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COBALTOCENIUM DIFFUSION COEFFICIENTS EVALUATION BY ELECTROCHEMISTRY IN ACETONITRILE AND DIMETHYL SULFOXIDE

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Cobaltocenium diffusion coefficients have been evaluated by electrochemistry in two organic solvents, acetonitrile or dimethyl sulfoxide, at different temperatures in the presence of tetrabutylammonium perchlorate as electrolyte. The data have been obtained by cyclic voltammetry, potential-step chronoamperometry, rotating disk electrode and differential pulse voltammetry for different cobaltocenium concentrations. Randles-Sevick and Cottrell equations have been used to calculate the diffusion coefficients. Validity of Stokes-Einstein equation has been checked in both solvents.

Keywords: cobaltocenium, cyclic voltammetry, chronoamperometry, diffusion coefficient, acetonitrile, dimethylsulfoxide

1. Introduction

Cyclic voltammetry is a commonly used method in the electrochemical characterization of redox species, offering important information on electron transfer kinetics involved in redox processes, system reversibility, and stereochemistry of the involved species.

Cobaltocene, $Co(C_2H_5)_2$ (Cc), is an organometallic complex similar to ferrocene, having Co atom "sandwiched" between two cyclopentadienyl rings. Cobaltocene has the tendency to form a stable cobaltocenium cation (Cc^+) in organic solvents by loss of an electron, at a standard potential of -1.33 V in respect with ferrocene-ferrocenium (Fc^+/Fc) couple:

$$Cc - e^- \leftrightarrow Cc^+ \quad (1)$$

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Both couples are recommended by IUPAC as suitable stable references that can be used both in conventional aprotic solvents and in room-temperature ionic liquids (RTILs) [1-12].

This paper focuses on the effect of the solvent on the electrochemical behavior of the $Cc^{+/0}$ couple in order to be used as internal standards for calibration purposes [13-15], especially in RTILs. The reported data have been obtained in two organic solvents: dimethyl sulfoxide and acetonitrile. The electrochemical processes were studied in the presence of tetrabutylammonium perchlorate, a quaternary ammonium salt, which has been used as background electrolyte. The diffusion coefficients of cobaltocenium have been determined in cobaltocenium solutions of different concentrations over a temperature range from 288 to 308 K from cyclic voltammetry and double potential-step chronoamperometry data.

2. Experimental

Materials

High purity acetonitrile (Sigma Aldrich, electronic grade, ≥99.999%) and dimethyl sulfoxide (Merck, ACS grade, ≥99.9 %) were used as solvents. Tetrabutylammonium perchlorate (TBAP) salt from Fluka (≥99.0%) and cobaltocene from Aldrich (reagent purity) have been used. All the experiments have been performed under argon. Solutions of 0.1 M TBAP in dimethyl sulfoxide (DMSO) or acetonitrile (CH_3CN) have been prepared and used as background. Different concentrations of cobaltocenium ranged from 0.4 to 3 mM have been investigated in both solvents.

Apparatus and procedure

The electrochemical studies were carried out using a thermostated cell connected to PGSTAT-12 AUTOLAB potentiostat. For cyclic voltammetry (CV), rotating disk electrode (RDE) and differential pulse voltammetry (DPV) studies both glassy carbon (GC) and platinum (Pt) disks (3 mm diameter) from Metrohm were employed as working electrodes. The auxiliary electrode was a platinum wire, whereas the reference electrode was Ag/Ag^+ couple (10 mM $AgNO_3$, 0.1 M TBAP in CH_3CN). The active surface of the working electrode was polished before each determination with diamond paste (1/4 µm) and then cleaned with the corresponding solvent. All measurements were carried out at 15, 25 and 35°C at different scan rates (0.1, 0.2, 0.3, 0.5 and 1 V/s).

For chronoamperometric measurements a glassy carbon disk (3 mm) was used as working electrode. The potential was stepped from 0 V to -1.3 V (the potential of Cc^+ reduction to Cc).

