Physical Sciences Section

p-DIMETHYLAMINOBENZALDEHYDRAZONE DERIVATIVES AS INDICATORS

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Two hydrazones were subjected to study. The first hydrazone was the *p*-dimethylaminobenzalde-hyde-benzoylhydrazone (DMB). This hydrazone was used to determine Cu^{2+} by spectrophotometric method. This method depends on the extraction of Cu-DMB complex in chloroform. Maximum absorption was attained at 440 nm at pH 7-10. The second hydrazone, *p*-dimethylaminobenzaldehyde-*p*-nitrophenylhydrazone (DMN) was tested as an acid-base indicator. DMN compound was studied in UV and visible regions at different pH-values. DMN compound was found to have two pK_a values, 3.31 and 9.1. DMN was tested as acid-base indicator. It gave satisfied results for (1) strong acid-strong base system (2) strong acid-weak base system (3) weak acid-strong base system. The result was found to have maximum error 2% with maximum standard deviation 1.59.

Key words: Hydrazones, Cu^{2+}, Acid-base indicator.

Introduction

Four hydrazones were used for spectrophotometric microdetermination of Cu^{2+} [1]. Cu^{2+} was also determined spectrophotometrically by extraction of its oxime [2] and porphine [3] complexes. The absorbance of the formed complexes were found to obey Beer's law which may be useful in microdetermination of Cu^{2+} ranging from 2-50 µg/L [2] and up to 1.5 µg [3] . Spectrophotometric determination of Cu^{2+} had been done using thiocarbamate as indicator [4]. The method was successful for a narrow concentration range (from 1 up to 5 µg Cu^{2+}/5 ml solution). In the present work, a more simple and convenient method was done with a wider concentration range (from 15.8 up to 158 µg/5 ml Solution).

It was known that some acid-base indicators had some limitations. Methyl-orange for example, could not be used as appropriate indicator for titrations involving a strong base and weak acid. The DMN compound gave satisfied results for systems 1- 3.

Experimental

Benzoylhydrazine, *p*-nitrophenylhydrazine and *p*-dime-thylaminobenzaldehyde were supplied by El-Nil Co. These compounds were pure based on the elemental analysis, so they were used without further purification. The organic compounds (methanol, ethanol, chloroform and acetic acid) were of high purity (A.R. or spectral grade products). 8% v/v ammonia solution was prepared by diluting the content of BDH concentrated volumetric solution vial. Stock solution of Cu^{2+} was prepared by dissolving $CuSO_4.5H_2O$ (BDH) in bidistilled water. A series of Cu^{2+} solutions of different concentrations were prepared by dilution.

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The two hydrazones DMB and DMN were synthesized by adding 0.05 mol of the required hydrazine to 0.05 mol solution of *p*-dimethylaminobenzaldehyde in methanol (10 ml) containing acetic acid (0.1 ml). The mixture was heated on water-bath for one hour. After cooling, the hydrazone derivatives that separated out was filtered off, washed with little ethanol, dried and then recrystallized from aqueous ethanolic solution. The melting point of the compounds were found to be 180-182°C and 170 (dec.) °C (uncorrected) respectively.

A series (I) of 2×10^{-5} M Cu^{2+} solutions of different pH-values (3.5-11.7) were prepared. The pH-values were adjusted with 8 % v/v ammonia solution using HANNA instruments H18519 pH-meter. To each 5 ml Cu^{2+} solution, equal volumes of 10^{-2} M DMB-chloroform solution were added. This mixture was shaken well for 5 min. The absorbance of organic layer measurements gave λ_{max} at 440 nm using 752 UV Grating Spectrophotometer.

Another series (II) of 5 ml Cu^{2+} solutions of different concentrations of pH= 9 were prepared. 5 ml of 10^{-2} M DMB-chloroform solution were added. The absorbance of organic layers of this series were measured at λ_{max}=440 nm after shaking for 5 min.

p-Dimethylaminobenzaldehyde-*p*-nitrophenylhydrazone was easily prepared and tested as an acid-base indicator.^{1}H-NMR and IR spectra of DMN were studied. IR and ^{1}H-NMR spectra were obtained from Unicam SP 1025 and Varian EM 90 MHz spectrometers respectively. A solution of 1 % acid-base indicator was prepared by dissolving 10 mg of DMN compound into 100 ml of 20 % ethanolic aqueous solution.

