DETERMINATION OF THE ACIDIC CHARACTER OF SOME AZO DYES BY POTENTIOMETRIC TITRATION[1]

*Potansiyometrik Titrasyon İle Bazı Azo Boyarmaddelerin Asidik Karakterlerinin Belirlenmesi**

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ÖZET

On altı tane azo boyarmadde 4-amino-5-hidroksinaftalin-2,7-disülfonik aside sübstitüe anilin bileşiklerinin kenetlenmesi ile sentezlendi. Sentezlenen bileşiklerin asidik karakterlerinin belirlemek için oda sıcaklığında standart sodyum hidroksit çözeltisi ile titre edildi (25 ±0.5˚C ; 0.1 M KCl). Sentezi gerçekleştirilen bileşiklerde sülfo gruplarının protonları bileşiklerin asidik karakterlerini belirlemek için titre edildi. Azo boyarmaddelerin titrasyonunda en uygun solvent olarak su belirlendi. Azo boyarmaddelerin içerdiği sodyum miktarı hem alev photometresi hemde potansiyometrik titrasyon kullanılarak tayin edildi. Titrasyonlar her bir azo boyarmadde için farklı konsantrasyonlarda tekrar edildi. Azo boyarmaddelerin bağıl standart sapmaları % 1 den daha küçük olarak hesaplandı. Bu bileşiklerin yarı nötralizasyon potansiyelleri ve PK_a değerleri potansiyometrik titrasyon eğrileri kullanılarak belirlendi.

ABSTRACT

Sixteen azo dyes have been synthesized coupling of the substituted aniline compounds with the 4-amino-5-hydroxynaphthalane-2,7-disulfonic acid mono sodium salt (H-acid). Prepared compounds titrated with standardized sodium hydroxide solution at room temperature (25 ±0.5˚C ; 0.1 M KCl) in order to determine their acidic character. In the synthesized compounds, protons of sulpho groups were titrated to have clear information about their acidic characterization. Water was determined as the most suitable solvent to the titration for azo dyes. Sodium content of azo dyes has been determined using both the potentiometric titration and flame photometer. The titrations were repeated for different concentrations of each azo dye. The relative standard deviations (RSD%) of the azo dyes were calculated <±1%. PK_a values and half neutralization potentials of these compounds were determined using the potentiometric titration curves.

Introduction

Potentiometric titration yields valuable information about the acidity or basicity of compounds, and widely used in biochemistry (Farkas and Kurzak,1990), analytical chemistry (Grosvenor,1982) and industrial chemistry (Jemasu and Iwamato, 1982). Azo dyes are widely used textile industry (Oh and Kang, 1996) as dye material, and generally contain two sulphonic acid groups. Acidity and basicity of some azo dyes were worked by many researchers (Serin and Kurtoglu, 1994). Potentiometric titration of these compounds can be carried out aqueous and non-aqueous media (Gunduz, 1986 ; Lycka and Jirman, 1987).

There are two main effects acidity or basicity of organic compounds, respectively, molecular structure and solvent effect (Taft, 1983; Hine, 1975; Gunduz, 1986). Many organic compounds with containing functional groups (NH_2, OH, -N=N-) exhibit weakly basic or weakly acidic properties in water (Fritz, 1973). Thus, Water is not suitable solvent to determine acidic and basic character of these groups.

When the literature on the determination of acidic character of sulpho groups, it can be seen that potentiometric titration in aqueous media has not been investigated. Acidic and basic characteristic of azo dyes have undetermined with classic titration method, because, determination of

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turning point with color indicator is impossible due to colorized azo dyes. Azo dyes containing sulpho groups were soluble in water and these compounds can be titrated in aqueous media.

In this study, some azo dyes containing sulpho groups were titrated potentiometrically with standardized sodium hydroxide. These azo dyes containing two sulpho groups were strongly acidic compounds in water. The synthesized compounds containing sulpho groups have two acidic protons, generally two basic turning points were observed at the end of titration. Water is the most common solvent used in titrimetric analyses due to its unique properties. The studies were performed in aqueous media with neutralization titration since synthesized compounds insoluble most organic solvents.

