Asian Journal of Chemistry Vol. 2, No. 1 (1990), 73–81

Polarographic Reduction of Aromatic Azo Compounds

P. N. GUPTA*, A. RAINA and V. K. BHAT

Department of Chemistry
Kashmir University, Srinagar-109 006, India

The polarographic reduction behaviour of 34 azo compounds has been investigated in a variety of buffers at different pH values. The electron-attracting or releasing ability of the substituents is related to their effect on $E_{1/2}$. Groups such as hydroxy, amino, methoxy etc. can enhance $E_{1/2}$ compared with unsubstituted ones provide evidence on the basis of directional dipole moments. The correlation coefficient between $E_{1/2}$ and pH has been found to have reasonably accurate value.

INTRODUCTION

Polarography of azo compounds in protic media undergo disproportionation (in certain non-symmetrical cases) via an intermediate hydrazo derivative[1,2], electrode reaction rate independent of pH[3] and various proposed mechanisms[4] of simultaneous electronation and protonation contrary to each other present complex behaviour towards reduction. Two $E_{1/2}-$pH equations in most cases[1,4] including geometric isomers of azobenzene(s)[5] have been explained on the basis of electronically distinct moities formed by dissociation. Abdel-Kadar and El-Arab[6] besides substantiating some established facts, showed reduction to be irreversible which has been confirmed in this study from $E_{1/2} \neq E^{\circ}$. Pattern of Hammett constants due to substituents on benzene/Naphthalene rings resembles favourably with reported ones[7].

A frequent problem of fitting a set of paired values to a linear $E_{1/2}-$pH equation was experienced because certain data was aimlessly neglected. Attempts have been made to utilise all data and to find the best estimate of constants as those that minimize sum of squares of deviations by process of differentiation w.r.t. variables. Correlation coefficient[8] $|r|$ of $E_{1/2}$ and pH relation has been calculated and found it close to 1.

This communication presents result of our investigation on polarography of 34 compounds including some commercial dyes. Most compounds show considerably high confident value of $|r|$.

EXPERIMENTAL

Compounds (I)-(XI) were prepared by treating nitrosobenzene with appropriately substituted amines. Compound (XII) was prepared from sulphanilic acid[1(d)], while solochrome yellow 2 GS (XXI), solochrome black PVS (XXVIII), eriochrome Violet B (XXIX), solochrome blue 2RL (XXX) and solochrome black WDFA (XXXIV) were obtained from

(I.C.I., India). Rest of compounds were synthesized by conventional diazotization method with $NaNO_2$ in HCl media followed by alkaline coupling. All compounds after recrystallizing twice and drying over BaO in vacuum desiccator were subjected to purity test spectrophotometrically, chromatographically, elemental analysis, inferred ca. 99% purity. Following compounds were investigated:

(I) trans-azobenzene, (II) 4-hydroxyazobenzene, (III) 4-sulphonic acid azobenzene, (IV) 4-nitroazobenzene, (V) 4-methylazobenzene, (VI) azobenzene 4-carboxylic acid, (VII) 4-acetylazobenzene, (VIII) 4-methoxyazobenzene, (IX) 4-aminoazobenzene, (X) 4-dimethylamino-azobenzene, (XI) 2-hydroxyazobenzene, (XII) 4,4′-disulphonic acid azobenzene, (XIII) 4,4′-dihydroxyazobenzene, (XIV) 2,2′-dihydroxyazobenzene, (XV) 3,3′-dihydroxyazobenzene, (XVI) 4-hydroxyazobenzene-4′-sulphonic acid, (XVII) 4-aminoazobenzene-4′-sulphonic acid, (XVIII) 4-dimethyl-aminoazobenzene-4′-sulphonic acid, (XIX) 4-dimethyl-amino-azobenzene-2-carboxylic acid, (XX) 2,4-diaminoazobenzene, (XXI) solochrome yellow 2GS, (XXII) 3,4-dihydroxy-4′-nitroazobenzene, (XXIII) 3,4-dihydroxy-4′-azobenzene sulphonic acid (XXIV), 2,4-dihydroxy-4′-azobenzene sulphonic acid, (XXV) 2-hydroxy-5-sulphonic acid-2′,4′-diamino azobenzene, (XXVI) 1-(2-hydroxy phenylazo)-2′-naphthol, (XXVII) 1′-(2-hydroxy naphthyl azo)-2-phenol-4-sulphonic acid, (XXVIII) solochrome black PVS, (XXIX) eriochrome violet B, (XXX) solochrome blue 2RL, (XXXI) 1-(2-hydroxy naphthyl azo)-2′-naphthol, (XXXII) 1-(2-hydroxy-naphthyl azo)-2′-naphthol-4-sulphonic acid, (XXXIII) 1-(2-hydroxynaphthyl azo)-2′-naphthol-7-nitro-4-sulphonic acid, (XXXIV) solochrome black WDFA.

