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The Isoelectric Point and the Points of Zero Charge of Fe-Al-Mg Hydrotalcite-like Compounds

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Abstract: The relation of the isoelectric point (IEP) and the point of zero net charge (PZNC) of the hydrotalcite-like compounds was discussed. It was found that the IEP does not equal to the PZNC and the IEP is higher than the PZNC. The structural positive charges existing in the HTlc, which cause the difference between the IEP and the PZNC. The effects of the structural positive charges of the HTlc on its IEP and PZNC are the same as the specific adsorption of metal cations.

Keywords: Isoelectric point, points of zero charge, potentiometric titration, hydrotalcite-like compounds.

In colloid and interface chemistry, the isoelectric point (IEP) is defined as the pH value at which the electrokinetic potential equals to zero; the points of zero charge (PZCs) are defined as the pH values, at which one of the categories of surface charge equals to zero[1]. Three operational categories may be defined [1]: (1) structural, denoted by σ_{st}; (2)adsorbed proton, denoted by σ_H; and (3)adsorbed ion, denoted by Δq. So, the PZCs have two standard definitions: (1) point of zero net proton charge(PZNPC, σ_H=0); and (2)point of zero net charge (PZNC, $\sigma_{st}+\sigma_H$=0). Extensive studies on the relationship between the IEP and PZCs have been reported[1-8], however, these work mainly emphasized the relationship between the IEP and PZNPC for some metal oxides and hydroxides with no structural charge, and it was found that the IEP and the PZNPC are equal in the absence of specific adsorption, and will move in different directions in the presence of specific adsorption[2, 5-8].

Hydrotalcite-like compounds (HTlc) have the general formula: $[M(II)_{1-x} M(III)_x(OH)_2]^{x+}A^{n-}_{x/n} \cdot mH_2O$, where M(II) is divalent metal ion, M(III) is trivalent metal ion, A is the charge compensating anions, x is the number of moles of M(III) per formula weight of compounds, m is the number of moles of co-intercalated water per formula weight of compounds[9,10]. HTlc simultaneously bear structural positive charges originated from isomorphic substitution and the proton charges resulting from the adsorption process, the effects of the structural positive charges on the IEP and the PZCs

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are questions of interest[11,12]. As far as the authors know similar research works have not been reported .

IEP was determined by the classical method of electrophoresis. Two series of HTlc suspensions containing different concentrations of background electrolyte NaCl, c=0.001, 0.010 mol/L, respectively, were prepared. The concentration of HTlc solid in all suspensions is 1 g/L and the pH of each suspension was adjusted to 8-12 with NaOH and HCl solutions. *Prior to* determining, the suspensions were stirred and kept at 25± 0.5°C for 24 h. The zeta potential (ζ) measurements of the Fe-Al-Mg-HTlc samples were carried out with DXD-II model Television Microelectrophoretic Instrument (made in Jiangsu Optical Instrument). Plotting ζ *vs* pH to obtain two ζ～pH curves for two concentrations, the crossover point of the two ζ～pH curves is IEP. PZCs were determined by potentiometric titration described in Ref.13, and the crossover point of $\Gamma_{OH-}-\Gamma_{H+}$～pH curves is PZNC.

Figure 1 Variation of Γ_{OH}-Γ_{H}^{+} of the sample 2 with pH

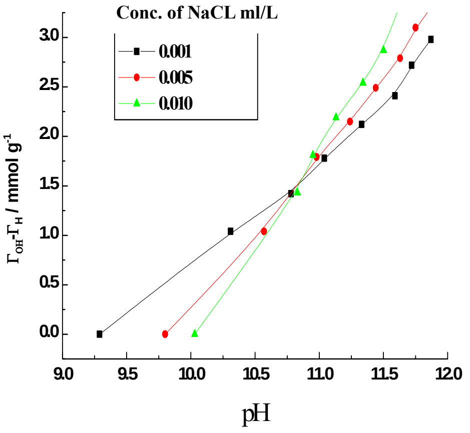
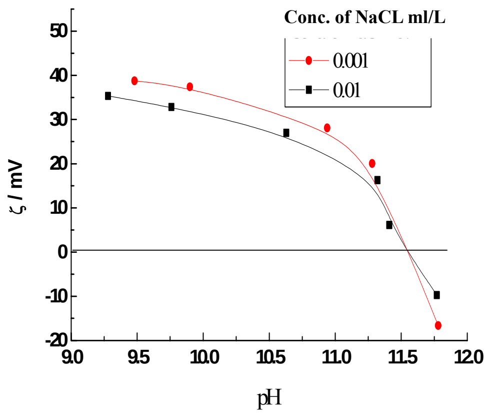


Figure 2 The ξ-pH relationships for sample 2



Typical ζ～pH curves and PT curves are shown in **Figure 1** and **2**, respectively, for Fe-Al-Mg-HTlc sample 2. Similar results were obtained for the other HTlc samples.

