PROTROPIC AND PHOTOPHYSICAL PROPERTIES OF 7-HYDROXYQUINOLINE IN X AND Y ZEOLITES

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Abstract − Diffuse reflectance and emission spectra of 7-hydroxyquinoline intercalated in the supercage of X and Y zeolites are compared with the absorption and emission spectra of aqueous 7-hydroxyquinoline solutions at various pH to understand protropic and photophysical properties of 7-hydroxyquinoline in zeolite microenvironments. Predominance of zwitterionic species with significant existences of the other three protropic equilibrium species, normal, protonated and deprotonated species in zeolite samples indicates that the major fraction of the molecules interact with strong acid and base sites of zeolite at an adsorbed position. Observed zeolite pHs of near neutrality are established by a near balance in numbers of many strong acid and base sites rather than by small numbers or weakness of acid and base sites. Excitations of nonzwitterionic species such as deprotonated species also give prevailing zwitterionic fluorescence, indicating that excited and ground proton transfer cycles of protropic species can be triggered by photons in organized zeolite media as well as in water.

INTRODUCTION

7-Hydroxyquinoline (7HQ)[†] exists as one of four protropic equilibrium species,[2] normal (N), protonated (P), deprotonated (D) and zwitterionic (Z) species, depending on equilibrium constants and sample conditions such as pH. The OH group and N atom in some hydroxyquinolines are known[2,7] to become more acidic and basic, respectively, in the first excited (π, π^*) singlet state[3] than in the ground state. Upon absorption of a photon the normal form of 7HQ in hydroxyl solvents is known[3-5] to undergo an excited state proton transfer process, forming the excited state tautomer form. Back proton transfer, following the relaxation of the excited tautomer form, replenishes photochemically depleted normal form in the ground state.[8,9] The participations of solvent molecules were reported[10,11] to be important in the excited and ground state proton transfers of hydroxyquinolines. The excitation of 7HQ protropic equilibrium species may also lead to an excited and ground state protonation and/or deprotonation cycle in water and zeolite environments.

Investigations on the photochemistry and photophysics of molecules adsorbed on solid surfaces have been vigorously carried out[12,13] since the investigations may provide a good insight into the photochemistry and photophysics of heterogeneity, surface and supramolecules. Drastically different effects of zeolites from those of solutions on encapsulated organic molecules have also been studied intensively in many research groups[14-16] since zeolites have well-defined structures, supercage effects and various unusual cation interactions. Studies on the microenvironmental effects of probe organic molecules trapped in the cages of zeolites have revealed rich informations on the interactions of introduced molecule with nearby and distant surroundings.[17,18]

Active acid and base sites of zeolites can be described in two types, Brönsted-Lowry and Lewis types as known in general. Brönsted-Lowry acid (base) site is able to transfer(accept) a proton from (to) the solid framework of zeolite to(from) an adsorbed molecule while Lewis acid(base) site can accept(donate) an electron pair from(to) an adsorbed molecules, forming a coordination bond between zeolite surface and an adsorbed molecule. Active sites in our present work about protropic equilibria and proton transfers would be explained better by Brönsted-Lowry definition rather than by the broader Lewis one. Acidic and basic properties of zeolites are known[19,20] to be dependent on Si/Al ratio as well as on preparation and treatment methods, dehydration temperature and zeolite structure. Zeolite acidity(basicity) decreases(increases) as Si/Al ratio decreases, as protons are exchanged with metal cations or as metal cations are exchanged with those of a lower charge density.[20]

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† *Abbreviations*: D, deprotonated species; 7HQ, 7-hydroxyquinoline; N, normal species; NaX, sodium-exchanged X zeolite; NaY, sodium-exchanged Y zeolite; P, protonated species; Z, zwitterionic species.

Interactions of acidic and basic sites in zeolites with the N and OH groups of 7HQ may exhibit interesting phenomena such as protropic equilibria, photon-initiated proton transfers, solvent effects, cage effects, etc.. It may be also possible to estimate the acidities of zeolites from relative equilibrium distributions of protropic species with known pK values.