All other reagents were guaranteed products of BDH and E. Merck.

Standard buffer solutions used were (i) Prideaux and Ward (H_3PO_4, phenylacetic acid, H_3BO_3 and NaOH) pH 2.0–11.9, (ii) Britton-Robinson (H_3PO_4, CH_3COOH, H_3BO_3 and NaOH) pH 2.0–12.0, (iii) Britton-Robinson (HCl, KH_2PO_4, citric acid, H_3BO_3, Veronal and NaOH) pH 2.5–12.0, (iv) German and Vogel (phenylacetic acid and sodium phenylacetate) pH 3.5–5.2, (v) McIlvaine (Na_2HPO_4 and citric acid) pH 2.2–8.0, (vi) Kolthoff (KH_2PO_4 and borax) pH 5.8–9.2, (vii) Clark and Lubs (H_3BO_3 and NaOH) pH 7.8–10.0, (viii) Sorensen (borax and HCl) pH 7.6–9.3.

Measurements were made on dropping mercury electrode in a Novak type cell in conjunction with Universal pen recording Polarograph (OH-105, Hungary). Temperature of cell was maintained at $25 \pm 0.1°$ by ultra thermostat (GDR) unless specified otherwise. The DME had capillary characteristics, 1.992 $mg^{2/3}\ s^{-1/2}$ at $h = 50$ cm, in Britton-Robinson buffer (pH 7) when short circuited. All potentials refer to SCE. Ionic strength $\mu = 1$ was maintained with $NaNO_3$. Solutions were deaerated with O_2 free N_2 before subjecting to analysis. Triton X-100 (0.0005%) was used as maximum suppressor when needed.

RESULTS AND DISCUSSION

Aggregating tendency of azo compounds in presence of ions induced complexity in reduction behaviour[9]. Based upon carefully designed experiments, concentration range was so selected to deprive them of this property and ensure all measurements in a monomeric form.

No appreciable effect of buffer constituents and their pH value on polarograms was noted. Waves were diffusion controlled as evinced from i vs. $h^{1/2}$; ivs. C and low temperature coefficient 1.10 to 2.75% K^{-1} (25°–40°). C-V curves, in general, were well formed; deformed mostly in German and Vogel and Prideaux and Ward buffers for derivatives of azobenzene. For a few compounds (V-VIII) Britton-Robinson buffer was excellent choice; in fact, this was decidedly the most favoured one. Kolthoff, Sorensen, Clark and Lubs buffers containing borax presented limitations; waves were ill-formed, if substances did not precipitate, commercial dyes (XXVIII), (XXIX) and (XXXIV) and 4-hydroxyazobenzene (II) gave reasonably good response. Another recently[10] used Stafford buffer consisting of dimethyl glutaric acid revealed no or ill-formed waves with most dyes.

Irreversible reduction envisaged from log plot supported fully from E_c° values determined by potential mediator method using freshly prepared $CrSO_4$ has been presented in Table 1 at pH 5.2 as a representative case. Difference is fairly low for azobenzene derivatives but is moderate to high for other two classes of compounds (XXVI-XXXIV). It can safely be concluded that reduction is not reversible. Weak adsorption of dye and increased rate of electron transfer due to association between buffer cation and (dye) anion is known[11] to influence the reduction pattern to depict the significant role of buffer constituents on reversibility.

