Effect of cetylammonium bromide micelles on decolouration of rosaniline hydrochloride by periodate: Experimental and theoretical approach

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Rosaniline hydrochloride (RH) is a triaminotriphenyl methane dye, which is widely used as biological stain, mordant, printing, in cotton tannings, and dyeing in textile industry. The reaction obeys first order kinetics with respect to RH and IO_4^-. The reaction is around hundred times faster in the presence of CTAB compared to aqueous medium under identical conditions. This is due to lower dielectric constant in micellar medium in which the transition state in more stabilized. The rate of the reaction increases with increase in concentration of CTAB up to 0.08 mol dm^{-3} and thereafter shows a limiting behavior with increase in micellar concentration. The monotonic increase indicates a unimolecular pathway. Using Menger and Portnoy'spre equilibrium kinetic model binding constant was found to be 21.84 mol^{-1} dm^3. This value was found to be in good agreement with the calculated binding constant K_M (= $p\overline{V}$) = 39.2, where p is partition co-efficient and $\overline{V}$ is molar volume. In order to account for the catalytic behavior of CTAB, theoretical calculations of single point energy and energy gap were done using GAUSSIAN 09 W program employing density functional theory (DFT) with Becke's three-parameters hybrid functional in combination of Lee-Yang-Parr functional implemented with LANL2DZ basis sets using conductor like polarizable continuum model (CPCM). (DFT/B3LYP/LANL2DZ/CPCM (solvent = water)). Based on the structures of RH, KIO_4 and CTAB, binding energies (BEs) were calculated for the dimer complexes RH-KIO_4 and RH-KIO_4-CTAB. BEs of the RH-KIO_4 and RH-KIO_4-CTAB systems have been found to be –60.4 kcal/mol and –70.4 kcal/mol, respectively. The high binding energy (RH-KIO_4-CTAB, –70.4 kcal/mol) indicates the catalytic behavior. The HLEG (HOMO-LUMO Energy Gap) measures the stability of the system. A large HLEG implies high stability (less reactive) and slight gap implies low stability (highly reactive). In this work, RH-KIO_4-CTAB system, the gap is reduced around 1.28 times than the RH-KIO_4 system which clearly indicates that the CTAB surfactant plays a vital role in this reaction. It explains that catalytic behavior of CTAB by theoretical approach.

Keywords: Catalysis, CTAB, decoloration, pseudo phase model, surfactants.

Introduction

Rosaniline hydrochloride (RH) which is a triaminotriphenyl methane dye, is widely used as biological stain, mordant, printing, in cotton tannings, and dyeing in textile industry[1–6]. These dyes enter the environment in natural waters. It is also an important constituent of Schiff's reagent as an indicator for the detection of aldehydes and ketones[7–9]. The intermediates of these dyes are also encountered in several organic and enzymatic reactions. Studies on the chemical reactions of these dyes are therefore important. Since rates of reactions change in the presence of micelles the oxidation reactions of the dye in the presence of micelles will be helpful in exploiting their use in industries.

Babatunde *et al.*[10-12] have studied the reduction of rosaniline hydrochloride extensively in tri oxo carbonate (IV), hydroxide ion and nitrite ions. In these reactions, a stoichiometry of 1:1 was found for rosaniline hydrochloride and the reductant. In the reaction of rosaniline hydrochloride with chlorite a stoichiometry of 1:2 was reported, the order of the reactions with respect to both the reactants was found to be two. The rate of reaction increases with increase in ionic strength[13]. In the reduction of rosaniline hydrochloride by

hydroxide ion[11], the rate of reaction decreases with increase in ionic strength. The oxidation of malachite green, brilliant green and crystal violet[14], other members of the tri amino tri phenyl methane dyes by peroxydisulphate was studied by Joshi *et al.* in the presence of different micellar media. London Singh *et al.*[15] have studied the effect of anionic and non-ionic micelles on nucleophilic addition reaction of rosaniline hydrochloride (RH) with hydroxide ion. Mishra *et al.*[16] were reported that rate enhancement (2.25 fold) of hydroxylation of rosaniline hydrochloride by NaOH in the presence of CTAB micelles. Padma *et al.*[17] studied fading of rosaniline hydrochloride by periodate (IO_4^-) in presence of reverse micellar systems. Since rates of reactions are altered in the presence of micelles, kinetic studies of rosaniline hydrochloride by periodate in the presence of CTAB micelles have been carried out and the results are presented in this paper.

