

Study on fluorescence spectra of molecular association of acetic acid-water

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Fluorescence spectra of acetic acid-water solution excited by ultraviolet (UV) light are studied, and the relationship between fluorescence spectra and molecular association of acetic acid is discussed. The results indicate that when the exciting light wavelength is longer than 246 nm, there are two fluorescence peaks located at 305 and 334 nm, respectively. By measuring the excitation spectra, the optimal wavelengths of the two fluorescence peaks are obtained, which are 258 and 284 nm, respectively. Fluorescence spectra of acetic acid-water solution change with concentrations, which is primarily attributed to changes of molecular association of acetic acid in aqueous solution. Through theoretical analysis, three variations of molecular association have been obtained in acetic acid-water solution, which are the hydrated monomers, the linear dimers, and the water separated dimers. This research can provide references to studies of molecular association of acetic acid-water, especially studies of hydrogen bonds.

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Fluorescence spectra of acetic acid as organic solvent, catalyst and quencher have been extensively studied. For example, the study of photochemical degradation and oxidation of ethylene terephthalate indicated that acetic acid as catalyst can make aromatic organic molecules emit fluorescence^[1]. 7-azaindole dimers and complexes of acetic acid and methanol can give off purple fluorescence when they are excited by laser^[2]. Collagen solution with acetic acid in distilled water as solvent exhibited fluorescence with a peak at 415 nm^[3]. Serving as food additive, preservative, and inhibitor, acetic acid also has been well studied at the end of the 20th century^[4], which showed that non-dissociative acetic acid could cause intermolecular acidification and proton transfer. Some investigators carried out the research of acetic acid in biological tissue disease diagnosis. For example, Zelenchuk *et al.* demonstrated that acetic acid molecules made fluorescence spectra of cervical cancer tissue more different from normal tissue so as to be more noticeable and distinguished^[5], which can provide theoretical basis for the diagnosis of cervical cancer.

In recent years, the molecular structures of acetic acid have attracted great interests. Hydrogen bonds play an important role in the process of molecular association of acetic acid. The molecular association of water, ethanol, acetic acid and the spatial structure of protein and nucleic molecule are all related to hydrogen bonds. Some studies showed that acetic acid-water solution was composed of three kinds of molecular structure, hydrated monomers (M_h), linear dimers (LDs), and cyclic dimers (CDs)^[6-8]. By analyzing acetic acid molecular clusters mass spectrometry, Akiyama *et al.* pointed out that the molecules of acetic acid were apt to gathering each other to form the chain structure in aqueous solution^[9]. Through the theories of quantum stoichiometry and molecular dynamics simulation, Chochołoušová

et al. analyzed the influence of acetic acid CDs and made conclusions that CD could not exist in aqueous solution, and acetic acid molecules were prone to form ring-opening multi-molecular association^[10]. In recent years, fluorescence spectra have been used extensively because of high sensitivity and selectivity^[11-14]. By studying acetic acid-water solution with fluorimetry, Liu *et al.* thought that the reason of acetic acid molecule emitting fluorescence is the electron transition of $n \rightarrow \pi^*$ in C=O— fluorophores, and the phenomenon of fluorescence quenching of acetic acid-water solution has been analyzed in theory^[11,12].

In this letter, the fluorescence spectra of acetic acid-water solution excited by ultraviolet (UV) light are studied, and the relationship between fluorescence spectra and the molecular association of acetic acid is discussed. The experimental results are analyzed and discussed. Three variations of molecular association from acetic acid-water solution, M_h , LDs, and water-separated dimers (WSDs) were obtained. The research can provide references to studies of molecular association of acetic acid-water, especially studies of hydrogen bonds.

The lifetime and steady-state-fluorimeter 900 (FLS900) and fluorescence lifetime and steady-state spectrometers which were made in Edinburgh Instruments Ltd. of UK were used in our experiment. The light source in steady-state spectrum was Xe 900, 450-W xenon arc lamp with continuous spectral distribution from 200 to 900 nm.

