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Comparison of diffusivities data of streptocyanine dyes by electrochemical and NMR-DOSY methods

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A B S T R A C T

Diffusivity data of streptocyanine dyes in acetonitrile were investigated using both transient voltammetric techniques and NMR-DOSY. Results of voltammetric measurements allow determination of the diffusion coefficient D values in the range of $1.2\text{--}1.6 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ for the target dyes. Deuterated acetonitrile solvent was used for NMR-DOSY experiments and diffusivities of streptocyanines are given after calibration of acetonitrile on its tracer diffusion value of D_{ACN}^* of 4.37×10^{-9} . The results for the two methods appear to be in good agreement allowing use of the convenient NMR-DOSY method to measure diffusivity of streptocyanine dyes at low concentrations and so giving a direct access to the number of exchanged electrons using limiting current electrochemical techniques. This last method affords a great advantage of obtaining diffusion coefficients by non-electrochemical method.

Keywords:

Diffusion coefficient

Self-diffusion

Mutual diffusion

Convolution potential sweep voltammetry

NMR-DOSY

1. Introduction

Streptocyanines, like cyanine dyes, are cationic conjugated organic compounds containing a chain made up of an odd number of carbon atoms between two nitrogen atoms [1,2]. Due to their photophysical properties, this class of compounds presents numerous applications, like photographic sensitizers [3,4], infrared-dye-sensitized solar cell [5], optical recording [6], nonlinear frequency doublers [7,8], or biological probes [9–12]. Cyanines are also known to possess interesting pharmacological properties [13,14].

Electrochemical methods are appropriated to the redox behavior study of these molecules as well as the understanding of their reaction scheme. For this purpose the convolutive cyclic voltammetry can be involved to access to their kinetic (k , the heterogeneous rate constant or α , the electronic transfer coefficient) and thermodynamic parameters (n , the number of exchanged electron, E° , the standard redox potential) [15]. Nevertheless because most of the electrochemical methods, including cyclic voltammetry involve simultaneously diffusion coefficient D , the electrochemical area of the working electrode, and the number of exchanged electron, n , estimation of the one requires the others. Consequently

determination of diffusion coefficient D by non-electrochemical methods could be of interest for electrochemists and constitutes the aim of this study.

Electrochemical and NMR-DOSY (Diffusion Ordered Spectroscopy) methods are both used widely for the quantification of diffusivity.

The self-diffusion (or intra-diffusion) coefficient D^* is directly related to the size of the molecule and refers to the diffusion in solution of uniform chemical composition, whereas the mutual diffusion (or inter-diffusion) coefficient D describes diffusion based bulk transport in the presence of concentration gradients. The difference between these two coefficients is described explicitly by Bearman [16] who demonstrated that at infinite dilution values of D and D^* are identical. Later, Least [17] has shown that at low concentrations self-diffusion and mutual diffusion coefficients are related by $D = D^* + CdD^*/dC$ where C is the total solute concentration. He has experimented that they are identical for dilute self-associating solutes. More recently, Bond et al. [18] compared diffusivity data derived from electrochemical and NMR investigations of the $\text{SeCN}^-/((\text{SeCN})_2)/(\text{SeCN})_3^-$ system in ionic liquids. The authors found that diffusivity data derived from concentration and field gradients respectively are in good agreement.

As there are no interaction or association between each streptocyanine molecules and between streptocyanine and electrolyte in

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acetonitrile, we were interesting in comparing diffusivity data of streptocyanine dyes by means of electrochemistry and NMR techniques at the low concentration usually involved in electrochemistry. Mutual diffusion D , plays a key role in convolutive voltammetry and has to be known to give access to kinetics and thermodynamics parameters. It could be indeed very convenient to get a direct access to the diffusion coefficient D by RMN-DOSY method: electrochemical methods could then provide directly the number of electron exchanged, n , by a simple use of the limiting current equation avoiding potentiostatic electrolysis.

2. Results and discussion

A family of streptocyanines with different polymethine chain length (5C-, 7C-, 9C-) (Fig. 1a-c) and one 5C- hemicarboxonium (Fig. 1d) were synthesized as previously described [19–23].

2.1. Electrochemical cathodic behavior of cyanines

The electrochemical reduction of each streptocyanine (1 mM) was studied by cyclic voltammetry using a glassy carbon electrode in anhydrous acetonitrile containing 0.1 mM tetrabutylammonium perchlorate (TBAP). For each experiment, the potential of the reference (silver wire) was always calibrated by adding ferrocene as internal standard.