Results and discussions

Experimental analysis:

The kinetic investigation of the decolouration of RH by IO_4^- has been carried out in the presence of CTAB micelles at constant ionic strength (μ) of 0.5 mol dm^{-3} under the experimental conditions [RH] << [IO_4^-], isolating RH. The reaction obeys first order kinetics with respect to RH and IO_4^-. The reaction is around hundred times faster in the presence of CTAB micellar medium compared to aqueous medium under identical conditions (Table 1).

The increase in rate is due to the lower dielectric constant of CTAB micellar medium compared to aqueous medium. The transition state in this reaction is less polar when compared with initial state which is more stabilized in CTAB micellar medium.

Effect of CTAB concentration:

The rate of the reaction increases with increase in CTAB concentration up to 0.08 mol dm^{-3} and thereafter a saturated behavior with increase in CTAB concentration (Fig. 1). The saturation limit indicates a unimolecular pathway.

The effect of CTAB can be explained using the pre-equilibrium kinetic model proposed by Menger and Portnoy[18] for a reaction mechanism shown in Fig. 2.

The rate law for a unimolecular reaction can be repre-

Table 1. Kinetic data for decolouration of RH by [IO_4^-] in presence of CTAB

[RH]×10^5 (mol dm^{-3})	[IO_4^-]×10^3 (mol dm^{-3})	[CTAB] (mol dm^{-3})	μ	T (K)	k'×10 (s^{-1})
1.12	1.0	0.0	0.5	300	0.03
		0.6			0.75
		1.0			1.12
		4.0			4.29
		8.0			6.53
		12.0			8.28
		20.0			12.1
		40.0			19.8
		60.0			27.5
		80.0			33.3
		100			35.7
0.11	1.0	40.0			56.3
0.28					36.7
0.56					22.7
0.84					20.9
1.12	0.5				4.10
	2.0				33.9
	3.0				55.8
	4.0				74.8
	5.0				106
1.12	1.0	40.0		313	589
				323	131
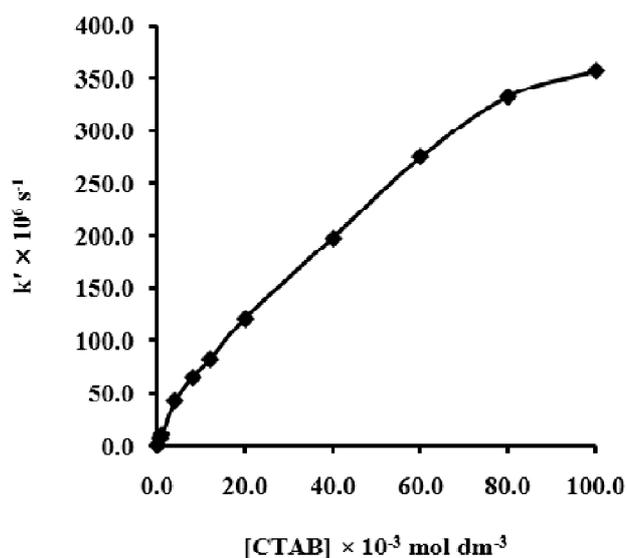
Fig. 1. Plot of k' vs [CTAB].

$$S + D_n \underset{K_S}{\rightleftharpoons} SD_n$$

$$k_W \big| \qquad \big| k_M$$

$$\longrightarrow \text{Products} \longleftarrow$$
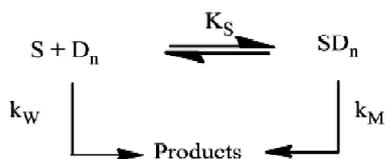
where S - Intermediate(X), D_n - CTAB, K_s - binding constant, k_w - rate constant in aqueous medium and K_M - rate constant in micellar medium

