ELSEVIER

Dyes and Pigments 41 (1999) 143–147

DYES and PIGMENTS

Determination of *p*Ka values of some azo dyes in acetonitrile with perchloric acid

M. Kurtoğlu[a], N. Birbiçer[b], Ü. Kimyonşen[c], S. Serin[a,*]

[a]*Department of Chemistry, Faculty of Science and Arts, University of Kahramanmaraş Sütçü İmam, 46100 Kahramanmaraş, Turkey*
[b]*Department of Textile Engineering, University of Kahramanmaraş Sütçü İmam, 46100 Kahramanmaraş, Turkey*
[c]*Başer Colgate, Bahçe, Adana, Turkey*

Received 4 September 1998; accepted 1 October 1998

Abstract

In this study, 10^{-4} M acetonitrile solutions of 15 azo dyes synthesized by coupling hydroxyl containing compounds such as phenol, 1-naphthol and 2-naphthol with diazonium salts obtained by the diazotisation of aniline and aniline derivatives were determined by potentiometric titration with perchloric acid in acetonitrile at room temperature. The turning points and the half neutralization potentials of these compounds were determined using the potentiometric titration curves obtained in order to calculate their pKa values. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Non-aqueous titrations; Potentiometric titrations; Basicity order; Azo dyes

1. Introduction

The effects of various substituents and of the solvents used on the behaviour of organic compounds in basic or acidic media has long been and still is of great interest [1–5]. The most important concepts used in the definition of acids and bases are acidity or basicity strengths, these concepts being related to ionisation equilibrium constants.

Water is the most common solvent used in titrimetric analyses due to its unique properties. However in spite of having some unique properties water is not a suitable solvent for the determination of the *p*Ka values of those organic compounds showing very weak acidic or basic character in aqueous media and those acids and bases which remain outside the pH scale developed as regards to aqueous media [1,3].

Compounds containing functional groups, and the acidic and basic character of these groups, have been investigated by various workers [5–10]. There are also literature studies in which the basic and acidic character of the functional groups of azo compounds, which are of industrial interest, have been examined [11,12]. These studies can be carried out in aqueous or non-aqueous media by spectrophotometric and titrimetric ways depending upon the compound [13]. The spectroscopic investigation of some azo dye showing tautomerism depending upon the alkanity of the media are particularly interesting [14,15]. Our study was carried out using potentiometric titration in non-aqueous media since the azo dyes prepared were soluble in organic solvents.

---

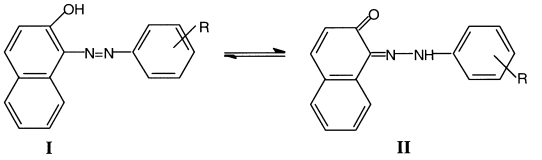
[*] Corresponding author.

PII: S0143-7208(98)00077-1

In this study, acetonitrile solutions of some of the azo dyes containing various functional groups (–Cl, $-NO_2$, $-CH_3$, –OH) were potentiometrically titrated with percholoric acid solution in acetonitrile. The structures of the azo compounds synthesised are listed in Table 1. The fact that these azo compounds are weakly basic necessitates the utmost care for their titrations. Acetonitrile, with a dielectric constant of 28.6, is a suitable non aqueous solvent for the titration of azo type dyes [16].

Azo dyes can exist as azo compounds or hydrazone compounds or their mixtures. Products from aminohydroxynaphthane-sulfonic acids are mostly formulated only as azo compounds or azo-hydrazone tautomerism is consciously omitted. Fedorov observed that monoazo dyes derived from chromotropic acid (4, 5-dihydroxy-2, 7-naphthalenedisulfonic acid) exist exclusively in the hydrazone form, while bisazo dyes are in the azo configuration [17].

Some time later, work was reported on the crystal structure determination of six azo pigments derived from β-naphthol. In the first three of these structures the accuracy of the work was insufficient to detect the hydrogen atoms, and the molecular configuration was assumed to be that of formula I. In the other three studies the accuracy of the work was improved and the positions of the hydrogen atoms were determined. These indicated that the 'azo' bond did not occur and the bridging was really due to a 'hydrazone' bond (II) [18].



Figs. 1 and 2 show the titration curves for two azo dyes, namely 4-(3'-chlorophenylazo)-1-naphthol and 4-(2′-methyl-5′-chlorophenylazo)-1-naphthol.