Aforementioned azo dyes were synthesized substitute aniline compounds and 4-amino-5-hydroxynaphthalane-2,7-disulfonic acid mono sodium salt, and which were shown in Fig. 1, 2, 3. The half-neutralization potentials, corresponding pK_1 and pK_2 values of azo dyes containing sulpho groups were given in Table I. Sodium content of azo dyes has been determined, both potentiometric titration and the flame photometer. The results are given Table II. By careful examination of the curves, half neutralization potentials of the azo dyes were determined and from these corresponding pK_a values were calculated. In calculations of pK_a values, 59 mV was taken as corresponding to one pK_a unit.

Experimental

Apparatus

All potentiometric titrations were carried out at 25 ±0.5˚C by using an Orion Model SA 720 digital pH meter, equipped with a glass electrode. A magnetic stirrer, a semimicro burette calibrated in 0,01 ml and 25 ml beaker was used for titration. The ionic strengths of solutions were adjusted with 0.1 M KCl.

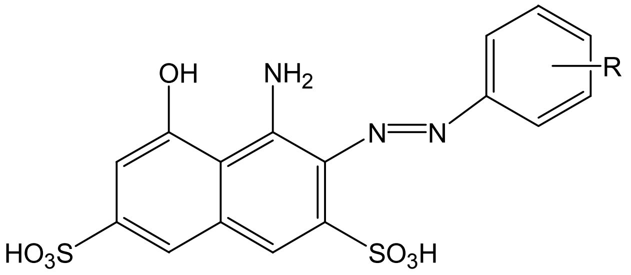
The saturated KCl solution of the calomel electrode was emptied and the electrode washed several times with distilled water. After drying, it was filled with saturated KCl solution in water. The flame photometer was used for nation of amount of sodium in the azo dyes.

Chemicals

Aniline and its derivatives, 4-amino-5-hydroxynaphthalane-2,7-disulfonic acid mono sodium salt, sodium hydroxide and other chemicals were purchased from Merck (Darmstadt, Germany). 4-Amino-5-hydroxynaphthalane-2,7-disulfonic acid mono sodium salt was recrystallized several times from ethyl alcohol-water (1:1) by the addition of hydrochloric acid to pH 3. For potentiometric titrations, 0.1 mol l^{-1} sodium hydroxide solution was prepared and standardized with potassium mono hydrogen phthalate. Azo dyes solutions were prepared 5.10^{-3} mol l^{-1} with freshly distilled water.

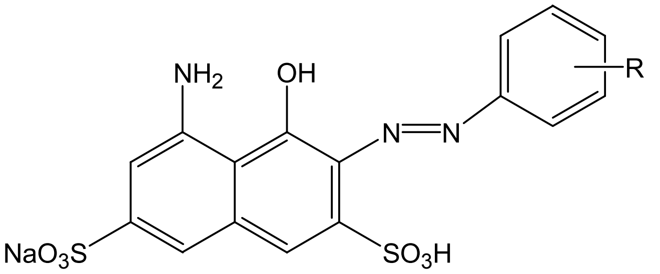
Synthesis of Azo dyes

Azo dyes used in Potentiometric titration were synthesized and purified according to the literature (Kırk otimer; Tunçel, 1996). Aniline derivative compounds have been diazotized that were coupled with 4-amino-5-hydroxynaphthalane-2,7-disulfonic acid mono sodium salt in alkaline and acidic media. Coupling to H-acid occurs in acidic media at the position ortho to the amino group, beside of this, in basic media at the position ortho to the hydroxyl group (Zollinger, 1995). All azo dyes were recrystallized several times from ethyl alcohol-water (1:1) by the addition of hydrochloric acid to pH 3. All organic impurities were then extracted by washing with small portions of diethyl ether. The precipitated dyes were dried under vacuum at 60˚C. The purity of all azo dyes were evaluated by thin layer chromatography. The formulae of the azo dyes were given in Fig. 1, 2 and 3, respectively.

