atoms C6 to C8) generally gave peak at around 1.42 nm. A hump at around 1.34 nm was also observed. For the alkylamines with chain lengths of C9 to C11, sharp peaks were obtained at about 1.79 nm to 1.92 nm with the exception of C10 which sometimes gave abruptly higher values. With increase in chain length from dodecylamine to octadecylamine (C12 to C18), the d-values increased proportionately from around 2.0 nm to 3.2 nm. All these values primarily showed the presence of smectites (Ray *et al.,* 2003). The alkylamines occupy the interlayers of smectites and replace the cations therein in a fashion similar to a Lewis acid (Jaynes
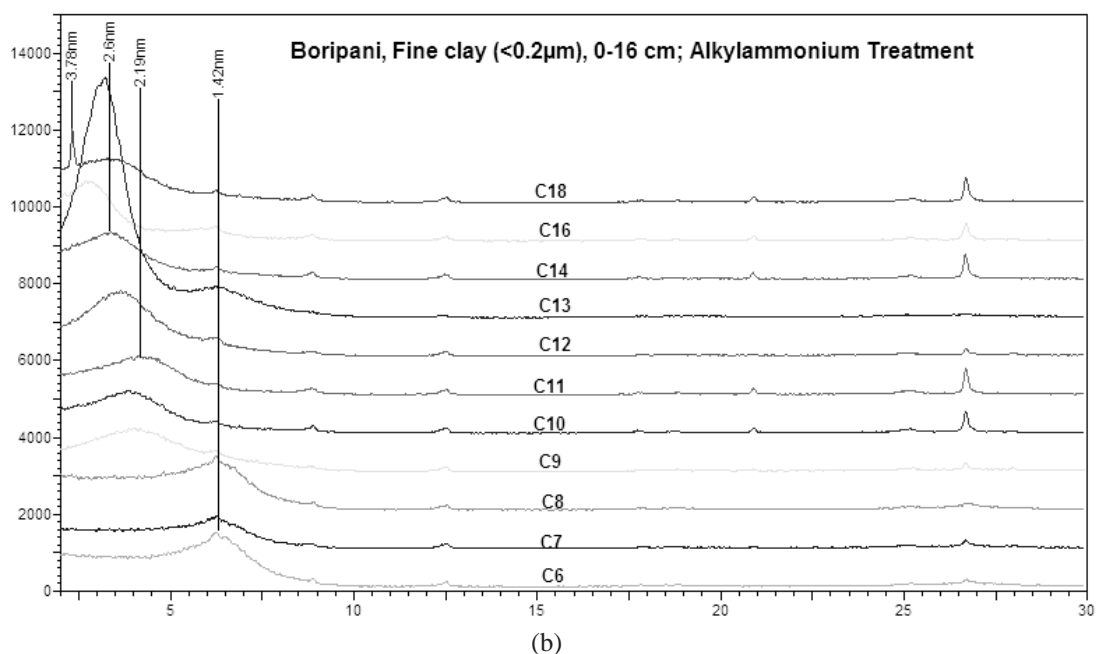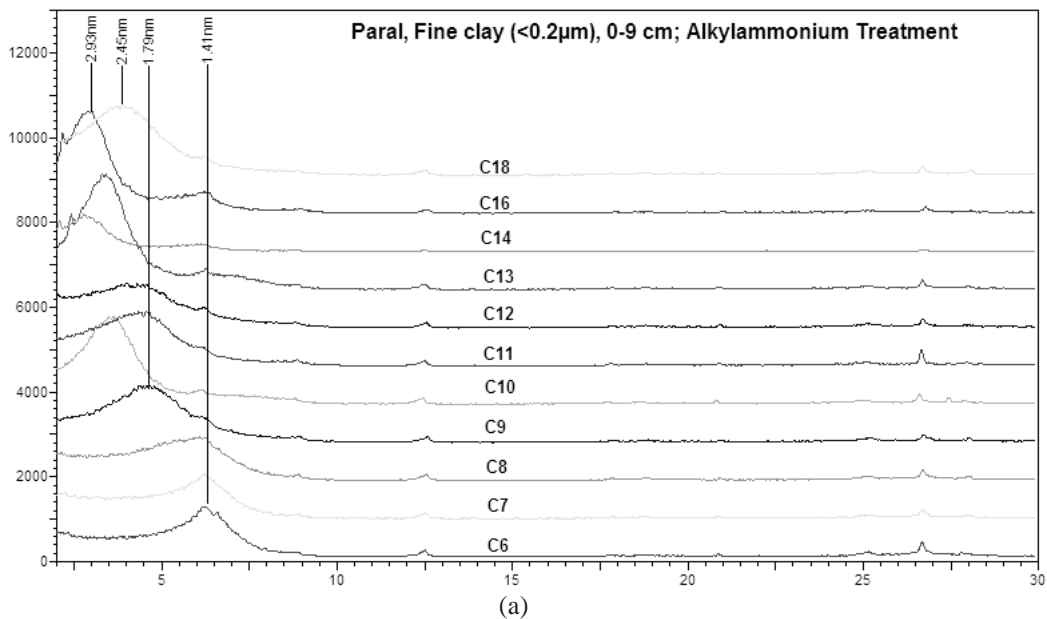
Fig. 2. *X-ray diffractograms of representative fine clay fractions treated with alkylammonium chlorides having number of carbon atoms C6, C7, C8, C9*, C10, C11, C12, C13*, C14, C16, C18 with respect to (a) Paralsoils and (b) Boripani soils*