Using these curves the half neutralisation potentials (HNP) were determined and their pKa values were calculated. In the calculation of pKa values 59 mV was taken as equal to 1 pKa unit. The half neutralisation potentials (HNP) and pKa values of the azo dyes investigated are listed in Table 1.

2. Experimental

2.1. Apparatus and chemicals

The titrations were carried out using an Orion model SA 720 digital pH meter having combined glass and calomel electrodes, with a magnetic stirrer and a semi micro burette with divisions of 0.01 ml. The internal KCl solution of the calomel electrode was modified for the non aqueous media [19].

The azo dyes were synthesized and dried in accordance to the literature [16,20]. All the chemicals and the solvents used in the study were purchased from Merck and used without further purification.

The azo dye solutions were titrated immediately after their preparation.

3. Results and discussion

The factors effecting the basicity of the compounds can be classified as follows:

i. inductive effects (substituent, alkyl and aryl effects);
ii. steric effects (F-strains and B-strains);
iii. solvent effects [9] (dipole moment, dielectric constant, acidity and basicity);
iv. hydrogen bonding;
v. resonance effects [21,22].

In this work it was observed that the inductive and resonance effects had a strong influence and that hydrogen bonding had weak effect on the basicity of some of the hydroxyl azo dyes in acetonitrile.

The —N = N– group is a weakly basic. However the basic character of this group is not greater than that of water due to resonance and inductive effects of the benzene ring. The potentiometric titration of this type compounds can conveniently be carried out in suitable organic solvents. Azo

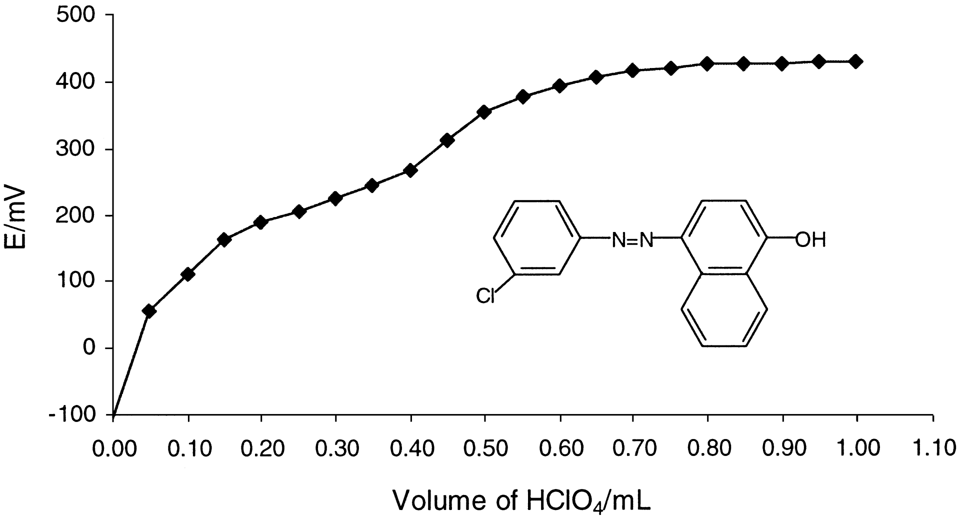


Fig. 1. Titration plot of 4-(3′-chlorophenylazo)-1-naphthol with $HClO_4$ in acetonitrile.

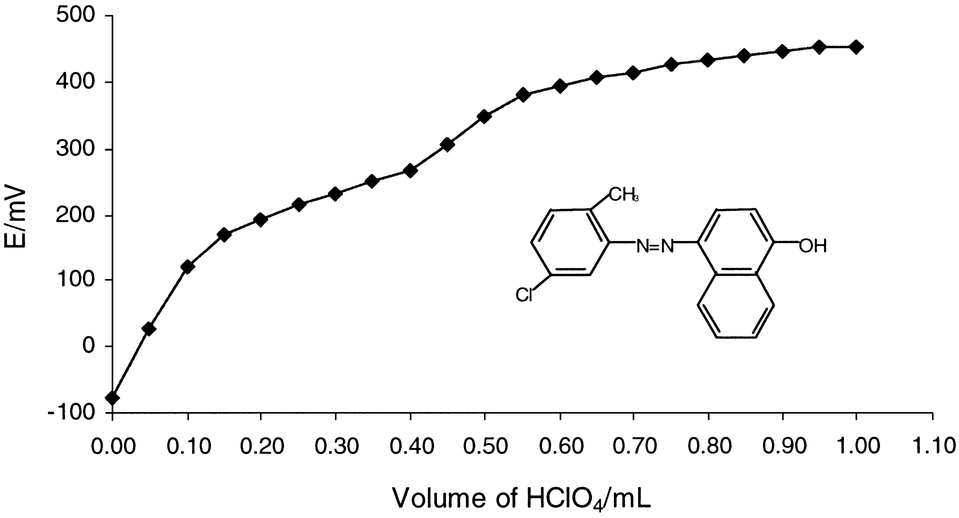
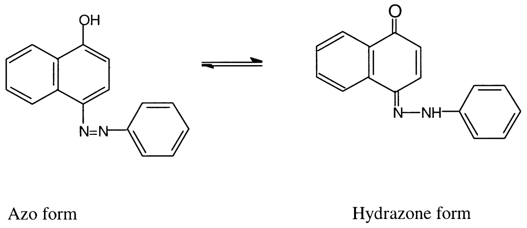


