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Studies on the adsorption of arsenic on calix[6]arene

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***p-tert*-butyl calix[6]arene (PTC6) was synthesized and characterized by solid- and liquid-state NMR and LC-MS techniques. The adsorption of arsenite and arsenate on calix[6]arene under different pH conditions and adsorbate doses was studied. The maximum adsorption of arsenic species on calix[6]arene was observed around neutral pH and the adsorption density of As (III) was higher than that of As (V). The adsorption of neutral H_3AsO_3 and negatively charged $H_2AsO_4^-$ molecules on calix[6]arene was attributed to the condensation reaction between hydroxyl groups of PTC6 and arsenic species. The complexation of arsenite with phenolic oxygen was confirmed by solid-state ^{13}C NMR CP-MAS. *Exo* attack mechanism was proposed to describe the interaction of arsenous and arsenic acid molecules with PTC6. The specific interaction between calix[6]arene and arsenic species was further substantiated by zeta-potential (ζ-potential) measurements and free energy of adsorption. The free energy of adsorption (ΔG^{o}_{ads}) estimated from Stern–Grahame equation was found to be 25 kJ/mole for As (III) and 19 kJ/mole for As (V). Copyright © 2010 John Wiley & Sons, Ltd.**

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Keywords: adsorption; arsenate; arsenite; ^{13}C NMR CP-MAS; *p-tert*-butyl calix[6]arene

INTRODUCTION

Calix[n]arenes are a class of phenol-formaldehyde macrocyclic oligomers that are available in variety of sizes and shapes depending on the number of phenolic units in the cyclic array and also on the nature of substituent attached to the aromatic nucleus. The size of the calixarene cavity can be modified by varying the reaction conditions. These molecules are particularly attractive in host–guest complex chemistry because of their ability to form inclusion complexes with metal ions and neutral molecules. Though calix[n]arenes were initially reported[1] in 1940, these molecules came to light after the base-induced one step synthesis of calixarenes was reported.[2] The calixarenes serve as vehicles of transport for metal ions, anions, and neutral molecules. Calixarenes were tried as electro-chemical and optical sensors, chiral recognition devices, modifiers, ion scavengers, phase transfer agents, and catalysts.[3] It has been established that the calixarenes can form coordinate complexes with alkali and alkaline earth metals, early transition metals like titanium, zirconium, vanadium, niobium, molybdenum, tungsten, and rhenium, late transition metals like iron, ruthenium, cobalt, nickel, iridium, palladium, platinum, copper, zinc, mercury, lanthanides, and actinides.[4,5] The intra-molecular hydrogen bonding plays a crucial role in the cavity-forming process and chemical reactivity of the host.[6] The insertion of phosphorous and arsenic atoms in the narrow rim of *p-tert*-butyl calix[4]arene was reported.[7] The mono arsenic derivatives with arsenic bonded to three of the four phenolic units of calix [4]arene and diarsenic derivatives with each arsenic bonded to two adjacent phenolic units with As—O—As bridges were proposed. Recently, the formation of stable five coordinate silicon and phosphorus derivatives with *p-tert*-butyl calix[4]arene was reported.[8] In the present study, the adsorption of arsenic on calix[6]arene was attempted. The calix[6]arene was preferred over calix[4]arene due to better selectivity and conformational flexibility. Above all, the ability of calix[6]arene to form inclusion complexes is better.[9] The solid-state ^{13}C NMR and zeta-potential (ζ-potential) measurements have been carried out to understand the interactions between arsenic and *p-tert*-butyl calix[6]arene (PTC6).

EXPERIMENTAL

Materials

p-tert-butyl phenol, formaldehyde, sodium hydroxide, petroleum ether, dichloromethane, potassium iodide, and sodium borohydride used for the synthesis of calix[6]arene were analytical grade chemicals procured from Merck whereas As_2O_3 and As_2O_5 were obtained from Acros organics, USA. The PTC6 was synthesized in the laboratory. The characteristics of the final product were found to match with the reported data.[10,11]

Density

AccuPyc 1340 Pycnometer was used for density measurements. It is highly accurate and works on the gas displacement technique. The pressure measured upon filling the sample chamber and then discharging it into a second empty chamber allows the

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computation of the sample solid phase volume.[12] The density of air dried PTC6 was estimated to be 1.44 gm/cm^3.