In the present paper we report a study on the protropic and photophysical properties of 7HQ adsorbed in the supercage of zeolites using absorption, diffuse reflectance and emission spectroscopic methods. It will be shown that most 7HQ molecules interact with strong acid and base sites of zeolite at a same time and that photons can initiate excited and ground state proton transfer cycles of 7HQ protropic equilibrium species in zeolite supercages as well as in water.

MATERIALS AND METHODS

7HQ was purchased from the Eastman Kodak and vacuum-sublimed. The pHs of aqueous solutions were adjusted using aqueous HCl, $HClO_4$ or NaOH solution. X and Y zeolites were synthesized, washed with doubly distilled hot water and dried in a vacuum oven. A Pyrex test tube containing zeolite was jointed with a vacuum port and maintained at 670 K for 2 h. The typical unit cell formulas are $Na_{80}(AlO_2)_{80}(SiO_2)_{136}\cdot250H_2O$ for sodium-exchanged X zeolite (NaX) and $Na_{56}(AlO_2)_{56}(SiO_2)_{136}\cdot250H_2O$ for sodium-exchanged Y zeolite (NaY). Then intercalation of a 7HQ molecule into a supercage of zeolite was carried as the following procedures which were established and confirmed with ^{129}Xe NMR spectroscopy previously.[21,22] 7HQ (~0.5 molecule per supercage) and zeolite powder were mixed under nitrogen atmosphere in a glove bag and transferred to a quartz tube. The tube was evacuated, sealed and maintained at 570 K for 12 h for 7HQ sublimation and encapsulation into zeolite supercages before it was slowly cooled down to room temperature to obtain a uniform distribution.

Home-made absorption and diffuse reflectance spectrometers were used to measure absorption spectra of solution samples and diffuse reflectance spectra of zeolite and nonsolution samples, respectively. In the diffuse reflectance spectrometer a wavelength-selected beam of a tungsten/deuterium lamp using a 0.25 m monochromator (Kratos, GM 252) was directed to a sample which was mounted on a tangent plane of an internally MgO-coated integrating sphere. Specular reflection-rejected diffuse reflectance of the sample was detected at a right angle from the illuminating beam using a Hamamatsu R374 photomultiplier tube and compared with the reflectance of MgO powder. For the measurements of emission and excitation spectra samples were excited by a wavelength-selected 1 kW xenon arc lamp (Schoeffel, LPS 255 HR) using a 0.25 m monochromator (Kratos, GM 252). Sample luminescence was collected from a right angle to the excitation beam and focused to a 0.25-m monochromator (Kratos, GM 252) which was attached with a Hamamatsu R376 photomultiplier tube. Emission spectra reported here were not corrected for the variation of the detector sensitivity as a function of wavelength.
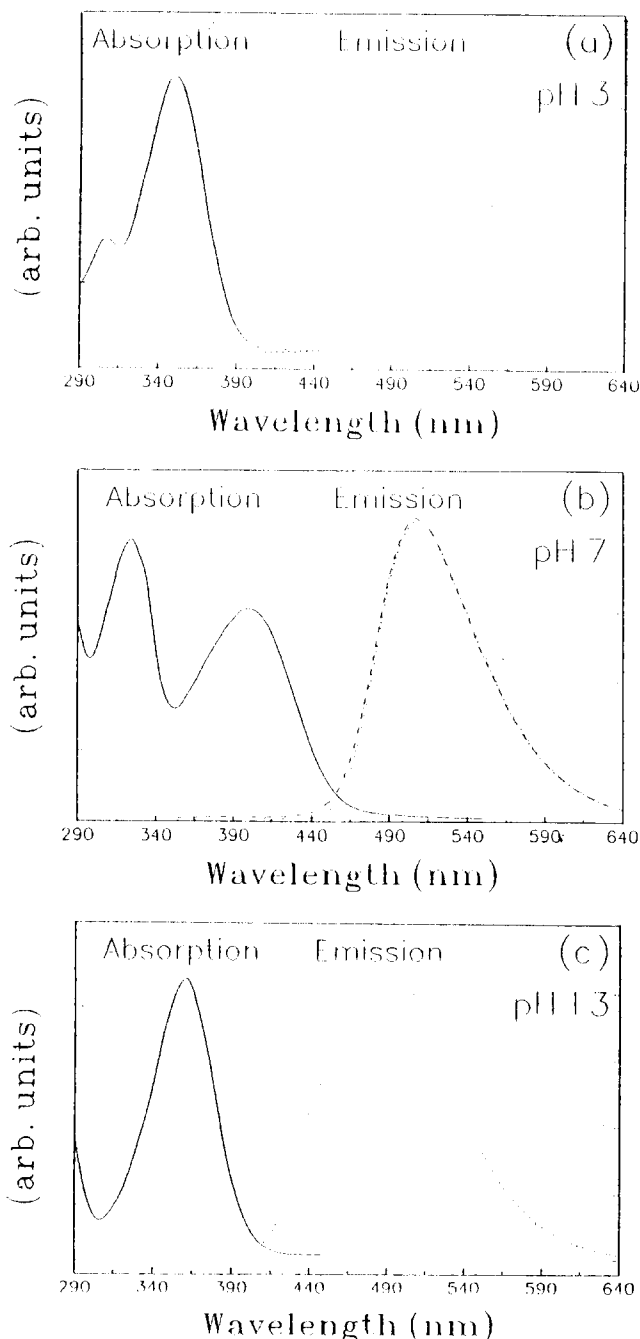