Maxima Suppression

Moderate to weak polarographic maxima in compounds e.g., (IX), (X), (XVII), (XVIII), (XX) and acute one with (XXI)[1(a)]), were eliminated by Triton X-100. This is based upon determination[12,13] of electrocapillary maxima, PZC etc., in separate set of experiments, and the choice is not arbitrary, $E_{1/2}-$pH relation.

Shift in $E_{1/2}$ with pH is an established fact, and this is clearly revealed in Table 1. Salient features of observed $E_{1/2}-$pH relationships are: (i) most of the substances revealed two $E_{1/2}$ — pH equations, (ii) substances (V-VIII), (XXIV)) and (XXVIII) show no break in entire pH range of 2–12, while compounds (IV), (IX), (XV), (XVI), (XIX), (XX), (XXII), (XXV) and (XXXIV) depict continuity in a limited acid-base range, (iii) yet another set of compounds reduce preferably in acid pH only and get precipitated in base media and/or not reduced at all. These observations are supported by literature and warrant no special explanation. However, calculated correlation coefficient[8] |r| underlines the special

TABLE 1

$E_{1/2}$—pH, CORRELATION COEFFICIENT |r| AND SUBSTITUENT EFFECTS OF AZO COMPOUNDS

Compound	Substituent	$E_{1/2}$—pH ($Y-X$)	pH–range	—|r|	$-E_{1/2}$/V vs.S.C.E. at pH 5.2	$-E^{\circ}_{c}$/V at pH 5.2	$\Delta E_{1/2}$/V	ρ	$\Sigma\sigma$
(I)	—	$Y = 0.0613–0.0605X$	2–7	0.998	0.250	0.23	—	—	—
		$Y = 0.0977–0.0509X$	7.5–12	0.991	—	—	—	—	—
(II)	4(OH)	$Y = 0.087–0.0718X$	2–6.4	0.965	0.28	0.25	0.03	0.14	0.21
		$Y = 0.11134–0.0777X$	7.2–12	0.976	—	—	—	—	—
(III)	4(SO_3H)	$Y = 0.1166–0.059X$	2–7.2	0.999	0.19	0.19	−0.06	0.14	−0.43
		$Y = 0.0923–0.045X$	8.3–12	0.964	—	—	—	—	—
(IV)	4(NO_2)	$Y = 0.2520–0.060X$	2–8.3	0.999	0.06	0.04	−0.19	0.14	−1.36
(V)	4(CH_3)	$Y = 0.0436–0.0614X$	2–12	1.000	0.275	0.25	0.025	0.14	0.18
(VI)	4(COOH)	$Y = 0.1029–0.059X$	2–12	0.999	0.210	0.19	−0.04	0.14	0.29
(VII)	4($COCH_3$)	$Y = 0.1244–0.161X$	2–12	0.999	0.19	0.18	−0.06	0.14	−0.43
(VIII)	4(OCH_3)	$Y = 0.0253–0.062X$	2–12	1.000	0.30	0.28	0.05	0.14	0.36
(IX)	4(NH_2)	$Y = 0.05–0.072X$	3.5–9.8	0.956	0.32	0.30	0.07	0.14	0.5
(X)	4[$N(CH_3)_2$]	$Y = 0.24–0.095X$	2–6	0.963	0.26	0.25	0.01	0.14	0.07
		$Y = -0.05–0.058X$	8–12	0.951	—	—	—	—	—
(XI)	2(OH)	$Y = 0.050–0.068X$	2–6	0.943	0.305	0.3	0.055	0.14	0.39

