

Two Crystal Structures of Dehydrated Sr^{2+} and Tl^+ Exchanged Zeolite A, $\text{Sr}_x\text{Tl}_{12-2x}\text{-A}$ ($x = 1.6$ and 5.45)

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Two crystal structures of dehydrated Sr^{2+} and Tl^+ exchanged zeolite A, $\text{Sr}_x\text{Tl}_{12-2x}\text{-A}$ ($x = 1.6$ and 5.45), have been determined by single-crystal X-ray diffraction techniques. Their structures were solved and refined in the cubic space group $Pm\bar{3}m$ at $21(1)^\circ\text{C}$. Both crystals were ion exchanged in flowing streams of mixed $\text{Sr}(\text{NO}_3)_2$ and TlNO_3 aqueous solution, followed by dehydration at 360°C and 2×10^{-6} Torr for 2 days. Full-matrix least-squares refinements of the dehydrated $\text{Sr}_{1.6}\text{Tl}_{8.8}\text{-A}$ ($a = 12.214(2)\text{\AA}$) and $\text{Sr}_{5.45}\text{Tl}_{1.1}\text{-A}$ ($a = 12.291(2)\text{\AA}$) have converged to final error indices, $R_1 = 0.055$ and $R_2 = 0.061$ with 286 reflections, and $R_1 = 0.072$ and $R_2 = 0.090$ with 217 reflections, respectively, for which $I > 3\sigma(I)$. In both structures, all Sr(II) ions are coordinated by three framework oxygens; Sr(II) to O(3) distances are $2.21(2)\text{\AA}$ for $\text{Sr}_{1.6}\text{Tl}_{8.8}\text{-A}$, and $2.31(1)\text{\AA}$ for $\text{Sr}_{5.45}\text{Tl}_{1.1}\text{-A}$, and Tl(I) to O(3) distances are $2.657(6)\text{\AA}$ for $\text{Sr}_{1.6}\text{Tl}_{8.8}\text{-A}$ and $2.845(8)\text{\AA}$ for $\text{Sr}_{5.45}\text{Tl}_{1.1}\text{-A}$, respectively. In each structure, the angle subtended at Sr(II), O(3)-Sr(II)-O(3) is $118.7(4)^\circ$ for $\text{Sr}_{1.6}\text{Tl}_{8.8}\text{-A}$ and $120.0(4)^\circ$ for $\text{Sr}_{5.45}\text{Tl}_{1.1}\text{-A}$. Sr^{2+} ions prefer to 6-ring sites and Tl^+ ions to 8-ring sites when total number of ions per unit cell is more than 8.

Introduction

The open frameworks of crystalline molecular sieve zeolites allow ready exchange of numerous cations and the sorption of a variety of small molecules. The physicochemical properties of zeolite A are influenced by the locations of the exchangeable cations. Because zeolite A crystallize in cubic system, the exchangeable cations usually occupy sites of high symmetry close to the oxygen atoms of the framework.^{1,2}

The unit cell of molecular sieve zeolite A has three eight-membered oxygen rings, eight six-membered rings, and twelve four-membered rings. The exchangeable cations in zeolite A can occupy a site near the center of the 6-ring (called β site), 8-ring (α site), or a site of the opposite of 4-ring (γ site). For example, in the dehydrated form of $\text{Na}_{12}\text{-A}$,³ eight sodium ions occupy the β sites, three sodium ions occupy the α sites and the twelfth sodium ion occupies a γ site. A knowledge of siting of these exchangeable cations within zeolite framework can provide a structural basis for understanding their physicochemical properties.^{1,2}

Up to this time, no structural studies of mixed cation system of Sr^{2+} and Tl^+ ion exchanged zeolite A have been reported. The present study has been initiated to investigate the site selectivity of cations in the crystal structure of Sr^{2+} and Tl^+ exchanged zeolite A. It would also be interesting to compare the structure of Sr^{2+} and Tl^+ exchanged zeolite A with those of zeolite A of different Sr^{2+} contents per unit cell. Furthermore, because of the high scattering powers of Sr^{2+} and Tl^+ , precise and reliable crystallographic determination should be easy to achieve.

Experimental Section

Crystals of zeolite 4A were prepared by Charnell's method.⁴ A single cubic crystal about 0.08 mm on an edge was lodged in finely drawn Pyrex capillary.

