

TABLE 2 — POLAROGRAPHIC AND DOUBLE-LAYER CHARACTERISTICS OF THE AQUONICKEL(II) COMPLEX IN RARE EARTH METAL NITRATES

$$[\text{Ni}(\text{H}_2\text{O})_6^{2+}] = 2.5 \times 10^{-4} \text{M}; \text{Temp.} = 25 \pm 0.2^\circ\text{C}; \text{Triton X-100} = 0.001\%$$

Base electrolyte (0.1M)	Maximum hydration number ^a	$E_{1/2}$ (V vs SCE)	Q_e kcal (at -1.10 V vs SCE)	$-E_{\text{max}}$ (V vs SCE)	$-q_m$ (μC)	ψ' -potential (at -1.1V vs SCE)
Mg(NO ₃) ₂	9	1.125	14.49	0.56	12.15	0.032
Ca(NO ₃) ₂	4	1.129	14.56	0.53	13.10	0.036
Sr(NO ₃) ₂	4	1.138	14.77	0.49	13.50	0.039
Ba(NO ₃) ₂	0	1.145	15.31	0.44	14.50	0.041

^aValues have been taken from ref. 9.

of a certain electrolyte, $\pi = a$ constant and $\sigma =$ dielectric constant of the working solution.

A perusal of the data given in Table 2 shows that with the change of cation from Mg²⁺ to Ba²⁺, (a) $E_{1/2}$ shifts to more negative side, (b) the activation energy, Q_e , of the electrode process is found to increase, (c) the potential of electrocapillary maximum, E_{max} , decreases from Mg²⁺ to Ba²⁺, (d) charge density on the electrode increases, and (e) the ψ' -potential becomes more positive.

These observations show that the electroreduction of Ni(H₂O)₆²⁺ is increasingly hindered with change of base electrolyte cation from Mg²⁺ to Ba²⁺, which may be explained as follows :

The size of the hydrated cation decreases⁹ in going from Mg²⁺ to Ba²⁺ (Table 2). The smaller the ion, greater is the possibility of approaching the interface, consequently increasing the adsorption at the electrode. According to Bockris and Reddy¹⁰, the adsorption of the cation to a considerable extent decreases the potential of zero charge, E_{max} , because of enhanced image interactions. Decrease in E_{max} leads to decrease in the potential which, in turn, results in the greater repulsion¹¹ between ψ' -potential layer and positively charged Ni(H₂O)₆²⁺ complex ion. This greater repulsion makes the reduction process more and more difficult¹².

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Electrochemical Oxidation of *o*-Anisidine at a Platinum Electrode†

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Anodic oxidation of *o*-anisidine at a platinum electrode has been studied using cyclic voltammetric and chronoamperometric techniques. A mechanism has been proposed for the oxidation process consistent with the electrochemical data and the products of this reaction. The data are also utilised in the evaluation of the diffusion coefficients of the electroactive species under consideration.

WE have reported earlier, our results on the electrochemical oxidation of *p*-anisidine¹, *p*-toluidine² and *p*-chloroaniline³. Previous work by Adams⁴ on *o*-anisidine with a carbon paste nujol electrode had indicated a half-peak potential of +0.68V vs SCE at a scan rate of 133 mV sec⁻¹ and at pH 2-4.

In the present investigation, cyclic voltammetry and chronoamperometry have been employed to study the electrochemical oxidation of *o*-anisidine at a stationary platinum wire electrode in different aqueous supporting electrolytes, covering a wide pH range. The data are also utilized to evaluate the diffusion coefficients of *o*-anisidine.

o-Anisidine (Eastman) was used as such. Its solution was prepared by first dissolving it in a minimum quantity of ethyl alcohol and then diluting with water to the required volume. Clarks and Lubs buffer (pH 1.32) phosphate buffer (pH 6.6), 1 N sulphuric acid, 0.1N sodium carbonate and 0.1N sodium hydroxide were used as the supporting electrolytes. The preparation of the solutions of the supporting electrolytes, the details of the instrument employed and the experimental procedure have been discussed in the earlier publication³.

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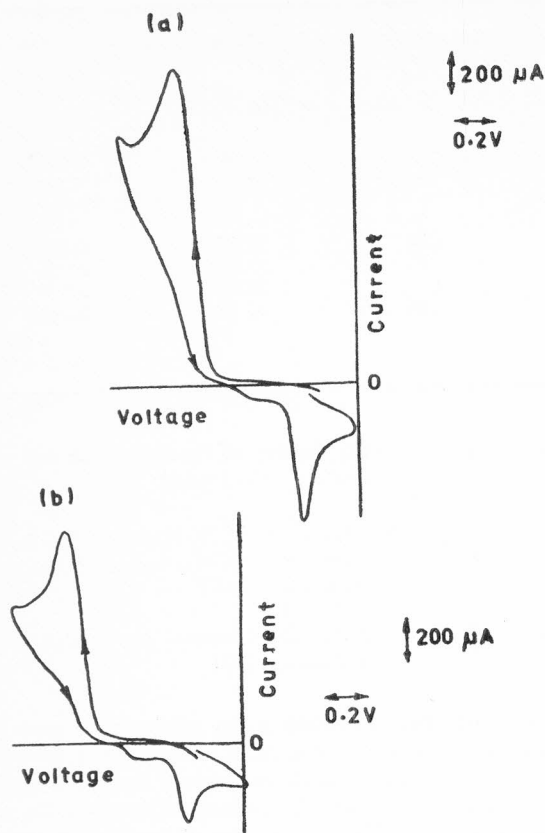