(XII)	4(SO_3H), 4′(SO_3H)	$Y = 0.164–0.0615X$	2–7	0.999	0.156	0.13	−0.094	0.14	−0.67
(XIII)	4(OH), 4′(OH)	$Y = 0.1085–0.12X$	2–7	0.999	0.51	0.45	0.26	0.14	1.86
(XIV)	2(OH), 2′(OH)	$Y = 0.158–0.0936X$	2–6.8	0.999	0.33	0.30	0.08	0.14	0.57
		$Y = -0.40–0.019X$	8–12	0.953	—	—	—	—	—
(XV)	3(OH), 3′(OH)	$Y = 0.08145–0.0616X$	2–8	0.974	0.23	0.20	−0.02	0.14	−0.14
(XVI)	4(OH), 4′(SO_3H)	$Y = 0.1056–0.066X$	5–12	0.950	0.24	0.20	−0.01	0.14	−0.07
(XVII)	4(NH_2), 4′(SO_3H)	$Y = 0.179–0.0879X$	3–6	0.942	0.28	0.23	0.03	0.14	0.21
		$Y = 0.02–0.058X$	7.5–12	0.990	—	—	—	—	—
(XVIII)	4[$N(CH_3)_2$], 4′(SO_3H)	$Y = 0.001–0.0585X$	2–6	0.957	0.30	0.28	0.05	0.14	0.36
(XIX)	4[$N(CH_3)_2$], 2(COOH)	$Y = 0.0414–0.0607X$	3.2–9.8	0.933	0.28	0.24	0.03	0.14	0.21
(XX)	2(NH_2), 4(NH_2)	$Y = -0.0295–0.0716X$	3.2–9.8	0.943	0.34	0.31	0.09	0·14	0.64
(XXI)	3(COONa), 4(OH), 4′(SO_3Na)	$Y = -0.0102–0.027X$	1.8–5.8	0.998	0.15	0.13	−0.10	0.14	0.07
		$Y = -0.0057–0.0258X$	6.8–10.4	0.980	—	—	—	—	—
(XXII)	3(OH), 4(OH), 4′(NO_2)	$Y = 0.0411–0.0611X$	2.2–7.4	0.973	0.28	0.26	0.03	0.14	0.21
(XXIII)	3(OH), 4(OH), 4′(SO_3H)	$Y = 0.0919–0.0596X$	3.9–6.4	0.949	0.22	0.21	−0.03	0.14	−0.21
(XXIV)	2(OH), 4(OH), 4′(SO_3H)	$Y = 0.105–0.08X$	2.2–12	0.935	0.31	0.29	0.06	0.14	0.43
(XXV)	2(OH), 5(SO_3H), 2′(NH_2), 4′(NH_2)	$Y = -0.049–0.0659X$	3.6–10	0.987	0.29	0.27	0.04	0.14	0.29

TABLE 1 (*cont.*)

Compound	Substituent	$E_{1/2}-\text{pH}$ $(Y-X)$	pH-range	$-\lvert r\rvert$	$-E_{1/2}$/V vs. S.C.E.	$-E^{\circ}_{3}$/V	$\Delta E_{1/2}$/V	ρ	$\Sigma\sigma$
					at pH 5.2				
(XXVI)	—	$Y = 0.040-0.067X$	2–6.5	1.000	0.31	0.22	—	—	—
		$Y = 0.0644-0.063X$	7.5–12	0.998	—	—	—	—	—
(XXVII)	4(SO$_3$H)	$Y = 0.020-0.060X$	2–6	0.999	0.29	0.21	−0.02	0.16	−0.13
		$Y = 0.0479-0.056X$	8–12	0.998	—	—	—	—	—
(XXVIII)	5(SO$_3$Na), 5′(OH)	$Y = 0.02267-0.031X$	1.8–11.5	0.976	0.13	0.07	−0.18	0.16	−1.13
(XXIX)	4(SO$_3$H), 4′(OH)	$Y = 0.021-0.060X$	2–6	0.999	0.29	0.21	−0.02	0.16	−0.13
		$Y = -0.0495-0.053X$	8–12	0.987	—	—	—	—	—
(XXX)	3(SO$_3$Na), 5(Cl)	$Y = 0.05-0.55X$	2.2–6	0.976	0.23	0.18	−0.08	0.16	−0.5
(XXXI)	—	$Y = 0.087-0.08X$	2–6.5	0.980	0.32	0.16	—	—	—
		$Y = 0.0972-0.075X$	7.5–11.2	0.999	—	—	—	—	—
(XXXII)	4(SO$_3$H)	$Y = 0.021-0.06X$	2–6	0.999	0.29	0.15	0.03	0.18	0.17
		$Y = 0.0442-0.052X$	7.2–12	1.000	—	—	—	—	—
(XXXIII)	4(SO$_3$H), 7(NO$_2$)	$Y = -0.0271-0.060X$	2–6	0.990	0.33	0.16	0.01	0.18	0.06
		$Y = -0.053-0.048X$	7–12	0.990	—	—	—	—	—
(XXXIV)	3(SO$_3$H), 6(NO$_2$)	$Y = -0.031-0.0699X$	4–10	0.990	0.39	0.19	0.07	0.18	0.39

