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SYNTHESIS, CHARACTERIZATION OF ORGANO CHEMO SENSORS AND THEIR APPLICATION FOR ANION DETECTION IN WATER SAMPLES

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ABSTRACT

Organo chemo sensors were used to detect fluoride ions in water samples and were synthesized by mixing two compounds in a 1:1 ratio with constant stirring for two hours using a stirrer with the addition of acetic acid and ethanol. The products were checked for a single spot using TLC paper. The experiment was taken further for the detection of fluoride ions by making a solution of chemo sensor and water sample at a 1:2 ratio and checked using a spectrophotometer and colorimeter. The values of absorbance were then compared with the standard solution containing fluoride ions. The formation of H - F bonding between the chemo sensors and fluoride ions in the water samples was confirmed. The results indicate the presence of fluoride ions in terms of ppm in the different water samples taken.

Keywords: Chemo Sensors, UV-Vis Spectrophotometer, Fluoride Ion, Colorimeter, Spectral Data.

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INTRODUCTION

Fluoride ions help to prevent cavities and demineralization of teeth by strengthening enamel and protecting it against tooth decay.[1] This class of compounds was discovered by Hugo Schiff in 1864.[2] When F^- ions were detected, the chemo sensor immediately displayed a strong color shift.[3] In this work chemo sensors contain an active azomethine group (–CH=N-) group.[4-6] The condensation reactions used for the preparation of chemo sensors are carried out efficiently in a solvent medium.[7,8] These organo chemo sensors are superior chelators, and because of their special quality, they have a place in both qualitative and quantitative analysis of ions in aqueous media.[9] They were also used as optical sensors in chromatographic applications for sensitive and selective applications.[10] Various chemo sensors that can detect fluoride ions were synthesized.[11-14] When F^- ions were detected, the chemo sensor immediately displayed a strong color shift. The consumption wise fluoride might be harmful or beneficial depending upon the amount of intake.[15]

EXPERIMENTAL

Materials and Methods

All chemicals used were procured from Sigma Aldrich. The IR spectra of the compounds were recorded on a PERKIN ELMER diamond top plate FT-IR spectrometer. The ^{1}H (400 MHz) NMR was recorded on a JNM ECZ 400 NMR spectrometer with $CDCl_3$. Crystallographic structure determined using RIGAKU MINIFLEX XRD instrument. Characterization of newly synthesized compounds was recorded on a CARY 60 UV-Vis spectrophotometer. The formed compound was checked by TLC on pre-coated silica gel aluminum plates using hexane: ethyl acetate (3:2).

General Procedure for Synthesis of Organo Chemo Sensors 3A-3G

For the synthesis of organo chemo sensors 3A-3G, substituted aromatic aldehyde and amine in the ratio 1:1 was stirred for two hours using a magnetic stirrer at room temperature with the addition of acetic acid and

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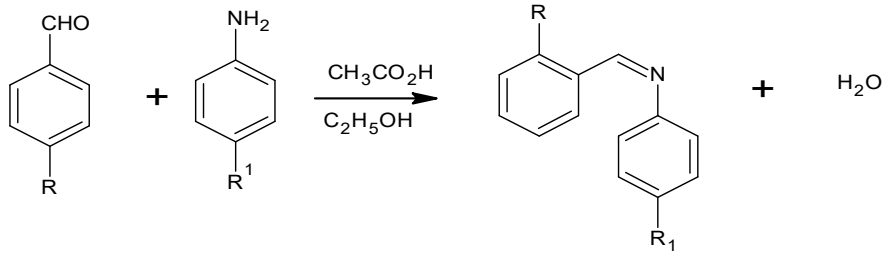
ethanol in a round-bottomed flask. The residue obtained was then washed using cold water and it was filtered and dried. The product was purified by recrystallization using ethanol at higher temperatures (40°C) using a Rota mantle. TLC was performed.



Colorimetric Detection

Water samples (1ml) mixed with chemo sensors (2ml) 3A/3B/3C/ 3D/3E/3F/3G and were made up to the mark 10ml using DMF. Maximum wavelength (λ max) was found for various wavelength filters. It was found to be 540 nm is the maximum wavelength.

