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Rapid, selective and direct spectrophotometric determination of aliphatic amines with m-dinitrobenzene

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Abstract

Color reaction has been studied for identification and spectrophotometric determination of aliphatic amines at room temperature by m-dinitrobenzene (m-DNB) as reagent. The λ_{max} value ranges from 458 to 570 nm. This is a simple and rapid method for determination of aliphatic amines in the acidic, water and acetone medium. Beer's law is verified for methylamine, dimethylamine, trimethylamine and n-butylamine in the range of 0.5–8 mg l⁻¹. The effect of pH on the molar absorptivity is investigated for a representative primary amine i.e. methylamine and it was observed that molar absorptivity increases from acidic to basic pH, with a sharp increase at pH 12. The kinetic of reaction was also studied and found that reaction time has marked effect on the molar absorptivity of electron donor–acceptor (EDA) complex. The detection of methyl amine has been reported in three real samples of water.

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Keywords: Spectrophotometry; Aliphatic amines; m-Dinitrobenzene

1. Introduction

For the detection of aliphatic amines different reagents are being attempted so as to get rapid, selective, stable and direct method. 1,2-Naphthaquinone-4-sulphonic acid sodium salt has been used widely and has a number of useful application as reagent for determination of primary amines in the sample of water. This reagent form violet color at pH 10.2–10.4 [1]. The interaction of n-alkylamine with chloranil has been investigated [2], which involves the participation of electron

donor–acceptor (EDA) complex between the primary aliphatic amine and chloranil resulting in mono and di-substituted products. Primary, secondary and tertiary amines, both aliphatic and aromatic amine, are shown to react with p-chloranil and form blue to purple color in dioxane/2-propanol (1:4 v/v) [3]. The colored compound formed was stable for 8 h at room temperature, depending on the amine and solvent used. Some new 9-substituted 10-methyl acridinium trifluoromethanesulfonates salt have been synthesized and shown to react in methanol with aniline and n-butylamine to form derivatives which absorb strongly at 445 and 439 nm, respectively [4]. The reaction between 1-fluoro-2,4-dinitrobenzene and aliphatic amines [5], 1-fluoro

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and 1-chloro-2,4-dinitrobenzene and aliphatic amine have also been studied [6]. Terephthaloylacetylene [7] form yellow or orange colored product with primary and secondary amines and may be used for their detection.

Quinoline-2-(carboxaldehyde) has been used as reagent for spectrophotometric detection of primary amines [8]. N-hydroxysuccinimidyl 4,3,2¹-naphthapyrone-4-acetate has been utilized for determination of primary and secondary amines at pH 8.5 that gave the corresponding derivatives with in 5 and 15 min [9].

9-Chloroacridine and 9-methoxyacridine reagents have also been used for the determination of aliphatic amines [10,11]. These methods need heating the analytical solution and require excess of acridine reagent in order to achieve the reproducible results. The interaction of several aliphatic amines as n-donors and dinitrobenzene as n-acceptors have been studied in n-hexane. The formation of electron EDA complex was proposed to explain the spectroscopic behavior of the mixtures [12]. The kinetic studied of 1,2-dinitrobenzene with aliphatic amine have been investigated in n-hexane [13] and benzene [14].

The goal of this study was to investigate the detection of aliphatic amines with a reagent which does not require any derivatization or catalyst or heating but should be simple, quick to react and forms stable colored complexes.

2. Experimental

2.1. Apparatus

A ECIL make UV–Visible double beam spectrophotometer model UV-5704 equipped with two quartz cells and a Orion make pH meter model 1720A were used for absorbance and pH measurements, respectively.

2.2. Reagents

The m-dinitrobenzene (m-DNB) (E. Merck, India), amines (S.D. Fine, India), acetone (E. Merck), HCl (E. Merck), HNO₃ (E. Merck), NaOH (E. Merck) were used. All reagents were

of analytical grade. Double distilled water was used when required.

2.3. Test solution

Stock solutions of different aliphatic amines were prepared by diluting 1 ml of (between 1.1 and 8.4 M) different amines solution to 10 ml by distilled water except in case of triethylamine and 1-naphthylamine (these solutions were prepared in acetone).

2.4. Reagent solution

Stock solution of m-DNB was prepared by dissolving 1 g of reagent in 100 ml of acetone.

2.5. Procedure for determination of aliphatic amines

Standard solution of aliphatic amines in concentration ranges from 0.5 to 8.0 mg l⁻¹ was taken in 20 ml standard flask. 1 ml of m-DNB solution was added to each flask. Then the solution was made upto mark with acetone, 0.1 M HCl and water, separately. The absorbance of the solution so prepared was determined at different wavelength (200–950 nm) against a blank solution at room temperature. The spectrum was recorded after different time intervals.