mention and is noted that |r| is numerically close to 1 in most cases reported herein. Surprisingly when this treatment was extended to data on solochrome yellow 2GS(XXI) reported earlier (Table 2) revealed predictably erroneous value $|r| > 50$, while reasonably accepted values emerged if data was subdivided into two parts of pH 1.8–5.8 and 6.8–10.4, sqq., with (XIV), $|r| = 0.68$ when data were calculated in one lot, while this ranges between 0.953–0.999 when considered in two portions (Table 1). In a way, correlation coefficient stresses the possible alteration in molecular form toward reduction at DME with pH and is accounted by distinctly different $E_{1/2}$ — pH equation.

TABLE 2

REPORTED DATA ON SOLOCHROME YELLOW 2GS[1](a)

pH	$-E_{1/2}$/V vs. SCE
1.8	0.05
2.2	0.07
3.3	0.11
4.8	0.14
5.8	0.16
6.8	0.18
8.0	0.21
9.15	0.25
10.4	0.27

$E_{1/2} = 7.14911 - 1.259$ pH
$|r| = 50.62$

Substituent constants $\Sigma\sigma$ at pH 5.2 as shown in Table 1 are reasonably similar to reported ones. However, marginal differences, if any, could be attributed to different experimental conditions[14]. Table 1, illustrates σ4-OCH$_3$ is −0.36 in (VIII)-negative value-indicating electron donation to nucleus, −0.18 for a weaker group 4—CH$_3$ (V), whereas electron withdrawing —NO$_2$ (IV) is more positive (+1.36) compared to 4—COCH$_3$ (VII) which is less positive (+0.43). The value of ρ measures the sensitivity of reaction to substituent effects in Hammett equation and has a constant value. Equation considers, in general, effect of aromatic ring substituents on side chain and the measured σ values signifies expected trend of reactivity on structure of azo compounds.

Electroreduction of azo/hydrazo system

Substituents bring about electron density variation at —N=N—, viz., —COOH, —SO$_3$H, facilitate a single two electron reduction of azo group simultaneously lowering the basicity of N-atoms in azobenzene to the extent that these are not protonised easily. Further, electron donating substituents produce an increase in electron density at azo bond in strong acid media ($pH > 2.0$) has been found to give double wave height compared to unsubstituted one, suggesting disproportionation[2,3] of hydrazo compound ($n = 4$). In base media ($pH = 9.8$) height of polarographic wave is smaller but still correspond to $n > 2$ indicating that disproportionation has occurred, maybe slowly. The latter situation continues to prevail at $pH \geqslant 12$. Some mechanistic variation can be anticipated when two or more substituents are present in a molecule; i.e., reinforcement of inductive and mesomeric effects favourably on the reducing moiety is likely to cause activation and vice-versa but a definite conclusion cannot be made unless some additional measurements are available, e.g., dipole moment etc.