Crystals of $\text{Sr}_{1.6}\text{Tl}_{8.8}\text{-A}$ and $\text{Sr}_{5.45}\text{Tl}_{1.1}\text{-A}$ were prepared using exchange solutions in which mole ratios of $\text{Sr}(\text{NO}_3)_2$ and

TlNO_3 were 1:1 and 100:1, respectively, with a total concentration of 0.05 M.

Ion exchange was accomplished by allowing the solution to flow past each crystal at a velocity of approximately 1.0 cm/sec for 5 days at $21(1)^\circ\text{C}$.

Crystals were dehydrated at 360°C and 2×10^{-6} Torr for 2 days. Microscopic examination indicated no crystal damage resulted from dehydrated procedures and both crystals remained colorless.

The space group $Pm\bar{3}m$ (no systematic absences) was used throughout this work for reasons discussed previously.^{2,5} Preliminary crystallographic experiments and subsequent data collection were performed with an automated, four-circle Enraf Nonius CAD4 single crystal X-ray diffractometer.

Molybdenum radiation was used for all experiments (K_{α_1} , $\lambda = 0.70930\text{\AA}$; K_{α_2} , $\lambda = 0.71359\text{\AA}$). The unit cell constants, as determined by a least-squares refinement of 25 intense reflections for which $10^\circ < \theta < 15^\circ$, are $12.214(2)\text{\AA}$ for $\text{Sr}_{1.6}\text{Tl}_{8.8}\text{-A}$, and $12.291(2)\text{\AA}$ for $\text{Sr}_{5.45}\text{Tl}_{1.1}\text{-A}$, respectively.

For each crystal, reflections from intensity-equivalent regions of reciprocal space (hkl , $h \leq k \leq l$ and $h\bar{l}k$, $h \leq l \leq k$) were examined using the ω - 2θ scan techniques. The data were collected using variable scan speed. The most reflections were observed at slow scan speeds, ranging from 0.13 to $0.17^\circ\text{min}^{-1}$ in ω .

The intensities of three reflections in diverse regions of reciprocal space were recorded after every 3 hours to monitor crystal and instrument stability. Only small, random fluctuations of these check reflections were noted during the course of data collection.

The raw data for each crystal were corrected for Lorentz and Polarization effects; the reduced intensities were merged and the resultant estimated standard deviation were assigned to each average reflection by the computer programs, PAINT and WEIGHT.⁶

An absorption correction was judged to be unimportant, and was not applied because the crystals used were very small cubes (μ_{MoR} for $\text{Sr}_{1.6}\text{Tl}_{8.8}\text{-A} \approx 0.7$ and μ_{MoR} for $\text{Sr}_{5.45}\text{Tl}_{1.1}\text{-A} \approx 0.3$). Of the 904 pairs of reflections for the de-

Table 1. Positional, Thermal^a and Occupancy Parameters for Dehydrated $Sr_xTi_{12-2x}-A$ ($x = 1.6$ and 5.45)Crystal 1. Dehydrated $Sr_{1.6}Ti_{8.8}-A$

Atom	Wyc. pos.	x	y	z	$^b\beta_{11}$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Occupancy
(Si,Al)	24(h)	0	1830(3)	3691(3)	19(2)	14(2)	18(2)	0	0	-0(4)	1 ^c
O(1)	12(h)	0	2180(10)	5000	40(10)	70(10)	16(9)	0	0	0	1
O(2)	12(i)	0	2990(10)	2990(10)	60(10)	39(7)	39(7)	0	0	30(20)	1
O(3)	24(m)	1143(6)	1143(6)	3340(9)	37(4)	37(4)	60(8)	30(10)	10(10)	10(10)	1
Ti(1)	8(g)	2586(1)	2586(1)	2586(1)	43(1)	43(1)	43(1)	-2(1)	-2(1)	-2(1)	0.625
Ti(2)	8(g)	1065(3)	1065(3)	1065(3)	45(2)	45(2)	45(2)	-3(5)	-3(5)	-3(5)	0.175
Sr(1)	8(g)	2000(20)	2000(20)	2000(20)	213(7)	213(7)	213(7)	360(20)	360(20)	360(20)	0.200
Ti(3)	12(i)	0	4569(3)	4569(3)	173(9)	140(4)	140(4)	0	0	-247(7)	0.200