Convolutive voltammetry, successfully applied to elucidate the mechanism of various electrochemical reactions, was involved in this study. The convoluted current $I(t)$ is given by Eq. (1) [24]:

$$I(t) = \frac{1}{\pi^{1/2}} \int_0^t \frac{i(u)}{(t-u)^{1/2}} du \quad (1)$$

where I is the convoluted current ($A s^{1/2}$), i the actual current, and t the time. It can be estimated from the algorithm suggested by Lawson and Maloy [25].

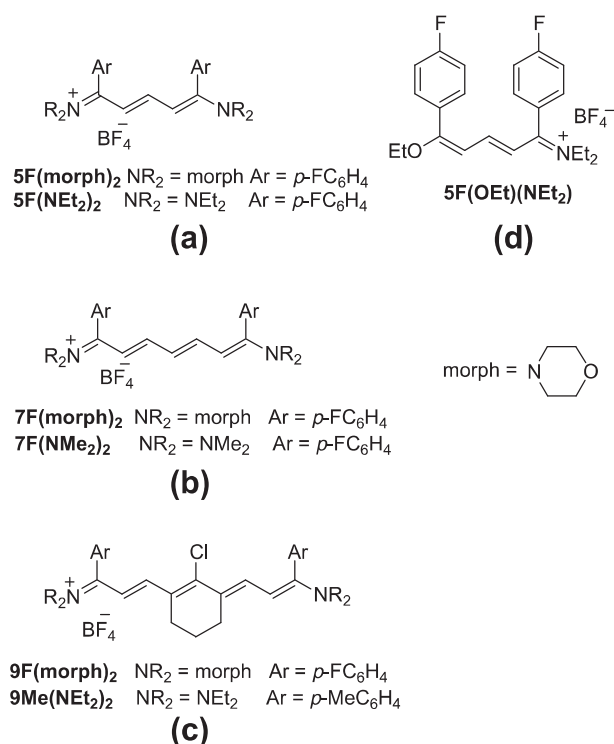


Fig. 1. Streptocyanines (a-c) and hemicarboxonium (d) used.

$$I(t) = I(k\Delta t) = \frac{1}{\pi^{1/2}} \sum_{j=1}^{j=k} \frac{i(j\Delta t - \frac{1}{2}\Delta t)}{\sqrt{k\Delta t - j\Delta t + \frac{1}{2}\Delta t}} \quad (2)$$

where j takes values of time in the range 0– t .

I_{lim} is the convoluted limiting value of $I(t)$ at 'extreme' potentials i.e. when the potential is driven to a sufficiently extreme value allowing to the concentration at the electrode to become zero. The current is thus controlled solely by the diffusion flux at the electrode.

At the plateau, the convoluted limiting current is expressed by:

$$I_{lim} = n \times F \times S \times C_p \times D^{1/2} \quad (3)$$

where n is the electron exchanged, S is the electrode area, D is the diffusion coefficient, C_p is the concentration of the streptocyanine [15].

Fig. 2 presents typical voltammetric (a) and convoluted (b) curves at different potential scan rates ($r = 0.05$ – $1 V s^{-1}$) obtained with the streptocyanine $5F(morph)_2$ exempted of the residual current. Curves show a nice peak of which the current magnitude increases versus the potential scan rate. The reverse scan does not indicate any signal, translating an irreversible behavior. The electrode area S was estimated from voltammetric curves obtained with ferrocene. The peak current was correlated to the electrode area and the scan rate r , according Eq. (4) [15]:

$$I_p = 269,000 \times S \times n_{Fer}^{3/2} \times D_{Fer}^{1/2} \times r^{1/2} \quad (4)$$

For reversible ferrocene oxidation: $n_{Fer} = 1$ and $D_{Fer} = 2.62 \times 10^{-9} m^2 s^{-1}$ in acetonitrile [26].

A linear evolution of i_p versus the potential scan rate $i_p = f(r^{1/2})$ allows access to the electrode area S with a relative error of 5%. Then the S value was used to determine diffusivity of each streptocyanine using Eq. (3) (results are shown in Table 1).

Note that, the determination of D value requires knowledge of the exchanged electron number n . The studied dyes, (5C-streptocyanines) present a reversible redox system in oxidation, involving one electron as shown in our work [27] and by Lenhard et al. who investigate n in a similar series of cyanines [28].