Figure 1. Absorption and emission spectra of aqueous 7HQ at pH 3 (a), 7 (b) and 13 (c). The emission spectrum in (a) was obtained after excitation of P species at 350 nm, the dotted emission spectrum and the dot-and-dashed one in (b) were after excitations of N and Z species at 320 and 400 nm respectively, and the emission spectrum in (c) was after excitation of D species at 360 nm.

RESULTS AND DISCUSSION

The dominant species of aqueous 7HQ at pH 3, as shown in Fig. 1(a), is P species in which the N atom is protonated. The emission spectrum with the peak at ~510 nm shows unusually large Stokes shift

from the absorption spectrum with the peak at ~350 nm. N and Z species are the major equilibrium species at pH 7 as seen in Fig. 1(b). The spectrally well separated absorption spectra of N and Z species with the lowest energy peaks at ~330 nm and ~400 nm respectively are a good contrast with the spectrally similar emission spectra of N and Z species excitations with both peaks at ~510 nm, respectively. The dominant D species, where the OH group is deprotonated, absorbs and emits a photon with the peaks at ~360 nm and ~490 nm, respectively, as shown in Fig. 1(c). Selective excitations of any aqueous protropic equilibrium species give us similar emission spectra regardless of their spectrally well distinguishable absorption spectra as presented in Fig. 1. All the emission spectra resemble the fluorescence spectrum emitted from the first excited singlet state of Z species. These facts indicate that the excitations of N, P and D species lead to photochemical reactions, forming Z^* species as the final product in the first excited singlet state. The emission spectrum of D species at pH 13 shows spectrally blue shift compared to the other three emission spectra in Fig. 1 and a left shoulder at ~450 nm which is due to D^* fluorescence. This indicates that Z^* fluorescence is less dominative in the emission spectrum of the pH 13 sample than in the other three emission spectra of Fig. 1.

The relative ground state energies[2] and the absorption peak wavelengths indicate that the relative energies in kJ/mol of the protropic equilibrium species at pH 7 are $N^*=P^*+10=D^*+20=Z^*+70$ in the first excited singlet state. In the ground state protropic species are equilibrated by the concentration ratios dependent on the relative ground state energies and pH. However, in the nonequilibrated excited state the relative energies tell us the direction of photochemical reactions since the initial reactant (the species excited) and the final product (Z^* species) have a large energy differences. Upon absorption of a photon the N atom and OH group of N species may compete to find H_3O^+ and OH^- ions respectively generating P^* or D^* species as a proton transfer reaction intermediate before the formation of Z^* species. Obviously, D and P species directly undergo protonation and deprotonation respectively with excitation and both result in Z^* species. Photochemically transformed Z^* pecies relaxes to the ground state of Z species radiatively or nonradiatively. Conversion of protropic equilibrium species into other species by photoninitiated excited state proton transfer breaks the protropic equilibria among species. The relaxation of the equilibrium perturbation will be accomplished as the extra amount of Z species returns to the photochemically depleted initial species by reprotonation
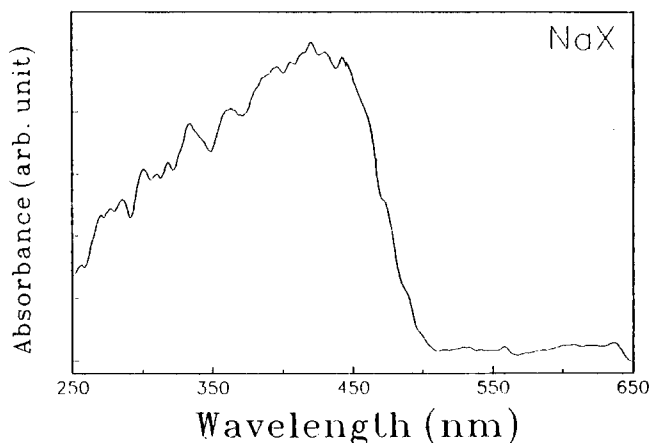