Well established geometrical models are known to provide means of investigating the effects of resonance or steric repulsion within the molecules based upon differences in calculated and observed values of dipole moments.[15] For the present purpose, it is enough to note direction of dipole moment values in solution, viz., ← for OH, NH_2, OCH_3, CH_3 etc. indicating overall electron donating effect and → for SO_3H, NO_2 etc., for electron withdrawing effect. This simply illustrates that with ←, $E_{1/2}$ should be higher compared with unsubstituted azobenzene as observed with compounds (II), (V), (VIII), (IX), (XX) etc. vide Table 1 and lower $E_{1/2}$ with compounds (III), (IV) etc. In a similar manner, with opposing substituents, $\overleftarrow{4\text{—}OH}$, $\overrightarrow{4-SO_3H}$, an intermediate value, close to unsubstituted one is expected e.g., with compounds (XVI) $E_{1/2} = -0.24V$ which is close to $E_{1/2}$ of azobenzene (I) having value $-0.25V$, while for (XVII) with $\overleftarrow{4\text{—}NH_2}$ and $\overrightarrow{4-SO_3H}$ as substituents a reasonable value of $-0.28V$ was appropriately justified. In view of large difference generally occurring among the moments of isomers, viz., azobenzene ($\mu = 0D$ for trans and $\mu = 3.0D$ for cis) different $E_{1/2}$ values under similar experimental conditions can be anticipated and has been observed experimentally[5] too. Thus availability of data on dipole moments of the azo compounds, alongwith structural collinearity with axis of benzene/naphthalene may provide a tool for predicting $E_{1/2}$ values with precision.

REFERENCES

1. (a) W. U. Malik and P. N. Gupta, *J. Electroanal. Chem. Interfac. Electrochem.*, **54**, 417 (1974).

   (b) T. M. Florence, *Aust. J. Chem.*, **18**, 609, 619 (1965).

   (c) F. G. Thomas, K. G. Boto in S. Patai (ed.), The Electrochemistry of Azoxy, Azo and Hydrazo Compounds, John Wiley, London. Chap. 12 (1975).

(d) J. W. Timberlake and J. C. Stowell, *Ibid.*, Chap. 4.

2. P. N. Gupta and A. Raina, *J. Indian Chem. Soc.*, **62**, 363 (1985); **63**, 246 (1986).
3. ______, *Bull. Electrochem.*, **4**, 989 (1988).
4. (a) T. M. Florence, *J. Electroanal. Chem. Interfac. Electrochem.*, **52**, 115 (1974).
   (b) J. P. Stradins and V. T. Glezer in A. J. Bard (ed.), Encyclopedia of Electrochemistry of Elements, Organic Section, Vol. 13–4, Marcel Dekker (1979).
5. P. N. Gupta and A. Raina, *J. Indian Chem. Soc.*, **65**, 495 (1988) and references given therein.
6. A. R. Abdel-Kadar and N. A. El-Arab, *Zanco*, Ser. A, **5**, 19 (1979).
7. P. Zuman, Substituent Effects in Organic Polarography, Plenum Press, N.Y., pp. 43–118 (1967).
8. C. L. Perrin, Mathematics for Chemists, John Wiley, pp. 161–2 (1970).
9. W. U. Malik and P. N. Gupta, *J. Electroanal. Chem. Interfac. Electrochem.*, **62**, 441 (1975); *Indian J. Chem.*, **15A**, 273 (1977); *J. Electrochem. Soc.* (*India*), **28**, 17, 137 (1979).
10. P. N. Gupta and A. Raina, *Ann. Chimica.*, **78**, 317 (1988).
11. T. M. Florence and Y. J. Farrar, *Aust. J. Chem.*, **17**, 1805 (1964).
12. P. N. Gupta, C. N. Kachru and S. A. Bhat, *J. Electrochem. Soc.* (*Japan*), **46**, 92 (1978).
13. P. N. Gupta, *Proc. Indian Acad. Sci.*, **88**, 317 (1979).
14. P. Nagy, I. Gorbe and A. Szakkos, *Rev. Roum. Chim.*, **15**, 881 (1970).
15. P. Sykes, A Guidebook to Mechanism in Organic Chemistry, Orient Longmans, New Delhi, Chap. 6 (1965).

[*Received*: 20 March 1989: *Accepted*: 10 August 1989] AJC–77