UV-Vis Spectroscopy

To determine the fluoride content in water samples in ppm at maximum absorbance, a standard solution of ammonium fluoride was prepared. It was then mixed with chemo sensors 3A/3B/3C/ 3D/3E/3F/3G and made up to the mark of 10 ml using DMF. Sample solutions of 1, 2, 3, and 4 NH_4F ppm were prepared in DMF. Absorption was observed at 540 nm for all the samples mentioned above. Finally, absorption for different water samples such as rainwater, tap, pool, and well water were detected. It was found that the observed values for rainwater in ppm were by the values found for the fluoride content in PPM for rainwater observed theoretically. Using organo chemo sensors 3A/3B/3C/3D/3E/3F/3G, the detection of fluoride ions would be beneficial and provide proper results.

RESULTS AND DISCUSSION

The organo chemo sensors 3A-3G were found to be close to their elemental values. The precipitate was filtered using cold water and then recrystallized in ethanol. The crystals obtained were dried for further analysis.

Compound 3A

Colour: Yellow, Yield 80%

^{1}HNMR ($CDCl_3$): δ 6.83-7.16 (m, 4H-Ar-H), δ 2.24 (s, 3H-CH_3), δ 6.32-7.00 (m, 4H-Ar-H), δ 4.89 (s, 2H-NH_2)

IR (KBr pellet): λ max 3109, 1605, 1511and1463cm^{-1}

Mass (m/z): 244.17 [M+]

Anal. Calcd for $C_{14}H_{13}N_2Cl$: C-68.71%; H-5.31%; N-11.45%; Cl-14.51%. Found: C-68.62%; H-5.22%; N-11.26%; Cl-14.31%

Compound 3B

Colour: Red, Yield 65%

^{1}HNMR ($CDCl_3$): δ 6.30-7.03 (m, 4H-Ar-H), δ 7.33 (s, 1H-CH), δ 7.42 (s, 1H-Ar-OH), δ 6.82-7.05 (m, 4H-Ar-H), δ 4.50 (s, 2H-NH_2)

IR (KBr pellet): λ max 3320, 1640, 1573 and 1451cm^{-1}

Mass (m/z): 212.25 [M+]

Anal. Calcd for $C_{13}H_{12}N_2O$: C-73.58%; H-5.66%; N-13.20%; O -7.54%. Found: C-73.42%; H-5.36%; N- 13.16%; O-7.23%

Compound 3C

Colour: White. Yield: 72%

^{1}HNMR ($CDCl_3$): δ 7.61-8.01 (m, 5H-Ar-H), δ 7.30 (s, 1H-CH), δ 7.15-7.42 (m, 5H-Ar-H), δ 3.4 (s, 3H-OCH_3)

IR (KBr pellet): λ max 3229, 1677, 1503 and 1489cm^{-1}

Mass (m/z): 269.3 [M+]
Anal. Calcd for $C_{16}H_{15}NO_3$: C-71.37%; H-5.57%; N-5.20%; O-17.84%. Found: C-71.25%; H-5.32%; N-4.92%; O-17.35%

Compound 3D
Color: Yellow, Yield: 63 %
^{1}HNMR ($CDCl_3$): δ 7.65-7.90 (m, 4H-Ar-H), δ 7.41 (s, 1H-Ar-OH), δ 10.59 (s, 1H-Ar-COOH), δ 7.43 (s, 1H-CH), δ 7.23-7.56 (m, 4H-Ar-H)
IR (KBr pellet): λ max 3340, 1731, 1599 and 1421cm^{-1}
Mass (m/z): 241.24[M+]
Anal. Calcd for $C_{14}H_{11}NO_3$: C-69.71%; H-4.56%; N-5.80%; O-19.91%. Found: C-69.42%; H-4.36%; N-5.72%; O-19.76%

Compound 3E
Color: Brown, Yield: 85%
^{1}HNMR ($CDCl_3$): δ 6.91-7.13 (m, 4H-Ar-H), δ 7.45 (s, 1H-CH), δ 11.21-12.16 (m, 1H-Ar-COOH), δ 3.52 (s, 3H-OCH_3), δ 7.41-7.86 (m, 4H-Ar-H)
IR (KBr pellet): λ max 3000, 1652, 1522 and 1489cm^{-1}
Mass (m/z): 255.29 [M+]
Anal. Calcd for $C_{15}H_{13}NO_3$: C-70.58%; H-5.09%; N-5.49%; O-18.82%. Found: C-70.22%; H-5.01%; N-5.23%; O-18.26%