3. Results and Discussion

The redox processes of Cc^+ in the range of cathodic potentials have been studied under argon by using CV, DPV and RDE methods (Fig. 1). Two successive one-electron reduction peaks (c1 and c2) were noticed during the negative scanning of potential in CV. They are seen in DPV as two peaks at potentials of -1.3 V and -2.3 V, respectively, being also in agreement with the two RDE waves (Fig. 1). Even if the number of involved electrons is the same (one) for c1 and c2 cathodic processes, the shape of the curves obtained for c1 and c2 is not the same. This influence is more visible on the DPV curve, where the first peak is bigger than the second one, and less noticeable on CV and RDE curves in Fig. 1. This behaviour is due to the superposition of oxygen reduction process, which occurs at about the same potential as c1 (oxygen is difficult to be removed from solution, and it is present in small traces, even after long Argon bubbling times). The study of the first electron transfer (c1) has been performed by CV and by chronoamperometry in order to calculate the diffusion coefficient of cobaltocenium.

3.1 Studies by cyclic voltammetry

The study of the first electron transfer (c1) has been performed at different scan rates by CV. The reversible couple (c1/c1') seen in CV has been examined for Cc^+ on different electrodes. In Table 1 are indicated the characteristic peak potentials (Ep_{c1} and $Ep_{c1'}$) for this couple on GC and Pt electrodes. The formal potential (E_f) for this couple is the same on both electrodes. The independence of the formal potential peak on the electrode material shows that the reduction of the cobaltocenium cation is a reversible ideal process, in agreement with the literature [12, 16, 17].

Table 1

Potentials of c1 cathodic peak for Cc^+/ Cc^0 couple on GC and Pt electrodes

Electrode	Ep_{c1}(V)	$Ep_{c1'}$ (V)	E_f (V)
GC	-1.297	-1.218	-1.257
Pt	-1.295	-1.220	-1.257

The reversible couple (c1/c1') seen in CV has been examined for different Cc^+ concentrations at three temperatures on GC working electrode in TBAP-acetonitrile and TBAP-DMSO, respectively. For comparison, the cyclic voltammograms obtained in DMSO and CH_3CN at the same temperature on glassy carbon electrode are shown in Fig. 2 a) and b), respectively, using the same scales for current and potential. It can be noticed that in CH_3CN the currents are higher than in DMSO, even if Cc^+ concentration is lower.

The obtained results are summarized in Tables 2 and 3. The voltammograms show the existence of symmetrical peak couple (c1/c1'), having almost equal values of cathodic (Ip_{c1}) and anodic ($Ip_{c1'}$) peak currents. The $Ip_{c1'}/Ip_{c1}$ ratio, ranged from 0.92 to 1.05 at the studied concentrations and scan rates, indicates the existence of a reversible redox process.

The peak-to-peak separation (ΔEp) between reduction (Ep_{c1}) and oxidation ($Ep_{c1'}$) peak potentials were found to be in the range between 0.78–0.115 V. The obtained ΔEp values are different from the theoretical value of 0.059 V for a one-electron transfer process due to uncompensated resistance (Ru) of the electrolyte, in agreement with other results [9, 16, 18]. Working at higher scan rates and higher concentrations, ΔEp absolute values increase as expected (Tables 2 and 3). Such behavior was also reported in acetonitrile, dichloromethane and their binary mixtures [19]. However, it can be seen, that at low concentration and low scan rates (where Ru is minimized) ΔEp approaches better the theoretical value for GC electrode.

Values of the formal potentials (E_f) were determined. An averaged value of -1.3 V vs. $Fc^+|Fc$ has been obtained (Tables 2 and 3). This value is independent on scan rate and concentration, and it is characteristic for the reversible first reduction couple of Cc^+.

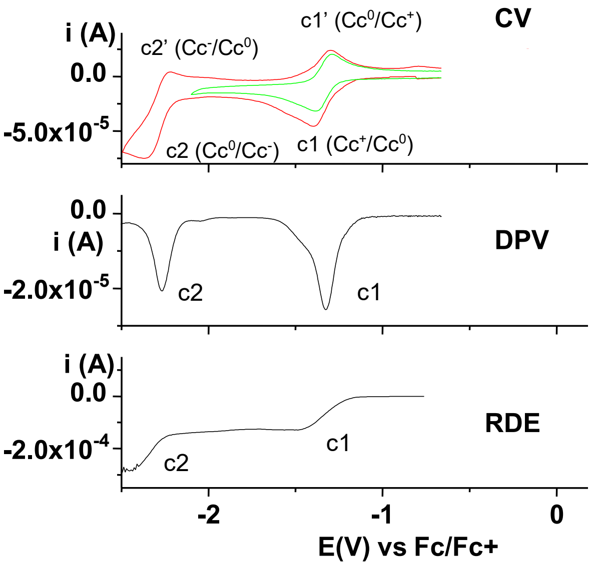

Fig.1. CV, DPV and RDE curves for Cc^+ in TBAP-CH_3CN 0.1 M at 25°C at 0.1 V/s on GC electrode

