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Role of sodium sulfite and β cyclodextrin as preservative of photographic developing agents

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Abstract

Para-aminophenol, *N*-methyl para-aminophenol sulfate and pyrogallol are used as photographic developer and their fluorescence intensity has been quenched in presence of acid, base, KCl, KBr, KI and oxygen. In presence of sodium sulfite fluorescence intensity of the compounds gradually increases with time. It has been established that in the steady-state fluorescence of these photographic developers the role of sodium sulfite is oxygen scavenger. In presence of β cyclodextrin, fluorescence intensity of these photographic developers increases due to steric restriction. Location and nature of the surrounding medium of the photographic developers in cyclodextrin have been ascertained from quenching study. The presence of two rotamers of aminophenols and substituted aminophenols has been established from fluorescence anisotropy study. The relative stability of the rotamers and the attachment of the compounds in the cavity of β cyclodextrin have been established on the basis of semiempirical AM1-SCI calculation.

Keywords: Photographic developers; Quenching; Preservative; Rotamer; Steric restriction

1. Introduction

A photographic emulsion when exposed to light, the silver salt (silver bromide, chloride or iodide) become activated and when the emulsion is placed in a developing solution the exposed, “activated” particles of silver salt are reduced chemically to black metallic silver [1–4], leaving the unexposed particles of silver salt unchanged. The conversion of silver ion into metallic silver is an oxidation–reduction process [1] and for the reaction one or more reducing agents—which photographers call “developers” are necessary. Some basic components of developers are *N*-methyl *p*-aminophenol sulfate (MAP), *p*-aminophenol (AP) and pyrogallol (PY), etc. As a result of the redox process, the basic components are converted into their oxidised form. When the basic components of developing solution are hydroquinone, resorcinol and catechol, the products of photochemical reactions are quinones [5].

In photography, the developing solution has been prepared by using alkali as activator, KBr as restrainer and sodium sulfite as preservative [6] in addition to the basic components of the developers. The photographic developers are generally neutral or slightly acidic in nature and hence activators are used to initiate the developing action. At appropriate concentrations, bromide ions restrain the rate of fog formation more than the rate of development in image areas. Such restrainer selectively usually improves picture quality. Selective restrainers of this type are called development antifoggants. Unintentional oxidation of the chemical reducing agent by oxygen dissolved in the developer solution may not only alter development kinetics but may also give coloured by products that can produce unattractive strains in the developed material. The role of preservative is to stop this oxidation. In stop bath treatment, the oxidation of the developing agents is checked by addition of 0.5% acetic acid.

In the photophysical studies of organic compounds, sodium sulfite is used as oxygen scavenger [7,8] and it enhances the fluorescence intensity of the compounds. Oxygen is a good quencher in singlet and triplet state

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photophysical studies of dyes [9,10]. The Stern Volmer constants of oxygen quenching predict that it is an effective quencher to alter the emission intensity of the fluorophore from S_1 and T_1 state.

Cyclodextrin (CD) is linked glucopyranose rings forming doughnut-shaped compound [11]. They are interesting microvessels for appropriate sized molecules. The cyclodextrin molecules have an internal cavity accessible to suitable guest molecules through an opening of 7.8 Å for β CD and the depth of β CD is 7.9 Å [12,13]. Depending on the cavity size, CDs are capable of encapsulating different guest molecules. The reduced polarity and restricted space provided by the CD cavity markedly influence a number of photochemical/photophysical properties [14–17].

The effects of sodium sulfite, potassium bromide, acid and alkali on the fluorescence spectrum of MAP, AP and PY have been investigated. Effect of β CD on the steady-state emission of the above compounds have also been investigated. The compounds have been optimized geometrically by using the semiempirical AM1 method to calculate different energy parameters [18]. The ground state energy, dipole moments in the ground and excited state and the transition energies to different excited electronic state of the compounds have been determined by the semiempirical AM1-SCI method [19]. From the quantum chemical calculations, an idea has been drawn about the stability of the rotamer as well as propositions have been given about the attachment of the compounds to the β CD cavity. Photophysical studies of the developers in β CD and sodium sulfite solution have been done to justify the use of β CD in exchange of sodium sulfite in photography.