Crystal 2. Dehydrated $Sr_{5.45}Ti_{1.1}-A$

Atom	Wyc. pos.	x	y	z	$^b\beta_{11}$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Occupancy
(Si,Al)	24(h)	0	1848(5)	3736(4)	23(6)	16(3)	20(3)	0	0	5(7)	1 ^c
O(1)	12(h)	0	2260(10)	5000	40(20)	20(10)	40(20)	0	0	0	1
O(2)	12(i)	0	2820(10)	2820(10)	60(20)	21(8)	21(8)	0	0	40(20)	1
O(3)	24(m)	1119(8)	1119(8)	3420(10)	61(8)	61(8)	30(10)	20(20)	0(1)	0(1)	1
Ti(1)	8(g)	2666(5)	2666(5)	2666(5)	26(3)	26(3)	26(3)	-11(7)	-11(7)	-11(7)	0.1375
Sr(1)	8(g)	1890(8)	1890(8)	1890(8)	250(3)	250(3)	250(3)	472(5)	472(5)	472(5)	0.6813

^aPositional and anisotropic thermal parameters are given $\times 10^4$. Numbers in parentheses are the esd's in units of least significant digit given for the corresponding parameter. ^bThe anisotropic temperature factor = $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. Rms displacements can be calculated from β_{ii} values by using the formula $\mu_{ii} = 0.225 a (\beta_{ii})$, where $a = 12.214(2)\text{\AA}$ for $Sr_{1.6}Ti_{8.8}-A$ and $a = 12.291(2)\text{\AA}$ for $Sr_{5.45}Ti_{1.1}-A$. ^cOccupancy for (Si) = 0.5; occupancy for (Al) = 0.5.

hydrated $Sr_{1.6}Ti_{8.8}-A$ and 917 for the dehydrated $Sr_{5.45}Ti_{1.1}-A$, only 286 and 217 pairs, for which $I > 3\sigma(I)$, respectively, were used in subsequent structure determinations.

Structure Determination

All structure calculations were done using the Structure Determination Package (SDP) programs supplied by Enraf-Nonius.⁶

Crystal 1. Dehydrated $Sr_{1.6}Ti_{8.8}-A$. Full-matrix least-squares refinement was initiated using the atomic parameters of the framework atoms [(Si,Al), O(1), O(2), and O(3)], obtained from the fully dehydrated Sr_6-A .^{7,8} Refinement with anisotropic thermal parameters converged to R_1 , $(\sum w(F_o - |F_c|) / \sum F_o) = 0.545$ and R_2 , $(\sum w(F_o - |F_c|)^2 / \sum wF_o^2)^{1/2} = 0.600$. A difference Fourier synthesis revealed a large and distinct peak at (0.25, 0.25, 0.25) with a height of 23.4(44) $e\text{\AA}^{-3}$ and (0.10, 0.10, 0.10) with a height of 9.4(44) $e\text{\AA}^{-3}$. Anisotropic refinement including these positions, Ti(1) and Ti(2), converged to $R_1 = 0.232$ and $R_2 = 0.295$. A subsequent difference Fourier synthesis revealed one peak at (0.0, 0.46, 0.46) with a height of 12.9(28) $e\text{\AA}^{-3}$, and at (0.20, 0.20, 0.20) with a height of 8.46(5) $e\text{\AA}^{-3}$. These were stable in least-squares refinement and anisotropic refinement including these positions, as Ti(3) and Sr(1), converged to $R_1 = 0.055$ and $R_2 = 0.061$.

It is easy to distinguish Ti^{4+} from Sr^{2+} ions because their ionic radii are quite different, 1.47 \AA and 1.12 \AA , respectively. Therefore their approach distances to zeolite oxygens are indicative, as have observed in Sr_6-A ,^{7,8} $Ti_{12}-A$,⁹ and $Ag_xTi_{12-x}A$ ($x = 2, 3, 4$, and 5).¹⁰

A final difference Fourier map showed no significant

Table 2. Selected Interatomic Distances(\AA) and Angles(deg)