The samples were tri-distilled water and high performance liquid chromatography (HPLC) acetic acid with the concentration of 36%, which was produced by Sinopharm Chemical Reagent Co., Ltd. In this experiment, the wavelength of exciting light was selected from 240 to 300 nm, the excitation slit was 2 nm, the emission spectrum scanning step was 1 nm, and the scanning

dwel time was 0.1 s at each wavelength.

A non-fluorescence quartz colorimetric utensil, whose length, width, and height are 10, 10, and 40 mm respectively, was used in this experiment. The aqueous solution of acetic acid-water mixture was prepared in the way of the total volume of acetic acid-water solution kept at 3 mL, and the volume percentages of HPLC acetic acid in the water solution were 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, and 100%, respectively. The emission spectrum for each sample was measured over three times. The measured spectra were stable on the whole. All the experiment was performed at room temperature.

According to Liu *et al.*^[11], acetic acid-water can absorb UV light with wavelength around 250 nm. In this experiment, the exciting light with wavelengths from 240 to 300 nm was used to irradiate acetic acid-water solution with the volume percentage of 50%.

When the exciting light wavelength is less than 246 nm, the emission spectrum is unobvious and not easily detected. Figures 1 – 4 show the fluorescence spectra of acetic acid-water solution of 50% volume percentage when excited by the UV light with wavelengths of 246 – 260, 260 – 270, 270 – 280, and 280 – 292 nm, respectively. Each emission spectrum has a Raman peak which is related to the wavelength of exciting UV light. The spectral intensity enhances and the location of the peak moves with the increase of exciting wavelength. In Figs. 1 and 2, there is a central wavelength located at 305 nm, whose spectral intensity is stronger and spectral location is changeless as the exciting wavelength is longer. This is an intrinsic fluorescence peak. When the wavelength is longer than 258 nm, the fluorescence intensity begins to

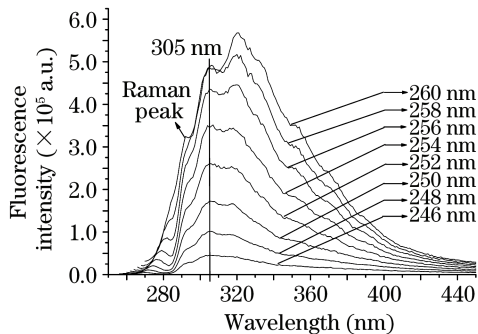


Fig. 1. Fluorescence spectra of acetic acid-water solution of 50% volume percentage excited by the UV light with wavelengths of 246 – 260 nm.

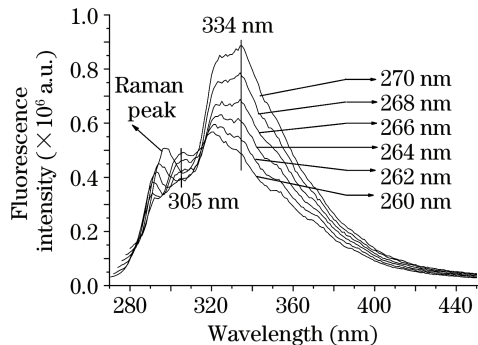


Fig. 2. Fluorescence spectra of acetic acid-water solution of 50% volume percentage excited by the UV light with wavelengths of 260 – 270 nm.

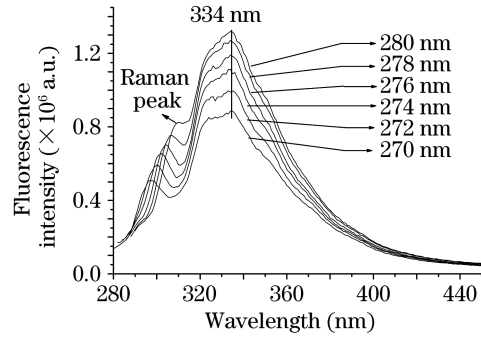


Fig. 3. Fluorescence spectra of acetic acid-water solution of 50% volume percentage excited by the UV light with wavelengths of 270 – 280 nm.