Table 2

Dependence of cathodic (E_{pc1}) and anodic ($E_{pc1'}$) peak potentials, peak potential separation (ΔEp), ratio of peak currents ($I_{pc1'}/I_{pc1}$) and formal potential (E_f) on Cc^+ concentration, temperature and scan rate (v) for Cc^+/ Cc^0 couple in DMSO on GC electrode

c (mM)	t (°C)	v ($V{\cdot}s^{-1}$)	E_{pc1} (V)	$E_{pc1'}$ (V)	-ΔEp (V)	$I_{pc1}/I_{pc1'}$	E_f (V)
0.75	15	0.1	-1.345	-1.267	0.078	1.04	-1.306
		0.2	-1.350	-1.260	0.090	1.05	-1.305
		0.3	-1.354	-1.259	0.095	1.05	-1.307
		0.5	-1.354	-1.258	0.096	1.03	-1.306
		1	-1.355	-1.253	0.102	1.03	-1.304
	25	0.1	-1.348	-1.262	0.086	1.03	-1.305
		0.2	-1.356	-1.261	0.095	1.04	-1.309
		0.3	-1.356	-1.260	0.096	1.01	-1.308
		0.5	-1.360	-1.259	0.101	1.08	-1.310
		1	-1.361	-1.253	0.108	1.06	-1.307
	35	0.1	-1.342	-1.257	0.085	1.03	-1.300
		0.2	-1.350	-1.255	0.095	1.01	-1.303
		0.3	-1.352	-1.254	0.098	1.00	-1.303
		0.5	-1.359	-1.250	0.109	1.03	-1.305
		1	-1.360	-1.245	0.115	1.03	-1.303
1.5	15	0.1	-1.353	-1.270	0.083	1.01	-1.312
		0.2	-1.361	-1.266	0.095	1.01	-1.314
		0.3	-1.366	-1.264	0.102	1.01	-1.315
		0.5	-1.367	-1.260	0.107	1.03	-1.314
		1	-1.368	-1.258	0.110	1.08	-1.313
	25	0.1	-1.345	-1.262	0.083	1.01	-1.304
		0.2	-1.355	-1.258	0.097	1.01	-1.307
		0.3	-1.358	-1.257	0.101	1.00	-1.308
		0.5	-1.358	-1.256	0.102	1.06	-1.307
		1	-1.358	-1.252	0.106	1.09	-1.305
	35	0.1	-1.341	-1.260	0.081	1.01	-1.301
		0.2	-1.345	-1.253	0.092	1.01	-1.299
		0.3	-1.348	-1.251	0.097	1.00	-1.300
		0.5	-1.358	-1.247	0.111	1.03	-1.303
		1	-1.359	-1.244	0.115	1.04	-1.302
3	15	0.1	-1.353	-1.269	0.084	1.03	-1.311
		0.2	-1.359	-1.266	0.093	1.03	-1.313
		0.3	-1.363	-1.263	0.100	1.01	-1.313
		0.5	-1.364	-1.259	0.105	1.04	-1.312
		1	-1.365	-1.251	0.114	1.05	-1.308
	25	0.1	-1.349	-1.261	0.088	1.04	-1.305
		0.2	-1.360	-1.261	0.099	1.05	-1.311
		0.3	-1.361	-1.260	0.101	1.03	-1.311
		0.5	-1.365	-1.254	0.111	1.02	-1.310
		1	-1.368	-1.259	0.109	1.04	-1.314
	35	0.1	-1.342	-1.254	0.088	1.01	-1.298
		0.2	-1.350	-1.252	0.098	1.00	-1.301
		0.3	-1.352	-1.251	0.101	1.02	-1.302
		0.5	-1.356	-1.250	0.106	1.06	-1.303
		1	-1.357	-1.250	0.107	1.04	-1.304