Fig. 2. Scheme of pseudo phase model.

sented by Menger[18], eq. (1).

$$k' = \frac{k_w + k_M K_M [C_M]}{1 + k_M [C_M]} \qquad (1)$$

where $C_M = C - CMC$ and C is the stoichiometry concentration of CTAB. k' is the observed rate constant in presence of CTAB micelle, k_W and k_M are the rate constants in water and micelle phase respectively, K_M is the binding constant of the ion-pair intermediate with the micelle. Eq. (1) rearranges to

$$\frac{1}{k' - k_w} = \frac{1}{k_M - k_w} + \frac{1}{(k_M - k_w) K_M C_M} \qquad (2)$$

According to eq. (2) the plot of $1/(k' - k_W)$ versus $1/C_M$ must be linear with a positive slope and intercept. Such a plot has been obtained and from the slope and intercept and the value of K_M was found to be 21.84 mol^{-1} dm^3 (Fig. 3). The ion pair intermediate of RH$\cdots$IO$_4^-$ is bound to a micelle only by hydrophobic interactions and for such interactions the partition coefficient p for each substrate with the micellar phase and water is given as $p = e^{-\Delta \mu / RT}$ where $\Delta \mu$ is the standard chemical potential ($p = 280$ for CTAB)[19]. The molar volume of the surfactant and is equal to 0.14 dm^3 mol^{-1} for CTAB micelles. Therefore the binding constant $K_M = p\overline{V} = 39.2$, which is of the same order and in good agreement with K_M obtained from eq. (2).

Computational analysis:

To understand the catalytic behavior of CTAB in the present system by computational analysis authors performed single point energy and HOMO-LUMO calculations. Single point energies and energy gaps were obtained from the method DFT/UB3LYP/LANL2DZ/CPCM (solvent = water) for RH, KIO$_4$, CTAB and also combined form of RH-KIO$_4$ and
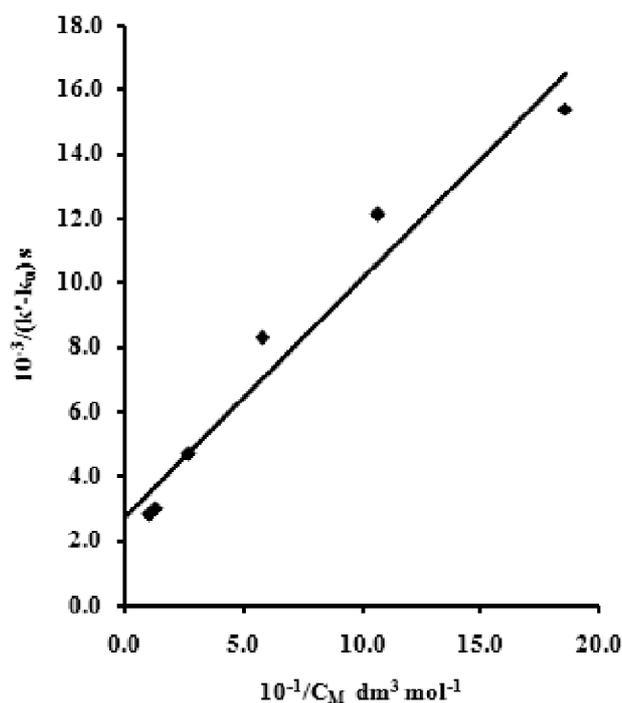

Fig. 3. Plot of $1/(k' - k_W)$ vs $1/C_M$.

RH-KIO$_4$-CTAB. Values are presented in Table 2. Binding energies (BEs) were calculated for the dimer complexes RH-KIO$_4$ and RH-KIO$_4$-CTAB. BE values for the complexes were obtained employing the supramolecular approach in which the sum of the energies of the constituting monomers is subtracted from the energy of the complex. BEs of the RH-KIO$_4$ and RH-KIO$_4$-CTAB systems have been found to be –60.4 kcal/mol and –70.4 kcal/mol, respectively. The above BE value fairly suggest that the substrates-surfactant complex RH-KIO$_4$-CTAB is more stable than the dimer complex RH-KIO$_4$. The high binding energy facilitates the rate of reaction. It shows that catalytic behavior of CTAB by theoretical approach.

