Diffusion Coefficients of C₆₀ and C₆₀[−] in Benzonitrile and Dichloromethane Solutions Containing Tetrabutylammonium Perchlorate, Measured by Potential-step Chronoamperometry

Yukihiro HISHIDA, Minako NISHI, Yukie BABA, and Haruko IKEUCHI[†]

Department of Chemistry, Faculty of Science and Technology, Sophia University,
7-1, Kioi-cho, Chiyoda-ku, Tokyo 102-8554, Japan

The diffusion coefficients of C₆₀ in dichloromethane and benzonitrile solutions containing 0.1 M tetrabutylammonium perchlorate were determined by single potential-step chronoamperometry at small disk electrodes. The diffusion coefficients of C₆₀ were obtained by curve fitting of the chronoamperograms to a theoretical equation by Shoup and Szabo. The values were $(1.4 \pm 0.3) \times 10^{-9}$ and $(4.1 \pm 0.3) \times 10^{-10}$ m² s^{−1}, respectively (the errors are 95% confidence limits). The diffusion coefficients of C₆₀[−] in these solutions were measured by double potential-step chronoamperometry. The ratios of the diffusion coefficients of C₆₀ to those of C₆₀[−] were obtained from theoretical curves of the ratios of the current at the second potential step to the current at the first one. The values of the ratios were 1.2 ± 0.2 and 1.0 ± 0.3 , respectively.

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Introduction

Fullerene C₆₀ is a valuable model molecule for solution chemistry and electrochemistry because of its spherical shape and its delocalized electron structure. The diffusion coefficient (*D*) of this molecule is one of the most suitable physical properties for studying the hydrodynamic features of solutes in solutions. *D*s have therefore been measured in various solvents by different techniques, such as electrochemical methods,^{1–7} ¹³C-NMR,^{8,9} Taylor dispersion,^{10,11} neutron scattering,^{12–15} and polarization interferometry.^{16,17} Among them, the electrochemical method is very conveniently used, because C₆₀ can be reduced in several successive one-electron transfer steps, Eq. (1), in the electrochemically observable potential window:

Dubois *et al.* measured the diffusion coefficients of C₆₀ as well as the half-wave potentials for reductions in various solvents containing different supporting electrolytes.¹ Krishnan *et al.* extended the research further by determining the diffusion coefficients of negatively charged fullerenes, C₆₀^{*n*−} (*n* = 0, 1, 2, 3).¹⁸ Such fulleride ions are also extremely interesting substances if they keep the spherical shape and the delocalized electronic structure. Many reports concerning the characterization of the UV-vis and near-IR absorption spectra of fullerene and fulleride ions have been presented.^{19–33} According to these reports, the possibility of the Jahn-Teller distortion from I_h symmetry of C₆₀[−] can not be completely excluded; the shape of C₆₀[−] is nevertheless supposed to be almost spherical and the size to be similar to that of C₆₀.^{3,18,24,29,30,33}

Some data of diffusion coefficients of C₆₀ (*D*_{C60s}), determined by electrochemical methods in similar experimental environments, are listed in Table 1. As can be seen in Table 1, one value of *D*_{C60} deviates from the other beyond the experimental error or/and the probable divergence that can come from insignificant differences of the experimental environment. One group of authors¹ deduced positive solvation numbers from their own data of *D*, while the others^{3,5} will have to claim negative ones in similar media if they perform the calculations. The data now available are not accurate or precise enough to be used for any discussion of the solvated state.

We have already developed a single-potential-step (SPS) chronoamperometric method to determine the *D*s of electroactive species in electrolyte solutions.^{34,35} This method has a routine to assess the accuracy of the values of obtained *D*s. Here, we applied the method to determine accurate and precise values of *D*_{C60} in dichloromethane (DM) and benzonitrile (BN) solutions containing 0.1 M tetrabutylammonium perchlorate (TBAP). We have also developed a method to determine *D*s of electrode reaction products by the double-potential-step (DPS) chronoamperometry.^{36,37} By this method, the diffusion coefficients of C₆₀[−] produced by the electrode reaction of C₆₀ in both solutions have been determined.