Performing calculation of uncertainties from previous Eq. (3) led to:

$$\frac{\Delta D}{D} = 2 \left(\frac{\Delta I_{lim}}{I_{lim}} + \frac{\Delta n}{n} + \frac{\Delta S}{S} + \frac{\Delta C_p}{C_p} \right) \quad (5)$$

Relative errors on both the limiting convoluted current and the concentration are negligible (<2%), main uncertainties come from the estimation of the electrode area, evaluated close to 10%; in these conditions the overall relative error on experimental diffusion value by electrochemistry can reach 20%.

2.2. Measurement of D^* by NMR-DOSY (Diffusion Ordered Spectroscopy) [29]

Intradiffusion (often called self-diffusion) is conveniently measured by NMR-DOSY techniques. The basic scheme for the determination of self-diffusion coefficient is the pulse field gradient spin-echo (PFGSE). The measurement is carried out by observing the attenuation of the NMR signals during a pulsed field gradient experiment. The degree of attenuation is a function of the magnetic gradient pulse amplitude and occurs at a rate proportional to the self-diffusion coefficient (D^*) of the molecule. In practice, a series of NMR diffusion spectra are acquired as a function of the gradient strength. It can be observed that the intensities of the resonances follow an exponential decay. The slope of this decay is proportional to the diffusion coefficient [30,31].

D^* values are function of temperature and viscosity as indicated from the Stokes–Einstein equation:

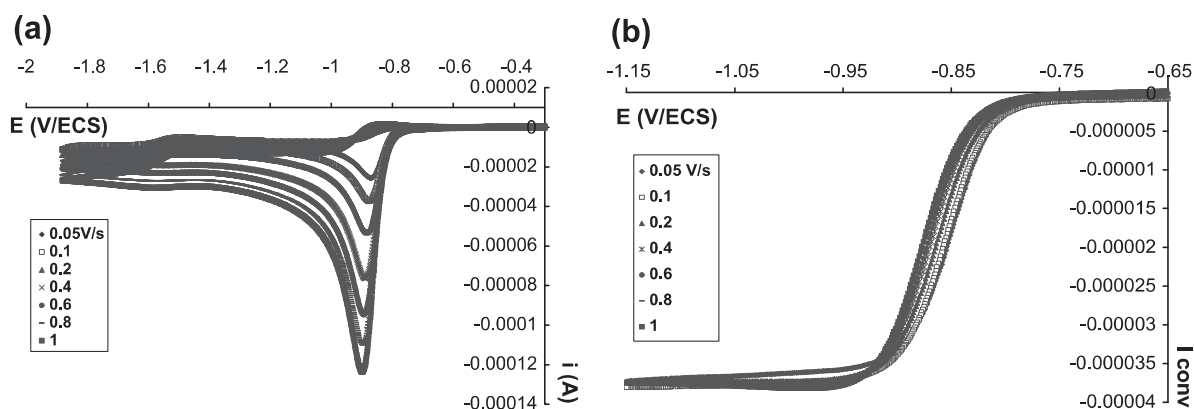


Fig. 2. Voltammetric (a) and convoluted (b) curves plotted on glassy carbon disk shaped, at different sweep rates ($0.05\text{--}1\text{ V s}^{-1}$) for reduction of $5\text{F}(\text{morph})_2$ at 1 mM , in acetonitrile and in presence of tetrabutylammonium perchlorate (TBAP) (0.1 mM). Residual current was removed and the potential is calibrated versus the ferrocene/ferricinium reference electrode. Auxiliary-electrode: Pt plate of 1 cm^2 ; Pseudo-reference electrode: Ag wire immersed in acetonitrile containing TBAP (0.1 mM).

Table 1
Operating parameters and data obtained by convoluted curves of Fig. 2.

