Studies on the Zetapotential of Calcite/p-Sulfonato-calix[4,8]arenes

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Zeta potential of calixarenes has been reported for the first time. The water-soluble calixarenes has been used as dispersion media in solid/liquid interface. p-sulfonato-calix[4]arene (PSC4) and p-sulfonato-calix[8]arene (PSC8) were synthesized and characterized by FTIR, NMR, mass spectrometry, and HPLC techniques. It was proved that the zeta potential is a fast and simple measurement to know the adsorption behavior of sufonato calixarnes on calcite. The chemisorption of p-sulfonato-calix[n]arene was confirmed by shift in iso electric point, adsorption studies and FTIR. The calculated free energy of adsorption value and its sign suggests the chemical interaction between the calcite surface and p-sulfonato calix[4]and[8]arene.

Keywords Chemisorption, particle size distribution, surface area, water soluble calixarenes, zeta potential

1. INTRODUCTION

Calixarenes are a class of supramolecules widely used in host-guest chemistry. Due to the lack of water solubility of calixarenes, the functional groups containing positive charge or negative charge were introduced on the wider rim and narrow rim. The introduction of functional groups on calixarenes is a challenging task.[1] The modified calix[n]arenes at upper/lower rim will play a major role in selective separation of fullerenes and to determine their inclusion behavior.[2] The selective binding of calcium and sensing of fluoride were already reported.[3–7] Shinkai et al. reported water-soluble calixarene derivatives bearing a sulfonato group on the wide rim and the hydrophobic alkyl groups on the narrow rim.[8] The sulfonato calix[n]-arenes can able to complex with (i) metal ions[9–11] such as Cu^{+2}, Zn^{+2}, Ni^{+2}, U^{+2}, Pb^{+2}; (ii) neutral molecules like acetonitrile, acetone, butanone, ethanol, propanol, naphthalene[12,13], (iii) anionic guests[14,15] like BF_4^-, $SO4^{-2}$, Cl^-, Br^-, I^-; (iv) antiviral, antibacterial, and catalytic activity[16–18]; (v) complexation with amino acids, peptides, steroids and biomedical applications.[19–21] Very recently

researchers reported that sulfonato-caix[n]arenes act as surfactants in stabilizing in magnetite nanoparticles and trans-Beta-carotene nanoparticles.[22,23] Zeta potential is an important parameter to know the electro kinetic behavior of solid/liquid interface. Zeta potential is a key factor in colloidal chemistry, paper industry, ceramics, cement, water purification, mineral processing, clay technology, paints, electro deposition, dairy products, cosmetics, pharmaceuticals.[24] Over the common surfactants the hydrophilic functional groups and hydrophobic cavity of calixarenes form the inclusion complexes, micelles and intermolecular complexes.[25] Generally, the critical mecellar concentration of surfactant is dependent of alkyl chains attached to the surfactant. But some of the calixarene derivatives critical mecellar concentration is independent of alkyl chains attached to the phenolic oxygen.[26] Thus, in the present study PSC4 and PSC8 were used as a adsorbate. This study was an attempt to understand the adsorption behavior of the PSC4 and PSC8 on calcite surface. Theoretically the expected interaction between the sulfonato calixarene and calcite are hydrogen-bonding, Π-stacking, vanderwaals, electrostatic and nonelectrostatic interactions.[27] We envisioned that the use of these sulfonato calixarenes as surfactant on calcite surface was helpful to overcome the difficulties arose in flotation of calcium minerals.

2. MATERIALS AND METHODS

5, 7, 17, 23,-Tetra-t-butyl-25,26,27,28 tetrahydroxy-calix[4]-arene and 5, 11, 17, 23, 29, 35, 41, 47-Octa-tert-butyl-49, 50, 51, 52, 53, 54, 55, 56-octa hydroxy calix[8]arene were

synthesized as described in literature.[28] The sulfonation was carried out with 98% sulfuric acid.[29,30]

2.1. Synthesis of PSC4 and PSC8

In a three-necked round bottom flask, 40 ml of 98% sulphuric acid was refluxed with p-tert-butylcalix[4]arene or p-tert-butylcalix[8]arene at $100°C$ with stirring in water bath. The 0.622grams of the calix[n]arene was added for each 10 minutes in around 2 hours. Then further 3 hours was refluxed with same condition. The reaction was monitored by TLC or by checking the solubility of the product in water. After finishing the reaction, obtained high viscous liquid was filtered trough crucible with vacuum. The residue dissolved in methanol and filtered through silica gel column results the clear brown color filtrate. The addition of 1 L of ethyl acetate to the filtrate results the light brown color precipitate. The collected PSC4 and PSC8 were kept in vacuum oven at $80°C$ for 24 hours to get anhydrous sulfonato calixarenes.