and Bigham, 1987).

The lower chain alkylamines usually form a monolayer of alkylamines in the interlayer and the resultant d-values are in the order of 1.36 nm (Lagaly, 1994; Ray *et al.*, 2003). Further increase in chain length resulted in bilayers (above 1.76 nm), pseudotrilayer (2.2 nm) and paraffin type 22Å to ∞ (Lagaly and Weiss, 1969, 1976). The mainly monolayer to bilayer transition indicates that these fine clays are of low charge smectites (Lagaly and Weiss, 1969; Malla and Douglas 1987; Laird *et al.,* 1987; Jaynes and Bigham, 1987). For the fine clay smectites under the study the integral monolayer and bilayer spacings were actually not obtained, indicating that the smectites are not homogeneous but non-integral and heterogeneous in nature with respect to lower carbon chain lengths. However, non-integrality is more conspicuous in case of higher chain lengths of carbon atoms from C12 to C18 compared to that showed by alkylamines with lower carbon chain length. This also suggests that the monolayers and bilayers succeed each other in a random manner (Lagaly, 1969; Ray *et al.,* 2003). The point where non-integrality ends in bilayer is the lower limit of charge density (Fig. 3). The point h1 in the figure where non-integrality begins in a monolayer is the upper limit of charge density. This non-integrality disappears as the d-spacing approaches 1.76 nm. The graphs in figure 3 show S-type curves where they depict transition from one layer to other. It is more homogeneous and integral if the curves are sharper in nature
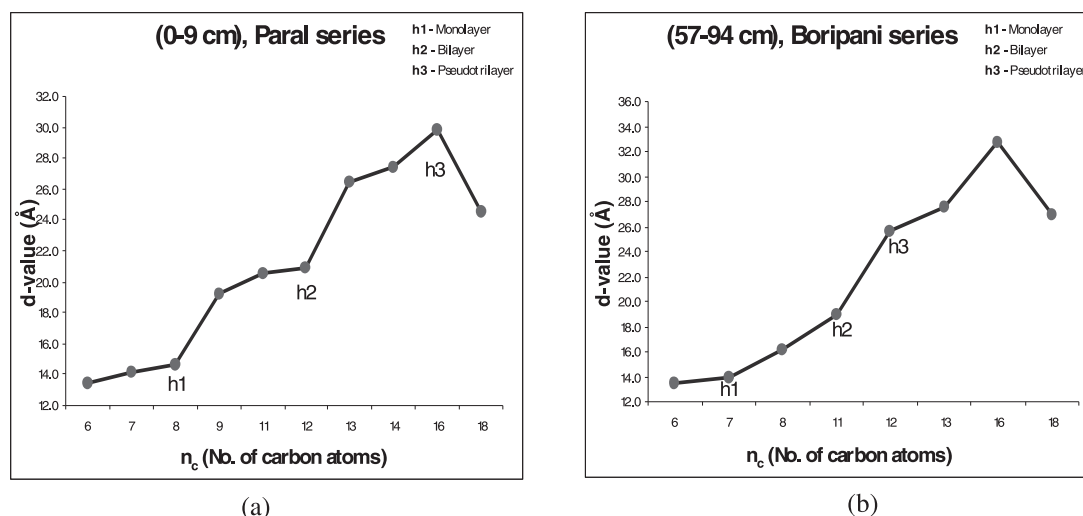
Fig. 3. *Relationship between d-spacings (001) of fine clays intercalated with alkylammonium chlorides and number of carbon atoms of representative soil fine clays with respect to (a) Paral series and (b) Boripani series*

and vice-versa. It is interesting to note in the figures that for Paral fine clays the transition from monolayers to bilayers is sharper compared to Boripani, where more gradual. This may indicate that the Boripani soils may be slightly hydroxy-interlayered as compared to Paral fine clays (Lagaly *et al.,* 1976; Ray *et al.,* 2006).