Surface area

Specific surface area of PTC6 was determined by using the sorption technique with Micromeritics ASAP (Model 2020) Surface area analyzer. Nitrogen and helium gases with a purity of 99.999% were used for the measurements. A known weight of PTC6 was taken in a standard sample tube with a filler rod, which is closed with seal frit and covered with an isothermal jacket to maintain the constant temperature during analysis. The analyzer is equipped with two independent vacuum systems: one for sample preparation and the other for sample analysis. In the first step, the sample tube containing PTC6 was evacuated to 50 μmHg for 2 h at 150 °C. In the second step, the sample tube was cooled with liquid nitrogen temperature, and is then exposed to nitrogen gas at a series of precisely controlled pressures. With each incremental pressure increase, the number of nitrogen gas molecules adsorbed on the PTC6 surface increases. The pressure at which adsorption equilibrium occurs is measured and the universal gas law is applied to determine the quantity of nitrogen gas adsorbed.[13] The isotherm was obtained by plotting a graph between the quantity of nitrogen gas adsorbed *versus* P/P_o values. Analysis of the isotherm yields the surface area of the material. The specific surface area of the PTC6 was found to be 46 m^2/gm.

NMR spectroscopy

Liquid state proton NMR, DEPT-NMR spectra were measured with a Bruker Avance 500 MHz set. TMS was used as an internal standard. 1H NMR spectra of PTC6 in $CDCl_3$ were recorded at various temperatures with an accuracy of ±1 °C. Solid-state ^{13}C NMR spectra were recorded by cross-polarization magic angle spinning technique[14] temperature operating at 7.04 T magnetic field (^{13}C 75.4 MHz) and room temperature. Samples were packed in 2.5 mm diameter ZrO_2 rotors and were spun with a frequency of 7 kHz at the magic angle spinning.

Zeta-potential measurements

The ζ-potential measurements were conducted using zeta acoustic sizer (DT 1200) equipped with a video system and auto titration unit supplied by Dispersion Technology, USA. The sample container is equipped with a pH probe, a stirrer, and a Colloid Vibration Current probe. The CVI Probe consists of two parts: a transmitting and a receiving transducer. The transmitting transducer consists of a piezoelectric transducer that converts a radio frequency (RF) pulse into acoustic energy. This acoustic energy induces dipole moments in the solid/liquid interface. The dipole moments from the particles add up to create an electric field, which can be sensed by a receiver as a ζ-potential.[15] The instrument was calibrated with the standard silica particles prior to the experiment.

Adsorption measurements

The standard solutions of As (III) and As (V) were prepared by dissolving a known quantity of As_2O_3 and As_2O_5 in 0.1 N NaOH. One hundred milliliters of arsenic solution at required pH was taken in a polyethylene bottle and a known quantity of PTC6 was added to the arsenic solution. The contents in the bottles were agitated in a laboratory shaker for 1 h at a constant temperature of 27 °C. During the equilibration, samples were collected with the help of micropipette at different time intervals, i.e., 10, 20, 30, 60 min and at 24 h. After equilibration, the solutions were filtered through a 0.2 μm membrane filter and filtrates were analyzed for arsenic. Hydride generator (HG-2000) coupled with an atomic absorption spectrophotometer (GBC Avanta) was used for arsenic analysis. Three replicate measurements with a relative standard deviation of 1% were taken and an average value was considered. The arsenic detection limit was 0.02 mg/L.