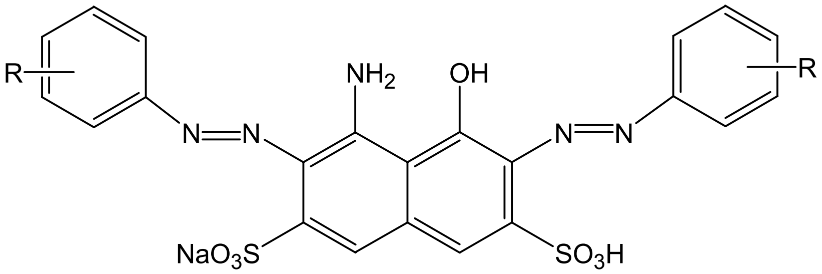


R = 3-NO_2 (1a), 4-NO_2 (1b), 3-Cl (1c), 4-Cl (1d), 2,5-Cl (1e)

Fig. 1. Structure of the 1 type azo compounds.



R = 3-NO_2 (2a), 4-NO_2 (2b), 3-Cl (2c), 4-Cl (2d), 2,5-Cl (2e), H (2f)
Fig. 2. Structure of the 2 type azo compounds.



R = 3-NO_2 (3a), 4-NO_2 (3b), 3-Cl (3c), 4-Cl (3d), 2,5-Cl (3e)
Fig. 3. Structure of the 3 type azo dyes.

Potentiometric Titration

The azo dyes were titrated with the 0,1 mol l^{-1} sodium hydroxide solution that has been daily adjusted. PH meter was standardized against an aqueous buffer solutions of pH: 4 and pH: 9. Dye solutions were titrated immediately after their preparation. All titrations were carried out manually and repeated for different concentrations of azo dyes. During the titration, the pH values and the volume of titrant regularly. The processing software allows the detection of turning points by the calculation of titration derivative curve (dpH/dV).

Results and discussion

The azo dyes derived from 4-amino-5-hydroxynaphthalane-2,7-disulfonic acid mono sodium salt were synthesized from the diazonium salts, for which substitute aniline derivatives were used. The azo dyes used in this work which were compounds of 4-amino-5-hydroxynaphthalane-2,7-disulfonic acid derivatives has been illustrated in Fig 1 and 2, 3, respectively.

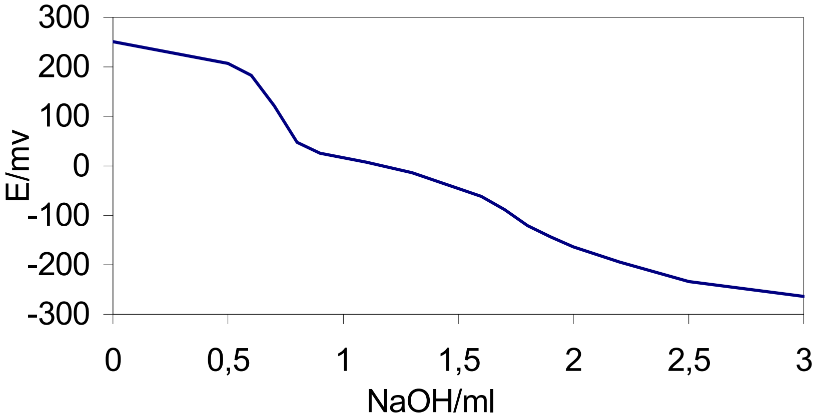


Fig. 4. Titration graph of 4-amino-5-hydroxynaphthalane-2,7-disulfonic acid with standardized sodium hydroxide in water.