2.6. Effect of pH

The absorbance reaction between methylamine and m-DNB was studied at different pH by adding 1 ml solution of m-DNB to 1 ml solution of methylamine and making the reaction mixture upto 20 ml with acetone, after adjustment of pH by adding 0.1 M solution of HNO₃ or NaOH.

2.7. Effect of other nitrogen containing molecules

The effect of other nitrogen containing molecules on the detection of aliphatic amines by m-DNB was studied by recording the spectra for different nitrogen containing compound mixed with m-DNB. One ml of reagent solution was mixed with 1 ml of different nitrogen containing

Table 1
Properties of EDA between different aliphatic amines and m-DNB

Serial number	Amine (concentration in mol l ⁻¹)	Amine dissolved in	Appearance of EDA complex	Minimum concentration detected (mg l ⁻¹)	Maximum concentration detected (mg l ⁻¹)	Minimum time, ϵ ($\times 10^2$ mol ⁻¹ cm ⁻¹)	Maximum time ϵ ($\times 10^2$ mol ⁻¹ cm ⁻¹)	λ_{\max} (nm)
1	Methylamine (5.1) [CH ₃ NH ₂]	Water	Pink	0.5	10.0	1 s (10.6)	2 days (14.5)	554.5
2	Ethylamine (3.5) [C ₂ H ₅ NH ₂]	Water	Purple	1.0	6.0	1 s (4.54)	1 day (78.14)	559.0
3	n-Butylamine(2.1) [CH ₃ (CH ₂) ₃ NH ₂]	Water	Light purple	1.0	8.0	1 s (7.35)	3 days (46.39)	569.0
4	Ethylenediamine(2.6) [H ₂ NCH ₂ CH ₂ NH ₂]	Water	Purple	1.0	6.0	1 s (46.38)	3 days (100.8)	557.5
5	1-Naphthylamine(1.1) [C ₁₀ H ₇ NH ₂]	Water	Yellow	1.0	6.0	3 h (85.0)	1 day (90.0)	556.0
6	Ethanolamine(2.6) [CH ₂ OHCH ₂ NH ₂]	Acetone	Orange	1.0	5.0	1 s (8.23)	3 days (15.34)	458.0
7	Ammonia(2.3) [NH ₃]	Water	Violet	1.0	6.0	2 h (4.22)	1 day (8.29)	551.0
8	Dimethylamine(3.5) [(CH ₃) ₂ NH]	Water	Violet	1.0	6.0	1 s (3.33)	1 day (57.3)	570.0
9	Diethylamine(2.1) [(C ₂ H ₅) ₂ NH]	Water	Light violet	0.5	8.0	1 s (60.7)	3 days (173.0)	552.0
10	Trimethylamine(2.7) [(CH ₃) ₃ N]	Water	Violet	0.5	10.0	1 s (13.09)	1 day (28.57)	560.0
11	Triethylamine(1.5) [(C ₂ H ₅) ₃ N]	Acetone	Pink	2.0	8.0	1 h (6.05)	2 days (16.31)	570.0

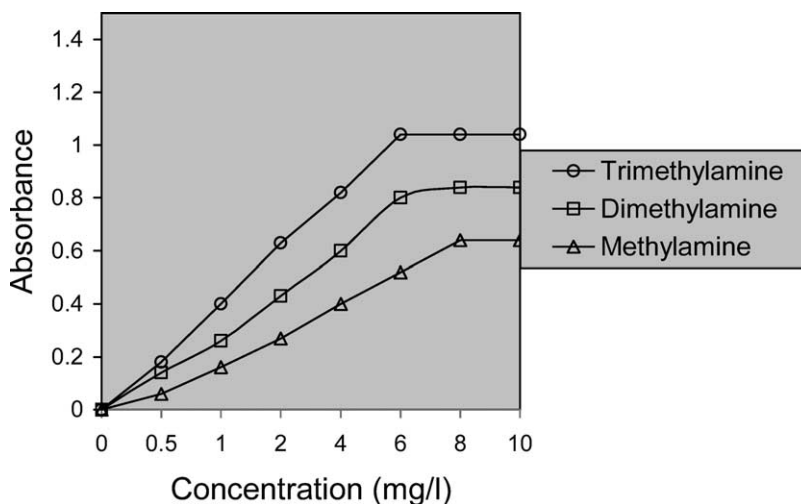


Fig. 1. Verification of Beer–Lambert's law.

solution (between 0.75 and 3.4 M) and made up to 20 ml by acetone.