The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of a molecule

Table 2. HOMO-LUMO analysis for the RH-KIOI$_4$ and RH-KIO$_4$-CTAB system

	HOMO (eV)	LUMO (eV)	HOMO-LUMO energy gap (eV)
RH-KIO$_4$	–5.93	–4.71	1.22
RH-KIO$_4$-CTAB	–5.67	–4.72	0.95

are well known as the frontier molecular orbitals. Fukui[20] was the one who first noticed the prominent role played by the HOMO and LUMO in leading chemical reactions. The HOMO-LUMO energy gap (HLEG) explains the chemical reactivity of a species. The HLEG analyses for the system without the catalyst, RH-IO_4^- and with catalyst RH-IO_4^--CTAB were conducted by the B3LYP/6-31G(d,p) level of study. This can be calculated by the subtraction of LUMO and HOMO energy values.

The positive lobes are represented by the green color scheme and the negative lobes are indicated by the red color scheme (Fig. 4). HOMO lobes are distributed throughout the two benzene rings in RH moiety where as LUMO lobes distributed over KIO_4 and one benzene ring in RH which is near to KIO_4 (Fig. 4a, 4b). This is because of weak interactions between O atoms in KIO_4 and C atoms in third benzene of RH which near to KIO_4. The HLEG 1.22 eV obtained. Whereas in RH-KIO_4-CTAB system the HOMO lobes exist at Br atom from CTAB and LUMO lobes spread around the KIO_4 molecule and N atom in third benzene ring in RH which is near to KIO_4 (Fig. 4c, 4d). Due to CTAB exist in RH-KIO_4^--CTAB system HOMO-LUMO lobes distribution changes this leads to decrease energy gap (0.95 eV) and enhance the rate of reaction. The HLEGs of the RH-KIO_4 and RH-KIO_4-CTAB are 1.22 eV and 0.95 eV respectively which indicate that the RH-KIO_4-CTAB is chemically more reactive than the RH-KIO_4 system. The HLEG measures the stability of the system. A large HLEG implies high stability (less reactive) and slight gap implies low stability (highly reactive). In this work, RH-KIO_4-CTAB system, the gap is reduced around 1.28 times than the RH-KIO_4 system which clearly indicates that the CTAB surfactant plays a vital role in this reaction. The HOMOs, LUMOs and HLEGs can be seen in the Table 2.

Experimental

All chemicals were obtained from Merck (India). Stoichiometry of the reaction indicate that one mole of RH reacts with one mole of IO_4^- which was determined by spectrophotometry using mole ratio method. The analysis of product was carried out by mixing equimolar amount of IO_4^- and RH. After the completion of the reaction a colorless solution indicating that destruction of the quininoid group was obtained and UV-Visible spectrum of the product showed no absorption peak at wavelength (λ_{max}) = 545 nm. However, the authors interest about catalysis because the product already reported[21].