2.2. Characterization of PSC4

Yield 48%, m.p. $277°C$, GC-Ms; 745, purity by HPLC; 99.5%. 1HNMR (500 MHz, D_2O) δ(ppm) 3.9 (bs, H, Ar-CH_2-Ar), (bs, H, 92H, 46H_2O exchangeable peak) 7.4 (bd, 16H, Ar-H); ^{13}C NMR (500 MHz, D_2O) δ(ppm); 153, 130, 128, 126, 30.6. DEPT-NMR (500 MHz, D_2O) δ(ppm) 30.6 (Bridged -CH_2-), 126 (Aromatic carbons).

2.3. Characterization of PSC8

Yield; 52%, m.p. $270°C$, GC-Ms 1489, purity HPLC 99.5%, 1HNMR (500 MHz, D_2O) δ(ppm) 3.83 (bs, 16H, Ar-CH_2-Ar), 4.7 (bs, 56H, 28H_2O exchangeable peak) 7.29 (bs, 16H, Ar-H); ^{13}C NMR (500 MHz, D_2O) δ(ppm) 153.3, 135.1, 128.0, 126.1, 30.5; DEPT-NMR(500 MHz, D_2O) δ(ppm) 30.44 (Bridged -CH_2-), 126.0 (Aromatic carbons).

2.4. Characterization

Bruker Avance-500 MHz NMR spectrometer was used to record the ^1H NMR, ^{13}C NMR, DEPT-NMR of the sample. The elemental analysis of the sample was obtained using an Euro Vectors Elemental analyzer (Italy). HPLC was performed using a Schimadzu instrument (Japan).

2.5. Mechanical Activation

A Fritsch pulverisette-5 planetary mill having agate bowl and balls (Fritsch GMBH, Germany) was employed for the mechanical activation of the calcite mineral. The calcite sample was activated in the planetary mill for 120 minutes with 200 rpm.

2.6. Electron Probe Micro Analysis

EPMA analysis was carried out using a JEOL, Super Probe JXA-8600 model electron microprobe operating with a current setting of 2×10-8A, with Standard Program International (SPI) mineral standards and using on-line ZAF correction procedures. EPMA results are shown in Table 1. The results indicated that the calcite sample is pure and contains 55% of CaO. Magnesium and iron content in these calcite samples varies from 0.43 to 0.51 and 0.21 to 0.27. All other elements present are in traces and insignificant.

2.7. Surface Area Measurements

Specific surface area and porosity of calcite samples were determined by nitrogen sorption technique with Micromeritics ASAP (Model 2020, USA) Surface area analyzer.

2.8. Particle Size Distribution

Laser diffraction method was used to measure the particle size by CILAS particle size analyzer (Model 1180, France). Depending on the size of the particle, required quantity of materials was dispersed in water. To avoid the agglomeration of particles ultrasonic vibrator was switched on during the measurement. The suspension was pumped through a detector and a laser beam. The equipment analyzes the particle size and also the weight percent of the fraction. The particle size distribution of calcite was shown in Figure 1.

2.9. Density

Density of calcite mineral was determined by gas displacement technique with AccuPyc 1340 Pycnometer (USA).

2.10. Zeta Potential Measurements

The zeta potential measurements[31,32] were conducted using zeta acoustic sizer (DT1200) equipped with video system and auto titration unit supplied by Dispersion Technology (USA).

TABLE 1
EPMA of calcite

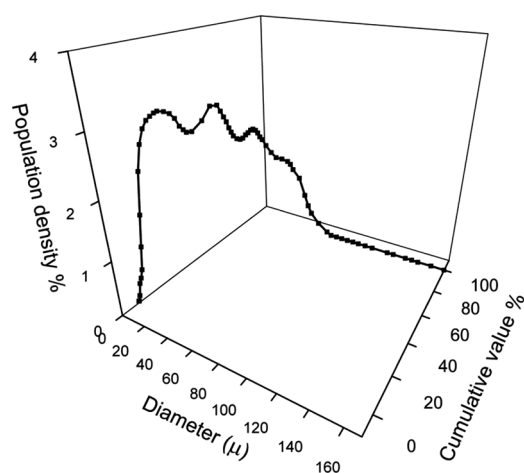|	1	2	3
CaO	55.20	55.41	55.36
FeO	0.23	0.27	0.21
Al_2O_3	—	0.08	—
MgO	0.51	0.50	0.43
MnO	0.10	0.09	0.11
ZnO	0.08	0.07	—
Cr_2O_3	0.01	0.03	0.02
V_2O_5	0.01	0.01	0.01
Total	56.14	56.46	56.14

FIG. 1.   Particle size distribution of calcite.