2.8. Determination of amine in real samples

Water samples were collected from the residual water reservoir, river passing nearby and human urine from the workers of the chemical industry situated in one of the industrialized city of India. These samples were collected at peak hours of working and on hourly basis. Ten such samples were collected and mixed to get the composite sample for each type of the sample (residual water, river water and human urine). Residual water and river water samples were filtered before use for detection purpose. 5 ml each type of the composite

sample was mixed with one ml of the reagent solution (m-DNB) and made up to 10 ml with distilled water.

3. Result and discussion

Table 1 shows that the absorbance of reaction mixture of different amines and m-DNB, absorbs at different λ_{\max} values in the visible region of absorption. It is observed that there is a definite

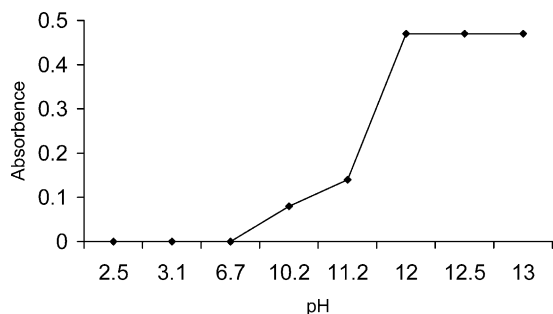


Fig. 2. Effect of pH on the absorbance of m-DNB–methylamine complex.

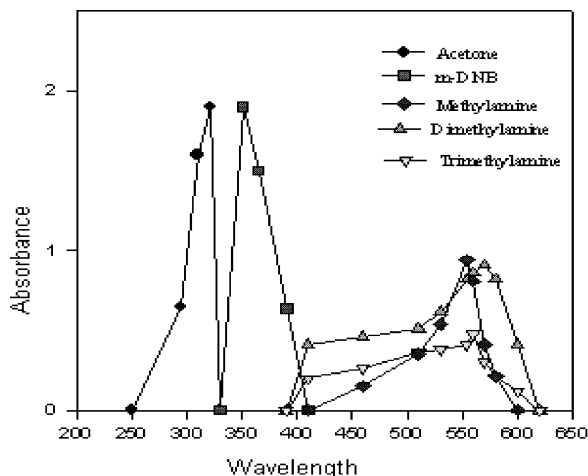
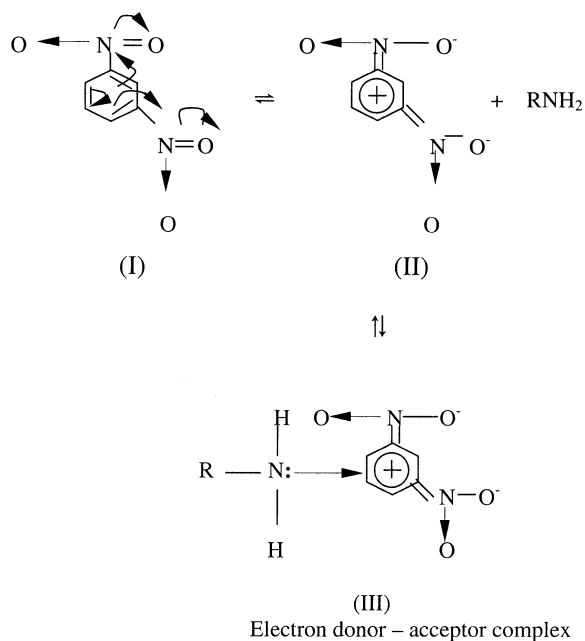


Fig. 3. Absorption pattern for EDA complexes of aliphatic amines with m-dinitrobenzene



Scheme 1.

shift of absorption wave-length as bathochromic shift from m-DNB to mixture of m-DNB + methylamine in acetone which absorb at 379 and 554.5 nm, respectively. This behavior shows that methylamine donates its non-bonding electron to π^*

energy state of m-DNB thus forming $n \rightarrow \pi^*$ EDA complex as per the Scheme 1 for pr-amine. All of pr- and sec-amines and only trimethylamine (tert-amine) react almost instantly with m-DNB while triethylamine, 1-naphthylamine and ammonia react slowly. Table 1 shows that molar absorptivity increases with time and EDA complexes of aliphatic amines with m-DNB are stable up to 24 h (for all of the pr-, sec- and tert-amines). Fig. 1 shows that Beer's law is verified for representative pr-amines (methylamine: concentration between 1 and 8 mg l^{-1} , n-butylamine: 1 and 6 mg l^{-1}), sec-amine (dimethylamine: 2–6 mg l^{-1}) and tert-amine (trimethylamine: 2–6 mg l^{-1}).