Compound 3F
Color: White, Yield: 81%
^{1}HNMR ($CDCl_3$): δ 7.63-7.85 (m, 5H-Ar-H), δ 2.42 (s, 1H-CH), δ 7.52-7.81 (m, 5H-Ar-H)
IR (KBr pellet): λ max 3568, 1708, 1532 and 1404cm^{-1}
Mass (m/z): 209.26 [M+]
Anal. Calcd for $C_{14}H_{11}NO$: C-80.38%; H-5.26%; N-6.69%; O-7.65%. Found: C-80.22%; H-5.16%; N- 6.58%; O-7.61%

Compound 3G
Color: Brown, Yield: 92 %
^{1}HNMR ($CDCl_3$): δ 7.15-7.65 (m, 5H-Ar-H), δ 2.62-3.10 (s, 1H-NH), δ 7.42-7.50 (m, 5H-Ar-H), δ 7.52-7.80 (m, 5H-Ar-H)
IR (KBr pellet): λ max 3893, 1672, 1588 and 1460cm^{-1}
Mass (m/z): 272.35 [M+]
Anal. Calcd for $C_{19}H_{16}N_2$: C-83.82%; H-5.88%; N-10.29%. Found: C-83.44%; H-5.72%; N- 10.09%

Table-1: Physical and Analytical Data of Organo Chemo Sensors (3A-3G)

Compound	Color	R	Molecular weight (g)	Molecular Formula	Yield (%)
3A	Yellow	CH_3	244.52	$C_{14}H_{13}N_2Cl$	80
3B	Red	H	212.22	$C_{13}H_{12}N_2O$	65
3C	White	H	269.29	$C_{16}H_{15}NO_3$	72
3D	Yellow	H	241.24	$C_{14}H_{11}NO_3$	63
3E	Brown	H	255.29	$C_{15}H_{13}NO_3$	85
3F	White	H	209.26	$C_{14}H_{11}NO$	81
3G	Brown	-	272.35	$C_{19}H_{16}N_2$	92

NMR Spectroscopy
The Nuclear magnetic resonance has confirmed the elements that were expected from the synthesis of chemo sensors 3A-3G.

IR Spectroscopy
The crystals obtained were taken for IR. The stretching frequency of 1621cm^{-1} indicates the formation of the chemo sensors 3A-3G with a C=N group.

XRD Analysis

XRD Analysis of the sample explains about the crystalline nature of the chemo sensors 3A-3G.

UV - Visible Spectroscopy

The solution of the water samples and chemo sensors 3A-3G resulted in the formation of an H - F bond which had a maximum wavelength value of 540nm. Chemo sensors 3A-3G in various water samples were taken for further analysis. The fluoride content in the sample was found to be below 1 ppm.

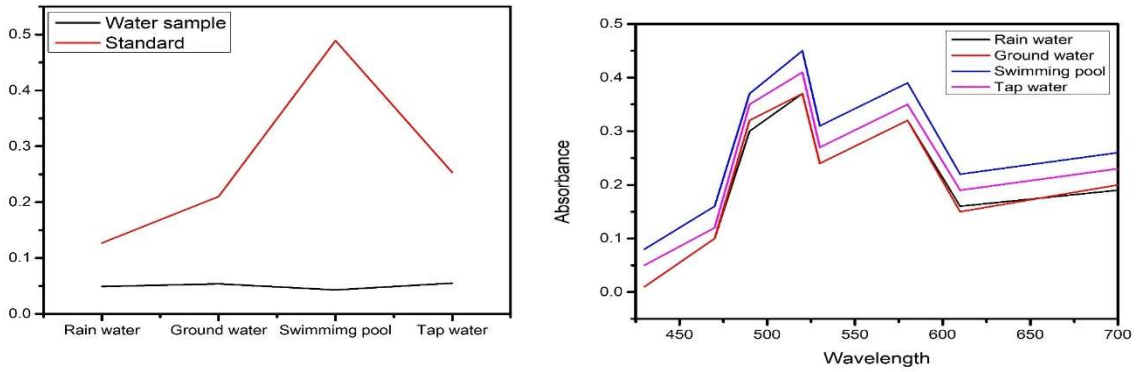


Fig.-2: Graphical Representation of Colorimetric Analysis and UV-Visible Spectroscopy for Fluoride Content

CONCLUSION

The organo chemo sensors synthesized were able to detect fluoride ions in different samples of water that were taken. The fluoride ion content was checked using spectrophotometric analysis for standard fluoride solution using its absorbance values, which were later compared with the absorbance values of the sample. The concentration of fluoride ions in different water samples that were taken was found to be 1 ppm.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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