Fig. 1 — Cyclic voltammograms of *o*-anisidine in (a) H₂SO₄ (b) Clarks and Lubs buffer

Typical cyclic voltammograms for *o*-anisidine in sulphuric acid and Clarks and Lubs buffer are shown in Fig. 1. In sulphuric acid, *o*-anisidine undergoes oxidation at +0.83V (vs SCE) and in the latter buffer at +0.85V. The reduction peaks occurring at +0.24 V (vs SCE) in both the cases may be due to the reduction of the oxidation product. In phosphate buffer, sodium carbonate and sodium hydroxide, this reduction peak is not noticed within the potential range applied. The cyclic voltammetric data of *o*-anisidine, presented in Table 1 show that E_p is dependent on the pH of the medium and the sweep rate. The electrochemical oxidation of *o*-anisidine has thus been found to proceed irreversibly. The number of electrons involved in the above oxidation is evaluated as two, using the

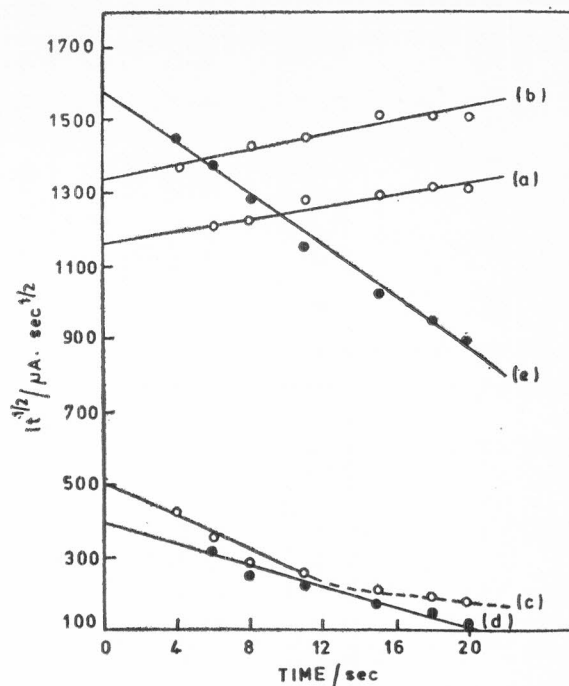
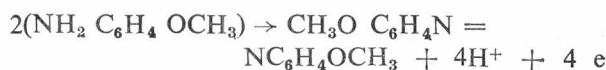


Fig. 2 — $it^{1/2}$ versus t plots of *o*-anisidine in (a) H₂SO₄, (b) Clarks and Lubs buffer, (c) phosphate buffer, (d) Na₂CO₃ and (e) NaOH

diffusion coefficient ($0.70 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$) of a similar sized molecule, *p*-methoxyphenol⁵, and αn_a values reported earlier⁶. The formation of 2,2'-dimethoxyazobenzene as the product of oxidation is borne out by the absorption spectral data. The oxidation of *o*-anisidine in acidic solutions or basic medium is, therefore, proposed to proceed as :



The variation of peak potential with pH also suggests the involvement of protons in the charge-transfer reaction. The i_p vs $v^{1/2}$ plot for *o*-anisidine in sulphuric acid is linear and hence the electrochemical oxidation of *o*-anisidine is found to be diffusion-controlled.

Step potentials employed for the chronoamperometric runs were chosen from the diffusion limited regions observed for the compound in various media.

TABLE 1 — CYCLIC VOLTAMMETRIC DATA FOR *o*-ANISIDINE

[Conc. of *o*-anisidine = 2.4 mM; sweep rate = v]

Sl No.	Sulphuric acid		Clarks and Lubs buffer		Phosphate buffer		Sodium carbonate		Sodium hydroxide	
	$v/\text{V sec}^{-1}$	E_p/V	$v/\text{V sec}^{-1}$	E_p/V	$v/\text{V sec}^{-1}$	E_p/V	$v/\text{V sec}^{-1}$	E_p/V	$v/\text{V sec}^{-1}$	E_p/V
1.	0.04	+0.83	0.05	+0.82	0.04	+0.60	0.04	+0.60	0.05	+0.57
2.	0.14	+0.83	0.29	+0.85	0.13	+0.68	0.13	+0.65	0.13	+0.63
3.	0.29	+0.84	0.45	+0.88	0.25	+0.74	0.29	+0.69	0.28	+0.66
4.	0.53	+0.84	0.70	+0.89	0.49	+0.80	0.57	+0.74	0.52	+0.68
5.	0.73	+0.85	—	—	0.71	+0.89	0.78	+0.79	0.72	+0.70

