

Environmental Effect on the Dissociation Constant of Substituted N-Benzylideneanilines in Aqueous Micellar System

¹Padmini Suna, ²Ashok K. Naik, ³Sagarika Panigrahi and ⁴Pramila K. Misra

Centre of Studies in Surface Science and Technology, School of Chemistry,
Sambalpur University, Jyoti Vihar-768019, Odisha, India.

Email: p.sunachem@gmail.com

Abstract -The environmental effect on the dissociation equilibria of some tailor made aldimines have been investigated in water and aqueous micellar systems of nonionic (TX100), cationic (CTAB) and anionic (AOS) surfactants. The dissociation constants have been determined by observing the absorption spectra of aldimine at different pH values. Results show that the pK values of these aldimines are influenced by the presence of surfactant. The results have been attributed to the surficial charge of the micelles and intramolecular H-bonding prevailing in o-substituted aldimines.

Keywords: Aldimine, dissociation constants, TX100; AOS, CTAB, Spectrophotometric method.

INTRODUCTION

Dissociation constants are important parameters to indicate the extent of ionization of molecules in solution at different pH values. Dissociation constants has essential role in many analytical procedures such as acid-base titration, solvent extraction, ion transport of organic compounds and complex formation. The acid-base properties affect the toxicity, chromatographic retention behavior, and pharmaceutical properties of organic acids and bases. Most of the theoretical study of modern organic chemistry is based on the observation of the effects on acid-base equilibrium of varying molecular structure [1].

Different methods are available for pK measurements such as solubility, potentiometric titration, spectrophotometry conductometry, HPLC etc. The solubility method is of limited accuracy and the sample concentrations required for potentiometry often result in precipitation of poorly soluble compounds, necessitating mixed solvent extrapolation methods [2] and further impacting sample through put. Spectrophotometric detection involves a rapid method for pK measurement employing a mixed-buffer linear pH gradient [3]. Here, we have used spectrophotometric method in triplicate thus repeating of each experiment to get accurate result.

The ability to solubilize a wide variety of compounds which are insoluble or slightly soluble in water is an important property of micelles. Micellar media are commonly used in different areas of analytical chemistry and several works have been done on these [4]. The incorporation of a solute into micellar systems can lead to important changes in its molecular properties. The additional important effects of micellar systems are that they can modify reaction rates by inhibiting or accelerating reaction rates, shift the equilibrium and, to some extent sway the nature of the products. Surfactants usually affect spectral parameters i.e. the intensity and absorption bands shift [5]. Micelles can affect the apparent pK values of the aldimine due to a combination of electrostatic and microenvironmental variations and type of the surfactant [6]. Moreover, the acid-base equilibrium involved in these systems are also influenced by surfactant.

Aldimine has been prepared by the condensation reaction of amines with carbonyl compounds through the elimination of water molecule. Owing to their physical and chemical properties, aldimines are mostly used in chemistry and due to the pharmacological activity it is used for industrial purposes [7].

EXPERIMENTAL MATERIALS

The aldimines, N-benzylidene-p'-chloroaniline, (o/p-OH)-benzylidene-p'- chloroaniline were synthesized and later were confirmed by their sharp melting point, TLC and the structure of these compounds are confirmed by spectral studies such as IR, NMR. TX100, AOS, CTAB were analytical grade commercial products from Merck (Darmstad, Germany). These aldimine were used without further purification. Standard stock solution of $5 \times 10^{-5} \text{M}$ of aldimine was prepared by dissolving appropriate amounts of aldimine in Dioxane. The stock solutions of surfactants were prepared by dissolving weighted amounts of substances in millipore water.

Apparatus

A Shimadzu uv-spectrophotometer controlled by a computer and equipped with a 1-cm path length quartz cell was used for UV-Vis spectral acquisition.