	$Sr_{1.6}Ti_{8.8}-A$	$Sr_{5.45}Ti_{1.1}-A$
(Si,Al)-O(1)	1.654(5)	1.636(7)
(Si,Al)-O(2)	1.66(1)	1.64(2)
(Si,Al)-O(3)	1.685(7)	1.686(9)
Sr(1)-O(3)	2.21(2)	2.31(1)
Ti(1)-O(3)	2.657(6)	2.845(8)
Ti(2)-O(3)	2.78(2)	
Ti(3)-O(1)	2.96(1)	
Ti(3)-O(2)	2.724(9)	
O(1)-(Si,Al)-O(2)	106.1(6)	106.1(6)
O(1)-(Si,Al)-O(3)	112.0(4)	112.5(6)
O(2)-(Si,Al)-O(3)	107.2(3)	103.3(5)
O(3)-(Si,Al)-O(3)	112.1(4)	109.4(5)
(Si,Al)-O(1)-(Si,Al)	151.1(2)	144(1)
(Si,Al)-O(2)-(Si,Al)	152.1(7)	176.8(7)
(Si,Al)-O(3)-(Si,Al)	139.5(6)	144.6(8)
O(3)-Sr(1)-O(3)	118.7(4)	120.0(4)
O(3)-Ti(1)-O(3)	91.1(2)	89.6(3)
O(3)-Ti(2)-O(3)	86.0(2)	
O(1)-Ti(3)-O(1)	110.5(1)	
O(1)-Ti(3)-O(2)	55.2(3)	

Numbers in parentheses are the estimated standard deviations in the units of the least significant digit given for the corresponding value.

peaks; one at (0.0, 0.5, 0.5) had peak height of 3.7(15) $e\text{\AA}^{-3}$ which was unstable at least-squares refinement.

Crystal 2. Dehydrated $Sr_{5.45}Ti_{1.1}-A$. Using the atomic

Table 3. Deviation of Atom(Å) from the (111) Plane at O(3)

Atom	Sr _{1.6} Tl _{8.8} -A	Sr _{5.45} Tl _{1.1} -A
O(2)	0.251(7)	-0.018(7)
Sr(1)	0.257(17)	0.008(6)
Tl(1)	1.505(1)	1.659(3)
Tl(2)	-1.715(2)	

A negative deviation indicates that the atom lies on the same side of the plane as the origin.

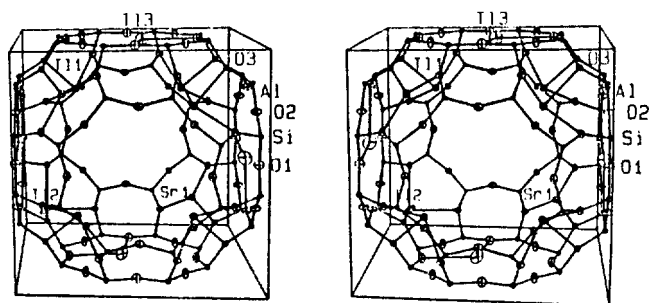


Figure 1. A stereoview of a large cavity of dehydrated Sr_{1.6}Tl_{8.8}-A. Five Tl⁺ ions at Tl(1), one Tl⁺ ion at Tl(2), two Tl⁺ ions at Tl(3), and two Sr²⁺ ions at Sr(1) are shown. About 60% of unit cells may have this stoichiometry. The remaining 40% of unit cells may have five Tl⁺ ions at Tl(1), two Tl⁺ ions at Tl(2), three Tl⁺ ions at Tl(3), and one Sr²⁺ ion at Sr(1). Ellipsoids of 20% probability are shown.

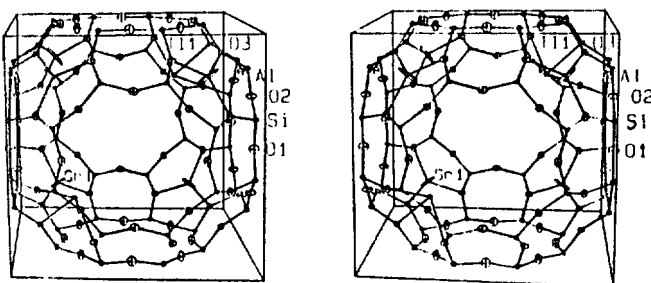


Figure 2. A stereoview of a large cavity of the dehydrated Sr_{5.45}Tl_{1.1}-A. Five Sr²⁺ ions at Sr(1) and two Tl⁺ ions at Tl(1) are shown. About 55% of unit cells may have this stoichiometry. The remaining 45% of unit cells may contain six Sr²⁺ ions at Sr(1). Ellipsoids of 20% probability are shown.

parameters of the framework atoms, Sr(1) and Tl(1) in the structure of Crystal 1, least-squares refinement was initiated. Anisotropic refinement of the framework atoms, Sr(1) and Tl(1) converged to $R_1 = 0.072$ and $R_2 = 0.090$.

