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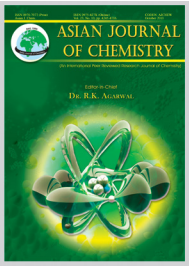

Electrochemical Study of the Complexation of Methyl Yellow with Some Metal Ions as a Model for Doped Poly Azo Compound

AMMAR A. IBRAHIM* and ROSIYAH YAHYA

Department of Chemistry, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia

*Corresponding author: E-mail: dr.ammar_1974@yahoo.com

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The electrochemical behaviour of the complexation of 4-dimethylaminoazobenzene (methyl yellow) with some metal ions has been evaluated using square wave voltammetry. The interactions between the azo compound with metal ions Co^{2+}, Cd^{2+}, Rb^{+}, Rh^{3+}, Ti^{3+}, Hg^{2+}, La^{3+} and Sc^{3+} were measured in phosphate buffer solution at pH 7. The slope obtained from the relationship between diffusion current (I_p) and concentration of azo compound is most steep for Sc^{3+} while Rb^{+} has the least steep slope. This indicates that amongst the metal ions investigated, Sc^{3+} has the most interaction with the azo compound.

Key Words: Electrochemical, Methyl yellow, Complexation, Metal ions, Square wave voltammetry.

INTRODUCTION

Many azo-compounds have been employed as dyes and are used as sensors to detect metal cations[1], non-metal anions[2] or organic compounds[3] as detection can be done efficiently by just simple UV-Visible spectrometer. Electrochemical detection of the azo dyes and their metal complexes have been evaluated to obtain the best experimental conditions for a highly sensitive detection of the analytes considered[4]. The behaviour of azo-conjugated metal compounds based on the d-π electronic interaction is described[5]. Recently, electrochemical methods have been employed to investigate azobenzene and 4-(2-pyridyl-azo-resorcine) compounds in phosphate buffer and Briton-Robinson solutions and their interactions with some metal ions at different pHs[6].

Amongst the azo compounds, 4-dimethylaminoazobenzene (methyl yellow) has been extensively applied as indicator in titration and is also an important redox indicator in catalytic kinetic spectrophotometry[7,8].

The electrochemical degradation of methyl yellow was investigated. The effect of pH, current, the supporting electrolyte and the substituent at the aromatic ring were investigated[9].

The reduction of *trans*-4-dimethylaminoazobenzene (methyl yellow) has been studied in acetonitrile in the absence and presence of added water. was more difficult to reduce than azobenzene with E= -1.995V, 390 mV negative of that of azobenzene, consistent with the very strong electron donating properties of the dimethylamino group[10].

Laitinen and Kneip[11] have investigated the electrochemical behaviour of 4-dimethylaminoazobenzene by polarography. They found that in acidic media the polarographic wave height corresponds to a four-electron reduction, whereas above pH 9 the wave height corresponds to a two-electron reduction.

The objective of this study is to measure complexes of methyl yellow with some metal ions using the polarographic analyzer. Square wave voltammetry technique was used because of its ability to measure at very low concentrations and short time. Some parameters like slope, intercept and correlation coefficient (R) of diffusion current (I_p) with concentration azo complexes will be compared.

EXPERIMENTAL

Preparation of phosphate buffer solution at pH = 7 was carried out by mixing different volumes of K_2HPO_4 and KH_2PO_4 to obtain the required pH. Metal ions were dissolved in distilled water to prepare a stock solution. The metal salts used were: RbCl, $RhCl_3$, $CdCl_2$, $Sc_2(SO_4)_3$ obtained from BDH and $CoCl_2$, $La(NO_3)_3$, $TiCl_3$, $HgCl_2$ obtained from Fluka.

Square wave voltammetric measurements were made using polarographic analyzer model (797 VA computrace Metrohm, which was connected to the computer). The working electrode was a mercury electrode, while the reference electrode was (Ag/AgCl) which was immersed in saturated solution of 3 M KCl. The auxiliary electrode was platinum wire.

RESULTS AND DISCUSSION

Square wave voltammetric technique was used to study the complexation of metals ions at pH = 7 in phosphate buffer. Results showed that all these metals do not have any peak

TABLE-1
EFFECT OF INCREASING THE CONCENTRATION ON I_p AND E_p IN A SOLUTION CONTAINING 2.99×10^{-6} M AND 4.98×10^{-6} M AZOCOMPOUND AT pH = 7

Metal conc. 10^{-6} (M)	2.99×10^{-6} M azo									
	$CdCl_2$		$RhCl_3$		$TiCl_3$		$Pb(NO_3)_2$		$HgCl_2$	
	Ep (V)	Ip (A) $\times10^{-8}$	Ep (V)	Ip (A) $\times10^{-8}$	Ep (V)	Ip (A) $\times10^{-8}$	Ep (V)	Ip (A) $\times10^{-8}$	Ep (V)	Ip (A) $\times10^{-8}$
0	-0.451	9.05	-0.451	9.05	-0.451	9.05	-0.451	9.05*	-0.451	9.05*
0.99	-0.451	7.90	-0.457	8.79	-0.451	7.69			-0.451	9.95
2.00	-0.451	6.52	-0.457	7.92	-0.451	7.14	-0.451	14.01		
2.99	-0.451	5.07	-0.457	6.76	-0.451	5.19			-0.451	9.42
3.98	-0.451	3.52	-0.457	6.00	-0.451	4.79	-0.451	13.21		
4.98	-0.451	2.60	-0.451	5.72	-0.451	3.71			-0.451	6.50
5.96	-0.451	2.13	-0.457	5.26	-0.451	3.57	-0.451	12.81		
6.95	-0.451	1.49	-0.457	5.13					-0.451	5.21
7.94							-0.451	11.11		
8.92									-0.451	4.61
9.90							-0.451	9.710		
10.88									-0.451	3.99
11.86							-0.451	7.910		
12.83									-0.451	3.33
Intercept		8.76×10^{-8}		9.02×10^{-8}		8.75×10^{-8}		1.58×10^{-7}		1.02×10^{-8}
Slope		-0.0114		-0.0063		-0.0096		-0.0062		-0.0059
R		-0.9870		-0.9749		-0.9800		-0.9785		-0.9617