The reaction was followed by measuring the absorbance of the unreacted RH at wavelength 545 nm using Shimadzu UV-1800 spectrophotometer. The experiments were carried out in a temperature controlled thermostat at 27±0.1°C. The reaction was initiated by adding IO_4^- (1.0×10^{-3} mol dm^{-3}) to the rosaniline hydrochloride (1.12×10^{-5} mol dm^{-3}) at ionic strength (0.5 mol dm^{-3}) and CTAB (0.04 mol dm^{-3}) under pseudo-first order conditions, [IO_4^-] >> [RH]. Plots of log (A_t) versus time (where A_t is the absorbance at time t) were found to be perfectly linear for at least 95% of the reaction.
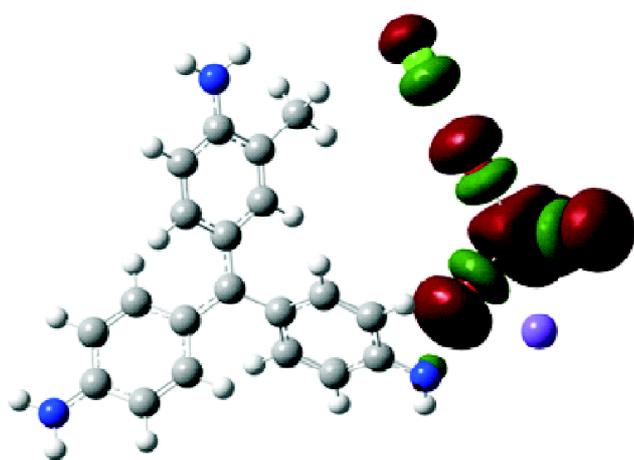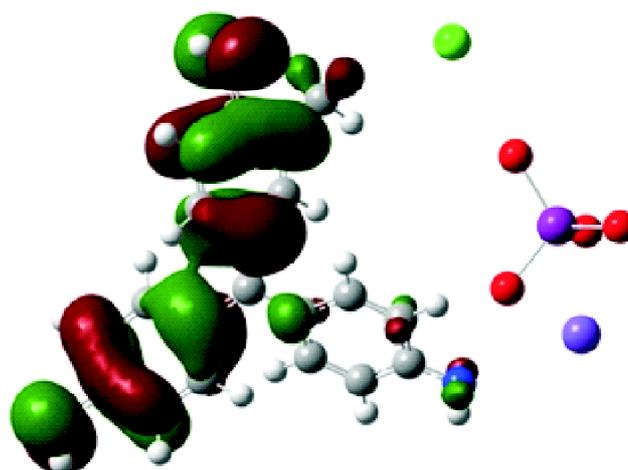

Fig. 4a. LUMO structure of RH-KIO_4.