TABLE 2 — DIFFUSION COEFFICIENT (D) DATA FOR *o*-ANISIDINE AT 24°C

[Conc. of *o*-anisidine = 2.4 mM]

Sl No.	Medium	$D \times 10^5$ (cm ² sec ⁻¹)	
		Cyclic voltammetric	Chrono-amperometric
1.	Sulphuric acid	1.81	1.08
2.	Clarks and Lubs buffer	1.24	1.47
3.	Phosphate buffer	0.38	0.21
4.	Sodium carbonate	0.29	0.21
5.	Sodium hydroxide	2.9	2.1

The $it^{1/2}$ versus t plots (Fig. 2) in different media show that the electrochemical oxidation of *o*-anisidine in the presence of phosphate buffer, sodium carbonate and sodium hydroxide is complicated by the formation of a film of the oxidation product in media of higher pH, thus reducing the effective surface area of the electrode causing the fall of current.

The diffusion coefficient data for *o*-anisidine evaluated from the cyclic voltammetric and chrono-amperometric data are given in Table 2. The values obtained by both the techniques are in reasonable agreement. Since the values arrived from chrono-amperometry are obtained from ($it^{1/2}$) values which are calculated by extrapolation of $it^{1/2}$ values to zero time, they are not likely to be affected by the complications associated with the surface state of the electrode.

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Electrochemical Oxidation of Anions of Diarylamine, Carbazole & Phenothiazine Derivatives

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The electrochemical oxidations of the anions of some diphenylamine, carbazole and phenothiazine derivatives have been investigated in DMSO-(*n*-Bu)₄NClO₄ system. The oxidation potentials of these anions are less than those of the corresponding parent molecules. The electron acceptor substituents decrease the reactivity of anions towards oxidation.

NO information is available concerning the oxidation of anions of secondary aromatic amines or heterocyclic nitrogen compounds, since all the previous studies¹⁻⁴ are restricted to the electrochemical oxidation of the molecular compounds in aqueous or organic solvents.

Apparatus used — Potentiostat model π 5848 (USSR), galvanometer M-254; rotatory machine (800 to 3960 rot./min), spectrophotometer "Mhitach 250" and a glass cell.

The cell is constructed of three compartments separated by sintered glass No. 2 and surrounded with jacket. The anodic compartment was a cylindrical glass tube of 50 ml volume. The two arms (10 ml capacity) were used as cathodes.

The electrodes consisted of a rotating platinum disc anode (2.53 cm diameter) and two platinum cathodes (a gauze-form) of surface area 1 cm². A SCE was used as the reference electrode.

Electrolyte — *n*-Tetrabutylammonium perchlorate was prepared by adding a hot alcoholic solution of Bu₄NBr with continuous stirring to a hot alcoholic solution of NaClO₄. The mixture was cooled, filtered, washed thoroughly with cold alcohol-water mixture (1:1), and recrystallized from aqueous alcohol, m.p. 213-212°C; Lit. m.p.⁵ 212.5-213.5°C.

Solvent — Dimethylsulphoxide (pure grade) was dried over calcium hydride for two days with the passage of a stream of argon, and finally distilled under vacuum over CaH₂ in argon atmosphere at 40-43°C/0.1 mm. Hg.

Procedure — A solution of 0.05 M *n*-Bu₄NClO₄ in 35 ml DMSO was placed in the anodic compartment, a stream of argon was passed for 40 min and a 2 × 10⁻³ M KOH solution was added. The measurements were carried out for three times, one before the addition of the investigated material, another in the presence of this material, and finally after the addition of KOH solution. The desired temperature was controlled using an ultrathermostat. A stream of argon was passed during the whole measurements.

The results obtained from the polarization curves are presented in Table 1.

Spectrophotometric measurements were carried out in DMSO with or without adding KOH. The concentration used of both the investigated material and KOH were equal and ranged from 1.0 × 10⁻³ to 1.0 × 10⁻⁴ M. The results are presented in Table 1.

In the present work the electrochemical oxidation of the following carbonions⁶⁻⁸ have been investigated: bis(2,4,6-tribromo)-diphenylamine (1), 2,4,6-trinitrodiphenylamine (2), bis(2,3,4,5,6-pentabromo)diphenylamine (3), 2,4,6-tribromo-2',4',6'-trinitrodiphenylamine (4), bis(2,4,6-trinitrodiphenylamine) (5), 2,4,6,2',4',6'-hexanitro-3-chlorodiphenylamine (6); 1,2,3,4,6,7,8,9-octabromophenothiazine (7), 1,3,6,8-tetrachlorocarbazole (8) and 1,2,3,4,5,6,7,8-octachlorocarbazole (9). These anions were generated by the interaction of KOH with the corresponding amine in DMSO (Eq. 1). This solvent was selected because of its high solubilizing power and stability during electrolysis.