



ELECTROCHEMICAL BEHAVIOUR OF METHYLENE BLUE IN NON-AQUEOUS SOLVENTS



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ARTICLE INFO

Article history:

Received 15 November 2014

Received in revised form 9 January 2015

Accepted 30 January 2015

Available online 19 February 2015

Keywords:

Cationic dye electro-reduction

Cyclic voltammetry

ESR

Solvent and Supporting electrolyte effects

Reaction mechanism

ABSTRACT

The electrochemical behaviour of methylene blue in solution of non-aqueous solvents with different supporting electrolytes was studied by cyclic voltammetry. Dye electro-reduction presents two well-defined processes of monoelectronic charge transfer yielding a free radical in the first process and an anion in the second electron transfer. Free radical and anion are long living species in some of the studied media. Effects of supporting electrolyte and solvent on the peak potentials, the peak current functions and the reversibility of the charge transfer processes are reported. A dissociation equilibrium of the dye in solution of non-aqueous solvents and the acid or base added determine markedly the electrochemical responses. In the particular cases of KOH/DMF or EDA basic media the chemical formation of the stable methylene blue radical was detected and it was characterized by EPR spectroscopy. A general reaction scheme is proposed.

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1. INTRODUCTION

Methylene blue (3,7-bis(dimethylamino) phenothiazin-5-ium chloride, 1^+Cl^- in Fig. 1) is a cationic dye, widely used in various fields related to chemistry and biology [1–3]. Main uses of 1^+Cl^- are associated with the determination of glucose, oxygen and ascorbic acid [4,5]. Also, 1^+Cl^- is one of the materials of high consumption in the dye industry, being used for cotton and silk painting [6].

The electrochemical behaviour of 1^+Cl^- has been the subject of numerous investigations performed in aqueous solutions [7–17], but the behaviour in non-aqueous solvents has been insufficiently studied, and the published results are very scarce [18].

The electrode process of 1^+Cl^- in aqueous media is illustrated in Scheme 1. It has been shown that 1^+Cl^- undergoes a fast two-electron transfer process without an evident separate electron transfer step, with only one cathodic wave and only one anodic wave being observed by cyclic voltammetry [7]. However, *in situ* ESR results provide evidence for the formation of a radical intermediate (Scheme 1, 1^\bullet) [19]. The intermediate is a short-lifetime radical, which combines with a proton and suffers an

electron reduction, yielding the non-paramagnetic leucomethylene blue (1H).

In special cases, two electron transfer processes are detected in the growth of 1H films and their electro-dissolution on bare gold (Au) and sulphur modified gold (Au-S) electrodes in methylene blue solutions. These processes are attributed to $1\text{H}^{+\bullet}$ and 1H formation in acid aqueous medium. The first cathodic process, at more positive potentials, is assigned to the reduction of 1^+Cl^- from solution with the formation of 1H. The second redox process, at more negative potentials, is due to the reduction of the dye adsorbed on the electrode surface with the formation of 1H [20].

It is well known that ionic dyes tend to aggregate in aqueous solutions, leading to the formation of dimers, and occasionally even higher order aggregates [21–23]. The aggregation of 1^+Cl^- in aqueous solution affects its colouristic and photo-physical properties, being therefore of special interest. However, is not possible to carry out a complete analysis of the results from studies on aggregation, since the influence of the medium, of the nature of the counter-ion, etc. has been sporadically investigated, and ambiguous interpretations are given.

We hypothesise that due to the particular structure of 1^+Cl^- (salt nature and aggregation possibilities) its electrochemical behaviour should be notably influenced by the composition of the medium in which the electrochemical reaction occurs. The

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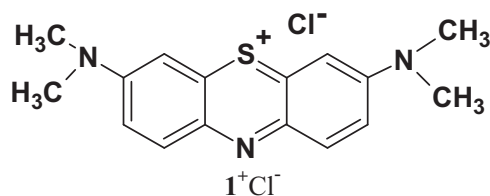


Fig. 1. Structure of methylene blue (1^+Cl^-).

understanding of the electrochemical behaviour of 1^+Cl^- in solution of non-aqueous solvents is interesting because it offers the possibility of transforming the molecule by particular ways of synthesis, that often are very complicated by traditional thermal routes [24]. It is known that the use of organic solvents has several advantages over water. The most accessible potential range in organic solvents allows easy detection of the processes of electro-reduction/oxidation in non-aqueous media that are hardly achievable in aqueous solutions.

This work focuses on the electrochemical reactivity of 1^+Cl^- in solution of non-aqueous solvents with a variety of supporting electrolytes, and in the presence of an anhydrous acid or a base added in order to ascertain if our proposed hypothesis is fulfilled.

2. EXPERIMENTAL

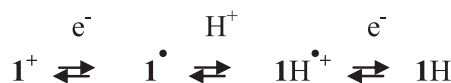
The investigation was performed on 1^+Cl^- in solution of six dipolar non-aqueous solvents, without and with H-bond ability, and with different strength as Lewis acids or bases [25], in presence of two supporting electrolytes (tetraethylammonium perchlorate (TEAP) and $LiClO_4$) in the absence and in the presence of an anhydrous acid (trifluoroacetic acid, TFA) or a base (KOH) added. Further, the studies were extended to other supporting electrolytes for acetonitrile (ACN), and ethanol (EtOH) solvents.

Solutions preparation and electrochemical experiments were carried out inside a glove box under dry nitrogen atmosphere. Non-aqueous solvents and inorganic compounds were purified by standard methods [26]. Solvents ACN, N,N-dimethylformamide (DMF), tetramethylurea (TMU), formamide (FM), EtOH and ethylenediamine (EDA) were dried with freshly activated 4 Å molecular sieves and stored in the dry glove box on freshly activated molecular sieve. 1^+Cl^- (Rhone Poulenc, Buenos Aires, Argentina) was successively re-crystallized from water and ethanol and its purity was thoroughly tested by thin layer chromatography.