Experimental

Chemicals

Fullerene C₆₀ (Tokyo Kasei Kogyo Co., Ltd., >99.9%) and TBAP (Nacalai Tesque, specially prepared for polarographic use, >98%) were used without further purification. The solvents, DM (Kanto Chemical Co. Inc., dichloromethane dehydrated, >99.5%) and BN (Sigma-Aldrich, HPLC grade, >99.9%) were used as received as soon as the bottles were opened.

[†] To whom correspondence should be addressed.
E-mail: h-ikeuti@sophia.ac.jp or haruko-i@gk9.so-net.ne.jp

Table 1 Values of the diffusion coefficients of C_{60} and C_{60}^{n-} in aprotic solvents containing 0.1 M electrolyte reported in references

Solvent	Electrolyte	$\frac{t}{^\circ\text{C}}$	$\frac{D_{C_{60}}}{10^{-10} \text{ m}^2 \text{ s}^{-1}}$	Method for measuring $D_{C_{60}}$	$\frac{D_{C_{60}^{n-}}}{D_{C_{60}}}$	Method for measuring $D_{C_{60}^{n-}}$	Reference
DM	TBAP	22 ± 1	4.4 ± 0.9	Rotating disk electrode voltammetry	0.50	Bulk electrolysis, rotating disk electrode voltammetry	1, 18
	TBAP	25	17	a.c. Voltammetry			5
	(TBA)BF ₄	25 ± 1	10.5 ± 1.2	Chronoamperometry at a disk electrode			6
BN	TBAP	22 ± 1	1.4 ± 0.3	Rotating disk electrode voltammetry	0.79	Bulk electrolysis, rotating disk electrode voltammetry	1, 18
	TBAP	25	2.6	a.c. Voltammetry	0.96	a.c. Voltammetry	3, 5
	(TBA)BF ₄ ^a	—	3.14	Steady-state voltammetry at ultramicrodisk electrodes			4

a. Concentration of the electrolyte is 0.05 M.

Apparatus

A computer-controlled potentiostat, Digital Universal Signal Processing unit HECS 326 with Head Box 326-2 (Fuso Seishakusho Ltd.), was used for the measurements of chronoamperometry, cyclic voltammetry (CV), and differential pulse voltammetry (DPV). The electrolysis cell was a glass cylinder equipped with three electrodes. The cell was set in a tight Faraday cage flushed with Ar, which worked as a thermostatic bath as well. The details of these devices have been reported elsewhere.^{4,36-38} The working electrode was a Pt-disk of 0.101 mm, 0.241 mm, or 1.002 mm radius imbedded in glass (locally made). These radii were determined by a measuring microscope. The reference electrode was an Ag | AgCl | 3 M NaCl aq. solution (BAS 11-2020), which was connected to the cell solution by double junctions (sample solution | supporting electrolyte solution | 3 M NaCl aq. solution), and the counter electrode was a piece of Pt wire (BAS 51-2222).

A UV-vis spectrometer (Hitachi; U-3210 or JASCO; V-560) was used for determining concentration of C_{60} , and a vis-NIR (380–1100 nm) spectrometer (Otsuka Electronics; Multi Channel Photo Detector Photol MCPD-7000, with a external light source Photol MC 2530) was used for monitoring the electrolysis progress in the optically transparent thin layer electrode (OTTLE) cell (home-made).^{39,40} These optical measurements were performed at an ambient temperature of 20 to 25°C.

The viscosities of the supporting electrolyte solutions were determined from the kinematic viscosities, which were measured at 25°C with an Auto-Viscometer equipped with Ostwald-Type viscometer cells (Shibayama Scientific Co. Ltd.; SS-102-L1), and from the densities, which were measured at 25°C with a density meter (Anton Paar; DMA 60 with Density Measuring Cell DMA 602).

Procedure

The concentrations of C_{60} in the TBAP/DM and TBAP/BN solutions were determined spectroscopically by the prominent absorption bands at 405 nm and at 407 nm, respectively, on the bases of calibration curves made for these electrolyte solutions. The molar absorption coefficient value of C_{60} was $(3.05 \pm 0.08) \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ in both electrolyte solutions. This value is acceptable compared with a reported value: $2.95 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ at 404 nm in pure *n*-hexane.²² The concentrations of C_{60} in the BN and DM solutions used for the electrolysis measurements were from 0.10 to 0.15 mM and from 0.14 to 0.28 mM, respectively.