Acetone (as solvent) lowers the molar absorptivity values for reaction mixture of m-DNB and different amines. However, this effect is more prominent when water or acid is used as solvent. This is because of interaction of protons of water or acid with non-bonding electrons of amines. The resultant spectra of different amines show the broad peaks due to mixing of acetone peak with the peak of amines. As a result of study for the effect of pH on the absorbance value it was observed that study could be done at pH between 10 and 14 with the best result at pH 12 (Fig. 2). This shows that alkaline medium is required for detection as the proton in acidic medium may

Table 2
Effect of different nitrogen containing compounds on absorption maxima of methylamine with m-DNB

Serial number	Compound (concentration in mol l^{-1})	Nature of peak	λ_{max} (nm)	Molar absorptivity (ϵ value)
1	Pyridine(1.8)	Sharp	352.0	165.4
2	Acetonitrile(2.9)	Sharp	353.5	81.95
3	Indole(2.1)	Broad	363.0	249.6
4	N,N-diethylaniline(1.07)	Broad	338.5	331.0
5	Dimethylaminebenzaldehyde(1.1)	Broad	338.5	332.0
6	Triethanolamine(1.0)	Sharp	354.0	330.0
7	Nitrobenzene(1.2)	Broad	337.0	247.6
8	Thiourea(1.2)	Sharp	374.0	152.07
9	Urea(1.6)	Sharp	365.5	124.68
10	Acetamide(1.2)	Sharp	365.5	124.81
11	Diphenylamine(1.2)	Broad	359.5	399.2
12	Benzamide(1.3)	Sharp	361.0	248.62
13	2,4-Dinitrophenylhydrazine(0.75)	Broad	368.5	397.4
14	Aniline(1.6)	Sharp	377.0	199.6
15	Nicotamide(1.2)	Sharp	365.0	249.5

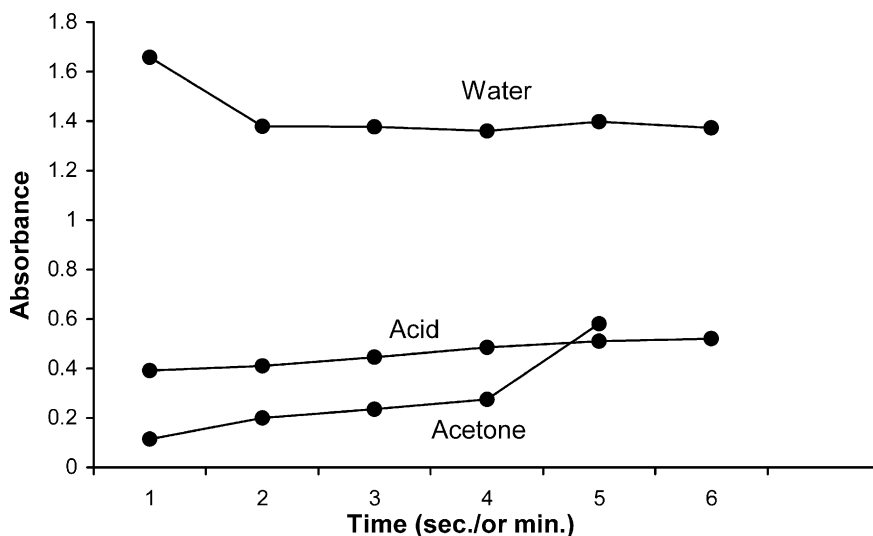


Fig. 4. Effect of solvent in detection of amine at 559 nm with m-DNB.

hamper the electron donating property of aliphatic amine as reported earlier [15].

Fig. 3 shows the absorption patterns for EDA complexes of aliphatic amines with m-DNB. The curves show different λ_{\max} values (between 458 and 570 nm) with different amines. For pr-aliphatic amine the λ_{\max} values could be seen in the order of n-butylamine > ethylamine > methylamine (followed by ammonia). As per Table 2, no interference is observed from other nitrogen containing molecules, in the detection of aliphatic amines with m-DNB. This shows the highly selective detection of aliphatic amines with m-DNB as reagent. The detection of aliphatic amines in aqueous environment is highly desirable due to the polluting nature of aliphatic amines [16]. Therefore, the detection of representative pr-, sec- and ter-aliphatic amines is attempted in aqueous media (acidic and water) as well as organic medium (acetone). Fig. 4 shows the effect of solvent in detection of aliphatic amines (represented by ethylamine) at 559 nm with m-DNB. The observations are (i) in acetone medium, with time the absorbance value increases while it decrease in water and almost no effect is seen in acidic media; (ii) the absorbance values are higher for aliphatic amines in water. Therefore, it may be

inferred that m-DNB is probably a good reagent for detecting the aliphatic amines in aqueous environment at microgram level of quantity, which could be exploited in water pollution studies. Therefore, this method of detection has been applied to three real water samples as detailed in Table 3, which suggests that methylamine, dimethylamine and trimethylamine could be accurately determined in residual water and river water while methylamine in all the three samples (residual water, river water and urine) by utilizing m-DNB as a reagent.