2. Experimental

AP, MAP and PY were of E. Merck products. These were crystallized thrice from their alcohol water mixture before use. Their characterization and purity were checked by emission measurement and the impurities were absent. Good quality of β CD was procured from Fluka and were used as received without further purification. Sodium sulfite, potassium chloride, potassium bromide and potassium iodide were of E. Merck product. Triply distilled water was used for the preparation of the experimental solutions. All the experiments were performed with air-equilibrated solutions. Shimadzu 1700 model UV–vis spectrophotometer and Spex Fluorolog F-III A spectrofluorimeter were used for the absorption and fluorescence measurement, respectively. The steady-state fluorescence anisotropy measurements were performed with a Hitachi spectrofluorimeter (F-4500) at 298 K and for anisotropy measurements the excitation and emission bandwidths were 2.5 nm each. The steady-state fluorescence anisotropies (r) were calculated using the following equation [10]:

$$r = \frac{I_{VV}(\lambda) - G(\lambda)I_{VH}(\lambda)}{I_{VV}(\lambda) + 2G(\lambda)I_{VH}(\lambda)} \quad (1)$$

where I_{VV} and I_{VH} are the intensities obtained with the excitation polarizer oriented vertically and the emission polarizer oriented vertically and excitation polarizer oriented in vertical and emission polarizer oriented in horizontal, respectively. $G(\lambda)$ is an instrumental factor representing the polarisation characteristics of the photometric system and is given by:

$$G(\lambda) = \frac{I_{HV}(\lambda)}{I_{HH}(\lambda)} \quad (2)$$

I term refer to parameters similar to those mentioned above for the horizontal position of the excitation polarizer.

For the geometry optimization, we have used the semiempirical AM1 method and for the determination of ground state energy, dipole moments in the ground and excited state and the transition energies to different excited electronic state, we have used the semiempirical AM1-SCI method supported by Hyperchem 5.01 package from Hypercube Inc., Canada. Utility of the AM1 and AM1-SCI method in getting reliable structural data has already been established [20,21].

3. Results and discussion

The absorption and fluorescence spectra of AP, MAP and PY have been studied at different pH. Absorbance of neutral species at $\lambda_{max}^{abs} = 295$, 300 and 266 nm for AP, MAP and PY, respectively, decreases with gradual addition of acid and alkali in the aqueous solution of the compounds. Fluorescence intensity of these compounds gradually decreases with increasing concentration of acid as well as alkali. In presence of alkali, phenolate ions are formed which is non-fluorescent, so concentration of neutral species in the medium decreases and hence fluorescence intensity also decreases. On the other hand, with gradual addition of acid fluorescence intensity gradually decreases, this is due to proton induced quenching [22]. As in presence of alkali phenolate ions are formed [23], so alkali helps to initiate the redox reaction in photography.

The absorption spectra of the compounds (AP, MAP and PY) in the presence and absence of KCl, KBr and KI in the aqueous solution show no observable change in spectral shape. With increasing concentration of KCl, KBr and KI quenching of fluorescence [24] of AP, MAP and PY occurs. The Stern Volmer quenching constant (K_{SV}) for KBr are 28.7, 40.2 and 48.3 $dm^3\ mol^{-1}$ (±10% error in each case) for MAP, AP and PY, respectively (Table 1). Using KCl and KI as

Table 1
Stern Volmer constants (K_{SV}) of quenching of fluorescence of photographic developers in presence of Cl^-, Br^- and I^-

Quencher	*N*-methyl *p*-aminophenol ($dm^3\ mol^{-1}$)	*p*-Aminophenol ($dm^3\ mol^{-1}$)	Pyrogallol ($dm^3\ mol^{-1}$)
KCl	25.8	38.3	46.1
KBr	28.7	40.2	48.3
KI	32.5	46.8	52