According to the crossover point in each figure, the IEP and the PZNC can be obtained. The chemical composition, structural charge density (x in mol electron charges/mol HTlc), IEP and PZNC results of Fe-Al-Mg-HTlc samples are listed in **Table 1**. It can be seen that the IEP does not equal to the PZNC and it is higher than the PZNC. In general, the IEP and the PZNC should be equal in the absence of specific adsorption, and will be different only in the presence of specific adsorption[2,5-8]. NaCl is usually considered as an inert electrolyte, so the specific adsorption does not occur in our investigated system, hence it can be concluded that the structural positive charges existed in the HTlc cause the difference between the IEP and the PZNC. As a general rule[2,5-8], the strong metal cation adsorption on an amphoteric colloid suspended in an electrolyte solution will lower its PZNC , but will raise its IEP, *i.e.*, IEP will be higher than PZNC; and the strong anion adsorption, on the contrary, will raise its PZNC but will lower its IEP, *i.e.*, IEP will be lower than PZNC. So, the effects of the structural positive charges of the HTlc on its IEP and PZNC are the same as the specific adsorption of metal cations.

Some interesting observations can be obtained in the plots of IEP and PZNC *vs* (x) (see **Figure 3**). Both the IEP and the PZNC of the HTlc are linearly related to its structural positive charge density (x), and the difference between the IEP and the PZNC increases with the increase of the x. If the curves of IEP～x and PZNC～x are extrapolated to x=0, a common intersection point between the two curves can be obtained . x=0 corresponds to pure brucite $Mg(OH)_2$, the equality of the IEP and the PZNC means that the structural charge is zero. Above results appropriately support our conclusion that the difference between the IEP and the PZNC is caused by the structural charges of the HTlc. The IEP or the PZNC value of brucite obtained at x=0 is about 11.75, which is in good agreement with the result of about 12 reported by Yoon *et al.*[14].

Figure 3 Variation of IEP and PZNC with structural charge density of Fe-Al-Mg-HTlc

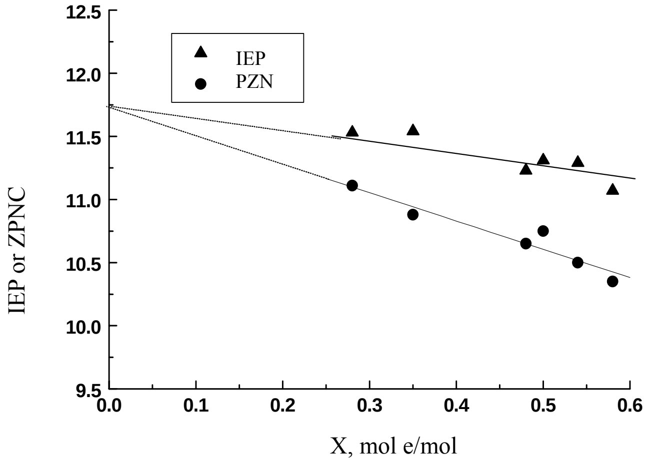


Table 1 The chemical composition, structural positive charge density, IEP and PZNC of Fe-Al-Mg-HTlc

Sample	Chemical Composition	X(mol e/mol)	IEP	PZNC
1	$[Fe_{0.13}Mg_{0.72}Al_{0.15}(OH)_2]Cl_{0.2}1(OH)_{0.07}$	0.28	11.53	11.11
2	$[Fe_{0.03}Mg_{0.65}Al_{0.32}(OH)_2]Cl_{0.14}(OH)_{0.21}$	0.35	11.54	10.88
3	$[Fe_{0.24}Mg_{0.52}A_{l0.24}(OH)_2]Cl_{0.12(}OH_{)0.36}$	0.48	11.23	10.65
4	$[Fe_{0.16}Mg_{0.50}Al_{0.34}(OH)_2]Cl_{0.12}(OH)_{0.38}$	0.50	11.31	10.75
5	$[Fe_{0.21}Mg_{0.46}Al_{0.33(}OH)_{2]}Cl_{0.11}(OH)_{0.43}$	0.54	11.29	10.50
6	$[Fe_{0.29}Mg_{0.42}Al_{0.29}(OH)_{2]}Cl_{0.10}(OH)_{0.48}$	0.58	11.07	10.35

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