RESULTS AND DISCUSSION

Effect of pH

Separate solutions of As (III) and As (V) with an initial concentration of 30 mg/L were taken and equilibrated with PTC6 at a desired pH for 1 h. For each experiment, 100 ml of arsenic solution was taken and equilibrated with 0.2 g of PTC6. The adsorbed arsenic at various pH values was estimated and the results are shown in Fig. 1. The maximum adsorption of arsenic species on PTC6 was observed around neutral pH. Calixarenes are unique molecules having super-acidic proton as well as super basic oxy-anion within the molecule. The dissociation of the first phenolic proton was reported to be below pH 1.0 while the last proton above pH 11.0.[16] Similarly, pKa values of arsenate[17] (2.20, 6.97, 11.5) and arsenite[18] (9.23, 12.13, 13.40) clearly suggest that arsenite exists as a neutral molecule and arsenate ($H_2AsO_4^-$) as an anion under the experimental pH of 6.00–7.00. The adsorption of neutral H_3AsO_3 and negatively charged $H_2AsO_4^-$ on PTC6 may be explained due to hydrogen bonding besides condensation reaction between hydroxyl groups of PTC6 and arsenite. The As $(OH)_3$ groups may polarize protons of PTC6 hydroxyl groups and facilitate attack at electrophilic sites[19] similar to that of condensation reaction proposed between arsenous acid and dithioerythritol.[20] Thus, the simultaneous ionization of hydroxyls of PTC6 and reaction with metal hydroxides via condensation mechanism can be suggested. In basic pH, the anions of arsenite and arsenate are expected to interact with polar —OH via hydrogen bonding mechanism. In

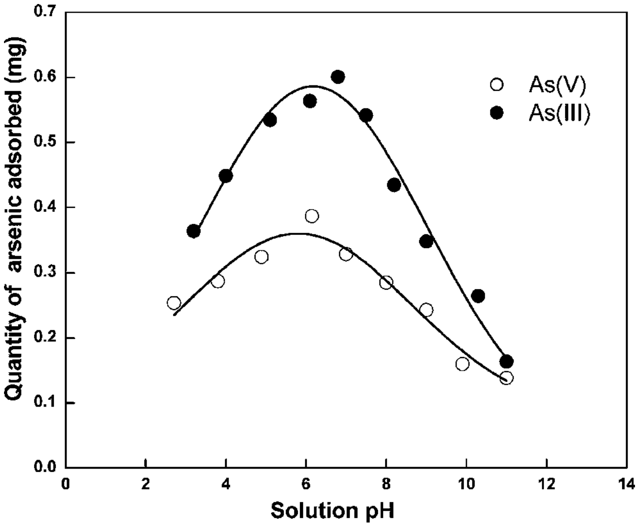

Figure 1. Effect of pH on the adsorption of arsenic

addition to the above mechanisms, π-metallated derivatives of calixarenes with the metals actually coordinated to the faces of the calixarene bowl could also be suggested.

Effect of arsenic concentration

The effect of arsenic concentration and equilibration time on adsorption density was studied. PTC6 (1.0 g) was taken and equilibrated with known volume and concentration of arsenic solution. The un-adsorbed arsenic content in the filtrate was estimated. The arsenic concentration was varied from 1.0 to 40.0 mg/L and the results are compiled in Fig. 2. By increasing the concentration of arsenic, the adsorption density increases and attains plateau beyond certain concentration. The adsorption density of arsenite remained same beyond 0.035 mg/m^2. In the case of arsenate, the plateau was observed at the adsorption density of 0.02 mg/m^2. It is evident that the effect of equilibration time on adsorption density is very marginal. The better adsorption of arsenite compared to arsenate may be explained due to favorable pyramidal symmetry and availability of phenolic —OH groups that facilitate condensation reaction. At saturation point, the number of PTC6 molecules and the adsorbed arsenite molecules were estimated to be 6.183×10^{20} and 6.31×10^{18}, respectively. The number of PTC6 molecules is roughly two orders more than the adsorbed arsenite molecules. The possibility of insertion of arsenite and arsenate molecules into the PTC6 bowl is remote as the diameter of the arsenite molecule[21] is higher (4.1 Å) compared to the annuli of the cyclic hexamer of PTC6 (2.4 Å). Thus the interaction of arsenic species is restricted to the —OH groups of PTC6. In aqueous medium, the adsorption density of arsenic can be improved by introducing hydrophilic groups at the wide rim of PTC6. The mono arsenic and diarsenic complexes can be expected between PTC6 and arsenic species similar to that of calix[4]arene.[8]

