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# Spectrophotometric Thermodynamic Study of Orientational Isomers Formed by Inclusion of Methyl Orange into β-Cyclodextrin Nanocavity

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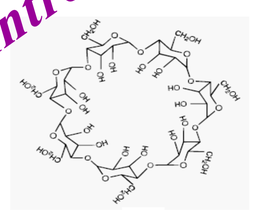
## Abstract

Spectrophotometry has been used to investigate the interaction between methyl orange, an azo dye as a guest, and β-cyclodextrin as the host. Inclusion of methyl orange into β-cyclodextrin nanocavity leads to two orientational isomers called inclumers, because of asymmetric structure of methyl orange. In order to calculate microconstants for inclumers, pure spectra for absorbing species in each media and enthalpies for inclusion equilibria, titration of methyl orange solution with β-cyclodextrin solution was performed in five different temperatures. Then globalization was performed to analyze the augmented data.

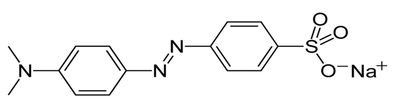
The recorded data at a constant temperature is rank deficient. This is so because there is a linear dependency between concentration profiles of inclumers. This problem is overcome through the augmentation of data recorded at different temperatures. This study has been performed in basic and acidic media to yield the microconstants and enthalpies for inclusion complexation equilibria in each media. Interaction of basic form of methyl orange with β-cyclodextrin in basic medium leads to two orientational isomers. But in acidic medium methyl orange has two tautomeric forms called ammonium and azonium. On the basis of former studies, inclusion of azonium form into β-cyclodextrin has been neglected for simplicity and inclusion of ammonium form is just modeled, because it forms more stable complexes. MATLAB software was used for the analysis of data. Newton-Raphson algorithm was used to produce concentration profiles and Newton-Gauss-Levenberg/Marquardt algorithm was used to optimize the parameters of interest.

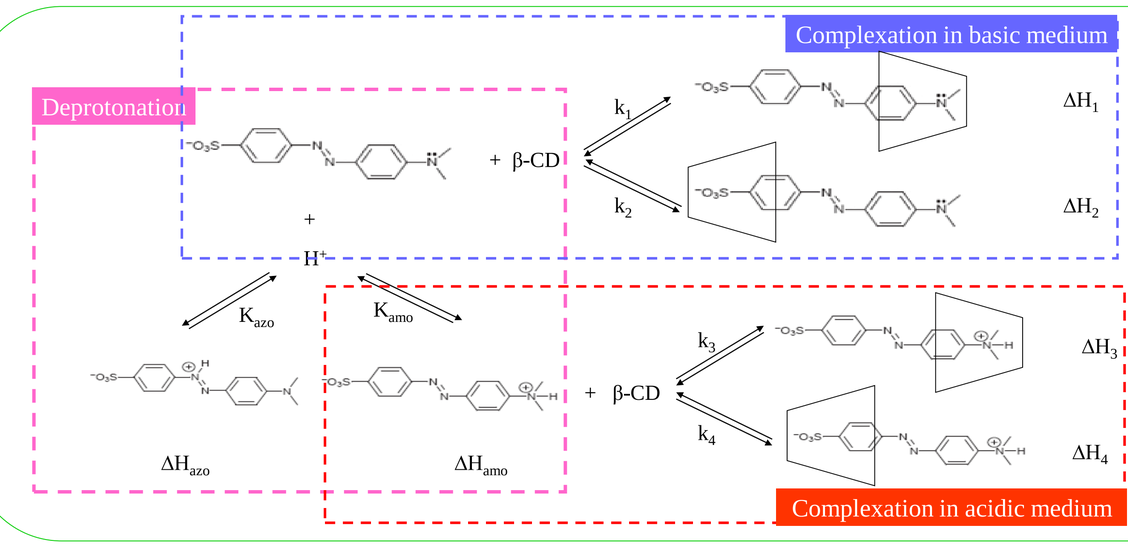
## Introduction



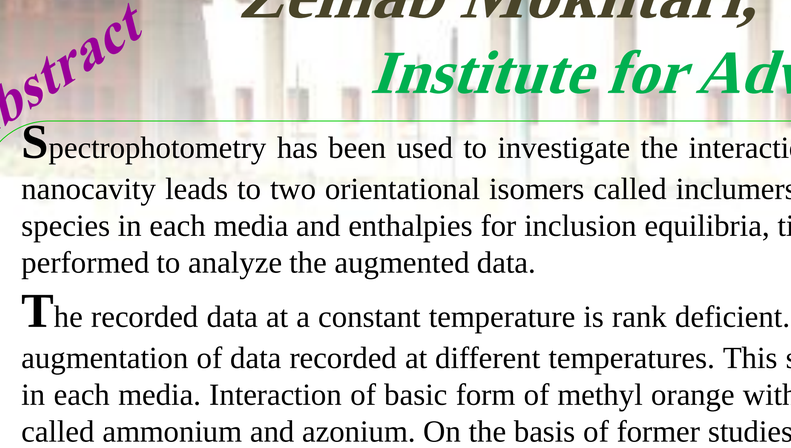
Cyclodextrins are cyclic oligosaccharides composed of D(+)glucopyranose units. They are cylinders with a hydrophilic exterior and a hydrophobic interior. Insertion of a hydrophobic guest in aqueous solutions of cyclodextrins leads to complexation which no covalent bonds are broken or formed. Cyclodextrins are widely used in drug delivery technology, food industry, chemistry and so on.
In this work β-cyclodextrin (β-CD) has been used, because of its availability and good solubility in water.