	MW (g mol^{-1})	C_p (mole m^{-3})	$S \times 10^6$ (m^2) ^a	$I_{\text{lim}} \times 10^{5b}$	$\Delta I_{\text{lim}}/I_{\text{lim}}$ (%)	$D \times 10^9$ ($\text{m}^2 \text{s}^{-1}$) ^c
$5\text{F}(\text{morph})_2$	512	1.05	9.96	3.75	3	1.38
$5\text{F}(\text{NEt}_2)_2$	484	1.07	7.69	3.30	3	1.58
$5\text{F}(\text{NEt}_2)(\text{OEt})$	457	1.05	7.07	2.80	1	1.53
$7\text{F}(\text{morph})_2$	538	1.02	6.91	2.56	2	1.47
$7\text{F}(\text{NMe}_2)_2$	454	1.09	7.00	2.98	6	1.63
$9\text{F}(\text{morph})_2$	639	1.56	7.31	3.92	7	1.27
$9\text{Me}(\text{NEt}_2)_2$	603	1.38	9.07	4.40	2	1.33

^a Electrode area obtained from ferrocene voltammetric curves according (4).

^b Convoluted limiting current for streptocyanine reduction, deduced from curves of Fig. 2.

^c Diffusivity of streptocyanines estimated using (3).

$$D^* = \frac{kT}{6\pi\eta R_H} \quad (6)$$

where k is the Boltzmann constant, T the temperature, η the viscosity of the solution and R_H is the radius of the solvated species. This equation shows that D^* is correlated to the temperature and the viscosity of the solution, and also of course to the size of the molecule.

This NMR-DOSY technique was applied to access to diffusion coefficient of target dyes in deuterated acetonitrile, with or without electrolyte (TBAP), within a relative error less or equal to 5%.

In the first sets of experiments, diffusion coefficient values were found to be similar in presence or absence of electrolyte. Thus, next experimental work was performed without electrolyte. As ferrocene is commonly used in cyclic voltammetry experiments to calibrate the potential and evaluate the surface of the working electrode, $D_{\text{ferrocene}}$ values are largely described in literature. So we used ferrocene in our NMR-DOSY experiments both to estimate its experimental D^* value by our method and compare to D value found in literature.

Streptocyanine (0.02 M) was dissolved in $\text{ACN-}d_3$, with or without ferrocene. Measurements of self-diffusion coefficients for each of the components were performed at 298 K on a Bruker AVANCE 400 spectrometer equipped with a TBO probe 5-mm direct detection, pulse field gradient (PFG) probe and a 10 A Highland gradient amplifier. The combination provides a z -gradient strength, g , of up to 34.05 G cm^{-1} . Experiments were performed by varying g and keeping all other timing parameters constant. The relationship between the echo attenuation and the self-diffusion coefficient, D^* ($\text{m}^2 \text{s}^{-1}$), is given by the Stejskal-Tanner relation [32]

$$I/I_0 = \exp[-\gamma^2 g^2 \delta^2 (\Delta - \delta/3) D^*] \quad (7)$$

where I is the measured signal intensity, I_0 is the signal intensity for zero g , γ is the gyromagnetic ratio for the ^1H nucleus, δ is the gradi-

ent pulse length, Δ is the time between the two gradients in the pulse sequence. Typically a Δ of 100 ms , a δ of $800\text{ }\mu\text{s}$ and varying from 1.703 (strength of 5%) to 32.35 (strength of 95%) G cm^{-1} in 15 steps were used. Used pulse program “stebppg1s” (stimulated echo bipolar gradient pulse pair 1 spoil gradient) which is furnished with the Bruker instrument [33]. The analysis of the PGSE NMR data was performed with implemented procedure in topspin software [34]. A typical curve showing the decrease of the intensity as a function of the gradient strength is presented in Fig. 3 for $5\text{F}(\text{morph})_2$. The resonance signal corresponds to the integrated area of the ^1H NMR signal between 7.168 ppm and 7.111 ppm . The gradient strength g , is varying from 1.703 to 32.35 G cm^{-1} (16 points). The topspin software allows a mono exponential fitting, of the type $I = I_0 \exp(-kg^2)$, from which self-diffusion coefficient D^* , of each component can be extracted.

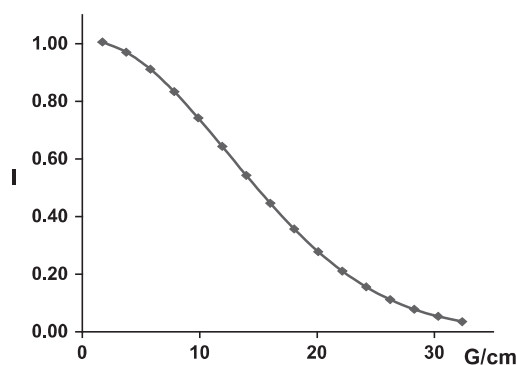


Fig. 3. Exponential decay of the intensity of the resonance for $5\text{F}(\text{morph})_2$ between 7.168 and 7.111 ppm . Dots: experimental values, solid lines: fit.

