The nature of clay-cation association dictates clay behaviour in aqueous suspensions

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Introduction

Dispersive behaviour of soil clays has been explained by soil scientists using hypotheses involving various electrical diffuse double layer forces generated between colloidal clay particles suspended in water (e.g. Quirk, 2001). In natural soils, however, clay particles in soil aggregates exist as complex heterogeneous intergrowths of different clay structures intimately associated with silt, sand and biopolymers, and are confined, without being in colloidal suspension in water. Stability of these aggregates when in contact with water depends on the nature and persistence of linkages between the particles which, in turn, are functions of the type of bonding such as covalent and ionic (Rengasamy and Sumner, 1998). In contrast to covalent bonds, ionic bonds are readily broken by water solvation as evidenced by the high solubility of ionic compounds. It has been documented that any given heteronuclear bond found in natural systems has a mixture of covalent and ionic character (Huheey *et al.*, 1993). The degree of ionicity (or covalency) of these bonds depends on the nature of cations (inorganic or organic) found on clay surfaces. The interactions between polar water molecules and the charged clay particles are functions of the ionicity of bonding involved (Rengasamy and Sumner, 1998). Several studies have attempted to describe the partial ionic character of covalent bonds on the basis of relative electronegativity of atoms (Pauling, 1967) or the molecular orbital electronegativity, particularly in diatomic molecules (e.g. Baird and Whitehead, 1964). However, no quantitative index for the ionic character of clay-cation bonds has been developed. Measurement of the electrophoretic mobility (velocity per unit electric field) of clays gives a measure of the net charge on the clay particle. The analysis of the forces on the solid can be carried out in terms of either charge or the electrostatic potential known as zeta potential. The stability of clay suspensions containing electrolytes, in terms of dispersion and flocculation, is a function of the distribution of charges and dipoles in the interfacial region (Hunter, 1981). In clay-cation systems, the potential-determining ions generate the surface charge. We derived the ionicity indices of the cations Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}, used in this study for the preparation of homo-ionic clays given in Table 1.

Results and discussions

Two soil clays (Urrbrae and Claremont) and Illite and Wyoming bentonite were saturated with cationic chlorides to prepare homo-ionic clays. The soils selection was based on their texture, clay mineralogy, electrical conductivity, pH and zeta potential measured on clay <2 μm clay fractions obtained from the soils without preliminary chemical treatment by the method described in

Churchman (2002). Turbidity, Zeta potential, and transmission electron microscopy were done on homo-ionic clays using standard procedures (Marchuk and Rengasamy, 2011).

With the decreasing ionicity index of cations clay dispersion (turbidity) and Zeta potential decreased while the mean particle size increased (Table1). When the results of all types of clays were combined, the relative zeta potential and relative turbidity were highly correlated with ionicity indices (Fig. 1). Strong relationships between ionicity indices of cations in clay-cation bonds and the clay behaviour such as dispersibility (measured as turbidity of suspensions), zeta potential and mean particle size confirm the hypothesis that the degree of ionicity in these bonds dictates the interaction with water molecules leading to separation of clay particles from aggregated clay domains and exposure of the surface charge.

Table 1. Ionicity indices , Zeta potential, Turbidity and the mean particle size of selected clays treated with cations.

Type of clay	**Li**	**Na**	**K**	**Mg**	**Ca**	**Sr**	**Ba**
				Ionicity index			
	0.93	**0.89**	**0.86**	**0.73**	**0.67**	**0.64**	**0.6**
				Zeta potential (ζ) mV			
Illite	-58.6	-57.9	-56	-36.8	-32.2	-30.8	-29.0
Urrbrae	-59.4	-57.8	-54.6	-34.9	-30.9	-27.3	-26.2
Claremont	-54.8	-50.1	-44.8	-26.2	-22	20.5	-19.6
Bentonite	-51	-50.1	-42.8	-37	-26.1	-24.4	-19.5
				Turbidity (NTU)			
Illite	867	755	743	553	303	106	96
Urrbrae	1769	1650	1410	420	180	109	90
Claremont	1869	1686	1577	1022	964	634	330
Bentonite	653	630	521	286	153	132	112
				Mean Particle size (µm)			
Illite	0.42	0.46	0.93	1.21	1.43	1.82	1.87
Urrbrae	0.38	0.39	0.66	0.81	0.93	1.33	1.41
Claremont	0.26	0.37	0.55	1.22	1.67	1.9	2.77
Bentonite	1.57	1.77	1.9	2.15	1.22	2.23	2.84

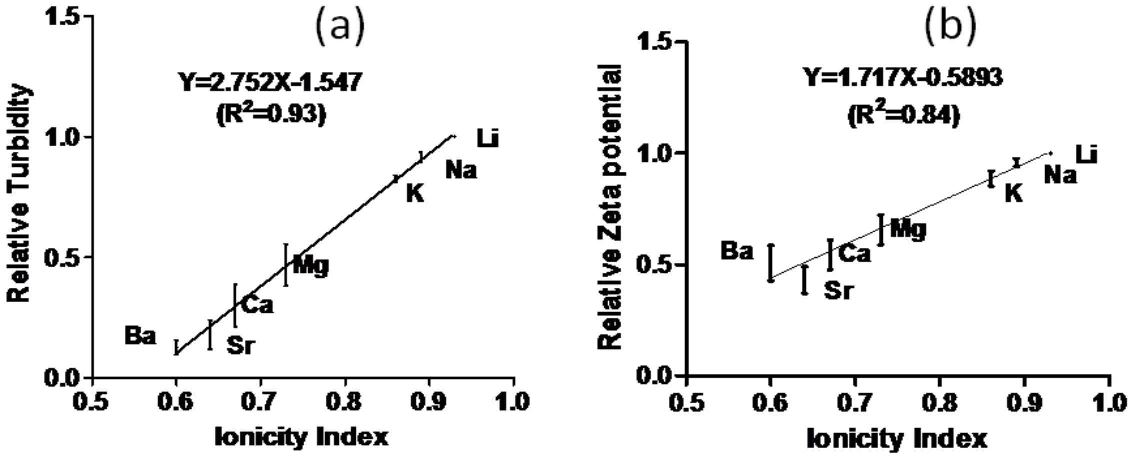

Fig. 1. Relationships between ionicity index of cations and a) relative turbidity and b) relative zeta potential.

As the ionicity index decreases in the following order $Li^+ > Na^+ > K^+ > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$, the tendency to covalency increases and hence, the proclivity to break the clay-cation bonds in water decreases. Thus the dispersion and zeta potential of homoionic clays increase in the same order while the mean particle size follows the reverse order.

Our results reveal the importance of both ionisation potentials and the charge of the cations in affecting the nature of clay-cation bonds. In this study, we considered the clay particle as an anion of large size and high charge and, therefore, decided that the polarizability of the cation dominates the nature of bonds. However, the results of correlations among the four types of clays studied show variations due to clay type. The strong relationship between relative zeta potential and relative turbidity of homoionic clays of all types suggest that the surface charge of clays can influence the ionicity index of clay-cation bonds. Future studies on clay behaviour should focus on relating ionicity index of cations to the surface charge on clays.

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