Table 2
Wavelength of absorption maximum (λ^{abs}_{max}) and fluorescence maximum (λ^{fl}_{max}) of photographic developers in different media

Compounds	In water		In presence of Na_2SO_3		In β cyclodextrin medium	
	λ^{abs}_{max} (nm)	λ^{fl}_{max} (nm)	λ^{abs}_{max} (nm)	λ^{fl}_{max} (nm)	λ^{abs}_{max} (nm)	λ^{fl}_{max}/nm
N-methyl *p*-aminophenol	300	385	300	388	300	378
p-Aminophenol	295	370[a]	292	394	292	377
Pyrogallol	266	352	266	354	266	349

[a] It represents the rotamer having torsional angle 42°.

quencher, the K_{SV} values for AP are 38.3 and 46.8 $dm^3\ mol^{-1}$ (±10% error), respectively (Table 1). So, it is clear that in photophysical study of photographic developers the role of restrainer is as quencher.

3.1. Excited state properties of the developers in sodium sulfite solution

On exciting the aqueous solution of AP, MAP and PY, at λ^{abs}_{max} = 295, 300 and 266 nm, respectively (Table 2), the absorbance and fluorescence intensity gradually decreases with time. The absorption spectra of the compounds show no observable change in presence and absence of sodium sulfite. The fluorescence intensity of the compounds in presence of sodium sulfite gradually increases with time. The rate constant (k) of enhancement of fluorescence intensity of the fluorophore have been evaluated using the equation $F = F_0 e^{kt}$. When $\ln F/F_0$ plotted against, t, yields good straight lines, justifying 1st order nature of the enhancement of fluorescence. There is no change in rate constant ($2.4 \times 10^{-2}\ min^{-1}$) with varying concentration of sodium sulfite.

In presence of Na_2SO_4 and even reducing agent $Na_2S_2O_4$, after spontaneous exposure of light at λ^{abs}_{max}, the behaviour of the compounds remains same as that in aqueous solution, i.e. fluorescence intensity decreases with time. In solution chemistry Na_2SO_3 exerts four activities: (1) it exhibits salt effect, (2) it is used as reducing agent in many organic reactions [25], (3) it also enhances pH of the medium [26] and (4) it removes dissolved oxygen.

As Na_2SO_4 and $Na_2S_2O_4$ have no influence on the fluorescence spectrum of AP, MAP and PY, so the reason of enhancement of fluorescence intensity in presence of Na_2SO_3 is neither salt effect nor reducing effect. As with increasing or decreasing pH of the medium fluorescence intensity decreases, so Na_2SO_3 do not exert pH effect to fluorescence intensity of the medium.

In nitrogen atmosphere, the aqueous solution of AP, MAP and PY exhibit no change in fluorescence intensity with time. So, the role of sodium sulfite is oxygen scavenger.

In presence of sodium sulfite, the fluorescence intensity of AP was enhanced with time having 13 nm red shifts in λ^{fl}_{max} (381–394 nm, Fig. 1) whereas for MAP and PY λ^{fl}_{max} has 3 and 2 nm red shift, respectively (Table 2). An attempt has been taken to explain the cause of shift from quantum chemical calculations.