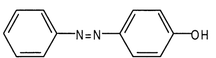
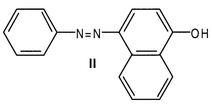
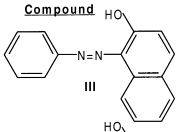
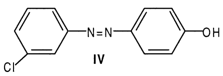
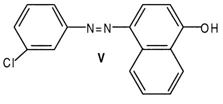
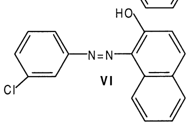
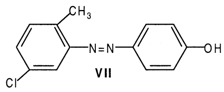
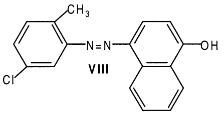
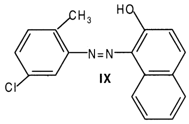
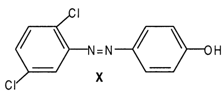
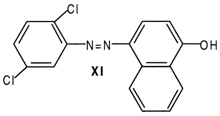
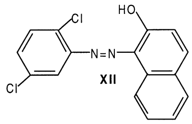
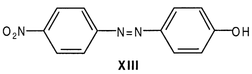
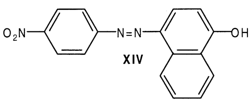
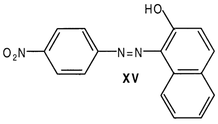
Fig. 2. Titration plot of 4-(2′-methyl-5′- chlorophenylazo)-1-naphthol with $HClO_4$ in acetonitrile.

compounds are generally represented by an azo form; however, some of them show azo-hydrazone tautomerism. A number of spectroscopic data have established that azo dyes, can exist in solution as hydroxy-azo or as quinone-hydrazone tautomers. Generally, the ratio of the azo-form to the hydrazone-form is much higher in organic solvents than in water, the hydrazone is favored by water and the azo by polar organic solvents [23,24].



Azo form hydrazone form since the electron density at the nitrogen atom attached to the phe-

Table 1
*p*Ka values and half-neutralisation potentials (HNP) of azo dyes titrated potentiometrically with $HClO_4$ in acetonitrile

Compound	HNP/mV	*pKa*	Compound	HNP/mV	*pKa*	Compound	HNP/mV	*pKa*
 I	205	3.60	 II	194	3.80	 III	215	3.44
 IV	210	3.52	 V	193	3.82	 VI	221	3.37
 VII	175	4.20	 VIII	173	4.16	 IX	182	4.05
 X	203	3.62	 XI	189	3.90	 XII	210	3.50
 XIII	220	3.34	 XIV	207	3.60	 XV	245	2.95

nolic ring in the azo dyes I, IV, VII, X and XIII is less than the electron density of the other nitrogen atoms of the azo group due to the electronic effect of the *p*-nitro group, it quite possible that the nitrogen atom of $-N=N-$ group attached to the ring can be protonated. In the case of 1-naphthol dyes (II, V, VIII, XI, XIV) it is possible to say that the nitrogen atom attached to the naphthalene moiety is protonated by analogy with their close similarity to the phenolic dyes. When 2-naphthol dyes (III , VI , IX, XII, XV) are investigated the nitrogen atom attached to the substituted benzene ring may also establish intramolecular hydrogen bonds with the O-H group of the 2-naphthol in addition to the phenolic or 1-naphthol dyes. Due to both the effect of the substituent groups and the formation of hydrogen bonds, it is highly probable that the nitrogen atom of the azo group may be protonised during its titration with perchloric acid.