2.11. Adsorption Studies

The standard solutions of PSC4 and PSC8 were prepared by dissolving a known quantity of PSC4 and PSC8 in double distilled water. One hundred milliliter of PSC4 or PSC8 soultion at required pH was taken in polyethylene bottle and known quantity of calcite was added to the PSC4 or PSC8 solution. The contents in the bottles were agitated in a laboratory shaker for 1 h at a constant temperature of 27°C. After the equilibration, the solutions were filtered through a 0.2 μm membrane filters. The filtrates were subjected to UV visible spectrophotometer to estimate the unadsorbed PSC4 or PSC8 by literature[33]

3. RESULTS AND DISCUSSION

3.1. Effect of pH on Adsorption

The equilibrium concentrations of PSC4 was estimated at pH 11.0 by UV visible absorption spectra at $\lambda_{max} = 284$ nm. The equilibrium concentrations of PSC8 was estimated at pH 12.5 by UV visible absorption spectra at $\lambda_{max} = 264$ nm. The amount of the adsorbed PSC4 or

PSC8 was calculated by subtracting the equilibrium concentration from initial concentration. The effect of the pH on adsorbed amount of PSC4, PSC8 on calcite surface was shown in Table 2. It suggests the adsorption of sulfonato calixarene on calcite was purely pH dependent. The coulombic attraction of PSC8 with calcite surface was more due to its deprotanation when compared to PSC4. The nonaggregating behavior of p-sulfonato-calix[n]arenes and high water solubility leads to well interaction with calcite surface.[34] Suga et al. reported that p-sulfonato calix[n]arenes form stable complexes with alkali and alkaline earth metal cations.[33] The adsorption density of PSC4 and PSC8 on calcite surface was maximum at pH 9.3 and 8.6 respectively.

3.2. Adsorption of PSC4 and PSC8 on Calcite

BET surface area, pore size, pore volume, and mean particle size pure calcite and sulfonato calixarene adsorbed on calcite are indicated in Table 2. The BET surface area of the calcite was greatly enhanced by the adsorption of water soluble calixarene on calcite surface. On the calcite surface, below the pH 5.0 the precipitation of p-sulfonato calixarene has been clearly observed. At below the pH 5.3 the precipitation of calcium-sulfonato calixarene will occur as zwitter ionic compound. The formation of and its shape depend on the pH of the solution. Houmadi et al. visually proved that the formation of sulfonato calixarene vesicles, micelles with the atomic force microscope and TEM studies. The shape and size of the vesicles or micelles is pure pH dependent,[35] hence the mean diameter of the calcite particle was increased 2–3 times of its original mean diameter.

3.3. FTIR Analysis

FTIR of PSC8, calcite, and PSC8 adsorbed on calcite at pH 8.6 were shown in Figure 2. The FTIR of calcite shows the broad band at $3428\,cm^{-1}$ refers the free hydroxyl groups, strong bands at $1448\,cm^{-1}$ and $879\,cm^{-1}$ are the

TABLE 2
Surface area, pore size distribution and particle size distribution of calcite in presence of PSC4 and PSC8

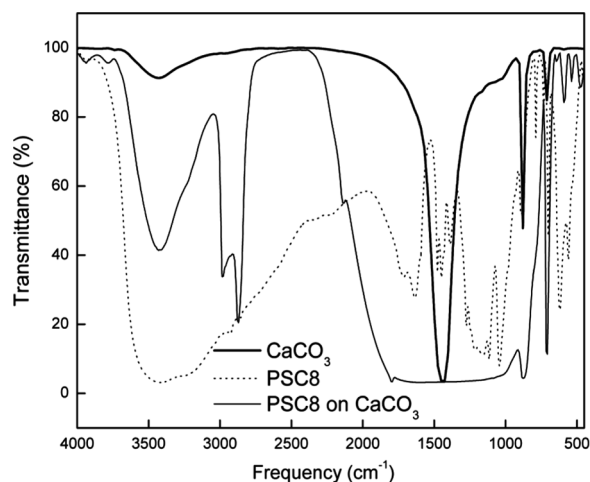| Sample	pH	BET surface area m²/gm	Adsorption pore volume cm³/gm	Adsorption pore size A°	Mean particle size distribution	Adsorption density mg/m²
Calcite	—	6.37	0.0098	64	8.3	—
PSC4 adsorbed	5.5	9.82	0.0157	64	30.2	0.6530
calcite	9.3	10.43	0.0213	75	20.6	0.9610
	12.5	8.59	0.0151	68	19.4	0.7100
PSC8 adsorbed	5.4	10.10	0.0170	71	34.0	0.5300
calcite	8.6	11.26	0.0203	74	24.2	0.7282
	12.6	10.20	0.0200	72	20.8	0.5000