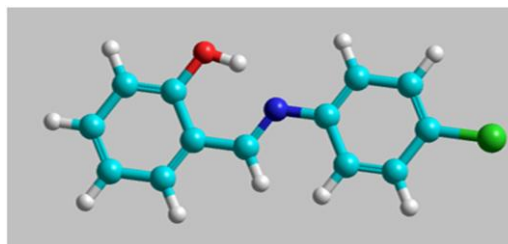


Fig 1: Structure of p-OH-benzylidene-p' chloroaniline

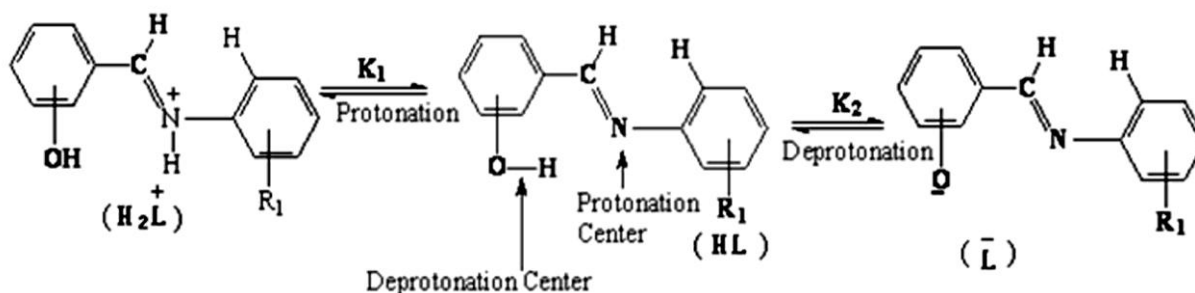


Fig.2: Protonation and deprotonation equilibria of the Aldimine

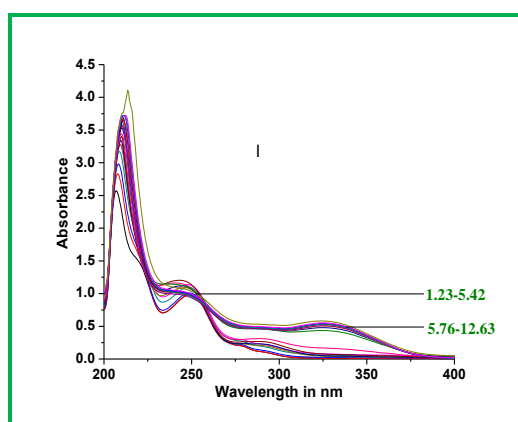
RESULTS AND DISCUSSION

Fig.2 describes the equilibria between different forms of aldimine. The dissociation constants relate the chemical activity of the cationic, neutral, anionic form of aldimine. In order to determine the influence of the nonionic surfactant (TX100), the anionic surfactant (AOS) and the cationic surfactant (CTAB) on dissociation constants, a series of experiments were run at above critical micellar concentration of TX100, AOS and CTAB.

Figure 3 show the absorption spectra of N-benzylidene-p'-chloroaniline, p-OH-benzylidene-p'-Cl aniline and o-OH-benzylidene-p'-Cl aniline at different pH values in

10% dioxane-water. The pK values of these aldimines have been investigated from their absorption spectra in 10% dioxane-water in absence and presence of TX100, AOS and CTAB.

It is interesting to note that the nature of the surfactant has a fundamental effect on each pure spectrum and this effect is apparently observed in different species of aldimine. Many papers have discussed the effect of micelle on the apparent pK values of the aldimines. It is observed the spectra of aldimines in TX100, AOS and CTAB micelles systems change with change in pH and from the change in wavelength maxima the pKa values of aldimine in these media has been calculated.