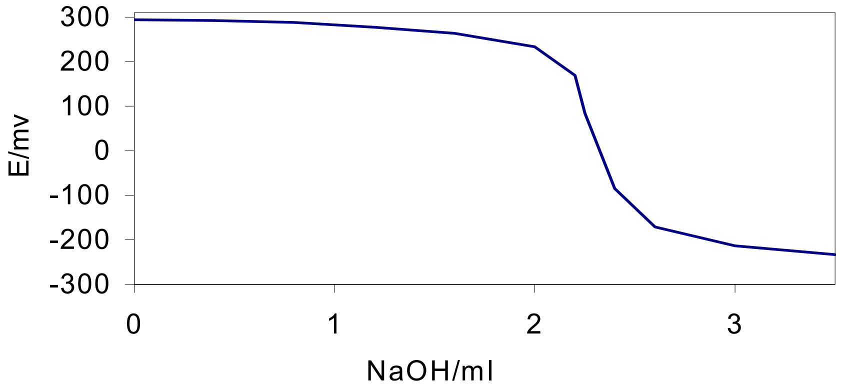


Fig. 5. Titration graph of 2c compound with standardized sodium hydroxide in water.

Azo dyes were titrated potentiometrically in aqueous media with standardized sodium hydroxide as titrant. In the synthesized compounds, protons of sulpho groups were titrated to give clear information about their acidic characterization. One or two well defined S-shaped end point (See Fig 4-5) was determined titration curve of the azo dyes. Turning points for azo dyes corresponded to one or two equivalent of base and related to the neutralization of the sulpho groups.

Table I. PK_a values, and half neutralization potentials (HNP) of azo dyes.

Compound	**pK_1**	**$^a RSD_1$%**	**HNP_1(mv)**	**PK_2**	**$^a RSD_2$%**	**HNP_2(mv)**
H-acid	3.44	0.3	200	8.45	0.7	-96
1a	3.23	0.6	213	7.42	0.3	-34
1b	3.26	0.6	211	7.20	0.6	-22
1c	3.20	0.4	214	7.41	0.4	-34
1d	3.16	0.7	217	7.38	0.5	-32
1e	3.19	0.5	215	6.93	0.2	6
2a	3.04	0.3	223	---	---	---
2b	2.75	0.3	241	---	---	---
2c	2.39	0.8	262	---	---	---
2d	2.29	0.9	267	---	---	---
2e	2.86	0.5	234	---	---	---
2f	2.63	0.7	248	---	---	---
3a	2.59	0.7	249	---	---	---
3b	2.78	0.3	239	---	---	---
3c	2.69	0.5	245	---	---	---
3d	2.27	0.6	270	---	---	---
3e	2.43	0.8	260	---	---	---

^{a}**RSD:** % relative standard deviation

The accuracy and precision of the proposed method were tested by five successive determinations carried out on the azo dyes. The results are given in Table I. As seen from the data in Table I, the mean values obtained by proposed method are in good agreement with value given for each azo dye and furthermore relative standard deviations were <±1 percentage. This indicates that the accuracy and precision of this method is satisfactory.

The acidity of sulpho protons is affected by the substituted azo groups on azo compounds. The sulpho groups of azo dyes were found more acidic than 4-amino-5-hydroxynaphthalane-2,7-disulfonic acid mono sodium salt itself since the Ar-N=N groups decreased the electron density. Amino and hydroxyl sites of azo dyes showed very weak basic character and acidic character in aqueous media, respectively. However, water is not suitable solvent for the determination of pKa value of these sites of azo dyes. Since aromatic amines are slightly ionized in water, they can be titrated easily in non-aqueous solvents (Skoog and West, 1988). Azo(-N=N-) groups of the azo dyes have very low basicity and the basic character of this group is not greater than that of water due to resonance and inductive effects of the benzene ring.

Acidity of naphtholic hydroxyl sites in compound 2 and 3 type are decreased by the effect of the azo-hydrazone tautomer and intramolecular hydrogen bonding (Breedereck and Schumacher, 1993; Fawcet, 1995) between azo and hydroxyl groups. Sulpho groups were more acidic then hydroxyl groups, therefore, acidity of naphtholic hydroxyl sites in the aqueous media was not considered.

Table II. Sodium content of the azo compounds.