Determination of layer charge of soil clays

Charge densities were calculated according to the above equations. For both monolayer and bilayer transition the charges are shown in table 3. The fine clay fractions (<0.2 μm) were used for the study to correct the error due to particle-size fraction. This error in calculation may occur due to the displacement of alkylammonium ions out of the interlayer space (Lagaly, 1994; Ray *et al*., 2003). The calculation for frequency distribution (Stul and Mortier, 1974) includes the vital steps of particle-size and the maximum and minimum values of layer charge were calculated from monolayer to bilayer transition shown in figure 2 (Lagaly and Weiss, 1969, Lagaly*et al.,* 1976, Ray *et al*., 2003). The average values were also calculated as shown in table 3. In this study charge density classes were made from the average charges calculated from the equation shown above (Lagaly and Weiss 1969, 1976). These charge density classes provide simple and reliable method for characterizing smectites. The quantity or frequency of each charge class was calculated (Table 3) and charge distribution diagrams were constructed (Fig. 3) (Stul

and Mortier, 1974; Lagaly and Weiss, 1976, Ray *et al.,* 2003, 2008). For the sake of brevity, details of the method of calculation is provided only for two depths in table 3 (Ray *et al.,* 2003). Peak migration curve analysis deduced by McEwan *et al.* (1961) and Ruiz Amil *et al*. (1967) was utilized here to calculate the frequency distribution of charge.

The average layer charge density varies from 0.307 to 0.353 mol(-)/$\{Si,Al)_4O_{10}(OH)_2\}$ for Paral fine clays and 0.328 to 0.360 mol(-)/$\{Si,Al)_4O_{10}(OH)_2\}$ for Boripani fine clays. In both soils, the layer charge decreases down the depth which may be due to the increase in smectite content with concomitant decrease in vermiculite and chlorite content (Ray *et al.,* 2006). This decrease is relatively more in Paral than Boripani soils. Another reason may be that both the soils' fine clays have negligible hydroxy-interlayering (Fig.1). The presence of hydroxy-interlayering has been reported to increase layer charge in some Vertisol smectites of Amravati and Ahmednagar districts of Maharashtra and Bellary district of Karnataka (Ray *et al.,* 2003, 2008, Deshmukh, 2009). The layer charges determined for Paral and Boripani are the lowest values reported till date for soils of India (Ray *et al,* 2003, Thakre, 2008, Ray *et al.,* 2008, Deshmukh 2009, Bhople 2010, Bhople *et al.,* 2011). Thus, the soils of Paral and Boripani have fine clay smectites which are of low charge and nearer to the bentonite (Wyoming) layer

Table 3. *Frequency distribution of various charge densities in fine clays of the soils of Paral*

Depth cm	No. of C-atoms	Act. D-value (Å)	Rearr-anged no. of C-atoms	Modi. D-value (Å)	Charge density {mol(-)/ $(Si,Al)_4O_{10}$ $(OH)_2$}	Bilayers/ Trilayers (%)	Freq. (%)	Avg. charge {mol(-)/ $(Si,Al)_4$ $O_{10}(OH)_2$}
0-9	6	13.4	6	13.4	0.484	0	0	0.353
	7	14.2	7	14.2	0.433	19	19	
	8	14.6	8	14.6	0.392	29	10	
	9	19.2	10	14.8	0.329	33	5	
	10	24.5	18	14.8	0.200	33	0	
	11	20.5	13	16.8	0.265	81	48	
	12	20.9	14	17.7	0.249	100	19	
	13	26.5	9	19.2	0.715	36*	36	
	14	27.4	16	20.1	0.444	56	20	
	16	29.8	11	20.5	0.608	66	10	
	18	24.5	12	20.9	0.597	100	34	
9-35	6	14.9	18	14.2	0.200	19	10	0.342
	7	15.3	8	14.3	0.392	21	2	
	8	14.3	12	14.6	0.283	29	7	
	10	26.4	6	14.9	0.484	36	8	
	11	19.6	7	15.3	0.433	45	9	
	12	24.3	10	16.7	0.329	100	55	
	14	29.8	11	19.6	0.608	45	45	
	16	30.9	14	20.1	0.498	57	12	
	18	23.9	16	21.2	0.444	100	43	

charge of 0.26 mol(-)/{Si,Al}$_4$O$_{10}$(OH)$_2$} (Ray *et al.,* 2003). These values are corroborated well with higher values of COLE, available water capacity, and CEC (Table 1). The smectites of the study area are of highly crystalline nature and charge is distributed in both tetrahedral and octahedral layers (Pal and Deshpande, 1987, Bhattacharyya *et al.,* 1993, Ray *et al.,* 2008). These smectites have almost negligible HI as envisaged from Ca, CaEG and K treated XRD graphs shown in figure