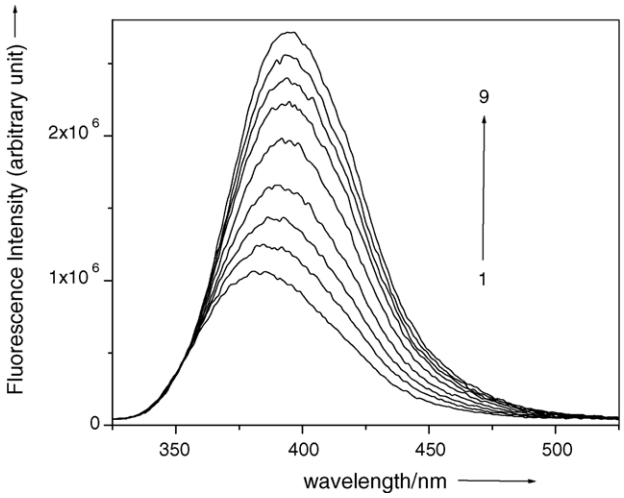

Fig. 1. Fluorescence spectra of *p*-aminophenol in presence of sodium sulfite at 303 K at different time. (1–9) represent: (1) 0 min, (2) 5 min, (3) 10 min, (4) 15 min, (5) 20 min, (6) 25 min, (7) 30 min, (8) 35 min and (9) 40 min.

3.2. Effect of microheterogeneous environment in preventing oxygen quenching

The absorbance of MAP in β CD medium increases with gradual addition of β CD in the solution (Fig. 2a). The fluorescence intensity of MAP enhances with blue shift on gradual addition of β CD in the probe solution (Fig. 2b). Maximum 10 mM concentration of β CD has been maintained in our experimental solutions and at 10 mM concentration of β CD the shift in λ^{fl}_{max} for MAP is 7 nm (Table 3).

With gradual addition of β CD in the aqueous solution of AP (Fig. 3) and PY absorbance gradually increases and their fluorescence intensity also increases with small blue shift in λ^{fl}_{max}. For AP, the shift is 4 nm whereas for PY the shift is 3 nm (Table 3). The enhancement of fluorescence intensity, may be due to imposition of some steric restriction on the above two

Table 3
Energy values and dipole moment of *p*-aminophenol and *N*-methyl *p*-aminophenol in ground and excited state at different torsional angles

	p-Aminophenol		*N*-methyl *p*-aminophenol	
	0°	42°	0°	42°
E_{S_0} ($eV\ mol^{-1}$)	−68.76	−68.75	−92.16	−92.16
E_{S_1} ($eV\ mol^{-1}$)	−65.26	−65.23	−88.58	−88.59
μ_{S_0} (D)	2.09	1.91	2.45	2.76
μ_{S_1} (D)	2.22	2.00	2.09	2.94