The titration results revealed that the most suitable solvent for these type of titrations was acetonitrile. The basicity order of the coupling components in acetonitrile was 2-naphthol > phenol > 1-naphthol. The *p*Ka values of compounds IV, v and VI obtained by coupling with phenol, 1-naphthol and 2-naphthol to 3-chloroaniline were 3.52, 3.82 and 3.37, respectively. The azo compound V was 0.3 *p*Ka more basic than the azo compound IV and the azo compound V was 0.15 *p*Ka more basic than VI. The basicity order of the compounds obtained by coupling the diazonium salts of aniline derivatives with phenol was found to be VII > X > I > IV > XIII. The $-CH_3$ group present in compound VII increased the basic character due to its electron donating ability. On the other hand the $-NO_2$ group on compound VIII which withdraws the electrons on the $-N=N-$ group by both inductive and resonance effects caused a decrease in basicity. Although Cl^- on *o*-position withdraws electrons due to its inductive effect, it also donates electrons by resonance. On the other hand Cl^- at the *m*-position only withdraws electrons by the inductive effect, which in turn decreases the basicity since there is no resonance effect at this position.

The basicity order of the compounds derived from 1-naphthol was found to be VII > XI > V > II > XI. The azo dye containing a $-NO_2$ group in this series shows a lower basic character compared with the other dyes. The order of basicity for the azo compounds obtained from 2-naphthol after the titration carried out in acetonitrile was: IX > XII > III > VI > XV.

One important finding of this study is that the azo compounds synthesized from 2-naphthol showed less basic character than those synthesized from 1-naphthol. For instance compound XV is more basic than compound XIV. This difference can be attributed to intra-molecular hydrogen bonding factors. In other words the $N \cdots H \cdots O$ hydrogen bond formed between the nitrogen atom in $-N=N-$ and the hydrogen atom of the hydroxyl groups blocks the unpaired electron pair on the nitrogen atom, thus decreasing the basicity.

Acknowledgements

The authors are grateful to the Department of Chemistry, University of Çukurova, Adana, Turkey, for providing laboratory facilities.

References

[1] Huber W. Titrations in non-aqueous solvents. London: Academic Press, 1967.
[2] Gündüz T, Gündüz N, Kiliç E, Kenar A. Analyst 1986;111.
[3] Fritz JS. Acid-base titrations in non-aqueous solvents. Boston, MA: Allyn and Bacon, 1973.
[4] Skoog AD, West MD, Holler FJ. Analytical chemistry. New York: WB. Sounders Corr. 1988.
[5] Taft RW. J Phys Org Chem 1983;14:242.
[6] Moran F, Celadon D, Severin MG, Vaonollo E. J Am Chem Soc 1991;113:9320.
[7] Fritz JS. Analytical Chem 1950;22:578.
[8] Streuli CA. Analytical Chem 1959;31:1652.
[9] Toren EC, Buck RP. Analytical Chem 1970;42:284–316.
[10] Lau YK, Saluja PPS, Kebark P, Alder W. J Am Chem Soc 1978;100:7328.
[11] Bredereck K, Schumacher C. Dyes and Pigments 1993;21:45.
[12] Fedorov LA, Sokolorskii?, Dvoskin, S. I. Zh Anal Khim 1987;10:1762.
[13] Abeta S, Akahori K, Meyer U, Zollinger H. J Soc Dyers Colour 1991;107:12.
[14] Bredereck K, Schumacher C. Dyes and Pigments 1993;21:23.
[15] Bredereck K, Schumacher C. Dyes and Pigments 1993;23:121.
[16] Serin S, Kurtoğlu M. Analyst 1994;119:2213.
[17] Lyçka A, Jirman J. Dyes and Pigments 1987;8:315.
[18] Whitaker A. J Soc Dyers Colour 1988;104:294.
[19] Kiliç E, Gündüz T. Analyst 1986;111:949.
[20] Kurtoğlu M. MSc. thesis, Institutation of Science, University of Çukurova, Adana, Turkey, 1993.
[21] Gündüz T, Kiliç E, Ertüzün V, Çetinel G. Analyst 1986;111:1439.
[22] Gündüz T. Gündüz N, Kiliç E, Kenar A. Analyst 1986;111:1345–7.
[23] Griffiths J, Hawkins C. J Chem Soc Perkin Trans 2. 1977;747.
[24] Kawashima N, Fujimoto N, Meguro K. Journal of Colloid and Interface Science 1985;103:459.