NMR Measurements

The solid-state ^{13}C NMR of PTC6 in the presence and absence of arsenic is shown in Fig. 3. It is apparent that in the absence of arsenic, signals related to aromatic carbons were observed at 147 and 125.5 ppm whereas signals corresponding to bridged methylene carbons and *tert*-butyl carbons were observed at

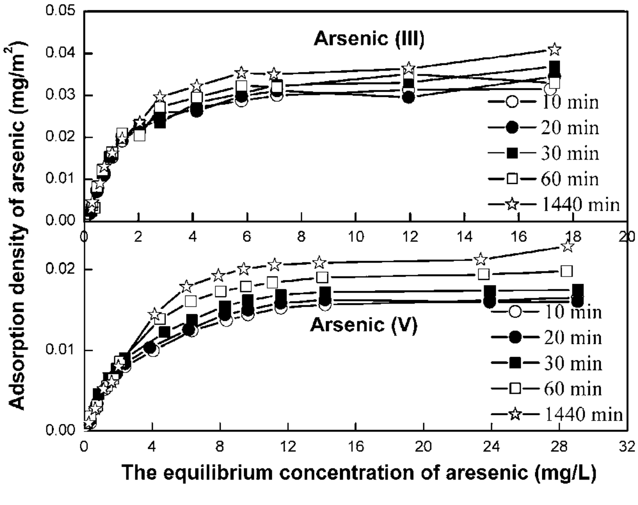

Figure 2. Effect of arsenic concentration on adsorption density

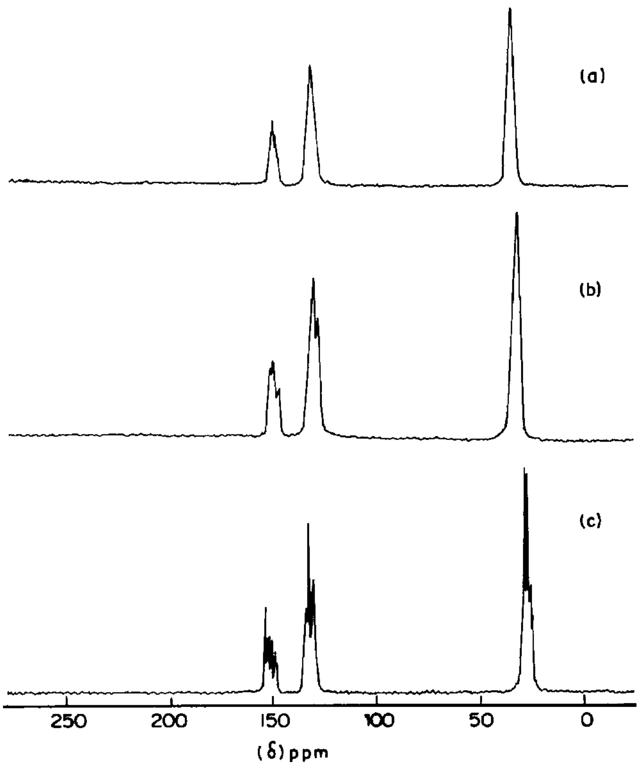

Figure 3. Solid-state ^{13}C NMR CP-MAS spectrum of PTC6. (a) In the presence of H_3AsO_4, (b) in the presence of H_3AsO_3, and (c) in the absence of arsenic