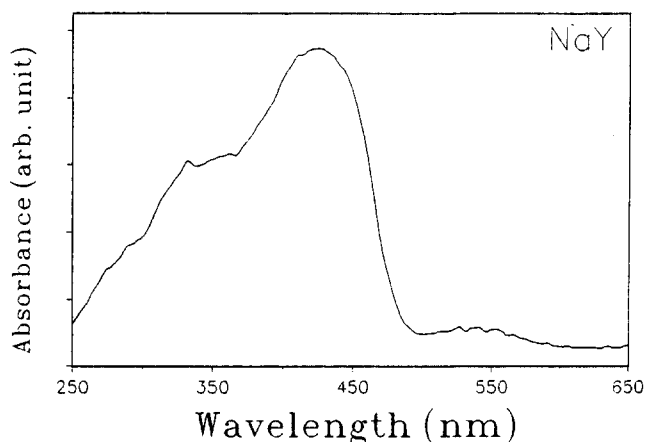Figure 2. Diffuse reflectance spectrum of NaX zeolite intercalated with 7HQ.

Figure 3. Diffuse reflectance spectrum of NaY zeolite intercalated with 7HQ.

and/or redeprotonation in the ground state.

The diffuse reflectance spectrum of NaX in Fig. 2, compared to the absorption spectra in Fig. 1, shows that absorption from every possible protropic species can be observed although that from Z species is most significant. The spectrum of NaY in Fig. 3 resembles that of NaX while the absorption contributions of N and Z species are enhanced and that of D absorption is reduced in NaY. Z species is dominant in NaY as described in the previous paper[3] where Z species was tentatively mentioned as the tautomeric form of 7HQ molecule since a zeolite was briefly tried to understand 7HQ proton transfers in methanol. NaY is more acidic than NaX since the silicon-to-aluminum ratio of 2.54 in NaY is higher than that of 1.23 in NaX.[19] (The weak absorption band near 550 nm is frequently observed even in 7HQ-free samples of NaY only as reported earlier.[12]) The decrease of D absorption and the increases of N and Z absorptions in NaY may be explained by the pH decrease of zeolite in NaY.

Using the reported pK values of 7HQ protropic equilibrium species in water[2] and estimating the relative fractions of those in zeolites from Fig. 2 and 3, we can estimate the macroscopic overall pH values of NaX and NaY as ~ 7 and ~ 8, respectively, assuming that the pK values of protropic species in zeolites are similar to those found in water. It is interesting to note that the relative fraction of Z species is much higher than that of N species in both zeolites NaX and NaY. Our suggestion that acidic and basic sites coexist at many different locations but in a same zeolite may explain well the predominant fraction of Z species as well as the large polarity and heterogeneity of zeolite. D species is produced when the N atom is attached to an active acid site but the OH group is not located to near a strong base site. Formations of the other three protropic species may also be explained in this way. Noticeable absorptions of P and D species at near neutral pHs of zeolites X and Y with the larger fraction of Z species than that of N species indicate indeed that the observed near neutral overall pHs of NaX and NaY are established by a near equivalence in numbers of many strong acid and base sites. Neutral pHs are established not by the small numbers or weakness of acidic and basic sites as observed in neutral solution systems.