Table 3

Dependence of cathodic (E_{pc1}) and anodic ($E_{pc1'}$) peak potentials, peak potential separation (ΔEp), ratio of peak currents ($I_{pc1'}/I_{pc1}$), and formal potential (E_f) on Cc^+ concentration, temperature and scan rate (v) for Cc^+/Cc^0 couple in CH_3CN on GC electrode

c (mM)	t (°C)	v ($V \cdot s^{-1}$)	E_{pc1} (V)	$E_{pc1'}$ (V)	$-\Delta Ep$ (V)	$I_{pc1}/I_{pc1'}$	E_f (V)
0.66	15	0.1	-1.308	-1.221	0.087	1.00	-1.265
		0.2	-1.311	-1.220	0.091	1.00	-1.266
		0.3	-1.312	-1.219	0.093	0.97	-1.266
		0.5	-1.316	-1.219	0.097	1.01	-1.268
		1	-1.328	-1.217	0.111	0.93	-1.273
	25	0.1	-1.296	-1.206	0.090	0.98	-1.251
		0.2	-1.300	-1.202	0.098	1.00	-1.251
		0.3	-1.303	-1.197	0.106	0.99	-1.250
		0.5	-1.310	-1.196	0.114	0.99	-1.253
		1	-1.322	-1.192	0.130	1.03	-1.257
	35	0.1	-1.296	-1.208	0.088	0.95	-1.252
		0.2	-1.297	-1.201	0.096	0.96	-1.249
		0.3	-1.300	-1.199	0.101	0.95	-1.250
		0.5	-1.308	-1.194	0.114	0.96	-1.251
		1	-1.318	-1.192	0.126	1.02	-1.255
0.72	15	0.1	-1.298	-1.217	0.081	1.03	-1.258
		0.2	-1.302	-1.214	0.088	1.00	-1.258
		0.3	-1.307	-1.208	0.099	0.99	-1.258
		0.5	-1.311	-1.210	0.101	1.00	-1.261
		1	-1.320	-1.200	0.120	1.02	-1.260
	25	0.1	-1.311	-1.228	0.083	1.00	-1.270
		0.2	-1.315	-1.222	0.093	0.98	-1.269
		0.3	-1.321	-1.222	0.099	0.98	-1.272
		0.5	-1.327	-1.219	0.108	1.01	-1.273
		1	-1.335	-1.218	0.117	1.01	-1.277
	35	0.1	-1.300	-1.212	0.088	1.02	-1.256
		0.2	-1.303	-1.206	0.097	1.02	-1.255
		0.3	-1.304	-1.202	0.102	1.01	-1.253
		0.5	-1.310	-1.200	0.110	0.97	-1.255
		1	-1.316	-1.198	0.118	0.97	-1.257
1.31	15	0.1	-1.323	-1.236	0.087	1.04	-1.280
		0.2	-1.326	-1.232	0.094	1.03	-1.279
		0.3	-1.329	-1.227	0.102	0.99	-1.278
		0.5	-1.337	-1.227	0.110	1.06	-1.282
		1	-1.338	-1.220	0.118	1.03	-1.279
	25	0.1	-1.311	-1.226	0.085	1.05	-1.269
		0.2	-1.318	-1.222	0.096	0.98	-1.270
		0.3	-1.323	-1.221	0.102	0.98	-1.272
		0.5	-1.330	-1.218	0.112	0.99	-1.274
		1	-1.335	-1.212	0.123	1.00	-1.274
	35	0.1	-1.309	-1.218	0.091	0.98	-1.264
		0.2	-1.315	-1.211	0.104	0.96	-1.263
		0.3	-1.317	-1.210	0.107	0.97	-1.264
		0.5	-1.324	-1.207	0.117	1.01	-1.266
		1	-1.330	-1.207	0.123	1.02	-1.269