Metal conc. 10^{-6} (M)	2.99×10^{-6} M azo				4.98×10^{-6}M azo			
	RbCl		$Sc_2(SO_4)_3$		$CoCl_2.6H_2O$		$La(NO_3)_3$	
	Ep (V)	Ip (A) $\times10^{-8}$	Ep (V)	Ip (A) $\times10^{-8}$	Ep (V)	Ip (A) $\times10^{-8}$	Ep (V)	Ip (A) $\times10^{-8}$
0	-0.451	9.05	-0.455	9.05	-0.455	9.64*	-0.455	9.64*
0.99			-0.455	8.98	-0.455	9.92	-0.455	9.56
2.00	-0.451	8.15	-0.455	7.60	-0.451	9.73	-0.455	9.53
2.99			-0.451	5.44	-0.451	8.76	-0.455	8.27
3.98	-0.451	7.24	-0.455	3.61	-0.451	7.92	-0.455	8.30
4.98			-0.451	3.40	-0.451	5.19	-0.451	6.64
5.96	-0.451	5.83			-0.451	3.87	-0.451	5.10
6.95					-0.451	3.10	-0.451	3.78
7.94	-0.451	4.99			-0.451	2.68	-0.451	2.86
8.92					-0.451	2.14	-0.445	2.71
9.90	-0.451	4.50						
10.88								
11.86								
12.83								
Intercept		9.04×10^{-8}		9.67×10^{-8}		1.16×10^{-7}		1.13×10^{-7}
Slope		-0.0049		-0.0134		-0.0114		-0.0100
R		-0.9929		-0.9707		-0.9761		-0.9803

*This point was removed at the regression

near the azo compound peak at -0.451 V. The parameters like slope, correlation coefficient and intercept were calculated from drawing the relation between diffusion current (I_p) and increasing the concentration of metal ions to the azo compound.

Table-1 shows the effect of adding metal ions to the solution containing azo compound in phosphate buffer solution of pH = 7 on reduction potential (E_p) and the current diffusion (I_p) of the azo-compound. The curves for $CdCl_2$ and $Pb(NO_3)_2$ to a solution containing azo compound in phosphate buffer solution at pH = 7 is depicted in Fig. 1.

From Table-1 all the correlation coefficients are more than ($R \approx 0.96$), meaning that there is an interaction (binding) between the azo compound with metal ions. Increasing of concentration ratio of metal ion to the azo compound leads to aclear decrease in (I_p) of compound. This decrease takes place because of the interaction between azo compound and metal ions in forming the complexed compound.

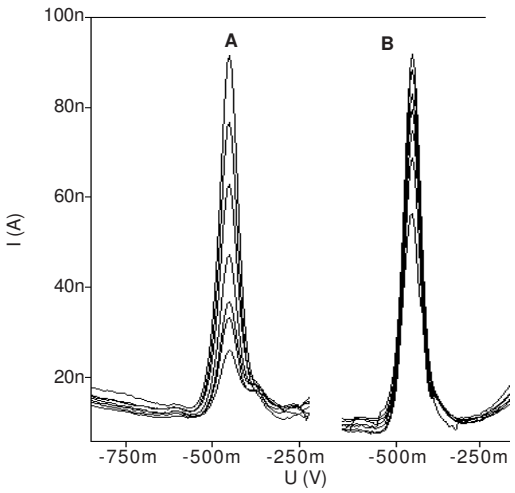

Fig. 1. Effect of added concentration for (1×10^{-6} M) from (A) $CdCl_2$ (B) $Pb(NO_3)_2$ in a solution containing azocompound at (pH = 7)

The slope value can give a good indication on the degree of the binding. Comparing the slope values of all the complexed compounds, Sc-metal complex has the highest binding (highest slope value) compared to Rb-metal complex which has the lowest binding value (lowest slope value) as shown in Fig. 2.

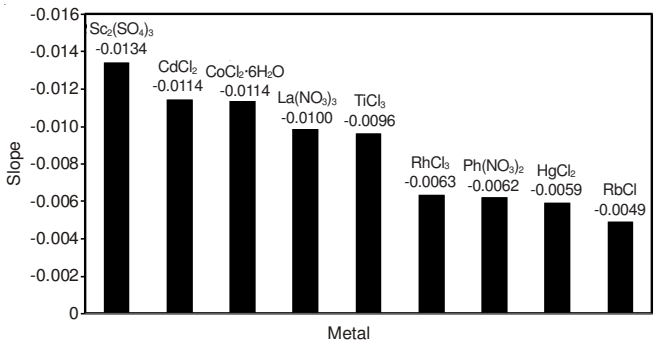

Fig. 2. Slope values of the complex construction from binding between azo compound with metals ions

Conclusion

The effect of adding metal ions to the azo compound leads to decrease the diffusion current, (I_p), of azo compound directly as seen from the slope values. This indicates that there is an interaction (or binding) between the azo compound with these metal ions, with Sc^{3+} having the most interaction.

The slope value obtained from this study gives useful information in choosing the best metal ion to be a dopant for interaction (binding) with poly azo compound.

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