Spectroscopic study of 8-hydroxyquinoline-5-sulfonic-acid-doped sol–gel transition metal ion optrode materials

Diane Arbuthnot, Xiao-jun Wang, E.T. Knobbe *

Department of Chemistry and the University Center for Laser Research Oklahoma State University, Stillwater, OK 74078, USA

Abstract

8-Hydroxyquinoline-5-sulfonic-acid-doped silicate gel has been found to exhibit optrode material characteristics suitable for the detection of transition metal ions. Analyte ion-induced perturbations of 8-hydroxyquinoline-5-sulfonic-acid-doped gels have been studied. Absorption, emission and excitation spectroscopic techniques were used to monitor complex formation processes in the composites in the presence of aqueous divalent zinc and cadmium species. Metal complexation has been observed to perturb the optical characteristics of incorporated 8-hydroxyquinoline-5-sulfonic acid dopants, as observed via continuous wave spectroscopy. Thus, the authors are presently investigating the utility of 8-hydroxyquinoline-5-sulfonic-acid-doped gels for use in remote optically interrogated chemical sensors. The larger ionic radius of Cd\(^{2+}\) was noted to slow the complexation rate with respect to Zn\(^{2+}\). Complexation rate is one method by which one may differentiate between these isoelectronic cations.

1. Introduction

Solid state optical sensors, to be used in detection of various analyte species have become the focus of much recent research in light of environmental concerns such as ground and surface water contaminants. These include the families of aromatic hydrocarbons as well as many of the heavy metal ions which are known to exist in solution [1,2]. Electrochemical sensors, in general, quantitate with a high degree of precision the presence of many analyte species, but remote discrimination between isoelectronic aqueous ions such as Cd\(^{2+}\) and Zn\(^{2+}\) is problematic.

In order to develop an optically coupled solid state device based on chelating probe species, several methods may be employed to immobilize organic molecules which are capable of binding aqueous transition metal ions. A primary method which has been used in the development of analytical ion exchange resins involves the use of immobilized ligands on silica gel, alumina gel and organic polymer-based columns [3,4]. Difficulties associated with the direct use of such methods in association with an optically coupled sensor include excessive scatter and absorption losses and leaching effects. We are presently investigating the use of sol–gel chemistry to entrap organic probe species into an inorganic host matrix which has previously been shown to exhibit good optical properties [5]. The low processing temperatures, relative ease of organic probe molecule entrapments and the porous nature of sol–gel-derived media make such systems a reasonable alternative to methods which have been previously investigated. The work reported herein investigates sol–gel-derived media such that ligating organic
probe molecules have been entrapped within a porous glassy matrix which can promote the transport of aqueous transition metal analytes. We have investigated the optode behavior of 8-hydroxyquinoline-5-sulfonic acid (HQSA)-doped sol–gel hosts with respect to aqueous Zn$^{2+}$ and Cd$^{2+}$ species.

Sol–gel–entrapped probe species and their ion complexes are readily distinguished by several spectroscopic methods, including luminescence and absorption spectroscopy. Fluorescent organic ligating molecules can be used to monitor complexation with metal ion analytes, as the luminescence characteristics of select probe molecules are distinctively perturbed by the presence of complexed ionic species. The use of continuous wave spectroscopy permits the study of complex formation on a time evolution basis. Differences between spectral features of metallorganic complexes containing closely related ionic species may allow specific ion quantitation to be performed. In addition to luminescence characteristics, absorption spectra may be used to evaluate both radiative and non-radiative transition events. Thus, a combination of spectroscopic techniques can enable one to distinguish between metallorganic complexes of isoelectronic species.

8-Hydroxyquinoline-5-sulfonic acid (shown in Fig. 1) has been widely studied as an analytical ion exchange reagent used in the complexation of transition metal ions [6–8]. This bidentate ligand molecule, and its various metal complexes, are readily studied through the use of absorption and fluorescence spectroscopy. HQSA has been reported to be highly selective for complexation with aqueous transition metal ions over competing alkali metal and alkaline earth ions [9]. Thus, enhanced sensitivity in the presence of large background amounts of IA and IIA metal ion species (as encountered in marine environments) may be realized. As with other organic ligands, HQSA is pH sensitive. It has been reported that a pH of ~4.5 or greater is needed for metal ion detection [10,11]. The spectral bands of HQSA complexes containing isoelectronic ions such as Zn$^{2+}$ and Cd$^{2+}$ may be distinguished, thereby permitting for differentiation of related analyte species. It has also been noted that the rate of complex formation is dependent upon the size and activity of the analyte ion species present. Fluorescence, pH and metal ion selectivity of HQSA have previously been reported [11–13], thereby making HQSA a good candidate for entrapment into sol–gel-derived inorganic glasses for the purpose of developing transition metal ion optode materials. The research presented herein seeks to expand on previously reported works, and to move toward the development of an optically coupled transition metal ion analyte probe material.