Table 2
Diffusion coefficients estimated by NMR-DOSY at 298 K.

Experiment	$D_{ACN}^* \times 10^9$ measured	$D_{Fer}^* \times 10^9$ measured	$D_{Fer}^* \times 10^9$ corrected ^a	$D_{Cyan}^* \times 10^9$ measured	$D_{Cyan}^* \times 10^9$ corrected ^a	Mean values
CH3CN	4.68					
Ferrocene	4.58	2.894	2.68			
5F(morph) ₂	4.35			1.38	1.40	
5F(morph) ₂ + fer	4.69	3.02	2.70	1.76	1.44	1.42 ± 0.02
5F(NEt ₂) ₂	4.54			1.61	1.44	
5F(NEt ₂) ₂ + fer	4.67	2.997	2.70	1.796	1.50	1.47 ± 0.03
5F(NEt ₂)(OEt)	4.70			1.846	1.52	
5F(NEt ₂)(OEt) + fer	4.80	3.203	2.77	1.89	1.46	1.49 ± 0.03
7F(morph) ₂	4.63			1.59	1.33	
7F(morph) ₂ + fer	4.47	2.752	2.65	1.42	1.32	1.32 ± 0.01
7F(NMe ₂) ₂	4.67			1.813	1.48	
7F(NMe ₂) ₂ + fer	4.484	2.814	2.70	1.556	1.44	1.46 ± 0.02
9F(morph) ₂	4.60			1.525	1.29	
9F(morph) ₂ + fer	4.48	2.847	2.74	1.341	1.23	1.26 ± 0.03
9Me(NEt ₂) ₂	4.92			1.875	1.33	
9Me(NEt ₂) ₂ + fer	4.86	3.203	2.71	1.774	1.28	1.31 ± 0.03

^a D^* are given with value of D_{ACN}^* calibrated at $4.37 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$.

D^* of ACN, ferrocene and streptocyanine were determined for each NMR-DOSY experiment. Results are presented in Table 2. As discrepancies appeared due to the great sensibility of the method, calibration is needed. D_{ACN}^* was calibrated on the value of the tracer diffusion coefficient of ACN at $4.37 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ which is the value found in literature [35]. Holz [36] also has been studying the effect of isotopic H-D substitution on self-diffusion coefficient for common used solvents and he showed that acetonitrile has a low dynamic isotope effect in the range of 5%.

Then corrected diffusion coefficients of ferrocene and streptocyanines can be obtained after calibration on D_{ACN}^* .

D_{Fer}^* was found at 2.71×10^{-9} which is in good agreement with the D_{Fer} value given by Ikeuchi et al. [26] in TEAP (0.1 M) acetonitrile solution ($2.62 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$). We can notice that the streptocyanine does not impact the diffusion of ferrocene as D_{Fer}^* and D_{Fer} are very close. D_{Fer}^* is around 2.71 ± 0.06 whatever the streptocyanine used or not and the presence or not of the electrolyte during the NMR experiment.

The ferrocene does not interfere with the streptocyanines molecules as their diffusion coefficient are similar with and without ferrocene (cf. Table 2).

Mean values of the two sets of experiments (with and without ferrocene) are presented in Table 2. Experimental errors during DOSY-NMR experiments are around 5%.

3. Conclusion

Evaluation of D^* by NMR-DOSY within the conditions described in the present study gave values in good agreement with diffusivity data derived from electrochemical results, as shown by the results presented in Tables 1 and 2 which are very similar. From our present study, we can deduce that using NMR-DOSY to determine the diffusion coefficient D , is suitable for dilute solutes. This method is more convenient than electrochemical method and is characterized by its high level of precision (relative error lower or equal to 5%) and reproducibility compared to the classical electrochemical method (relative error 20%). Nevertheless, note that this method needs calibration by a known self-diffusion coefficient of another species which was the acetonitrile here. Indeed NMR-DOSY is a direct method, allowing a rapid estimation of the diffusion coefficient in acetonitrile. Therefore, the number of exchanged electron n could be easily determined from the value of the convoluted limiting current and the value of D (using Eq. (3)) avoiding preparative electrolysis at controlled potential and its experimental problems.

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