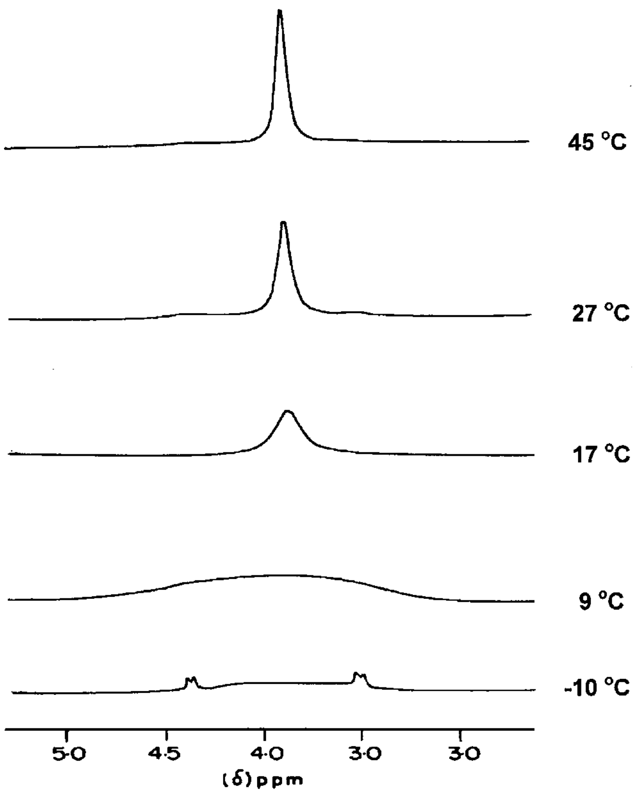

Figure 4. The temperature-dependent ^1H NMR spectrum for bridged methylene protons of PTC6

31 and 34 ppm, respectively. However, in the presence of arsenite, all these signals were broadened and shifted towards higher ppm. It was observed that the signals related to aromatic carbons were shifted from 147 to 151 ppm and 125 to 130 ppm. The signals corresponding to bridged methylene carbons and *tert*-butyl carbon were shifted to 37 ppm. Thus the solid-state NMR data confirm the complexation of As (III) with phenolic oxygen. Many researchers[22–27] have adopted the ^{13}C NMR CP-MAS technique to study the complexation and orientation of organic molecules such as chloroform, acetone, toluene, and carbon disulphide with calixarenes. Similarly, the same down field chemical shift observed in the case of As (V) indicates that the phenolic oxygen were either mono coordinated or dicoordinated with As (V). Thus, the NMR data clearly indicate that the PTC6 molecule has become rigid after the adsorption of arsenic species. The flexibility of the PTC6 molecule was studied by recording the variable temperature ^{1}H NMR spectrum shown in Fig. 4. It is apparent that the signal ascribed to bridged methylene was split into a pair of doublet at low temperatures. One doublet corresponds to four exo hydrogens and another doublet corresponds to four endo hydrogen. At higher temperatures, all the eight hydrogens will give one broad singlet (Fig. 4) indicating that the PTC6 molecule can rotate freely through σ-bonds of Ar-CH$_2$-Ar. Due to this, PTC6 can generate variety of conformations and coordination interactions, with guest molecules. The coalescence temperature of the PTC6 molecule was observed around 9 °C. This is in agreement with the data reported[28] for PTC6 in CDCl$_3$. The flexible nature of PTC6 at the coalescence temperature was affected after the co-ordination of arsenic molecules with PTC6. The uptake mechanism of arsenous and arsenic acid molecules is shown in Fig. 5. The arsenous acid and arsenic acid molecules can interact with PTC6 in two ways: the first one is *endo* attack (i.e., through arene cavity) and the second one is *exo* attack (i.e., through phenolic groups). The *p-tert*-butyl groups sterically hinder the endo attack of arsenite or arsenate molecules. Thus, the favorable *exo* interaction of arsenous or arsenic acid molecule was suggested in the proposed uptake mechanism.

Zeta-potential measurements

The adsorption of arsenic on PTC6 was examined by ζ-potential measurements and the results are shown in Fig. 6. It is apparent that the PTC6 is negatively charged below pH of 5.4. In the presence of electrolytes such as NaCl and NaNO$_3$, the magnitude of the ζ-potential increases, while the iso-electric point of PTC6 remains constant. It was also observed that the ζ-potential of PTC6 is increased considerably above pH 11.6. Sodium hydroxide was added to change the pH to alkaline during ζ-potential measurements. At pH $\geq$ 11, the sodium cation may form dimeric and polymeric units with PTC6. Hanna *et al.*[29] have reported the selective formation of calyx dianions (PTC6-2Na) with the alkali metal carbonates. Since the de-protonation of PTC6 is expected from pH 1.0, the molecule should exhibit negative charge.