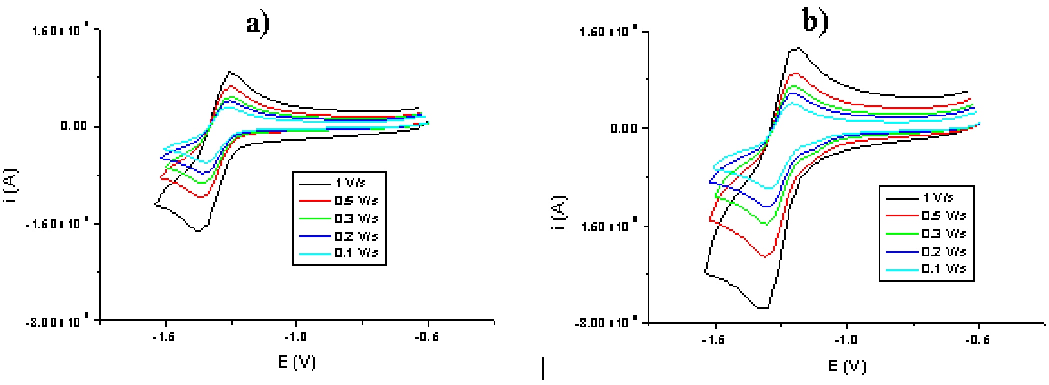

Fig. 2. CV curves at different scan rates at 15°C in: a) DMSO ([Cc$^+$] = 3 mM) and b) CH_3CN ([Cc$^+$] = 0.66 mM)

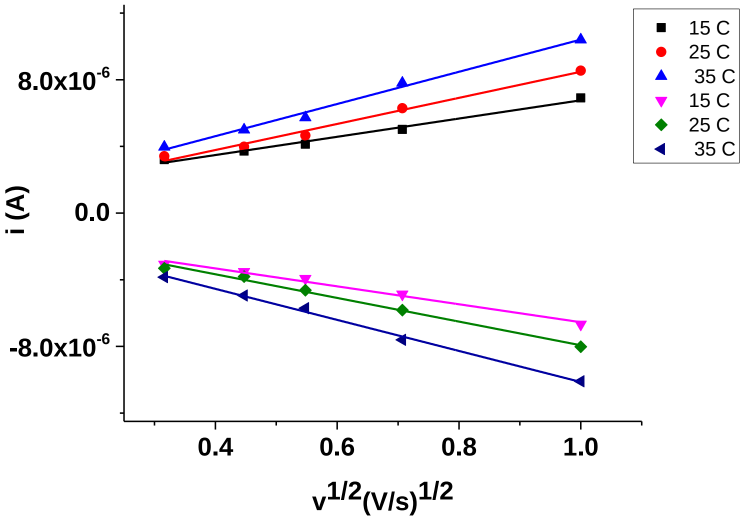

Fig. 3. Dependence of cathodic and anodic peak currents on the square root of the scan rate for Cc$^+$ (0.75 mM) in DMSO at different temperatures

Calculation of diffusion coefficient by cyclic voltammetry

The peak currents for different concentrations of Cc$^+$ and temperatures have been plotted versus the square root of the scan rate [20, 21]. Linear dependences have been obtained, as in shown for instance in Fig. 3, indicating that mass transport occurs by linear diffusion.

The slopes of these linear dependences were used for the calculation of the diffusion coefficients according with the Randles-Sevick equation (2), where i_p is the reduction peak current (A), n is the number of electrons involved in the transfer, A is the electrode area (cm^2), D is the diffusion coefficient (cm^2/s), c is the concentration of Cc$^+$ (mole/cm^3), and v is the scan rate (V·s^{-1}).

$$i_p = 268600 \cdot D^{\frac{1}{2}} \cdot n^{\frac{3}{2}} \cdot A \cdot c \cdot v^{\frac{1}{2}} \qquad (2)$$

The results are given in Table 4 for both solvents at the studied temperatures. It can be seen that the diffusion coefficients increase with temperature and are slightly dependent on concentration. This is a particular aspect observed in these systems, which can suggest an association of the electroactive dissolved substance in the supporting electrolyte, as was previously described by other researchers [12].

The obtained diffusion coefficients for cobaltocenium are five times smaller in dimethyl sulfoxide than in acetonitrile. Their values in both solvents are of the same order of magnitude as those mentioned in literature [5, 11, 12, 17].