2. Experimental procedures

Samples of HQSA-doped silica gel were made by a modification of the sonogel method described by Esquivias and Zarzycki [14]. A 1:4 molar ratio of tetraethylorthosilicate (TEOS) to a 0.001M aqueous HQSA solution was utilized. Five drops of 0.4N HCl per 23 ml of sol were added to catalyze the hydrolysis reaction. Upon the completion of hydrolysis, the pH of the sol was adjusted to 4.8 by dropwise addition of a dilute NH$_4$OH/EtOH solution. The samples were then cast into polystyrene cuvettes, covered and allowed to gel. Following gelation, the covers were perforated to allow slow evaporation of residual solvents. Dried xerogels were obtained within approximately 2 weeks. Probe-doped gel specimens were subsequently used for optode behavior and characterization.

Complex formation in HQSA-doped gels was observed by measuring analyte-induced perturbations to the absorption and luminescence characteristics of the gel-entrapped HQSA parent molecule. Xerogels were soaked in 10 mM aqueous solutions of Cd$^{2+}$ and Zn$^{2+}$ ions. The time-evolution of complex formation was observed using continuous wave fluorescence spectroscopy. Following complexation, the gels were removed from the aqueous solutions and dried.

![Fig. 1. Parent probe molecule: 8-hydroxyquinoline-5-sulfonic acid (HQSA).](image-url)
for 48 h. Complexed and uncomplexed HQSA containing gel specimens were then used to quantify changes to the absorbance characteristics of HQSA probe molecules as a result of Zn(II) and Cd(II) complex formation.

Excitation and emission features were measured using a Spex model F112A spectrofluorometer. 1.85 nm (excitation) and 0.86 nm (emission) band passes were used during the cw luminescence measurements. Absorbance spectra of the solid state complexed and non-complexed HQSA-doped gels were measured using a Cary 5 spectrophotometer (2.0 nm spectral band pass).

The degree of complex formation between HQSA and the aqueous IIIB analytes was observed by monitoring the emission intensity at 540 nm continuously for 240 min using an excitation wavelength of 396 nm.

3. Results

The absorption spectra of HQSA-doped xerogels are shown in Fig. 2. The three curves correspond to the free parent (A), cadmium complexed (B) and zinc complexed (C) HQSA gel dopants, respectively. In the case of the parent HQSA, the absorption spectrum exhibits a maximum peak at 308 nm with a broad shoulder centered at 360 nm. The 360 nm band is observed to increase in amplitude upon Zn$^{2+}$ and Cd$^{2+}$ metal ion complexation, as seen in curves B and C of Fig. 2. The absorbance bands for the parent, cadmium complexed and zinc complexed HQSA were deconvoluted into a pair of Gaussian peaks using Sigmaplot software. The deconvoluted bands and residuals associated with the parent HQSA species are shown in Fig. 3. Peak areal ratios ($A_{308\text{ nm}} / A_{360\text{ nm}}$) were found to be 0.72 for the free parent, 0.33 for the cadmium complex and 0.23 for the zinc-HQSA complex. For the parent HQSA, a tail beyond 420 nm was noted that did not correlate with the simple two-peak Gaussian model. A smaller, third peak centered at approximately 450 nm was hypothesized and substantially reduced the residuals, but this relatively small peak was ignored for the purpose of areal ratio calculations. Upon complexation with the analyte ions, evidence for the existence of a small peak at 450 nm disappeared.