Cyclic voltammetry (CV) experiments were performed in a conventional undivided gas-tight glass cell with dry nitrogen gas inlet and outlet. The working electrode (WE) was a 3 mm diameter vitreous carbon disk encapsulated in Teflon, and the counter-electrode (CE) was a 2 cm² Pt foil. An Ag^+ (0.1 M, ACN)/Ag reference electrode (to which all reported potentials are referred) was used. Prior to each electrochemical measurement the WE was polished with alumina up to 1 μm, and then thoroughly ultrasonically rinsed with water; final drying was performed with dry nitrogen gas.

Peak current intensities for the first electro-reduction process (I_{cp1}) increased linearly with the square root of the potential sweep rate (ν) in the range 0.050–0.300 V/s.

ESR spectra were obtained at room temperature with a Bruker EMX-Plus spectrometer, using the 9.7 GHz frequency (X band).



Scheme 1. Electrode process of 1^+Cl^- in aqueous media.

Uv–vis absorption spectrophotometric measurements were recorded using a Shimadzu UV – 1800 spectrophotometer.

3. RESULTS

The CV behaviour, mainly the reduction process, of 1^+Cl^- in solution of the different solvents and supporting electrolytes investigated without and with acid or base added is qualitatively described below. Quantitative results are shown in Tables 1–4. Rationalization of the results is under the subtitle: 4. Discussion.

3.1. Cathodic behaviour

3.1.1. 1^+Cl^- in ACN solution

1^+Cl^- in ACN solution with TEAP as supporting electrolyte was electro-reduced in CV experiments in two separated quasi-reversible one electron transfer steps (cathodic peak 1/anodic peak 1, cp1/ap1, and cathodic peak 2/anodic peak 2, cp2/ap2) with cathodic peak potentials $E_{cp1} = -0.73$ V and $E_{cp2} = -1.54$ V (Fig. 2, dotted line). CV experiments performed with different supporting electrolytes show that there is an effect of the supporting electrolyte on the separation between cathodic peaks ($\Delta E = E_{cp1} - E_{cp2}$) and on the peak current intensities measured for the first charge transfer (Fig. 2, full line and Table 1). The effect of the initial concentration of 1^+Cl^- ($[1^+Cl^-]_0$) in ACN solution with TEAP or $NaClO_4$ as supporting electrolyte on the current function ($cf = I_p/\nu^{1/2} [1^+Cl^-]_0$) for the first electro-reduction step (cf_{cp1}) of 1^+Cl^- is shown in Fig. 3.

When the electro-reduction of 1^+Cl^- was measured in solution of ACN with TEAP in the presence of TFA or KOH, a changed CV behaviour was observed. Some examples of such behaviours are shown in Fig. 4. In presence of added TFA (Fig. 4 dotted line, e.g. molar ratio = $R_{acid} = [TFA]/[1^+Cl^-]_0 \approx 67$) only one electro-reduction peak at $E_{cp1,acid} = +0.030$ V was observed. R_{acid} ratio value had effect on $E_{cp1,acid}$ and on the peak current intensity ($I_{cp1,acid}$) (results not shown). $I_{cp1,acid}$ increased up to reach a maximum value and $E_{pc1,acid}$ shifted toward more positive potentials with increasing R_{acid} . In presence of added KOH only one electro-reduction peak with a greater $I_{cp1,base}$ was observed at more cathodic potential than in the absence of base. $E_{cp1,base}$ shifted towards more cathodic values and $I_{cp1,base}$ increased with the increase of the molar ratio $R_{base} = [KOH]/[1^+Cl^-]_0$. A typical example of this behaviour is shown in Fig. 4 (dashed line), for $R_{base} \approx 91$ ($E_{cp1,base} = -1.24$ V). The addition of KOH to the initial blue solution of 1^+Cl^- in ACN/TEAP electrolytic solution caused a colour change of the solution. For $R_{base} > ca 2$, the initial blue solution acquired an intense purple colour.

Measured CV for a solution of 1^+Cl^- in ACN with $LiClO_4$ instead of TEAP as supporting electrolyte is shown in Fig. 5. 1^+Cl^- electro-reduction (Fig. 5, full line) occurs at $E_{cp1} = -0.73$ V (quasi-reversible) and $E_{cp2} = -0.99$ V (irreversible), being the more

Table 1

Effect of the supporting electrolyte on the current function for 1^+Cl^- first electro-reduction step (cf_{cp1}). Solvent: ACN; $[1^+Cl^-]_0$: 11 mM; scan rate: 0.2 V s⁻¹.

Supporting electrolyte (conc.)	cf_{cp1}^a ($AV^{-1/2} s^{1/2} M^{-1} 10^{-3}$)	$\Delta E = E_{cp1} - E_{cp2}$ (mV)
TBAP (0.34 M)	12	780
TEAl (0.10 M)	13	840
TEAP (0.10 M)	14	820
NaI (0.10 M)	14	550
TEAP (0.10 M) + $LiNO_3$ (25 mM)	21	–
KSCN (0.10 M)	21	660
$Mg(ClO_4)_2$ (0.10 M)	36	0
$LiClO_4$ (0.10 M)	43	270
$NaClO_4$ (0.10 M)	52	580

TEAP: tetraethylammonium perchlorate; TBAP: tetrabutylammonium perchlorate.

^a Current function ($cf = I_p/\nu^{1/2} [1^+Cl^-]_0$).

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