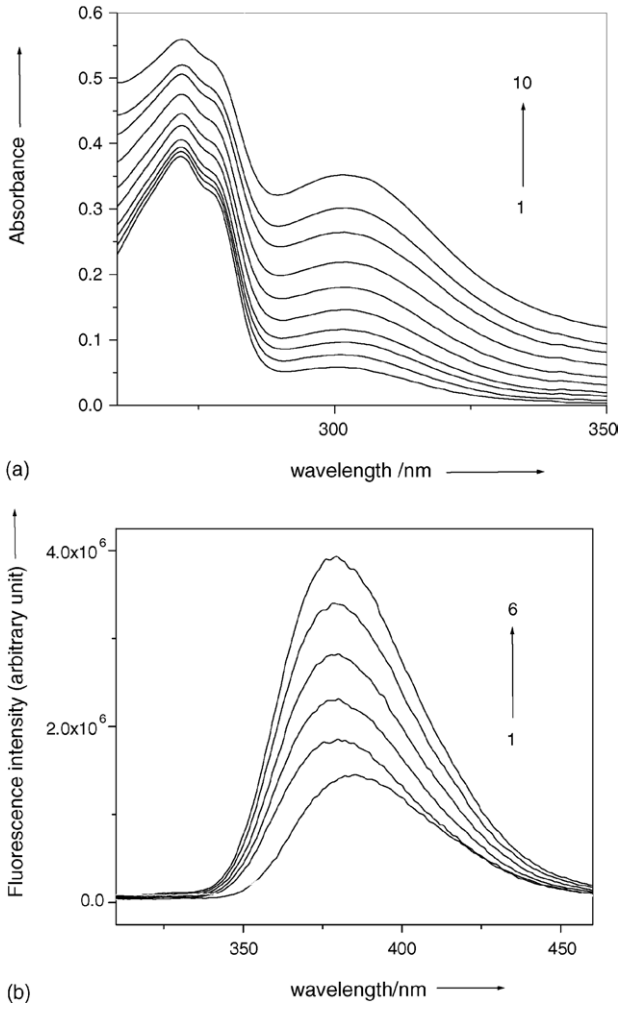

Fig. 2. (a) Absorption spectra of N-methyl p-aminophenol sulfate in β cyclodextrin medium; [β CD]: (1–10); (1) 0 mM, (2) 1.52 mM, (3) 3.06 mM (4) 4.52 mM, (5) 5.36 mM (6) 6.12 mM, (7) 7.62 mM, (8) 8.26 mM, (9) 9.13 mM and (10) 10.00 mM. (b) Fluorescence spectra of *N*-methyl *p*-aminophenol sulfate in β cyclodextrin medium; [β CD]: (1–6); (1) 0 mM, (2) 4.05 mM, (3) 5.40 mM, (4) 6.86 mM, (5) 8.58 mM and (6) 10.00 mM.

compounds. As the fluorescence maximum has a blue shift so from the photophysical studies of the compounds in solvents of different polarity, it may be guessed that the compounds are associated to a less polar environment compared to water. Therefore, the incorporation of MAP, AP and PY in the β CD cavity is likely.

3.3. Quenching study

The effect of CDs on collision quenching processes of the compounds has been studied in detail. In most cases, the quenching is inhibited by inclusion in CDs [27,28], since the trapped molecule is less accessible to the quencher. Steady-state fluorescence quenching study of AP, MAP and PY has been performed at 10 mM concentrations of β CD solutions with increasing concentration of KI (0.001–0.01 M). For AP, MAP and PY, it has been observed that the fluorescence

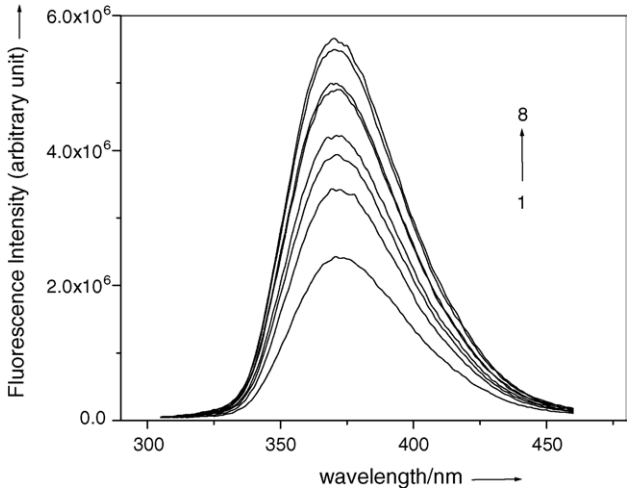

Fig. 3. Fluorescence spectra of *p*-aminophenol in β cyclodextrin medium; [β CD]: (1–8); (1) 0 mM, (2) 1.52 mM, (3) 3.23 mM, (4) 4.94 mM, (5) 6.22 mM, (6) 7.37 mM, (7) 8.72 mM and (8) 10.00 mM.

intensity remains same after addition of KI in the solution and there is no change in fluorescence intensity with increasing concentration of KI. So, from this study we can conclude that the compounds are associated within the cavity of β CD.

From semiempirical (AM1) calculation, the molecular diameters of AP, MAP and PY have been calculated for the optimized geometry of these compounds. It has been observed that the maximum diameter of MAP, AP and PY is 7.8, 6.6 and 5.9 Å, respectively. The lateral diameter of MAP and AP is 4.36 Å. So, the compounds can enter in the CD cavity easily. Quenching results also support the above explanation. Though MAP, AP and PY enter into the cavity, there has less shift in λ_{max}^{fl} compared to that in water. These results are a clear indication of the loose fit of compounds within the cavity of β CD (Fig. 4), which is large enough to include the guest together with low-ordered water molecules [29].