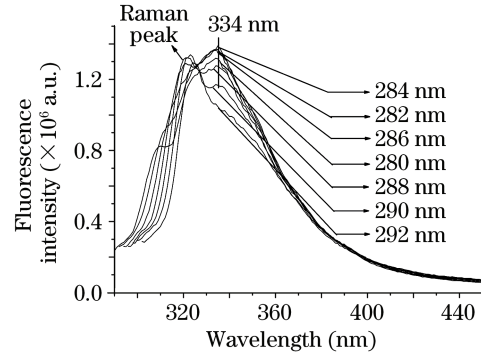


Fig. 4. Fluorescence spectra of acetic acid-water solution of 50% volume percentage excited by the UV light with wavelengths of 280 – 292 nm.

decrease, which means that the fluorescence peak at 305 nm can obtain the strongest intensity when the acetic acid-water solution is excited by the 258-nm light. When the wavelength increases to 270 nm, Raman scattering begins to have greater influence on the fluorescence peak at 305 nm, at the same time, the fluorescence peak at 334 nm appears and its intensity is stronger as the exciting light wavelength is longer. In Figs. 3 and 4, Raman peak gradually covers the fluorescence peak at 305 nm, and the fluorescence intensity with the peak at 334 nm continues to enhance with the increase of exciting wavelength. The intensity comes to be weak while the incident light wavelength is longer than 284 nm, which means that the fluorescence intensity gets the strongest value when the acetic acid-water solution is excited by the 284-nm light. As the exciting light wavelength increases to 292 nm, the fluorescence peak at 334 nm is affected and covered by the Raman peak gradually.

The fluorescence spectra of acetic acid-water solution with 10 different volume percentages induced by exciting light with the wavelength of 284 nm are shown in Fig. 5. For the fluorescence emitting area around 334 nm, there is a nonlinear relation between the fluorescence intensity and the acetic acid volume percentage. The fluorescence intensity enhances with the increase of acetic acid volume percentage, and attains the maximum when the acetic acid volume percentage is 80% and then decreases when the percentage is more than 80%. Comparing the fluorescence intensities of solutions with different volume percentages at 334 nm, the relation between the fluorescence intensity and the volume percentage is shown in Fig. 6. The molar percentage of acetic acid is

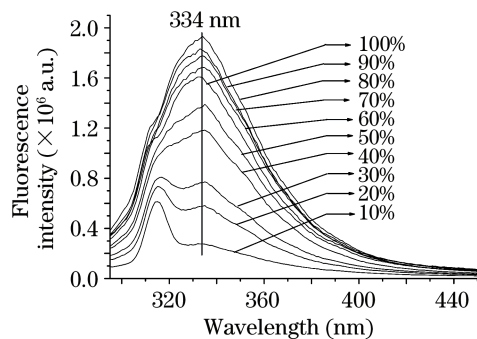


Fig. 5. Fluorescence spectra of acetic acid-water solution with various volume percentages induced by the exciting light with wavelength of 284 nm.

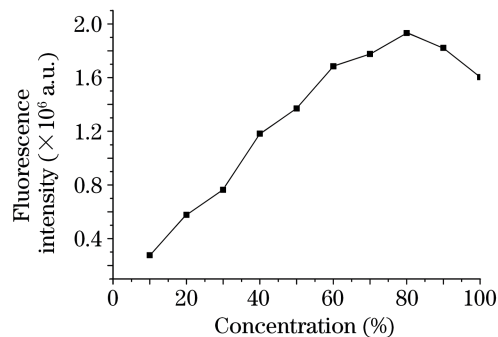


Fig. 6. Relationship between fluorescence peak intensity and acetic acid volume percentage at 334 nm.

is about 55% when the acetic acid volume percentage is 80%, i.e., the ratio of molar volume percentage of acetic acid molecules and water molecules is about 1:1, approximately mixed by the same molar volume percentage.