FIG. 2.   FTIR spectrum of calcite, PSC8 and PSC8 adsorbed calcite at pH 8.6.

characteristic bands for CO_3^{-2} anion C-O stretching vibrations.

The FTIR of PSC8 show the broad band from 3150 to $3500 \, cm^{-1}$ shows the phenolic hydroxyls and sulfonic acid –OH stretching of PSC8. The band at $1636 \, cm^{-1}$ corresponds to asymmetric –CH stretch of methylene group. The doublet bands at 1477, $1449 \, cm^{-1}$ in the FTIR spectra of PSC8 suggests the −C=C− stretching vibrations. The bands at $1390 \, cm^{-1}$/1274 to $1114 \, cm^{-1}$ refers the asymmetrical/symmetrical stretching bands S=O group. The band at $1043 \, cm^{-1}$ refers the C-O stretching vibration of PSC8.

The FTIR of PSC8 adsorbed calcite show the band at $3410 \, cm^{-1}$ refers the free hydroxyls groups of PSC8. This suggests the phenolic groups are oriented upward to the calcite surface. The bands at 2981 and $2873 \, cm^{-1}$ corresponds to asymmetric and symmetric –CH stretch of bridged methylene groups, respectively. The bands corresponding to S=O group became broad bad indicates the chemical interaction of sulfonic groups with calcite surface. In the case of free PSC8 that bands at 733, 720, and $620 \, cm^{-1}$ are characteristic bands for Ar-S stretching vibrations. But on the calcite surface these band positions are shifted to $711 \, cm^{-1}$ clearly indicates the specific interaction between calcite surface and sulfonate groups of calixarene. In the case of PSC4, the same results were which confirms the chemical interaction of PSC4 on calcite surface.

3.4. Zeta Potential Studies

Zeta potential of calcite mineral as a function pH was shown in Figure 3, revealing that the pure calcite iso electric point (iep) pH = 8.2. Below the iep the calcite mineral exhibiting the positive charge, where above the iep it is exhibiting the negative charge. In the presence of
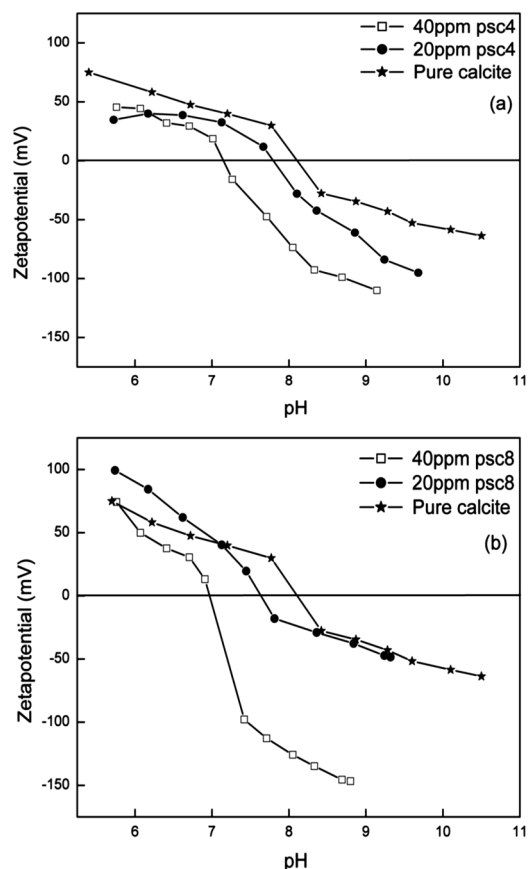

FIG. 3.   Zetapotential of (a) calcite/PSC4 (b) calcite/PSC8 as a function of pH.