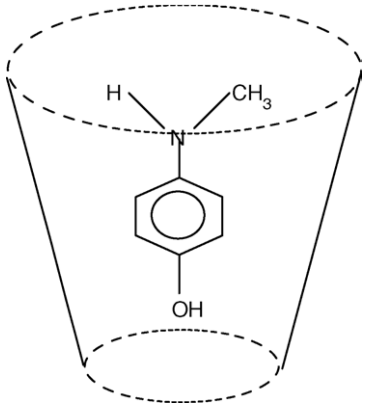

Fig. 4. Proposed model of inclusion of *N*-methyl *p*-aminophenol into the β cyclodextrin cavity.

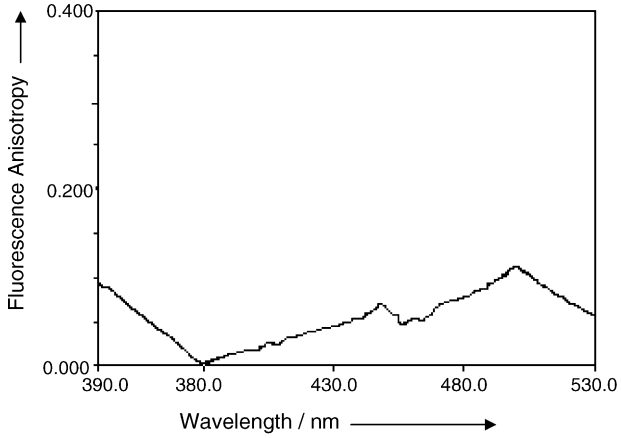

Fig. 5. Fluorescence anisotropy of *p*-aminophenol at different wavelength.

3.4. Anisotropy study

Fluorescence anisotropy depends upon the rotational diffusion of the fluorophore and the rotational diffusion changes with changing viscosity of the medium as well as size and shape of the diffusing species. Generally, fluorescence occurs from the lowest singlet excited state and hence fluorescence anisotropy is independent of emission wavelength. For the compounds having two rotamers (Fig. 6) in the excited state, fluorescence anisotropy changes depending upon the emission wavelength [10] of the rotamers. The fluorescence anisotropy of PY in aqueous solution is 0.01 and enhances to 0.12 at 10 mM concentration of β CD. So, inclusion of pyrogallol in β CD cavity has been confirmed.

For AP and MAP, the change in fluorescence anisotropy is complex. The fluorescence anisotropy value decreases with increasing wavelength and becomes zero at λ^{fl}_{max} and then increases after passing through zero (Fig. 5). This dependence was attributed to the two excited states of AP and MAP. So, existence of two rotomers (Fig. 6) has been confirmed in the excited state of *p*-aminophenol and *N*-methyl *p*-aminophenol. From the normalized fluorescence spectra of AP in aqueous solution in absence and presence of Na_2SO_3 it has been observed that two rotamers IIA and IIB of AP have λ^{fl}_{max} at 370 and 394 nm, respectively.

3.5. Quantum chemical calculations and intramolecular rotation

The ground state (S_0) geometries of the molecules have been optimized using the AM1 method. Subsequently, AM1-SCI (singly excited configuration interaction) has been performed to get the ground state energy (E_g), dipole moments in the ground and excited states and the transition energies ($\Delta E_{i\rightarrow j}$) to different excited electronic states. For the CI calculations, we have considered only the single electronic transitions between all the configurations (around 100 in number) within a predefined energy window (13–14 eV, depending on the molecular system) from the ground state.