Table 4

Diffusion coefficients ($10^{5}\cdot D$, cm^2/s) for Cc$^+$ at different temperatures and concentrations in DMSO and CH_3CN

c, mM \ t (°C)	15	25	35
in DMSO			
0.75	0.150	0.300	0.620
1.5	0.054	0.084	0.094
3	0.035	0.041	0.048
in CH_3CN			
0.66	1,089	1.450	1.705
0.72	0.897	1.032	1.450
1.31	0.300	0.319	0.332

The values of diffusion coefficients were plotted versus concentration at all studied temperatures. Linear interpolation was used to find the values of diffusion coefficient in both solvents corresponding to a concentration of 1 mM (interpolate value) and the results can be seen in Table 5.

Table 5

Diffusion coefficients ($10^{5}\cdot D$, cm^2/s) for Cc$^+$ 1 mM (interpolate value) in DMSO and CH_3CN for different temperatures

solvent \ t (°C)	15	25	35
DMSO	0.12	0.22	0.26
CN_3CN	0.81	1.01	1.25

3.2. Stokes-Einstein behavior

Stokes-Einstein equation (shown in eq. 3) predicts that a linear relationship between diffusion coefficient and the reciprocal of viscosity is observed for a simple diffusing species.

$$D = \frac{k_B \cdot T}{6 \cdot \pi \cdot r \cdot \eta} \qquad (3)$$

where D is the diffusion coefficient, k_B is the Boltzmann constant, r is the cobaltocenium hydrodynamic radius (assuming the molecule is spherical) and T is the temperature.

In order to show if Stokes-Einstein relationship applies for Cc^+ in DMSO and CH_3CN, respectively, dynamic viscosity product (D·η)/T for both investigated solvents was calculated. The results are shown in Table 6. For the investigated temperature domain the mean values are of about $1.23 \cdot 10^{-16}$ N·K^{-1}. The values of the dynamic viscosities were taken from literature [22].

Table 6

Diffusion coefficient of Cc^+ and dynamic viscosity product *vs.* temperature in DMSO and ACN

T (K)	η (mPa·s) [22]	$D \cdot \eta \cdot 10^{16}/T$ (N·K^{-1})
	in DMSO	
288.15	2.422	0.96
298.15	2.012	1.47
308.15	1.694	1.43
	in ACN	
288.15	0.406	1.09
298.15	0.370	1.15
308.15	0.340	1.27

3.3. Dependence of diffusion coefficients on temperature

Arrhenius type equation (4) was used to quantify the variation of the diffusion coefficient in the investigated domain of temperatures.

$$D = D_0 \cdot e^{-\frac{E_D}{RT}} \qquad (4)$$

where D_o is the pre-exponential factor, E_D is the activation energy for diffusion (J), R is the universal gas constant and T is the absolute temperature (K).

Plot of lnD against $1/T$ resulted in straight lines. In Table 7 are given the values obtained for the activation energy for diffusion, E_D, in each solvent for Cc^+ concentration of 1 mM. E_D value in DMSO (28.7 kJ/mol) was found to be almost double in respect to that obtained in acetonitrile (16 kJ/mol). These results are in agreement with the fact that more viscous ionic liquids have correspondingly larger activation energies.

Table 7

Activation energy of diffusion for Cc^+ (1 mM) in DMSO and CH_3CN

solvent	slope (K)	E_D (kJ/mole)
DMSO	-3450	28.67
CH_3CN	-1923	15.98

3.4. Calculation of diffusion coefficient by chronoamperometry

Double potential step chronoamperometry was also performed in Cc^+ solutions in DMSO and acetonitrile, respectively, in order to calculate the diffusion coefficients. The slope of linear plot of i versus $t^{-1/2}$ was used in the Cottrell equation (5) in order to determine the diffusion coefficient [23].

$$i = n \cdot F \cdot A \cdot c \cdot D^{\frac{1}{2}} \cdot \pi^{-\frac{1}{2}} \cdot t^{\frac{1}{2}} \tag{5}$$

In equation (5), n is the number of electrons involved in the process, $n = 1$, F is the Faraday constant, c is the concentration of Cc^+ ($mole \cdot cm^{-3}$), A is the area of the electrode (cm^2), and t is the time (s). The dependence of the current versus the inverse of the square root of time was found to be linear, when plotted with a zero intercept for different concentrations of Cc and temperatures, as seen in Figs. 6a and b.