1 (Ray *et al.,* 2008). Thus the sodic environment of Paral soils was not able to effect HI in smectites and cause increase in layer charge. The low and comparable range of layer charge values [0.307-0.360 mol(-)/{Si,Al}$_4$O$_{10}$(OH)$_2$}] in contrasting soil environments of high sodicity on one hand (Paral soil) and no imprints of sodicity on the other (Boripani soils), also suggest that layer charge is a permanent characteristic of layer silicate minerals which is unlikely to change even under

long-term sodic environment. The presence of HI which has been reported to increase the layer charge in some other soil clay minerals was not necessarily due to sodicity but acquired from sources primarily from high rainfall regions where acidic conditions prevailed (Pal *et al.,* 2012, Deshmukh *et al.,* 2012). On the other hand, alkaline conditions in soils are likely to remove the HI in smectites, especially the aluminium hydroxy-polymers (AHP) as Al is amphoteric in nature. The AHPs are usually in six fold co-ordination state, $[Al(OH)_x(H_2O)_y]^{(3-x)+}$ where $x+y = 6$. The process of removal of AHP with normal sodium citrate (pH 7.3) from acid soils has been described by Tamura (1958). For soils dominated with smectites, HI was effectively removed by sodium salt of ethylene diamine tetraacetic acid (Ray *et al.,* 2008; Deshmukh, 2009; Khuspure, 2012). However, in the context of smectite

dominated soils, the HI materials are dominated by hydroxy-polymers of Fe and Mg with moderate amounts of AHP (Ray *et al.,* 2008; Deshmukh, 2009). Therefore, it appears that sodic environment in smectitic soils are not likely to increase

Table 4. *Layer charge of Paral and Boripani soil fine clays.*

Depth (cm)	Avg. charge$\{mol(-) / \{(Si,Al)_4O_{10}(OH)_2\}\}$
Paral soil	
0-9	0.353
9-35	0.342
35-69	0.342
69-103	0.317
103-132	0.317
132-150	0.307
Boripani soil	
0-16	0.360
16-44	0.348
44-57	0.341
57-94	0.328

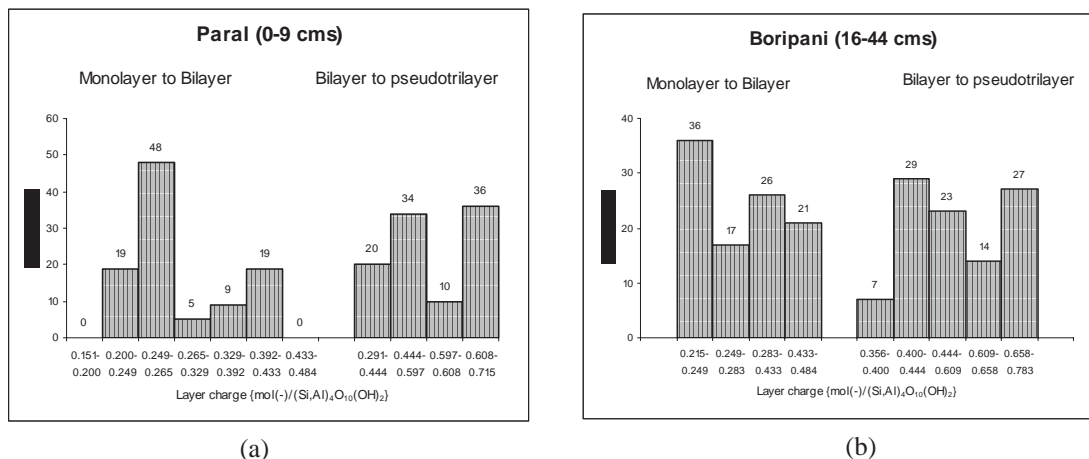(a)   (b)

Fig. 4. *Frequency distribution of charge density of representative soil fine clays for (a) Paral series and (b) Boripani series*

the layer charge, but on the other hand may partially remove the HI from smectite interlayers and decrease the layer charge.

Conclusions

The layer charge densities determined for Paral and Boripani soils are the lowest values reported till date for smectitic soils of India. Paral and Boripani soils have low charged fine clay smectites nearer to the layer charge of bentonite (Wyoming) having 0.26 mol(-)/$\{Si,Al\}_4O_{10}(OH)_2$. In spite of the fact that Paral soils are sodic in nature, it did not lead to hydroxy-interlayering in the smectite interlayers and thus did not result in an increase in layer charge.

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