The processes of metal complex formation were monitored by observing changes to both excitation and emission spectra of entrapped HQSA in the presence of aqueous transition metal ions. The time-evolution of HQSA emission spectra in the presence of zinc cations are shown in Fig. 4, where time 0
min corresponds to the emission spectrum of parent HQSA prior to introduction of aqueous Zn$^{2+}$ species. A broad emission band, centered at 535 nm, was observed to arise and increase in intensity as complex formation proceeded. Red-shifting of the peak associated with the free parent HQSA (490 nm) was noted upon complex formation with Zn(II). No further qualitative changes to the noted spectral characteristics were observed after 60 min, although the overall emission intensity increased as a function of complexation time over a period of approximately 3.5 h. A similar behavior is observed upon the introduction of aqueous Cd$^{2+}$, as seen in Fig. 5. Cd$^{2+}$-HQSA emission features were found to be substantially the same as in the Zn$^{2+}$ case, although peak emission intensities for the Cd$^{2+}$ complex were found to be lower overall.

Excitation spectra for the HQSA complexes of Zn$^{2+}$ and Cd$^{2+}$, utilizing an emission wavelength of 535 nm, are shown in Figs. 6 and 7, respectively. The spectrum for the Zn$^{2+}$ complex indicates an excitation doublet at 325 and 365 nm. Blue-shifting of the complex peak with respect to that of the parent peak was observed, with concomitant intensity increases. Similar behavior was observed upon addition of Cd$^{2+}$ (Fig. 7).

The progress of complex formation reactions, as determined by spectral changes in emission intensity, may be observed as shown in Fig. 8. Complexation rates between HQSA and the two isoelectronic analytes are substantially different and may permit specific ion detection when correlated to absorbance and
luminescence spectral band feature shifts and concomitant changes in the associated areal peak intensities.

Fig. 7. Time-evolved excitation spectra of cadmium complexed HQSA. Time 0 min is the parent HQSA; time 40 min is the observably saturated cadmium-HQSA peak.

Fig. 8. Degree of complexation as a function of time of HQSA with 0.1M Cd$^{2+}$ and 0.1M Zn$^{2+}$. O, HQSA-Zn; ●, HQSA-Cd.

4. Discussion

Perturbations to the absorbance and luminescence spectra of parent HQSA probe species, upon the introduction of aqueous IIB transition metal ions, may be correlated to the formation of specific metalorganic complexes. Changes in the relative intensities of the absorption band doublets found in HQSA-doped silicate gels, upon exposure to aqueous zinc and cadmium solution, have been attributed to such processes. Results indicated that integration of the absorption doublet, following a simple Gaussian deconvolution, and subsequent comparison of the two peak areas readily promotes discrimination between isoelectronic cations such as zinc (II) and cadmium (II). Thus, the HQSA-doped gel specimens behave as an optode material which may be used in the detection of aqueous transition metal ion analytes.

Continuous wave luminescence spectroscopy is also a useful method by which one may observe complexation in such systems. Introduction of aqueous IIB transition metal ion analytes resulted in substantive perturbations to the emission and excitation spectra with respect to the free reporter probe, although the differences were found to be much subtler than in the case of absorption spectroscopy.

Complexation as a function of time can also be utilized to correlate the absorbance/luminescence data with the activity of select ionic species. Results indicate that cadmium has substantially slower complexation kinetics under the given conditions. This behavior has been attributed, at least in part, to the larger ionic radius of Cd(II) with respect to Zn(II). Differing complexation rates can augment ion discrimination and determine overall activity levels when correlated to absorbance (peak wavelengths, areal intensities) and shifts in the luminescence spectral band features.

5. Conclusions

Silica gels made via the sol–gel process were doped with 8-hydroxyquinoline-5-sulfonic acid and studied for potential use as an optode sensor material. These composite media were treated with aqueous divalent zinc and cadmium solutions, and the
complexation process was studied through the use of absorption and continuous wave luminescence spectroscopy as a function of analyte species. Absorbance spectra of the parent and its complexed forms were determined, and peak areal ratios of the subsequent doublets were found to promote differentiation between Zn(II) and Cd(II) in aqueous solution. Fluorescence characteristics of the entrapped reporter molecule were observed to vary as a function of exposure time to Zn\(_{aq}^{2+}\) and Cd\(_{aq}^{2+}\) solutions; a shift of the parent peak and a concomitant increase in the peak intensity were noted. Zinc and cadmium complexes were observed to have substantially similar luminescence spectra, although doublet areal ratios may be used to distinguish the two. Complexation rates of the two isoelectronic cations with HQSA were studied and appear to be a function of the size of the cation. In summary, HQSA-doped silica gel specimens were found to be a good candidate system for the detection and differentiation of isoelectronic transition metal ions using complementary optical interrogation methods.

References