The emissions of 7HQ-intercalated NaX and NaY show similar spectra each other with both peaks at ~ 490 nm respectively, while the emission spectrum of NaX has an enhanced relative intensity at 450 nm which is due to D fluorescence as observed in aqueous 7HQ solution at pH 13 (Fig. 1(c)). The emission spectra after excitation at 340 nm, the wavelength where Z species is least effectively excited compared to the other three species, have the typical characteristic of Z* fluorescence. This fact indicates that excitations of nonzwitterionic species initiate excited state proton transfer processes, forming Z* species as the final product in the first excited singlet state, also in organized zeolite media as found earlier in water. Excitation of Z species obviously does not initiate a proton transfer process as reported previously.[3]

Observation of excited state proton transfer between an adsorbed 7HQ molecule and zeolite acid (base) site within the lifetime of the 7HQ excited state is really interesting. Freezed hydrogen bond between proton donor and acceptor in zeolite acts as a stable transition state intermediate of proton transfer reaction. The reaction may proceed immediately upon absorption of a photon via this prebuilt intermediate. If proton transfer reaction occurs between distant donor and acceptor, a proton from the donor has to migrate the distance between the donor and the acceptor species before the excited
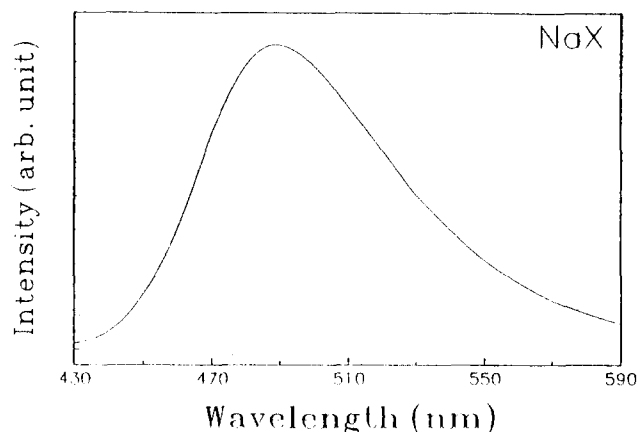

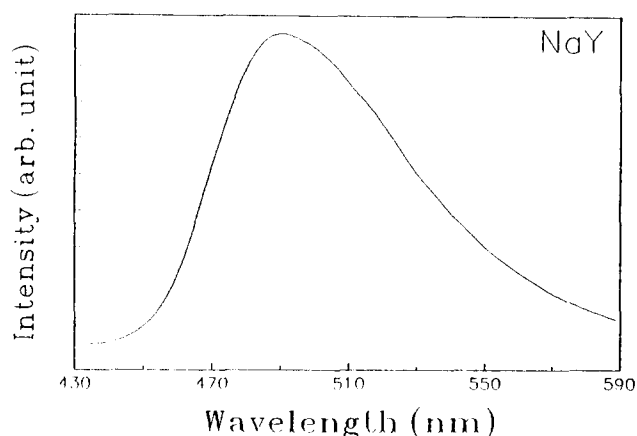Figure 4. Emission spectrum, excited at 340 nm, of 7HQ-adsorbed NaX zeolite.

Figure 5. Emission spectrum, excited at 340 nm, of 7HQ-adsorbed NaX zeolite.

precursor relaxes to the ground state. Since the number of 7HQ molecule was adjusted to 0.5 per supercage and the numbers of acidic and basic sites are reported[23] to be ~ 0.7 per supercage in NaY, some distant migration might be needed for excited state proton transfer in a supercage since a unit cell with 8 supercages has a molar mass of $\sim 19,000$g. Following the relaxation of photochemically transformed Z* species, back proton transfer process in the ground state may proceed in slower time scales as shown in water.

Careful studies on these photon-initiated proton transfer cycles in organized zeolite media using picosecond fluorescence and microsecond transient diffuse reflectance spectrometers, which are under construction in our lab, may reveal some vital informations on reactions, kinetics, so-called transition state properties, migration and equilibria. Our incomplete study, however, has made us observe some important results. The predominance of Z species with significant existences of the other three protropic species and the observation of near neutral overall zeolite pHs indicate that the major fraction

of 7HQ molecules interact with both acidic and basic sites of zeolite at a given adsorbed position. Excitations of nonzwitterionic species such as deprotonated species also give governing zwitterionic emission, indicating that an excited and ground state proton transfer cycle can be triggered by a photon in organized zeolite media as well as in water.

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