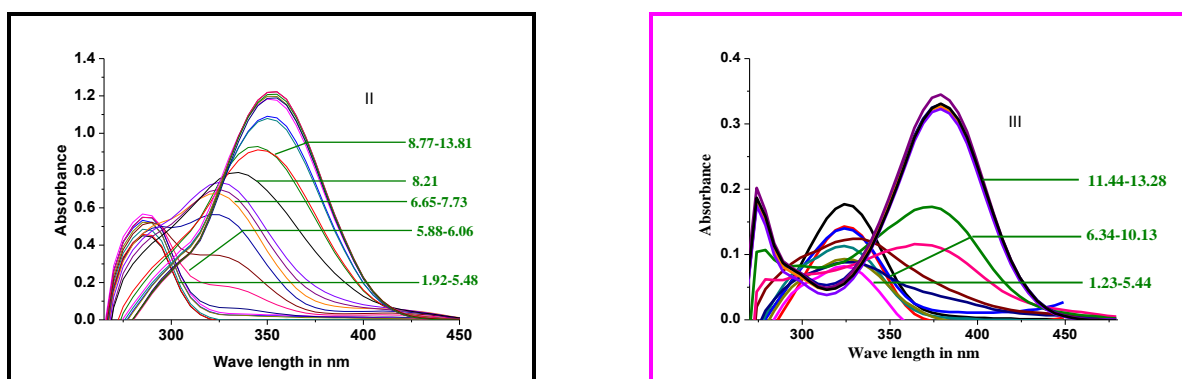


Fig. 3: Absorption spectra of N-benzylidene-p'-chloroaniline(I), p-OH-benzylidene-p'-Cl aniline(II) and o-OH-benzylidene-p'-Cl aniline(III) at various pH

It has been observed that wavelengths of absorption of these aldiminea in non-ionic TX100 micellar system do not vary but shows a slight variation as compared to aqueous system (about 3-4 nm in wavelength) in presence of ionic surfactant due to greater interaction with the charged hydrophilic part of surfactants. The dissociation constant (pK) of aldimines has been determined from the plot of λ_{max} vs. pH (a representative plot has given in Fig.4) and from Henderson's equation[8].

$$pK_a = pH + \log \frac{A_b - A_x}{A_x - A_a}$$

where, A_x = Absorbance of the compound at any pH,

A_a = Absorbance of strongly acid solution of the compound and

A_b = Absorbance of strongly alkaline solution of the compound.

Both the method gives approximately same values within the limits of ± 0.5 .

Table1:

Aldimine	I		II		III	
	pK_1	pK_2	pK_1	pK_2	pK_1	pK_2
Water	5.59	-	6.24	8.73	5.92	9.67
AOS	5.65	-	6.22	9.66	6.04	11.26
CTAB	4.06	-	4.27	8.45	4.98	10.68
TX-100	5.21	-	6.03	8.78	5.27	9.77

The pK values depend on absorption spectrum variation at different pH in aqueous and all micelles systems. In presence of AOS, it has been observed that there is an increase in dissociation constant (pK_1) of aldimine as compared to aqueous system and cationic /non-ionic micellar system because of interaction of anionic

hydrophilic part of surfactant with H_2L^+ . So pK_1 increases. pK_1 values in presence of cationic surfactant is always lower than other two micellar systems due to positive surface charge of CTAB which allows deprotonation favourably by repelling the H^+ ion by its cationic head groups. Thus the equilibrium is shifted towards HL. The ionic species of aldimine does not have considerable interaction with TX100, so its pK_1 is lower than aqueous system.

The aldimines formed from o-hydroxysubstituted group dissociates at higher pH (higher pK_2) due to the possibility of intramolecular H-bonding as shown in Fig.5 resulting in the formation of a six membered ring which gives large stabilization to the -OH substituted aldimines. The hydroxyl substituted aldimines (II, III) undergo ionization of -OH group with increase of pH and the equilibrium shift from neutral aldimine to ionized (negatively charged) aldimine. So, aldimine I does not have pK_2 . Since all the aldimines are localized in the palisade