The values of diffusion coefficients from chronoamperometric measurements (Table 8) are in a good agreement with those obtained from cyclic voltammetry measurements (Table 4).

Table 8

Diffusion coefficients ($10^5 \cdot D$ in cm^2/s) for Cc^+ at different temperatures (t) and concentrations (c) in DMSO and CH_3CN from chronoamperometry

c(mM) t (ºC)	15	25	35
in DMSO			
0.75	0.13	0.306	0.385
1.5	0.061	0.081	0.161
3	0.006	0.012	0.019
in CH_3CN			
0.66	1.429	1.962	2.757
0.72	0.833	1.298	1.454
1.31	0.482	0.573	0.971

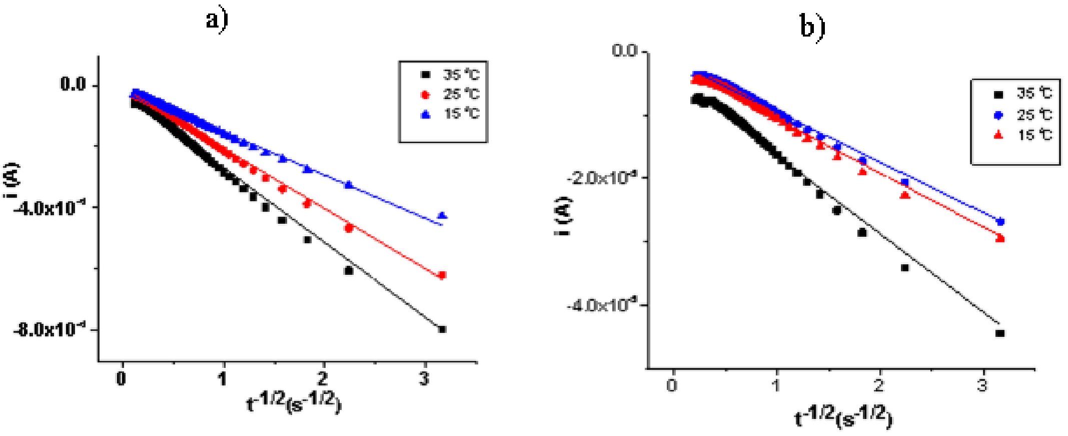

Fig. 6. Plots of chronoamperometric current i(A) vs. the inverse of the square root of time for Cc^+ at different temperatures in DMSO (a) and CH_3CN (b)

In order to determine the diffusion coefficient by chronoamperometry for Cc^+ concentration of 1 mM in both solvents, linear equations were used. The obtained values at different temperatures are given in Table 9.

Table 9

Diffusion coefficients determined by chronoamperometry ($10^5 \cdot D$) in cm²/s for Cc 1 mM (interpolated value) in DMSO and CH_3CN for different values of temperature

solvent t(°C)	15	25	35
DMSO	0.11	0.22	0.28
CN_3CN	0.77	1.01	1.22

Table 10

Comparison of diffusion coefficients ($10^5 \cdot D$ in cm²/s) for Cc^+ at 25°C

Solvent	D^a (cm^2s^{-1})	D^b (cm^2s^{-1})	D^c (cm^2s^{-1})
DMSO	0.22	0.30	-
CN_3CN	1.01	1.36	1.9

D^a- diffusion coefficient according to present paper by CV and chronoamperometry at 1 mM;
D^b- diffusion coefficient according to ref. [11] at 0.8 mM;
D^c- diffusion coefficient according to ref. [12].

4. Conclusions

The redox proccess of Cc^+/Cc has been highlighted by CV, DPV and RDE methods in two aprotic organic solvents, acetonitrile and dimethyl sulfoxide, in order to use it as internal standards for calibration purposes. It has been confirmed that the first reduction process is reversible. The ratio of the anodic and cathodic peak current is close to unity. The peak to peak potential difference shows deviations from the ideal value of 0.059 V at 25°C, due to the uncompensated solution resistance.

The diffusion coefficients for Cc^+ were calculated in both solvents at different temperatures and concentrations. The diffusion coefficients increase with temperature and slightly decrease with concentration. The obtained diffusion coefficients for cobaltocenium are five times smaller in dimethyl sulfoxide than in acetonitrile. The activation energy of diffusion in DMSO was found to be almost double than that obtained in acetonitrile.

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