Methyl orange (MO) is an azo dye which is widely used as acid-base indicator in chemistry. Its structure shows an asymmetric molecule with two different ends having different tendency to hydrophobe cavity of β-cyclodextrin.

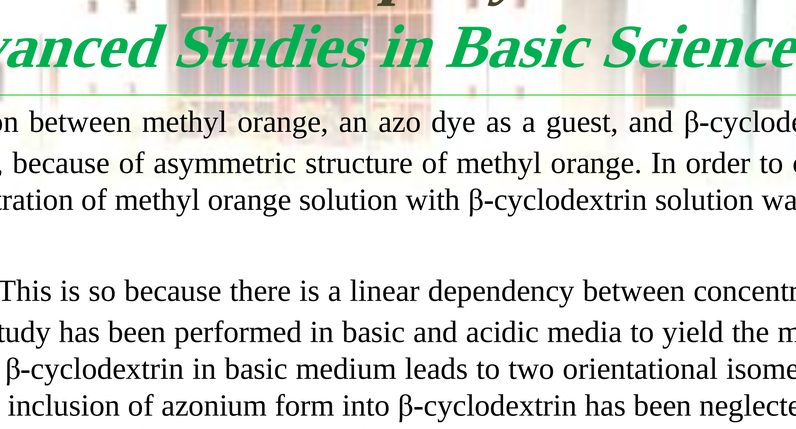




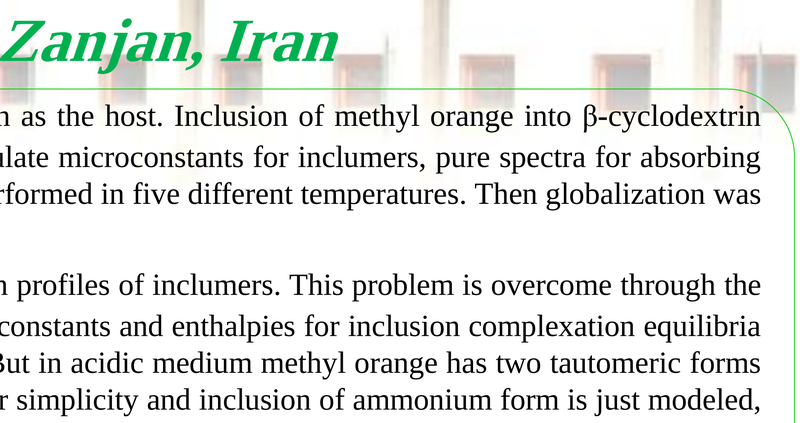

## Simulation




Spectrophotometric titration of MO with NaOH at 10, 20, 30, 40 and 50 °C




Spectrophotometric titration of MO with β-CD at 20, 25, 30, 40 and 50 °C




Spectrophotometric titration of MO with β-CD at 10, 20, 30, 40 and 50 °C

## Experimental

### Deprotonation




Spectrophotometric titration of MO with NaOH at 10, 20, 30, 40 and 50 °C

### Complexation in basic medium




Spectrophotometric titration of MO with β-CD at 20, 25, 30, 40 and 50 °C

### Complexation in acidic medium




Spectrophotometric titration of MO with β-CD at 10, 20, 30, 40 and 50 °C

## Results

| Deprotonation | | Complexation (basic medium) | | Complexation (acidic medium) | |
|---|---|---|---|---|---|
| $pK_{amo}$ | 2.67 | $\log k_1$ | 3.11 | $\log k_3$ | 5.28 |
| $pK_{azo}$ | 3.11 | $\log k_2$ | 2.83 | $\log k_4$ | 3.94 |
| $\Delta H_{amo}$ | -9.87 (kcal/mol) | $\Delta H_1$ | -1.04 (kcal/mol) | $\Delta H_3$ | -8.16 (kcal/mol) |
| $\Delta H_{azo}$ | -6.20 (kcal/mol) | $\Delta H_2$ | 5.49 (kcal/mol) | $\Delta H_4$ | -12.87 (kcal/mol) |

## References

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