Results and Discussion

The absorbance of organic layer measurements oil series (I) showed maximum extraction of Cu-DMB complex at

pH 7-10 (Fig. 1), while that of series (II) achieved Beer's law over the Cu^{2+} concentration range of 5 x 10^{-5} M up to 5 x 10^{-4} M (Fig. 2.) These results indicate that DMB compound could be considered as spectrophotometric indicator for microdetermination of Cu^{2+} (from 15.8 up to 158 µg/5 ml).

IR spectrum showed (C=N band) - at 1600, (N-H band) at 3300, (NO_2 band) at 590, (C-N band) at 850 cm^{-1} and (N=O stretching band for symmetrical and asymmetrical $ArNo_2$) at 1330 and 1510 cm^{-1} respectively. On the other hand ^{1}H-NMR (DMSO-d_6) showed signals, at δ 2.7 (5, 6H) for the two methyl groups at δ 6.8--7.8 (m,9H) for the aromatic protons as well as the CH proton, and the NH proton of the hydrazone residue at δ 10.5 ppm.

The absorption spectra of the DMN compound in 50 % ethanol-water (v/v) was studied in the UV and visible regions at different pH-values (from 2 up to 12.4). Britton Robinson
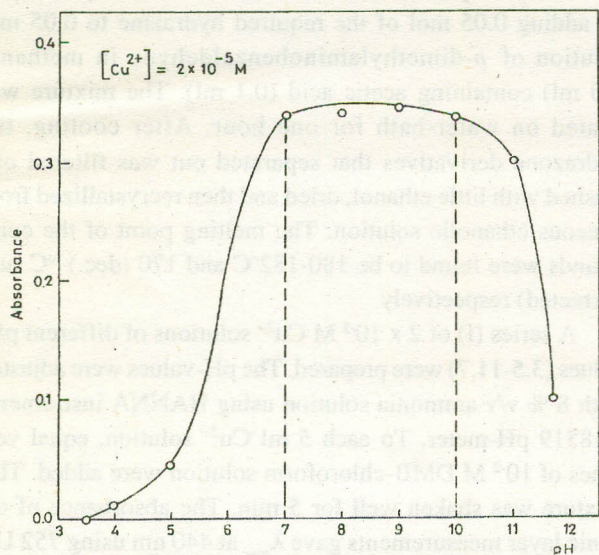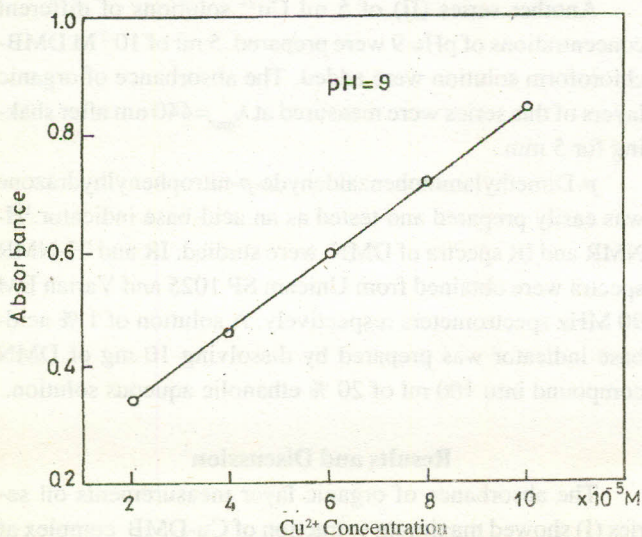
[5] universal buffer series were used to control the pH-value. The spectra obtained indicate that the intensity of absorption bands are dependent on the pH-value of the medium. The absorption band at 440 nm and 310 nm increased as the pH increased up to 10 (Fig.3). The change of absorbance according to the change of pH leads to the appearance of an isobestic point at 360 nm indicating the existence of an equilibrium between two different forms of DMN compound, the hydrazone-form and the hydrazo-form. At pH = 12, the colour of the buffered mixture changes from pale-yellow into violet due to the formation of the azo-form, as indicated from the spectrophotometric measurements where λ_{max} is shifted from 440 nm to 480 nm (Fig. 3).
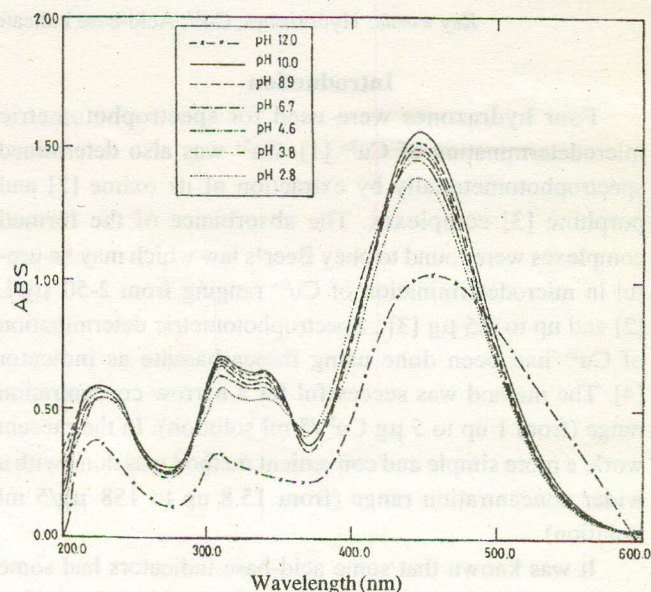