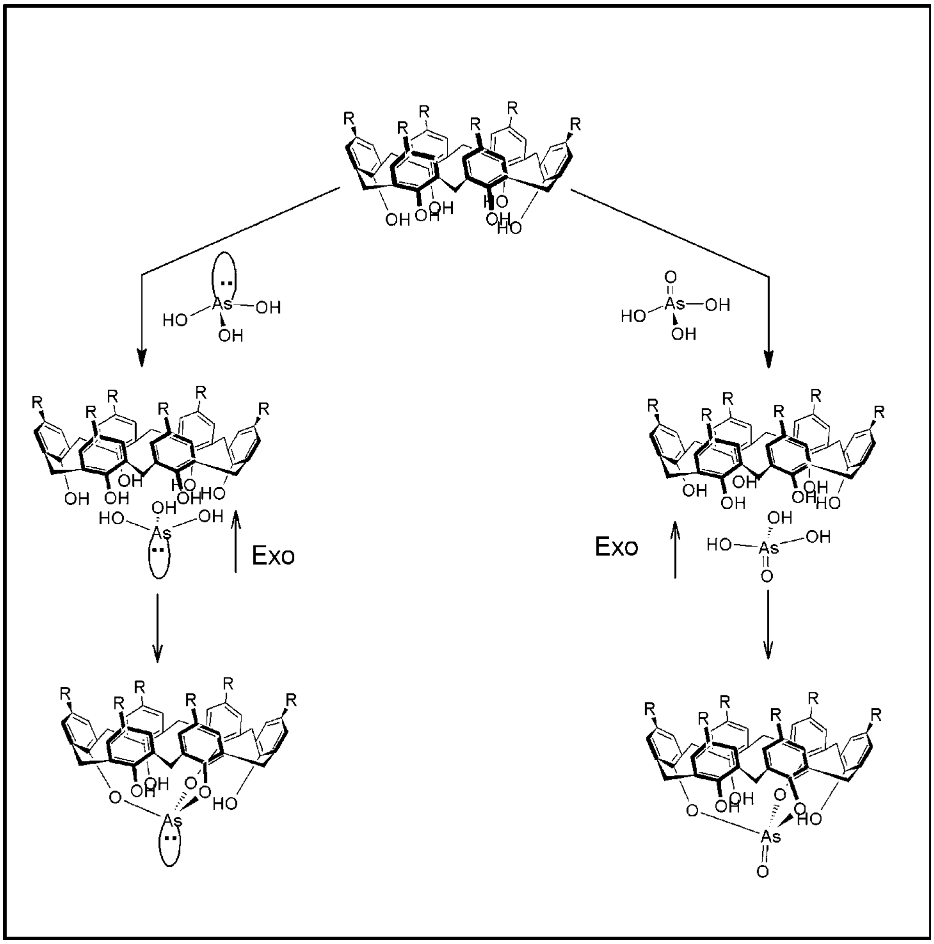

Figure 5. The interaction of arsenous and arsenic acid molecules with *p-tert*-butyl calix[6]arene (In reaction mechanism R = *tert*-butyl group)