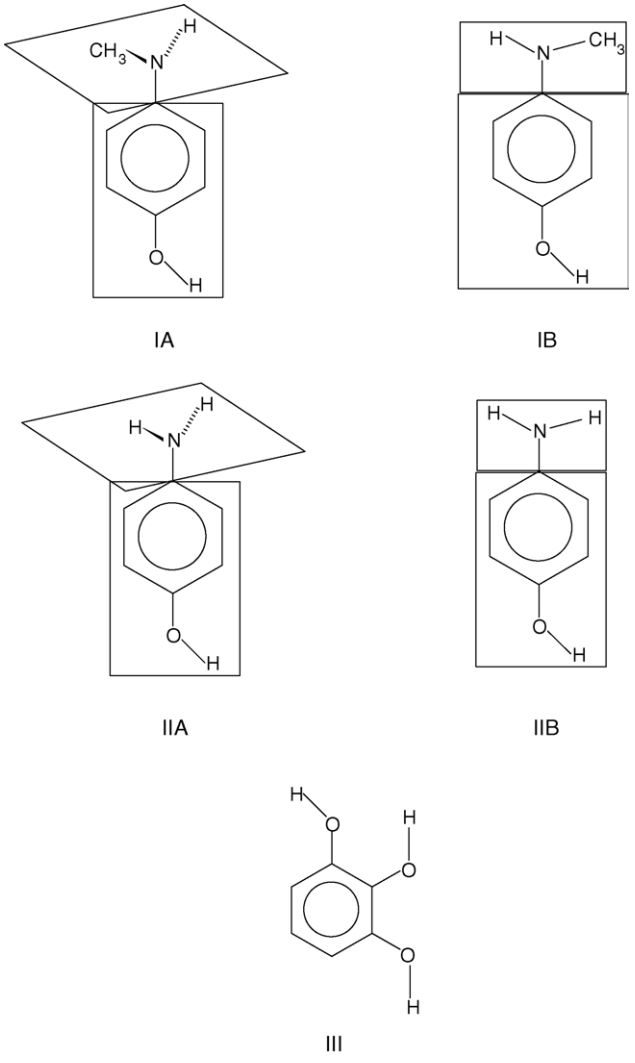

Fig. 6. Structure of (IA) non-planar *N*-methyl *p*-aminophenol, (IB) planar *N*-methyl *p*-aminophenol, (IIA) non-planar *p*-aminophenol, (IIB) planar *p*-aminophenol and (III) pyrogallol.

To find the relative stability of the different rotational conformers (rotamers), the torsional angle between the benzene plane and the plane, which contain the $–NH_2$/−NHMe group, has been preset to different values followed by a full optimization of all other geometrical parameters.

It is known [30–33] that aniline is nonplanar in the ground electronic state with the $–NH_2$ plane being at about 42° with respect to the ring plane. It has also been shown that the hydroxyl group in phenol lies in the plane of the ring [34]. For MAP, a bulky methyl group is present on the nitrogen atom and hence it can never attain the planarity. From AM1-SCI calculation, it has been observed that the energy difference $\left(\Delta E_{S_0\rightarrow S_1}\right)$ of MAP is less (Table 3) for the rotamer having torsional angle 42° (IA). So, for MAP, it is expected that there is no shift in λ^{fl}_{max} in sodium sulfite solution and the expectation agreed with the experimental observation.

AP has two rotational isomers (Fig. 6) [35]: (1) non-planar C_S point group (IIA) and (2) planar C_{2V} point group (IIB). In

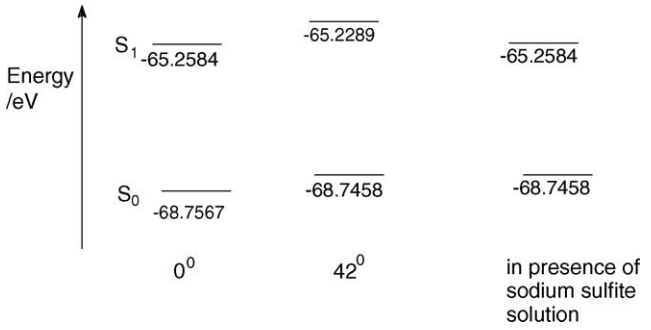

Fig. 7. Energy level diagram of *p*-aminophenol in vacuum when (1) torsional angle is 0°, (2) torsional angle is 42° and (3) in presence of sodium sulfite.