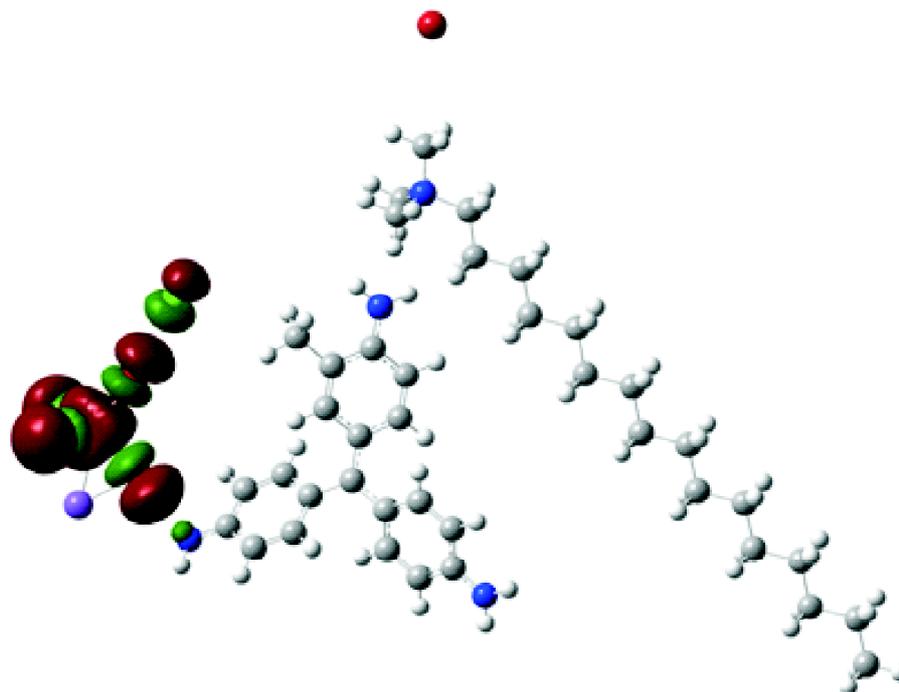**Fig. 4b.** HOMO structure of RH-KIO_4.
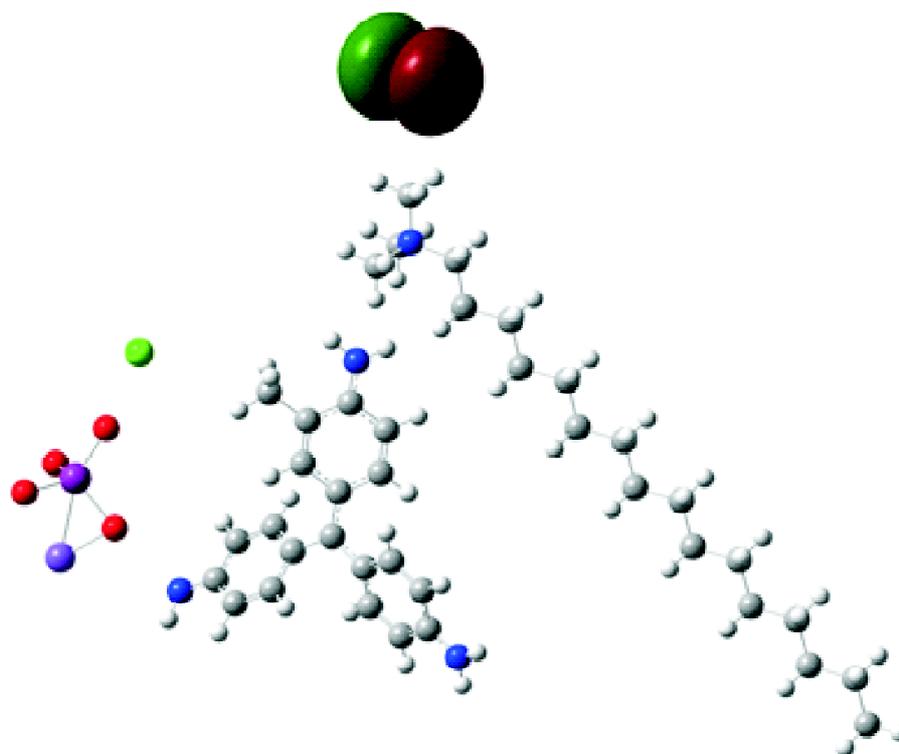
Fig. 4c. LUMO structure of RH-KIO$_4$-CTAB.

Fig. 4d. HOMO structure of RH-KIO$_4$-CTAB.

The kinetic data are the averages from triplicate runs with a reproducibility ±3%. Critical micellar concentration (CMC) of CTAB determined by surface tension measurements under the present experimental conditions was found to be 2.62×10^{-3} mol dm^{-3}. The theoretical calculations of single point energy and energy gap were done using GAUSSIAN 09 W program[22] employing density functional theory (DFT) with Becke's three-parameters hybrid functional in combination of Lee-Yang-Parr functional[23,24] implemented with LANL2DZ basis sets using conductor like polarizable continuum model (CPCM). In this method water consider as solvent (DFT/B3LYP/LANL2DZ/CPCM (solvent = water)).

Conclusions

The reaction between rosaniline hydrochloride and periodate is around hundred times faster in CTAB micelles compared to aqueous medium under identical conditions.

Since CTAB is an ionic surfactant, in addition to micellar medium effect and proximity effect of reactants, ionic strength of ionic micellar surface and electrostatic interactions between reactants and ionic head groups have effect on rates of reactions.

The effect of CTAB on the rate of the reaction confirms to a unimolecular pathway as shown by limiting behavior in a rate-surfactant profile.

The value of K_M obtained from the plot of $1/k'$ vs $1/C_M$ was found to be 21.84 mol^{-1} dm^3 and is of the same order as the calculated value i.e. 39.2.

This reasonably large binding constant is indicative of a strong interaction between reactants and CTAB micelles.

BEs of the RH-KIO$_4$ and RH-KIO$_4$-CTAB systems have been found to be –60.4 kcal/mol and –70.4 kcal/mol, respectively. The above BE value fairly suggest that the substrates-surfactant complex RH-KIO$_4$-CTAB is more stable than the dimer complex RH-KIO$_4$.