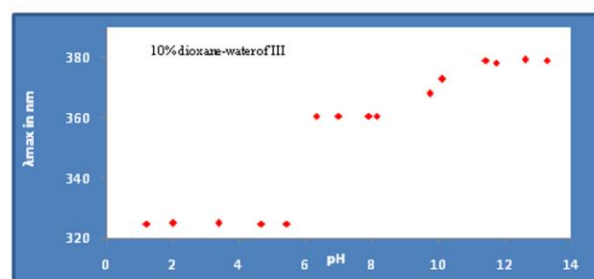


Fig.4: Representative plot of λ_{max} vs. pH of o-OH-benzylidene-p'-Cl aniline(III)

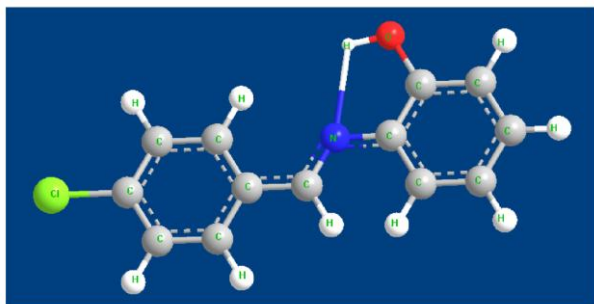


Fig.5:3D structure of III showing intramolecular H-bonding

region of micelles [9] as evident from the UV-spectral studies, higher pH is required to ionize the aldimines in anionic micelles compared to that of the water environment. The difficulties in removal of the H^+ ion from negatively charged surface of the micelle may also add to the enhancement of the pK_2 of **II** and **III** compared to that of water. The dissociated hydroxyl substituted aldimine is strongly attracted to the CTAB surface by both hydrophobic as well as electrostatic interaction due to its absolute positive charge on its head and hence distinct spectral shift is observed for ionized hydroxyl substituted aldimines. The effect is more prominent for aldimines with p-OH substituted aldimines than o-OH substituted ones possibly due to the existence of intramolecular H-bonding in the later. It is already known that the nonionic micelles provide a neutral environment, thus pK_2 in presence of nonionic micelles are nearly similar to water.

CONCLUSION

In this work, we distinguish the behavior of dissociation constants of aldimine in absence and presence of TX100, AOS and CTAB micellar media at 27°C studied by multiwavelength spectrophotometric method. Results

show that the pK_a values of aldimines are influenced by the presence of micellar media as interaction with micellar aggregates induces significant pK_a shifts which can be rationalized in terms of partitioning of species and electrostatic contribution.

ACKNOWLEDGEMENT

The authors thank University Grant Commission, New Delhi for providing a project to PKM and UGC, New Delhi for Fellowship to PS and AKN. Support of the UGC (DRS) and the FIST (DST) to the department is also highly acknowledged.

REFERENCES

- [1] C. Ogretir, S. Aydemir, M. Duran, M. S. Kılıckaya J. Chem. Eng. Data 2010, 55, 1477.
- [2] S. K. Poole, S. Patel, K. Dehring, H. Workman, C.F. Poole J Chromatogr A 2004, 1037, 445.
- [3] S. Panigrahi, M. Chakravorty, P. K. Misra J Colloid and Interface Sci 2007, 306, 137.
- [4] A. Safavi, H. Abdollahi Talanta 2001,53, 1001.
- [5] E. Pramauro, E. Pellezzeti Anal. Chim. Acta 1981, 126, 253.
- [6] G. S. Hartley, J. W. Roe Trans. Faraday Soc. 1940, 36, 101.
- [7] S. Panigrahi, P. Suna, P. K. Misra Colloids and Surfaces A: Physicochem. Eng. Aspects 2012, 415, 349.
- [8] J. Reijenga, A. Hoof, A. van Loon and B. Teunissen Anal. Chem. Insights 2013, 8, 53
- [9] R.H. Contreras, J.C. Facelli, D.G. Kowalewski Org. Magn. Reson. 1982, 20, 4.