The accuracy of all the molar absorptivity values reported in Table 1 and 2 is $\pm 0.5\%$ and standard deviations (S.D.) are between 0.001 and 0.005 (for five replicates). In Table 3, the accuracy of results are between ± 0.5 and $\pm 1.0\%$ and S.D. nearly 0.001 (for six replicates).

4. Conclusion

m-DNB has been shown as a reagent for rapid detection of aliphatic amines in aqueous medium. It forms stable electron donor acceptor complexes with almost all type of aliphatic amines viz pr-, sec- and tert-amine. Detection could be done at

Table 3
Determination of different aliphatic amines in real samples with m-DNB

Amine/sample	Sample S-1 (residual water)			Sample S-2 (river water)			Sample S-3 (human urine)		
	Amine found (ppm)	Average (ppm)	% Detection, S.D.	Amine found (ppm)	Average (ppm)	% Detection, S.D.	Amine found (ppm)	Average (ppm)	% Detection, S.D.
Methylamine	0.062, 0.064, 0.062, 0.061, 0.063, 0.062	0.06233	98 ± 0.5, 0.0009	0.092, 0.094, 0.093, 0.092, 0.096, 0.095	0.09366	98 ± 0.5, 0.0014	0.086, 0.088, 0.084, 0.086, 0.086, 0.084	0.08566	96 ± 0.5, 0.0001
Dimethylamine	0.048, 0.049, 0.046, 0.047, 0.048, 0.045	0.04716	98 ± 1, 0.0013	0.032, 0.034, 0.032, 0.033, 0.032, 0.034	0.03283	96 ± 1, 0.0008	–	–	–
Trimethylamine	0.042, 0.044, 0.043, 0.041, 0.042, 0.043	0.04316	96 ± 1, 0.0018	0.024, 0.024, 0.026, 0.026, 0.024, 0.025	0.02483	96 ± 1, 0.0008	–	–	–

microgram levels in the visible region of spectrum without any interference by a number of nitrogen containing compounds other than aliphatic amines. This detection method could be used for water pollution studies.

References

- [1] A.I. Vogel, Textbook of Quantative Chemical Analysis, fifth ed, ELBS and Longman, 1989, p. 705.
- [2] P.C. Dwivedi, A.K. Banga, J. Phys. Chem. 85 (1985) 1769.
- [3] R.E. Smith, W.R. Davis, Anal. Chem. 56 (1984) 2345.
- [4] J.W. Dunning, J.T. Stewart, Talanta 38 (1991) 631.
- [5] L. Forlani, E. Marianucci, P.E. Todesco, Gazz. Chim. Ital. 122 (1992) 9349.
- [6] L. Forlani, J. Chem. Soc., Perkin Trans. 8 (1993) 1525.
- [7] R.K. Tiwari, A.K. Saxena, P.S. Venkataramani, Indian J. Chem. 41B (2002) 384.
- [8] H. You-Zung, L. Jinping, M.V. Novotny, W. Donald, Research Corp Technologies Inc, Patent Number: 19901016 US 598508.
- [9] X. Liu, H. Wang, S.C. Liang, H.S. Zhang, Anal. Chim. Acta 441 (2001) 45.
- [10] J.T. Steward, T.D. Shaw, A.B. Ray, Anal. Chem. 41 (1969) 360.
- [11] J.T. Steward, D.M. Lotti, J. Pharm. Sci. 59 (1970) 838.
- [12] J.O. Singh, J.D. Anunziata, D. Jorge, J.J. Silber, Can. J. Chem. 63 (1985) 903.
- [13] S.M. Chiacchiera, J.O. Singh, J.D. Anunziata, J. Silber, J. Chem. Soc., Perkin Trans. 2 (1987) 987.
- [14] S.M. Chiacchiera, J.O. Singh, J.D. Anunziata, J. Silber, J. Chem. Soc., Perkin Trans. 2 (1988) 1585.
- [15] B.P. Puri, L.R. Sharma, M.S. Pathania, Principle of Physical Chemistry, S.L.N. Chand and Co, Jalandhar, India, 1998, p. 1291.
- [16] H. Brieger, W.A. Hodes, Ind. Hyg. Occup. Med. 3 (1951) 287.