Asian Journal of Chemistry Vol. 16, No. 3 (2004), 1353–1358

Interactions between Nitrophenylhydrazinium Chloride and Surfactants in Aqueous Solutions

JAMIL K.J. SALEM
Chemistry Department, Al-Azhar University, P.O. Box 1277, Gaza, Palestine, via Israel
E-mail: Jamils22@yahoo.com

In the present study, the interaction of *p*-nitrophenylhydrazinium chloride (Nphh) with sodium dodecyl sulfate (SDS), cetyltrimethylammonium bromide (CTAB) and Triton X-100 (TX-100) in aqueous solutions have been investigated by means of UV-Vis spectroscopy. Interactions between Nphh and surfactants (CTAB and TX100) around their critical micelle concentration (CMC) did not show any spectral shifts. At surfactant concentration above 0.01 M, a red-shifted absorption band appeared in the spectra of the Nphh molecule. On the other hand, a blue-shifted absorption band appeared at low SDS conceniration (*ca.* 0.002 M). The appearance of a red-shifted absorption band occurred at SDS concentration above 0.05 M. Electrostatic, charge transfer and hydrogen bonding interactions play an important role in the growth of red-shifted and blue-shifted absorption bands in the spectra of Nphh molecule.

Key Words: Interactions, Surfactants, Nitrophenylhydrazinium chloride.

INTRODUCTION

Surfactants play an important role in many chemical reactions, forming micelles and reversed micelles in aqueous and nonaqueous media respectively due to the presence of polar head groups and nonpolar long chain hydrocarbons[1].

The appearance of extra absorption bands has been observed when various electron acceptors are solubilized in different surfactant solutions above the critical micelle concentration (cmc)[2–5]. Marked changes also occur in the spectra of organic anions in the presence of surfactant micelles. Cationic surfactants induce changes in the spectra on anionic dyes such as 2-naphtholate, bromophenol blue, dansylglycine and methyl orange[6–9]. Also, anionic surfactants interact with cationic dyes[10]. Not only surfactants are able to induce spectral changes, but also synthetic polymers have been shown to aggregate with dye molecules in aqueous solution. Charged as well as nonionic polymers have been shown to interact with azo dyes such as methyl orange[11–16]. It has been shown that interactions between cationic polymers and methyl orange induce marked reductions in reduced viscosity[17]. The origin of the spectral shifts is still a matter of debate in the literature.

Nitrophenylhydrazinium (Nphh) ion possesses unique character of acting both as an electron donor and as an electron acceptor. To obtain a better understanding of the role of surfactants in exhibiting the electron donor-acceptor characteristics of Nphh, investigations of spectral properties of Nphh in various surfactant solutions are required and the results are reported.

EXPERIMENTAL

p-Nitrophenylhydrazinium chloride was obtained from Merck (purity > 99%) and stored in a vacuum desiccator over P_2O_5 for several days before use. Sodium dodecyl sulfate, cetyltrimethylammonium bromide and Triton X-100, were 99% pure from Merck-Schuchardt, and were used as received. All other chemicals used were also reagent-grade products. Double distilled water was used.

UV-Vis absorption spectra were recorded on a Shimadzu-1601 UV-Vis spectrophotometer. The instrument cell holder was thermostated at 30 ± 0.02°C. Nphh concentration was 27 μM. All solutions were prepared in 0.015 M HCl to prevent the oxidation of Nphh in the solution.

Interactions between Nphh and SDS were also determined by conductivities on AC-13 conductivity-meter with a cell constant of 1.03 cm^{-1}. Solutions in the conductivity cell were stirred magnetically and thermostated at 30 ± 0.02°C. The specific conductivity was determined by applying the solvent correction.

RESULTS AND DISCUSSION

Absorption spectra of Nphh have been recorded in aqueous and different nonaqueous solvents. The wavelengths of maximum absorption of Nphh are positioned at 328, 329, 333, 340 and 402 nm in water, acetonitrile, ethanol, diethyl ether and acetone, respectively. These results show that the position of the maximum absorption band of Nphh is sensitive to medium effects; therefore, it can be used as solvatochromic reporter molecule.

The spectra of Nphh upon addition of different concentrations of SDS are shown in Fig. 1 (Table-1). Successive additions of small concentrations of SDS decrease the absorption band at 328 nm. Further additions of SDS give rise to a new band at 416 nm. The red-shifted new band appears at 0.06 M SDS. The new band decreases gradually while its intensity increases. The disappearance of the short-wavelength absorption band at 0.02 M SDS results in a sharp increase in the intensity of the long-wavelength absorption band.