Fluorescence spectra of acetic acid-water solution with 10 various volume percentages induced by the exciting light with the wavelength of 248 nm are showed in Fig. 7. According to Fig. 7, when the exciting wavelength is 248 nm, the fluorescence peak of acetic acid-water solution at 305 nm is the most prominent characteristic peak whose fluorescence intensity reaches the maximum when the acetic acid volume percentage is 50%.

The relationship between the fluorescence peak intensity and the volume percentage is shown in Fig. 8, which indicates that the fluorescence peak intensity at 305 nm enhances with the increase of acetic acid volume percentage, attains the maximum at 50% volume percentage, and then weakens with it, while upturns as the acetic

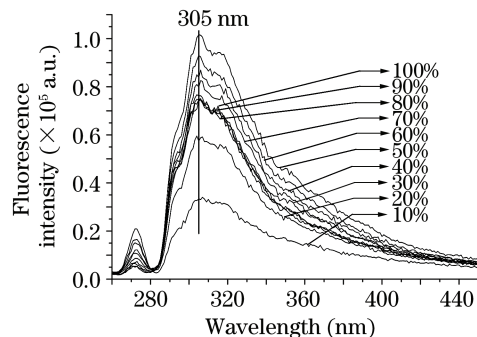


Fig. 7. Fluorescence spectra of acetic acid-water solution with various volume percentages induced by the exciting light with wavelength of 248 nm.

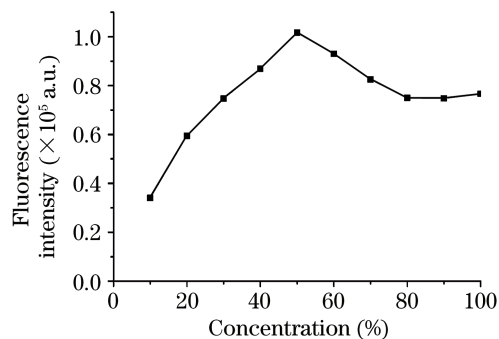


Fig. 8. Relationship between fluorescence peak intensity and acetic acid volume percentage at 305 nm.

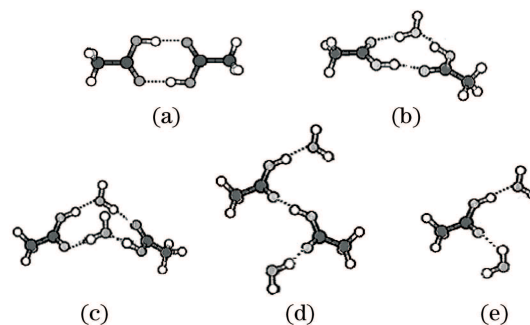


Fig. 9. Molecular associations in acetic acid-water solution. (a) CD; (b) ac1w (WSD); (c) ac2w (WSD); (d) LD; (e) M_h .

acid volume percentage is more than 80%.

The existing research results^[10,15–21] have indicated that in light water environments, water molecules interacted with CDs (see Fig. 9(a)), separated original hydrogen bonds and formed association WSD through new hydrogen bonding reaction. With the growth of the numbers of water molecules, more and more different WSDs formed, of which the maximal probabilities of occurring were ac1w and ac2w — acetic acid CD separated by one and two water molecules, forming new cyclic structures through hydrogen bonds, as shown in Figs. 9(b) and (c). Gathering of water molecules can break in hydrogen bond of cyclic structure and form LD with open structure, as shown in Fig. 9(d). When the molar percentage of acetic acid diluted by water is 50%, equivalent to the volume percentage of 77%, the volume percentage of LD obtains the maximum. Keeping on diluting, the hydrogen bond between two water molecules in LD is also separated by water molecules, and the new molecular association M_h is formed owing to abundant water molecules, as shown in Fig. 9(e). There are three kinds of hydrogen bond reactions in both association LD and WSD, $C=O \cdots H-O$ between acetic acid molecules and water molecules, $O-H \cdots O$ and $C=O \cdots H-O$. The difference between them is that the structure of WSD is closed-end cycle while the structure of LD is an open chain, which causes the discrepancy of bonding angle, bonding length, and bonding energy of hydrogen bonds formed among homogeneity atoms in different associations, and forms various hydrogen bond reaction.