A subsequent difference Fourier map was almost flat and revealed no significant peak. The final structural parameters are represented Table 1. Interatomic distances and angles are given in Table 2.

The full-matrix least squares program used in all structure determination minimized $\sum w|\Delta F|^2$. The weight (w) of an observation was the reciprocal squares of $\sigma(F)$, its standard deviation. Atomic scattering factors¹¹ for O⁻, (Si, Al)^{1.75+} (the average of Si⁰, Si⁴⁺, Al⁰, and Al³⁺), Sr²⁺, and Tl⁺, all properly modified to include the real compounds(f') of anomalous dispersion corrections, were used.¹²

Discussion

In the dehydrated Sr_{1.6}Tl_{8.8}-A structure, Tl⁺ ions occupy three different crystallographic sites. 5.0 Tl(1) and 1.4 Tl(2) ions per unit cell are distributed over two nonequivalent threefold axes positions (Figure 1). 2.4 Tl⁺ ions at Tl(3) are associated with 8-ring oxygens. 1.6 Sr²⁺ ions at Sr(1) occupy a 3-fold-axis site near 6-rings (Figure 2).

In the dehydrated Sr_{5.45}Tl_{1.1}-A, both 1.1 Tl⁺ ions at Tl(1) and 5.45 Sr²⁺ ions at Sr(1) are associated with 6-ring oxygens. There are no 8-ring cations. The positions of Sr(1) and Tl(1) are similar to those of Sr(1) and Tl(1) in the structure of dehydrated Sr_{1.6}Tl_{8.8}-A (see Table 1 and 2).

The Tl⁺ ions at Tl(1) occupy similar positions as found in dehydrated Tl₁₂-A⁹ and Ag_{12-x}Tl_x-A ($x = 5$ and 5.5).^{10,13} These Tl⁺ ions at Tl(1) occupy threefold-axis positions near 6-ring, recessed *ca* 1.505(1)Å for Sr_{1.6}Tl_{8.8}-A and 1.659(3)Å for Sr_{5.45}Tl_{1.1}-A into the large cavity from the (111) plane at O(3). The Tl(1)-O(3) distance is 2.656(6)Å for Sr_{1.6}Tl_{8.8}-A and 2.845(8)Å for Sr_{5.45}Tl_{1.1}-A, respectively. The distance may be, in part, virtual because only a single average O(3) position is determined for each structure.

1.1 Tl⁺ ions at Tl(2) in the structure of dehydrated Sr_{1.6}Tl_{8.8}-A lie relatively far inside the sodalite cavity. These Tl⁺ ions extend 1.715 Å into the sodalite cavity. These cations are trigonally coordinated to their respective set of three O(3) framework oxide ions at 2.78 Å.

2.5 Tl⁺ ions at Tl(3) are associated with 8-ring oxide ions and located in the plane of the 8-oxygen ring, but not at their centers in order to make favorable approach to the framework oxide ions; Tl(3)-O(2) = 2.724(9) Å and Tl(3)-O(1) = 2.96(1) Å.

The lack of agreement between the sum of the ionic radii of Tl⁺ and O²⁻, 2.79 Å and those observed 2.66, 2.78, 2.845 and 2.724 Å, involving Tl(1), Tl(2) and Tl(3), respectively, is primarily due to a result of the unusually low liganacy of these cations in dehydrated structures. Similar situations have been observed in the other zeolite structures.⁹

In both structures, Sr²⁺ ions at Sr(1) lie on threefold axes of the unit cell. The Sr²⁺ ions of Sr_{1.6}Tl_{8.8}-A extend 0.257 Å into the large cavity from the (111) plane at O(3). The Sr²⁺ ions of Sr_{5.45}Tl_{1.1}-A lie almost at the centers of 6-ring planes. These cations approach three zeolite framework oxygens at O(3) at a distance of 2.21(2) Å for Sr_{1.6}Tl_{8.8}-A and 2.31(1) Å for Sr_{5.45}Tl_{1.1}-A, respectively. The corresponding Sr-O distance for dehydrated Sr₆-A is 2.34(1) Å.⁷ For comparison, the sum of the Sr²⁺ and O⁻ radii is 2.44 Å.¹⁴ The O(3)-Sr(1)-O(3) angle is 118.7(4)° for Sr_{1.6}Tl_{8.8}-A and 120.0(4)° for Sr_{5.45}Tl_{1.1}-A, the idealized trigonal planar angles.