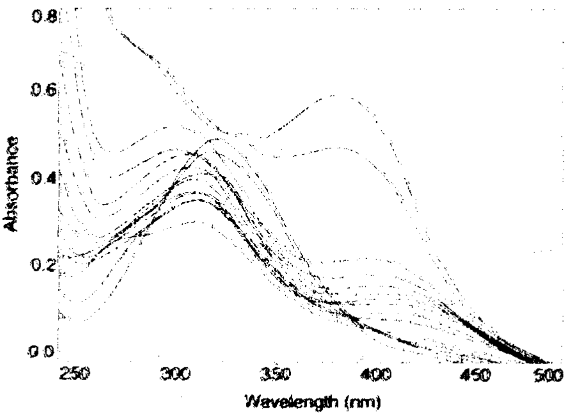

Fig. 1. Spectral changes observed for Nphh at various SDS concentrations

TABLE-1
DEPENDENCE OF MAXIMUM WAVELENGTH (λ_{max}) AND ABSORBANCE (Abs) OF Nphh ON SDS CONCENTRATION

[SDS] (Mm)	λ_{max} (nm)	Abs.
0.0	328	0.503
2.0	325.5	0.476
4.0	321	0.426
12	319	0.317
20	318	0.368
30	318	0.386
40	318	0.385, 0.134
60	316, 416	0.414, 0.148
80	314, 414	0.443, 0.164
120	312, 411	0.469, 0.176
160	308, 407	0.481, 0.200
200	308, 402	0.534, 0.237
300	389	0.490
400	387	0.610

In order to examine the interaction of Nphh molecules to SDS micelles more closely, conductivity titrations of Nphh solution with SDS solution were carried out. Typical results are shown in Fig. 2. Initially, the titration curve of SDS-Nphh is linear with a slope close to that of the SDS-water reference system, indicating that all added SDS is nonassociated with Nphh. This means that electrostatic repulsion between the negatively charged nitro group of Nphh and the main groups of SDS of the same charge would be responsible for the blue shift taking place in the maximum absorption band of Nphh from 328 nm to 316 nm at SDS concentration range from 0 to 0.06 M. Then, there is a change into a new linear region with a considerable lower slope. As this happens at a surfactant concen-

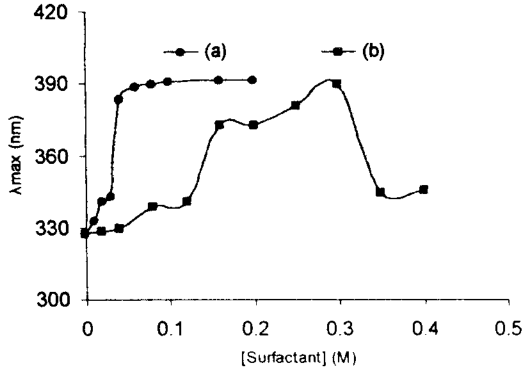

Fig. 2. Conductance of SDS solution in the absence of Nphh (a) and in the presence of 27 μM Nphh (b) at 30°C.

tration *ca.* 0.06 M, binding of the SDS micelles to Nphh is implied. The appearance of a new band (416 nm) supports this interpretation. This is due to electrostatic interaction between the positively charged hydrazinium group of Nphh and the negatively charged main group of SDS micelles. It might also be explained a contribution of hydrogen-bonding interactions between the sulfate main group and the hydrazinium group in the Nphh molecule. The importance of hydrogen-bonding interaction is evident from the influence of acetone on the spectral shift of Nphh absorption band. This occurs only through the interaction between the carbonyl group of acetone and the hydrazinium group of Nphh molecule. As seen from Table-1 and Fig. 2, there is a clear correlation between the abrupt changes in slope in the conductivity curve of SDS-Nphh and the long-wavelength absorption band (416 nm) appearance at 0.06 M SDS. This means that certain minimum SDS conceniration is needed for marked complex formation between Nphh and SDS to take place. At concentrations below 0.06 M SDS, the only interactions taking place in solution are of general electrostatic repulsion nature.

Examination of the spectral behaviour of equilibrated samples of Nphh in aqueous TX-100 and CTAB solutions is shown in Fig. 3. Both surfactants at low concentrations do not induce any spectral shift in the maximum absorption band of Nphh molecule. However, upon increasing surfactant concentration above 0.01 M, the maximum absorption band gradually shifts to a longer-wavelength absorption band up to 390 nm. In case of TX-100, the maximum absorption band increases with increasing TX-100 concentration and a plateau is reached at 0.08 M TX-100. On the other hand, the maximum absorption band increases with CTAB concentration and approaches maximum shift (390 nm) at 0.30 M CTAB and then shifted again to shorter wavelength (345 nm) as the CTAB concentration increases up to 0.4 M. The origin of the long-length absorption band in case of TX-100 might be explained by considering the hydrophilic main group (hydroxyl group) to be the site of interaction. The oxygen atom of this group donated lone pair electron to the electron accepting nitro group on Nphh which produce charge

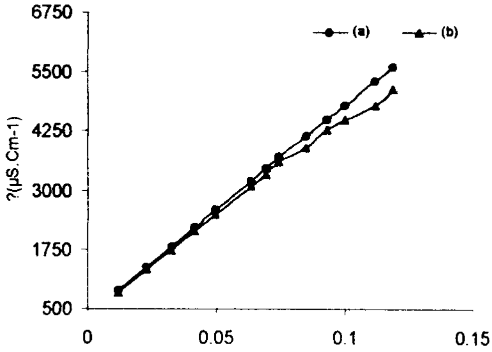

Fig. 3. Effect of [TX-100] (a) and [CTAB] (b) on the position of the wavelength of maximum absorption of Nphh in aqueous solution at 30°C. [NPhh] = 27 µM.