When the acetic acid volume percentage is about 80%, the association LD shown in Fig. 9(d) is the primary molecular structure of solution. When it is less than 80%, some LDs transform into M_h , while for the percentages more than 80%, LD begins to transform into

WSD. Thereby, the volume percentage of LD reaches its maximum as that of the acetic acid is about 80%. Analysis suggests that in all experimental spectra, the fluorescence intensity of 334 nm attains the maximum with 80% solution volume percentage. This is relevant to LD which reaches the maximal volume percentage at this state. Whereas the decrease of fluorescence intensity with acetic volume percentages more than 80% is related to the transformation of molecular association from LD to WSD.

When the UV light with the wavelength of 284 nm irradiates acetic acid-water solutions of various volume percentages, the excited fluorescence intensity varies at volume percentages more and less than 80%, but the location of spectral peak is changeless obviously. Therefore, the transformation of molecular association from LD to WSD does not cause alteration of fluorescence energy level intervals of emission electrons in acetic acid molecules. Because hydrogen bond formed by fluorophore in the ground state before being excited can alter the molar absorptivity, the decrease of fluorescence intensity at 334 nm when the acetic volume percentage is more than 80% shows that the molar absorptivity emitted by fluorescence at 334 nm corresponding to LD is larger than that of WSD.

When the acetic acid volume percentage is less than 50%, the association M_h shown in Fig. 9(e) is the prominent molecular structure. In this experiment, the changes of fluorescence peak intensity with acetic acid volume percentage appear apparent diversity at more and less 50%, which is related to the transition of acetic acid solution association from M_h to LD. It is analyzed that changing the association of hydrogen bond reaction has brought different quantum yield $Y_F = \frac{N_{em}}{N_{ab}}$, where N_{em} is the emission photon number, and N_{ab} is the absorption photon number. The quantum yield of fluorescence is the important luminescent parameter of fluorescent materials. The fluorescence intensity of solution is $F = 2.3Y_F I_0 \varepsilon bc$, where I_0 is the incident light intensity, b is the length of liquid pools, c is the concentration of solution, and ε is the molar absorptivity. With the exciting light of 248 nm, the fluorescence quantum yields of solution with volume percentages of 40%, 50%, 60%, 80%, and 90% are 2.16%, 2.51%, 2.24%, 1.97%, and 2.02%, respectively. The fluorescence quantum yield of LD is lower than that of M_h , which gives rise to the declination of fluorescence intensity at acetic acid volume percentages more than 50%. Similarly, the relation between fluorescence intensity at 305 nm and solution volume percentages of more and less than 80% is corresponding to another change of intermolecular association, i.e., the transformation from LD to WSD. Due to the difference in hydrogen bond reaction, the fluorescence quantum yield of WSD is a little higher than that of LD, and the fluorescence intensity upturns.

From the above discussion, we can draw the following conclusions. Firstly, when the exciting light wavelength is longer than 246 nm, excitation spectra of acetic acid-water solution can be observed. There are two characteristic fluorescence peaks located at 305 and 334 nm. The optimal excitation wavelengths of the two fluorescence peaks are 258 and 284 nm, respectively. Secondly, when the acetic acid-water solutions are induced by UV light with the wavelength of 284 nm, the change of fluorescence

intensity of fluorescence peak at 334 nm is corresponding to the transformation of molecular association from LD to WSD as the acetic acid volume percentage is more than 80%. Thirdly, when the acetic acid-water solutions of different volume percentages are induced by the UV light with the wavelength of 248 nm, there is obvious difference of relationship between fluorescence intensities less and more than 50% and 80% around the fluorescence peak at 305 nm and the volume percentage of acetic acid-water solution, which corresponds to the transformation of molecular association $M_h \leftrightarrow LD$ and $LD \leftrightarrow WSD$, respectively.

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