The fractional occupancy observed at Sr²⁺ ions at Sr(1) of Sr_{5.45}Tl_{1.1}-A indicates that about 55% of unit cells may have five Sr²⁺ ions at Sr(1) and two Tl⁺ at Tl(1) and the remaining 45% of unit cells may have six Sr²⁺ ions at Sr(1). Similarly, in the structures of Sr_{1.6}Tl_{8.8}-A, about 60% of unit cell may have five Tl⁺ ions at Tl(1), one Tl⁺ ion at Tl(2), two Tl⁺ ions at Tl(3) and two Sr²⁺ ions at Sr(1), and the remaining 40% of unit cell may consist of five Tl⁺ ions at Tl(1), two Tl⁺ ions at Tl(2), three Tl⁺ ions at Tl(3) and one Sr²⁺ ion at Sr(1).

The electrical neutrality of zeolite A crystal is achieved by the inclusion of cations (Na⁺ ions in Na₁₂(AlO₂SiO₂)₁₂·27H₂O). Twelve Na⁺ ions are exchangeable. When the ca-

tions are fully exchanged with bivalent cations such as alkaline earth metal ions, six cations per unit cell are introduced.² When the cations are monovalent, twelve cations per unit cell are introduced.

The present crystal structures of dehydrated $\text{Sr}_{1.6}\text{Ti}_{8.8}\text{-A}$ and $\text{Sr}_{5.45}\text{Ti}_{11.1}\text{-A}$ indicate that Sr^{2+} ions preferentially occupy 6-ring sites and Ti^+ ions occupy 8-ring sites when the total number of ions per unit cell is more than 8. This result is reasonable considering ionic radii of $\text{Ti}^+(1.47 \text{ \AA})$ and that of Sr^{2+} ion (1.12 \AA).¹⁴ Larger Ti^+ ion will better fit to larger 8-ring site over 6-ring. These result are also consistent with those from the structures of $\text{Ag}_9\text{Cs}_3\text{-A}$,¹⁵ $\text{Ag}_9\text{Rb}_3\text{-A}$,¹⁶ $\text{Ag}_{6.5}\text{Ti}_{5.5}\text{-A}$,¹³ and $\text{Ag}_{9.3}\text{K}_{2.7}\text{-A}$.¹⁷ In those structures, larger Cs^+ , Rb^+ , Ti^+ , and K^+ ions are also associated with the 8-ring oxygens.

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Potential Profiles and Capacitances of an Ideally Polarizable Electrode in a point Charged Electrolyte

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The effects of the charged metal on the overall electrostatic potential profiles and the capacitances of the electrical double layer are brought out. A model with a simplified jellium and a point-charged electrolyte is utilized in the present calculations. Electrons are assumed not to penetrate electrode surface due to a strong screening of electrolyte at the interface. Electron density functions and ion density functions are obtained, which are also based upon the Poisson equation and Boltzmann equation on either side of the interface. A complete potential profile starting from bulk electrode and ending at bulk electrolyte is obtained by connecting the two potential profiles (one inside the metal electrode, the other inside the electrolyte) with proper boundary conditions. In spite of the simplicity of the model, the present model reveals the importance of the effect of the charged metal on the electrostatic potential profile and the electrical double layer capacitances. The results are discussed and compared with the predictions by Gouy Chapman theory.

Introduction

Since the early works of Gouy, Chapman and Stern (GCS),¹ considerable attention has been paid to the study of the electrical double layer by a number of researchers. Models for the study of one sided electrode interface mostly consist of an ideally polarizable electrode (IPE) which is perfectly flat and smooth, and an electrolyte. The electrolyte is treated as charged hard spheres immersed in a dielectric

continuum. Most of the studies have been devoted to improve the GCS theory of the electrical double layer, that is, on the electrolyte side by mean spherical approximation and its generalization,² the hypernetted chain approximation and its derivatives,³ the modified Poisson-Boltzmann and the Born-Green-Yvon type theories.⁴ On the other side of the electrical double layer, the effect of the charged electrode has been relatively neglected for the following suggested reasons. i) when a potential is applied to the electrode, the