The high binding energy facilitates the rate of reaction. The HLEGs of the RH-KIO$_4$ and RH-KIO$_4$-CTAB are 1.22 eV and 0.95 eV respectively which indicate that the RH-KIO$_4$-CTAB is chemically more reactive than the RH-KIO$_4$ system.

The HLEG measures the stability of the system. A large HLEG implies high stability (less reactive) and slight gap implies low stability (highly reactive).

In this work, RH-KIO$_4$-CTAB system, the gap is reduced around 1.28 times than the RH-KIO$_4$ system which clearly indicates that the CTAB surfactant plays a vital role in this reaction.

References

1. H. J. Conn, "Biological stains, a hand book on the nature and uses of the dyes employed in biological laboratory", 7th ed., Baltimore, Maryland, 1961.

2. R. W. Sabins, "Handbook af Biological Dyes and Stains: Synthesis and Industrial Applications", John Wiley & Sons, New York, 2010.

3. E. Gurr, N. Anand, M. K. Uma and N. R. Ayyangar, "The Chemistry of Synthetic Dyes", ed. K. Venkataraman, Academic, New York, 1974.

4. C. Carate, M. Evelegh and R. Zawyiswski, US Pat. Appl. Publ. US 2007065893 (*Chem. Abstr.*, 2007, **146**, 333652).

5. U. Narang, W. S. C. Nicholson, A. Sherbondy and G. N. Szabo, US Pat. Appl. Publ. US 2003007946 (*Chem. Abstr.*, 2003, **138**, 78490).

6. S. N. Anderson and J. B. Wilson, US Pat. Appl. Publ. US 2003059379 (*Chem. Abstr.*, 2003, **138**, 276252).

7. S. K. Goyal, *J. Environ. Monitor.*, 2001, **3(6)**, 666.

8. C. F. A. Culling, "Handbook of micro pathological techniques", 2nd ed., Butterworths, London, 1963.

9. L. D. Smith and V. W., US Pat. Appl. Publ. US 2005120919, (*Chem. Abstr.*, 2005, **143**, 93331).

10. O. A. Babatunde and I. K. Adamu, *Eur. J. Sci. Res.*, 2009, **31(2)**, 237.

11. J. F. Iyun, A. O. Peters and O. A. Babatunde, *Indian J. Chem. A*, 2002, **41A(5)**, 967.

12. O. A. Babatunde, *World. J. Chem.*, 2009, **4(1)**, 39.

13. Y. Mohammed, A. C. Ethoniu and V. A. Tasku, *Trakia. J. Chem.*, 2011, **9(2)**, 1.

14. H. M. Joshi and T. N. Nagar, *Asian J. Chem.*, 2002, **14(3-4)**, 1763.

15. R. K. London Singh, *E-J. Chem.*, 2012, **9(3)**, 1181.

16. P. K. Mishra, L. N. Panda, B. K. Mishra and G. Behera, *Indian J. Chem. A*, 1988, **27A(11)**, 959.

17. M. Padma, P. Shyamala and D. Suneetha, *J. Indian Chem. Soc.,* 2017, **94(4)**, 381.

18. F. M. Menger and C. E. Portnoy, *J. Am. Chem. Soc.*, 1967, **89(18)**, 4698.

19. I. V. Berezin, K. Martinek and A. K. Yatsmirskii, *Russ. Chem. Rev.*, 1973, **42(10)**, 787.

20. K. Fukui, T. Yomezawa and H. Shingu, *J. Chem. Phys.*, 1952, **20**, 722.

21. K. K. Patil, *Der. Chemica. Sinica.*, 2011, **2(6)**, 245.

22. Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery (Jr.), J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

23. A. D. Becke, *J. Chem. Phys.*, 1993, **98(7)**, 5648.

24. M. Burkhard, S. Andreas, S. Herman and P. Heinzwerner, *Chem. Phys. Lett.*, 1989, **157**, 200.