Fig. 1. Effect of pH on the extraction of Cu-DMP complex.

Fig. 3. Electronic absorption spectra of 1 x 10^{-4} M in different buffer solutions.
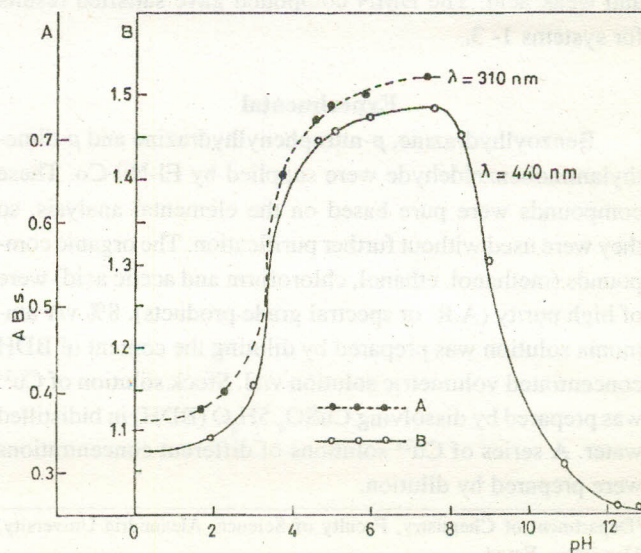

Fig. 2. Beer's low achievement.

Fig. 4. Absorbance – pH curves.

The change of absorbance with pH changes can be utilized in determining the dissociation constant using half-height method [6].This method is based on the fact that at the half-height of the absorbance-pH curve, the dissociated and undissociated species exist in equivalent quantities, thus:

$$pK_a = pH, \text{ at } A_{\frac{1}{2}}$$

where $A_{\frac{1}{2}} = \dfrac{A_{max} - A_{min}}{2}$

The DMN compound was found to have two pKa's, They were 3.31 and 9.1.

The variation of absorbance with pH at 440 nm includes two infections (Fig. 4). This indicates that two equilibriums can be traced by this method. The pK_a value 3.31 corresponds to the equilibrium between the hydrazo-form which is dominant into acid medium and the hydrazone-form which is dominant in neutral and slightly alkaline media, while the pK_a value 9.1 corresponds to the equilibrium between the hydrazone-from and the azo-form which is dominant in strong alkaline medium. Nearly, the same pk_a values were obtained from the Collecter method [7].
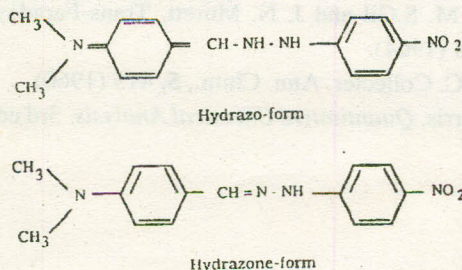

Hydrazo-form

Hydrazone-form

TABLE 1. STANDARDIZATION OF HCl SOLUTION BY STANDARD Na₂CO₃ SOLUTION, USING DMN INDICATOR.