Compound	**% Na**		**Compound**	**% Na**	
	Na^{a}	**Na**^{b}		**Na**^{a}	**Na**^{b}
H-acid	1,60	1.54	**2d**	4,79	4,81
1a	1.35	1.46	**2e**	4,47	4,52
1b	1,03	0,98	**2f**	5,16	5,22
1c	1,06	1,02	**3a**	3,59	3,65
1d	1,60	1,52	**3b**	3,59	2,63
1e	1.89	2.01	**3c**	3,72	3,76
2a	4,69	4,74	**3d**	3,72	3,71
2b	4,69	4,70	**3e**	3,34	3,36
2c	4,79	4,72	-	-	-

^{a}Flame photometer data
^{b}Potentiometric titration data

The acidity of sulpho groups of 1-type azo dyes was increased in this order, namely H-acid, 1a, 1b, 1c, 1e, 1d as the nitro and choloro groups decrease the electron density on the ring. Chloro groups have most effect on pK_a value, which increased acidity (Table I). These results are consistent with these reported pK_a values (Table I). H-acid, 1a, 1b, 1c, 1d, 1e azo dyes were titrated and two turning point were observed at the end of the titration. In the 1-type azo dyes, pK_1 values were approximately same while pK_2 values changed dramatically. On the side of coupling to 4-amino-5-hydroxynaphthalane-2,7-disulfonic acid mono sodium salt, acidity of 2-sulpho group increased due to the inductive and resonance effect (Serin and Kurtoglu, 1999) to the ring. However, the acidity of the other sulpho group showed small differences (see Table I). Therefore, first proton has been removed from the 7-sulpho group while second proton from 2-sulpho group. As a result of this 7-Sulpho proton corresponded to the pK_1, and 2-sulpho proton corresponded to the pK_2.

Less titrant was consumed at the equivalent point due to unremoved sodium atoms of sulpho groups of the 2 and 3-type azo dyes. Sodium determination has been carried out by both potentiometric titration and the flame photometer; the results were given in Table II.

PK_a values of 2 and 3-type azo dyes were affected not only by inductive and resonance effect but also unremoved sodium atoms. First turning point of 2 and 3-type compounds were observed. However, The second turning point of these compounds disappeared due to the unremoved sodium atoms in sulpho groups. PK_1 values below the three show that increases acidity at only one turning point of these azo dyes.

References

FARKAS, E., KURZAK B., 1990. J. Coord. Chem. 22, 145.

GROSVENOR, V. L., 1982. Analytical Chemistry. 57, 837.

JEMASU, I., IWAMATO, T., 1982. Analytical Chemistry. 54, 35.

OH, S. W., KANG, M. N., CHO, C. W., LEE, M. W., 1996. Dyes and Pigments. 33, 119-135.

SERIN S., KURTOGLU M., 1994. Analyst. 119, 2213.

BREEDERECK, K, SCHUMACHER C., 1993. Dyes and Pigments. 23, 121.

GÜNDÜZ, T., GÜNDÜZ, N., KILIÇ, E., KENAR, A.,1986. Analyst. 111, 1345-1347.

LYCKA, A., JIRMAN, J., 1987. Dyes and pigments. 8, 315.

TAFT, R. W., 1983. J. Phys. Org. Chem. 14, 242.

HINE, J., 1975. Structural Effects on Equilibria, Organic Chemistry, *Wiley*, New York.

GÜNDÜZ, T., KILIÇ, E., ERTÜZÜN, V., ÇETINEL, G., 1986. Analyst. 111, 1439.

FRITZ, J. S., 1973. Acid-base Titrations in Non-Aqueous Solvents. Allyn and Bacon, Boston.

KIRK OTIMER. Volume 2, p. 869.

TUNÇEL, M., 1996. MSc. thesis, Institution of science, University of Çukurova, Adana, Turkey.

ZOLLINGER, E., 1995. Diazo Chemistry; p 215. 1995.

SKOOG, A. D., WEST, M. D., HOLLER, F. J., 1988. Analytical Chemistry. p 250. W. B. Saunders Company, New York.

FAWCET, J., KEMMİT, R., RUSSEL, D. R., SERİNDAĞ, O., GÜZEL, B., SERİN, S.,1995. Acta Cryst. p. 139-141.

KURTOGLU, M., BIRBIÇER, N., KIMYONŞEN, U., SERIN S., 1999. Dyes And Pigments. 41, 143.