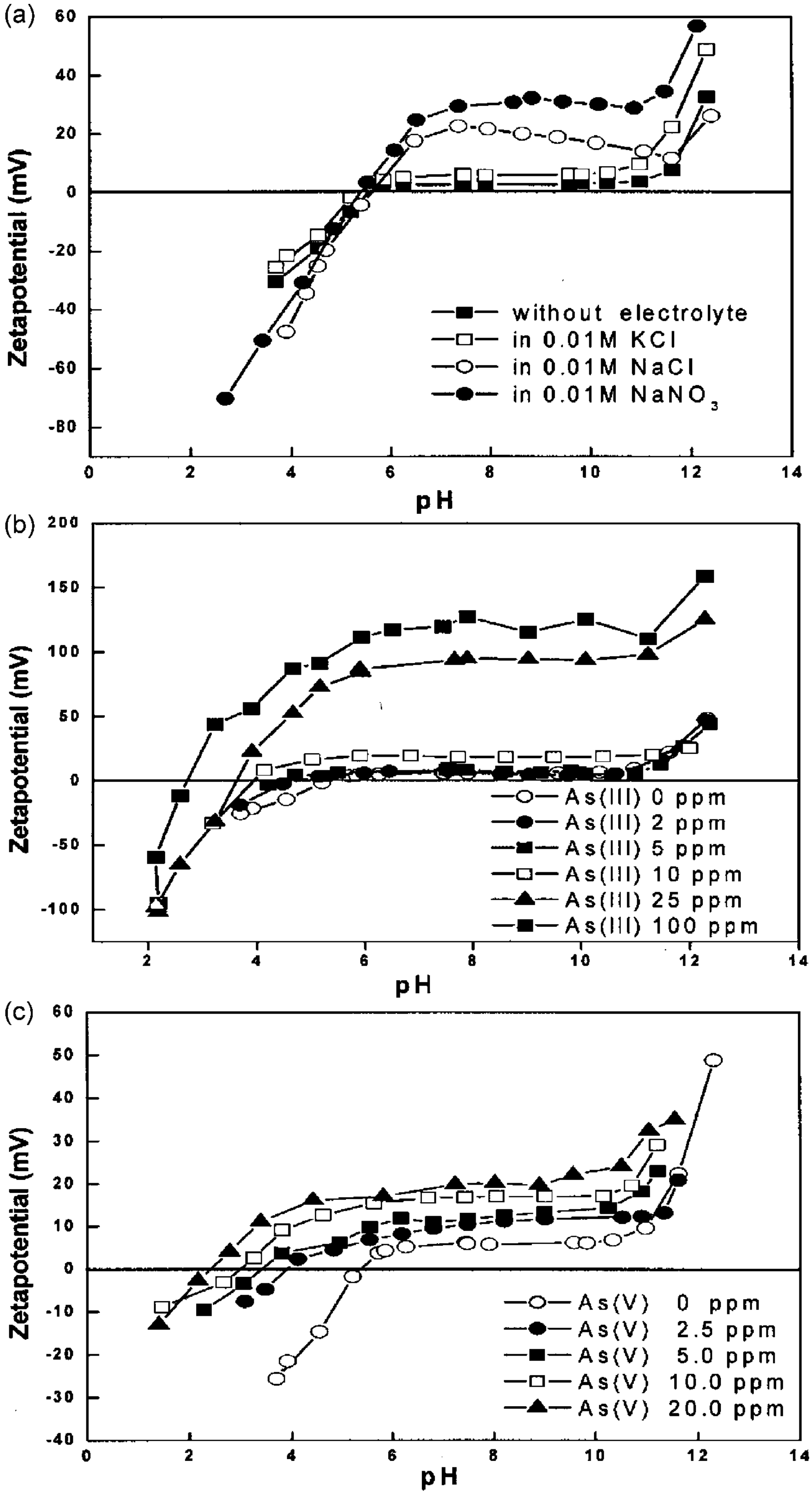

Figure 6. (a) The effect of electrolyte on ζ-potential of PTC6 as a function of pH, (b) the effect of H_3AsO_3 concentration on ζ-potential of PTC6 as a function of pH, and (c) the effect of H_3AsO_4 concentration on ζ-potential of PTC6 as a function of pH

Contrary to this, positive ζ-potential was observed. It could be interpreted due to the interaction of metal ion with PTC6. The ζ-potential of potassium–PTC6 complex[30] and ruthenium and cobalt calix[6]arenes[31] were reported to be positive. The reactivity of calixarenes is influenced by the ring size of calix anion and degree of de-protonation.[30] The effect of As (III) and As (V) concentrations on the ζ-potential of PTC6 is shown in Fig. 6(b) and (c). In both the cases, the shift in iso-electric point and the increase in the magnitude of the ζ-potential reveal specific interaction between arsenic and PTC6. The shift in iso-electric point towards lower pH was attributed to the specific interaction.[32–34] Thus, it is evident that the interaction between arsenic and calixarene could be described as specific interaction.