HCl Concentration Mx10⁻³		
Taken	Found	% Error
	9.87	-1.3
10	9.89	-1.1
	9.91	-0.9
	50.0	0.0
50	50.5	+1.0
	50.0	0.0
	101	+1.0
100	100	0.0
	101	+1.0
	302	+0.8
300	301	+0.3
	303	+1.0
	1010	+1.0
1000	1009	+0.9
	1012	+1.2

Standard deviation from true value = 0.32.

the acid-base indicator has a lemon-yellow colour in acid solutions, orang in neutral and slightly alkaline solutions, and violet in strong alkaline solutions. Three systems were studied using the new synthesized indicator: (1) strong-acid-strong base system, (2) strong acid-weak base system, (3) weak acid-

TABLE 2. TITRATIONS BETWEEN NaOH AND HCl SOLUTIONS USING DMN INDICATOR.

HCl as titrant			NaOH as titrant		
NaOH Concentration Mx10⁻³			HCl Concentration Mx10⁻³		
Taken	Found	%Error	Taken	Found	%Error
	9.88	-1.2		10.20	+2.0
10	9.90	-1.0	10	10.18	+1.8
	9.91	-0.9		10.15	+1.5
	49.91	-0.18		50.04	+0.8
50	50.00	0.00	50	50.05	+1.0
	50.00	0.00		50.00	0.0
	100.8	+0.8		98.0	-2.0
100	100.5	+0.5	100	98.2	-1.8
	100.0	0.0		99.0	-1.0
	302.5	+0.8		295.2	-1.7
300	301.7	+0.6	300	293.0	-2.0
	303.0	+1.0		294.1	-2.0
	1005	+0.5		988.3	-1.2
1000	1001	+1.2	1000	985.0	-1.4
	1009	+0.9		993.0	-0.7
Standard deviation = 0.79					1.56

TABLE 3. TITRATIONS BETWEEN NH₄OH AND HCl SOLUTIONS, USING DMN INDICATOR.

HCl as titrant			NH₄OH as titrant		
Concentration Mx10⁻³			HCl Concentration Mx10⁻³		
Taken	Found	%Error	Taken	Found	%Error
	9.91	-0.9		11.0	+1.0
10	9.93	-0.7	10	11.4	+1.4
	9.91	-0.9		11.8	+1.8
	49.7	-0.6		51.00	+2.0
50	49.5	-1.0	50	50.75	+1.5
	49.6	-0.8		51.00	+2.0
	99.1	-0.9		102.0	+2.0
100	99.0	-1.0	100	101.4	+1.4
	99.5	-0.5		101.3	+1.3
	303	+1.0		303.1	+1.0
300	299	-0.3	300	304.2	+1.4
	302	+0.7		304.3	+1.4
	1008	+0.8		988.0	-1.2
1000	1010	+1.0	1000	985.2	-1.5
	1005	+0.5		984.4	-1.6
Standard Deviation	= 0.83				1.59

Table.4. Titrations Between NaOH and CH$_3$COOH Soluitons Using DMN Indicator.

CH$_3$COOH as Titrant			NaOH as Titrant		
NaOH Concentration Mx10^{-3}			CH$_3$COOH Concentration Mx10^{-3}		
Taken	Found	%Error	Taken	Found	%Error
10	10.1	+1.0	10	9.80	-2.0
	10.1	+1.0		9.83	-1.7
	10.1	+1.0		9.85	-1.5
50	50.0	0.0	50	50.0	0.0
	50.0	0.0		50.0	0.0
	49.8	-0.4		49.5	-1.0
100	100.5	+0.5	100	99.0	-1.0
	101.0	+1.0		98.0	-2.0
	100.8	+0.8		99.3	-0.7
300	303.1	+1.0	300	295.1	-1.6
	302.8	+0.9		294.0	-2.0
	303.0	+1.0		296.3	-1.2
1000	1010.0	+1.0	1000	985.0	-1.5
	1009.0	+0.9		987.0	-1.3
	1009.2	+0.9		980.3	-2.0
Standard Deviation =	0.87				1.50

strong base system. Tables (1-4) represent the results attained for the three systems. Results listed in Tables 1-3 are comparable with that obtained using methyl-orange indicator. For titrations involving a strong base and weak acid (system 3),

methyl orange would be an entirely inappropriate indicator. Phenoplhthalein would be a much more appropriate choice [8]. The DMN indicator gave satisfied results for systems 1,2 and 3. This could be considered as an advantage for DMN indicator. The new indicator gave results of maximum error 2 % and maximum standard deviation 1.59 which are satisfactory to use it as good acid-base indicator.

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