transfer interaction between TX-100 as electron donor and Nphh which acts as electron acceptor[18]. On the other hand, addition of CTAB up to 0.3 M leads to the formation of ion pairs in which the head group of CTAB (trimethyl ammonium group) is attached to the nitro group on Nphh molecule[19, 20]. Further addition of CTAB above 0.3 M results in electrostatic repulsive inieraction between the positively charged main group of CTAB and positively charged hydrazinium group of Nphh molecule. Furthermore, the electrostatic repulsion component in the interaction region is missing with TX-100 that could also explain the lowering of the interaction concentration of TX-100 as compared with that of CTAB.

These results are fully reconcilable with the role of hydrophilic interactions in the spectral shifts of Nphh molecule. This is confirmed by the fact that the interactions between Nphh and surfactant are present in nonaqueous solutions. Red-shifts of 74, 15, 12, and 5 nm were observed upon addition of acetone, dimethylformamide, diethylether and ethanol, respectively. These results again confirm that hydrophilic interactions (electrostatic, hydrogen-bonding and charge transfer) are important for aggregation of organic molecules. In another study, aggregation of azo dyes with cationic amphiphiles was reflected by the appearance of a blue-shifted band in the spectra of the dyes at low surfactant concentrations. This study implies that next to electrostatic interactions hydrophilic stacking of the aromatic parts of the azo dyes is also important in the aggregation process[21].

Conclusion

Results show that the position of the maximum absorption band of Nphh is sensitive to the type of surfactant (*i.e.*, anionic, cationic and nonionic) and its concentration. Therefore, Nphh shows solvatochromic behaviour in aqueous micellar solutions. Growth of red-shifted (*ca.* 390 nm) band is produced only through electrostatic, charge transfer and hydrogen-bonding interactions with surfactant micelles. The red-shifting observed for micellized Nphh cannot be attributed to hydrophilic interactions. This is confirmed by the fact that the interactions between Nphh and surfactant micelles are present in ethanol and acetone solutions. The electrostatic repulsion is thought to be the origin of the blue-shifted band in SDS micelles.

ACKNOWLEDGEMENT

The author is grateful to Al-Azhar University of GAZA for its support.

REFERENCES

1. J.H. Fendler and E.J. Fendler, Catalysis in Micellar and Macromolecular System, Academic Press, New York (1975).
2. S. Muto, K. Deguchi, K. Kobayashi, E. Kaneko and K. Meguro, *J. Colloid. Interface Sci.*, **33**, 475 (1970).
3. S. Muto, K. Deyuchi, Y. Shimazaki, Y. Aono and K. Meguro, *J. Colloid. Interface Sci.*, **37**, 109 (1971).
4. S. Muto and K. Meguro, *Bull. Chem. Soc. (Japan)*, **46**, 1316 (1973).

5. S. Muto, Y. Aono and K. Meguro, *Bull. Chem Soc. (Japan)*, **46**, 2872 (1973).
6. O.A. Amire and H.D. Burrows, Surfactants in Solution, Plenum Press, New York (1986).
7. E.L. Colichman, *J. Am. Chem. Soc.*, **73**, 3385 (1951).
8. G.A. Davis, *J. Am. Chem. Soc.*, **94**, 5089 (1972).
9. F. Quadrifoglio and V. Crezenzi, *J. Colloid. Interface Sci.*, **35**, 447 (1971).
10. M.G. Neumann and M.H. Gehlen, *J. Colloid. Interface Sci.*, **135**, 209 (1990).
11. I.M. Klotz, G.P. Royer and A.R. Sloniewsky *Biochemistry*, **8**, 4752 (1969).
12. H. Yamaoto and A. Nakazawa, *Biopolymers*, **23**, 1367 (1984).
13. H. Yamaoto, A. Nakazawa and T. Hayadawa, *J. Polym. Sci., Polym. Lett.*, **21**, 131 (1983).
14. K. Hamada, M. Fujita and M. Mitsuishi, *J. Chem. Soc. Farad. Trans.*, **86**, 4031 (1990).
15. W. Kim, S. Lee and K. Seo, *Macromol. Chem. Phys.*, **195**, 449 (1994).
16. K. Kobayashi and H. Sumimoto, *Macromolecules*, **13**, 234 (1980).
17. G. Vlang and T.B. Engberts. *Langmuir*, **10**, 2583 (1994).
18. B. Benoy and M. Sushil, *J. Surf. Sci. Tech.*, **3**, 49 (1987).
19. R. Dutta and S. Bhat, *Bull. Chem. Soc. (Japan)*, **66**, 2457 (1993).
20. R. Dutta and S. Bhat, *Colloids Surf.*, **106**, 127 (1996).
21. B. Rrixt, M. Jessica and J. Engberts, *Langmuir*, **15**, 1083 (1999).

(*Received*: 23 September 2003; *Accepted*: 3 March 2004) AJC-3368