Free energy of adsorption

The NMR and ζ-potential study clearly suggests that the adsorption of arsenic on PTC6 is mainly due to specific chemical interaction. The free energy of adsorption was calculated for both As (III) and As (V) from the adsorption measurements. Adsorption densities around plateaus were taken for these calculations. The magnitude of free energy of adsorption ($-\Delta G^{o}_{ads}$) was calculated from the Stern–Grahame equation.[33]

$$\Gamma_d = zrCe^{\frac{-\Delta G^{o}_{ads}}{RT}} \quad (1)$$

where Γ_d is the adsorption density (mole/m^2), r is the effective radius of the adsorbed ion in m, C is the equilibrium concentration (moles/L), R is the gas constant, T is the absolute temperature, and z is the valency of the adsorbed ion. Equation (1) can be rearranged as

$$\Delta G^{o}_{ads} = -RT\ ln\left[\frac{\Gamma_d}{zrC}\right] \quad (2)$$

Table 1. Free energy of adsorption with reference to equilibration time and H_3AsO_3 concentration

		Free energy of adsorption (kJ/mole)				
		Equilibration time (min)				
S. no.	Initial concentration of As (III) (mg/L)	10	20	30	60	1440
1	1	21.617	23.804	23.993	23.687	24.392
2	2	22.820	23.886	24.316	24.803	25.185
3	4	24.762	25.189	25.415	25.552	25.273
4	6	25.277	25.182	25.445	25.620	25.594
5	8	25.135	25.229	25.052	25.332	25.298
6	10	24.916	25.134	24.487	25.187	25.024
7	12	24.396	24.315	23.752	24.183	24.535
8	14	23.811	23.397	23.226	24.122	24.335
9	16	23.117	23.043	22.582	23.340	23.554
10	18	22.428	22.527	22.231	22.723	22.951
11	20	22.035	22.127	20.982	22.196	22.462
12	30	20.844	20.700	20.328	21.127	21.220
13	40	19.993	20.160	20.138	20.043	20.583

Table 2. Free energy of adsorption with reference to equilibration time and H_3AsO_4 concentration

		Free energy of adsorption (kJ/mole)				
		Equilibration time (min)				
S. no.	Initial concentration of As (V) (mg/L)	10	20	30	60	1440
1	1	18.364	19.210	19.823	19.823	19.124
2	2	19.434	19.584	20.034	19.423	19.426
3	4	19.421	19.417	19.649	19.412	19.616
4	6	19.320	19.151	19.325	19.168	19.156
5	8	18.858	18.980	19.144	19.353	19.290
6	10	18.093	18.315	18.214	18.681	18.964
7	12	17.536	17.642	17.784	18.197	18.562
8	14	17.089	17.244	17.411	17.765	18.075
9	16	16.863	16.965	17.143	17.423	17.743
10	18	16.549	16.647	16.791	17.112	17.366
11	20	16.105	16.200	16.335	16.613	16.870
12	30	14.892	14.861	15.062	15.372	15.614
13	40	14.452	14.383	14.583	14.952	15.310

The ΔG^{o}_{ads} values calculated from adsorption isotherms are shown in Tables 1 and 2. The magnitude of the (ΔG^{o}_{ads}) values indicates weak chemisorption of arsenic on the PTC6 surface.

CONCLUSIONS

The adsorption of arsenite and arsenate on PTC6 was studied. The maximum adsorption of arsenic on PTC6 was observed around neutral pH. The interaction between arsenic species and PTC6 was explained in terms of hydrogen bonding and condensation reaction between hydroxyl groups of PTC6 and arsenic species. The ζ-potential measurements indicated the specific interaction between PTC6 and arsenic. The ^{13}C NMR CP-MAS spectra suggested the coordination of arsenic to PTC6. The free energy of adsorption (ΔG^{o}_{ads}) calculated by the Stern–Grahame equation was found to be 25 kJ/mole for As (III) and 19 kJ/mole for As (V). The magnitude of the (ΔG^{o}_{ads}) values and the NMR data indicates weak chemisorption between arsenic and PTC6 surface.

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