case of many *p*-substituted anilines it has been observed that the UV excitation spectra conforms more to the C_{2V} symmetry point group than the C_S [29]. As in presence and absence of Na_2SO_3 absorbance of the compounds remains same and hence the energies and properties of the ground state (S_0) of AP remains unaltered in presence of sodium sulfite. Usually AP remains in C_S point group as –NH_2 prefers the arrangement in which it makes an angle 42° to the phenyl ring (IA). In presence of sodium sulfite, the nonplanar (C_S) is converted into the planar (C_{2V}) arrangement after prolong irradiation of AP at $\lambda_{max}^{abs} = 297$ nm. After removal of the light source, the C_{2V} rotamer (IIB) is converted into C_S rotamer (IIA) and hence the interconversion of the rotamer occurs due to continuous light exposure on AP in presence of sodium sulfite whereas in absence of sodium sulfite the quenching of AP by dissolved oxygen predominates and such conversion does not occur. Therefore, for AP in presence of sodium sulfite, the energy of S_0 may be equal to the energy of S_0 of 42° rotamer and the energy of S_1 may be equal to the energy of S_1 of 0° rotamer when it is continuously irradiated on the λ_{max}^{abs}. From this new type of arrangement (Fig. 7) in the energy levels of AP, there is 3 nm shifts in λ_{max}^{fl} in vacuum. As in the presence of sodium sulfite solution, the excited singlet state (which has higher dipole moment, Table 3) of AP will be stabilized more compared to the ground singlet state, so the red shift will be more in presence of sodium sulfite solution compared to the vacuum due to identical arrangement in energy levels.

Greater is the dipole moment in the energy levels, solvent dipoles will stabilize these energy levels in greater extent by the reorientation of the solvent dipoles. AM1-SCI calculations data (Table 3) predicts that the dipole moment of excited states of MAP is high when torsional angle is 42° (for 42° rotamer $\mu_{S_1} = 2.94$ D and for 0° rotamer $\mu_{S_1} = 2.76$ D) and hence this arrangement is preferred in emission study in polar atmosphere surrounding MAP. As the dipole moment of the excited state of AP is higher compared to that in ground state, so, S_1 stabilises more compared to S_0 with increasing polarity of the solution. As a result a large red shift in the fluorescence spectrum of AP is expected with increase in polarity of the medium and that is observed in the experiment. Similarly from the theoretical calculations of AP the dipole moment of 0° rotamer ($\mu_{S_0} = 2.09$ D and $\mu_{S_1} = 2.22$ D) is greater compared to 42° ($\mu_{S_0} = 1.91$ D and $\mu_{S_1} = 2.00$ D) rotamer (Table 3). So, on continuous exposure to AP the instantaneous conversion in the excited state from C_S to C_{2V} can also be explained from dipole moment values.

4. Conclusion

In presence of sodium sulfite, the enhancement of fluorescence intensity of the photographic developers occur due to removal of oxygen and for AP the red shift in fluorescence maxima occur due to conversion from C_S to C_{2V} point group. In β CD medium, oxygen quenching is prevented due to incorporation of MAP, AP and PY inside the cavity. Like sodium sulfite, β CD has an equal effect on preventing photographic developers from the contact of oxygen. So, β CD may be used as a preservative in photographic formula in exchange of sodium sulfite. For MAP the dipole moment of ground and excited state is maximum when torsional angle is 42°. For AP, the dipole moment is maximum when the torsional angle is 0°, and thus, the instantaneous conversion from C_S to C_{2V} occurs. From the data of energy levels and dipole moments the most stable rotamer of MAP has torsional angle 42°. In presence of sodium sulfite, AP exhibit a new type of arrangement of the energy levels.

The development kinetics may be controlled on addition of β CD with varying concentration of it. As in higher concentration of β CD the developers are encapsulated in the cavity, so it may be used in stop bath treatment also.

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