p-sulfonato calix[4] and [8] arenes the iep of calcite was shifted to lower pH. This indicates the chemical interaction between the calcite and sulfonato calix[n]arene. The shift in iep of PSC8 was more when compared to the PSC4. The pK_a values of the OH groups of p-sulfonate groups suggests their super-acidic and super-basic oxy-anion nature.[36] In the case of PSC4 the first deprotanation occurs at $pk_{a1} = 3.3$, corresponding $\Delta H^o = 2.6 \, kJ/mole$ indicates the weak proton-oxygen interaction of hydroxyl groups at the narrow rim. But the second deprotanation was occurs at $pk_{a2} = 11.5$, corresponding $\Delta H^o = -25.9 \, kJ/mole$ indicates the very strong circular hydrogen bonding. In the case of PSC8 the first, second, third and fourth deprotanation occurs at 3.5, 4.3, 7.9, and 10.5, respectively.[33] Hence at higher pHs the upper and lower rim of the PSC4 and PSC8 becomes hydrophilic and specific interaction was more preferable. Where the hydrophobic mid region may not form any interaction with calcite surface. The columbic attraction of parallel orientation of PSC4 or PSC8 causes the minimization of positive charge and shift in iep toward the lower side. The PSC4 molecules are aligned such a manner that all sulfonate groups are facing toward calcite surface (i.e., parallel orientation) and phenolic groups may

align toward aqueous phase. The possible parallel and perpendicular orientations of PSC4 on calcite surface was shown in Figure 4. The FTIR and zetapotentail studies suggest the parallel orientation of calixarene on calcite surface.

3.5. Calculation of Free Energy of Adsorption

The anionic surfactants adsorbing at an oxide mineral surface, the free energy of adsorption was calculated by the following equation.[37]

$$\Delta pH = -\frac{ZF^2\Gamma_m}{2.0303RTC_\delta}\left[\frac{1}{1+\frac{55.5}{c_0}\exp\left(\frac{\Delta G_{sp}^0}{RT}\right)}\right]$$

ΔG_{sp}^0 = Free energy of adsorption

Γ_m = Adsorption density calculated from cross-sectional area of adsorbed-sulfonato calix[4] arene, that is, and [8]arene in mole/cm^2

Z = Valency of the p-sulfonato calix[4] and [8]arene

F = Faraday constant

C_δ = For oxide/water interfaces 20 µfarad/cm^2

ΔpH = Shift from the original iso electric point

R = Ideal gas constant in J/K mole,

T = Temperature in K.

C_o = For the unit shift of iso electric point the concentration of the water-soluble calixarene in mol/L.

The average cross sectional area 140 A^{o2} was considered for eight membered calixarene,[38] where 106 A^{o2} for four membered calixarene.[39] For both PSC4 and PSC8 on calcite the calculated negative free energy of adsorption was around 28–35 kJ/mole. The sign and magnitude suggests

FIG. 4. The representation of PSC4 and schematic illustration of PSC4 localization on calcite surface.

the chemical interaction between the sulfonated calixarene and calcite surface.

4. CONCLUSIONS

The adsorption of water-soluble calixarenes on calcite was studied. The FTIR and adsorption studies reveal the chemical interaction of PSC4 and PSC8 on calcite surface. The shift in isoelectric point indicates the chemisorption of PSC4 and PSC8 on calcite. The calculated free energy of adsorption. (ΔG_{sp}^0) and its magnitude confirms the chemisorption of water-soluble calixarene on calcite surface.

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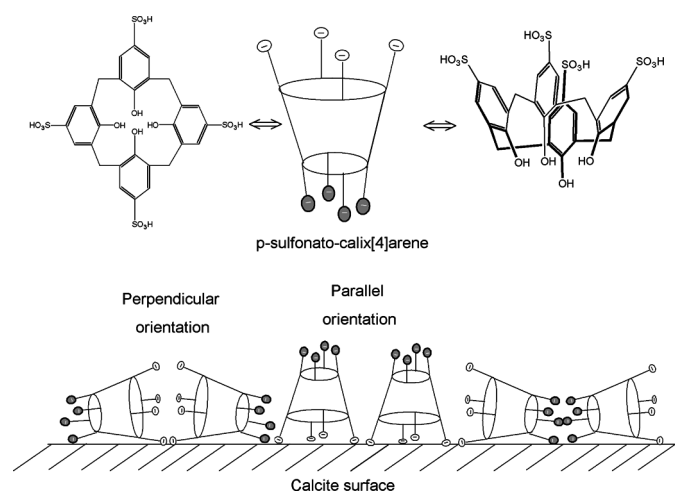[19] Memmi, L., Lazar, A., Brioude, A., Ball, V., and Coleman, A.W. (2001) *Chem. Commun.*, 2474–2475.

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