CV and DPV were performed for determining the electrolysis potentials of SPS- and DPS-chronoamperometry. Figure 1 is a typical example of CV and DPV results of C_{60} obtained in 0.1 M TBAP/DM solution. By using the OTTLE cell, we measured the vis-NIR absorption spectral changes of wavelength from 0.6 μm to 1.1 μm during the electrolysis at the first potential step, $E_1^{(n)}$ (here $n = 1, 2, \dots$) and at the second potential step, E_2 (see Fig. 1). These results will clarify the products of the electrolysis and the stability of them.

We can determine $D_{C_{60}}$ by SPS-chronoamperometry when the potential step is $E_0-E_1^{(n)}$. We can also determine $D_{C_{60}^{n-}}$ (here $n = 1, 2, \dots$) by DPS-chronoamperometry: $E_0-E_1^{(n)}-E_2$. In both cases, C_{60}^{n-} should be exclusively produced by the electrolysis at $E_1^{(n)}$, and the produced C_{60}^{n-} should be oxidized to C_{60} at E_2 in one electrochemical reaction step. E_2 can be set at the potential $E_1^{(n')}$ (here $0 < n' < n$) where C_{60}^{n-} oxidized to $C_{60}^{n'-}$. Of course, the product of the first potential step, C_{60}^{n-} has to be unreactive in the solution during the period of the measurement. Electrolysis in the OTTLE cell was performed to clarify these problems.

$D_{C_{60}}$ is calculated by curve fitting of the experimental diffusion current-time (I_1-t) curves by SPS-chronoamperometry to the theoretical equation of Shoup and Szabo, Eq. (2):⁴¹

$$|I_1| = \pi F a m c D [1 + \pi^{-1/2} (a^2/Dt)^{1/2} + 0.2732 \exp\{-0.3911(a^2/Dt)^{1/2}\}], \quad (2)$$

where F is the Faraday constant, a is the radius of the disk electrode, c is the bulk concentration of the electroactive species, and m is the charge number of the electrode reaction. Because this equation contains two adjustable parameters, we can determine two quantities experimentally. One of them is D , and the other could be c , which is actually known. We assessed the reliability of the D value obtained by how well the curve fitted to the equation and how close the c value obtained (c_{obsd}) was to the known one determined by spectroscopy (c_{anal}). The details of the procedure of the measurement and the routine of calculation have already been reported.^{34,38} The accuracy of the D values obtained by this method has also been discussed elsewhere.³⁵

For determining $D_{C_{60}^{n-}}$ (here $n = 1, 2, \dots$), we measured current-time (I_1, I_2-t) curves by DPS-chronoamperometry of potential steps $E_0-E_1^{(n)}-E_2$ (see Fig. 1). No simple theoretical equation is available for the I_2-t curve. The current at the second potential step (I_2), which is the electrode reaction current of the species produced at the first potential step, can not be expressed by a simple equation, because the concentration of the produced species and its distribution around the electrode

Fig. 1 (a) Results of CV (potential scan speed: 50 mV s⁻¹) and (b) DPV (potential scan speed, 5 mV s⁻¹; pulse amplitude, 10 mV; pulse width, 100 ms; eight sampling points of every 10 ms during the pulse) of 0.173 mM C₆₀ in 0.1 M TBAP/DM solution, measured by a 1.002 mm radius Pt-disk electrode at 25°C.

are controlled by the duration time of the first potential (τ) and the D of the original species, not only by D of the produced species, t and a . However, we can determine the ratio of $D_{C_{60}^-}$ to $D_{C_{60}}$ by comparing the experimental $I_2(t)/I_1(t - \tau)$ vs. $\{t/(t - \tau)\}^{-1/2}$ curve to the theoretical curves for several different values of the D -ratio, which were derived by means of digital simulation. The details of the derivation of the theoretical curves³⁶ and the procedure of the experiment and the calculation have been described elsewhere.^{36,37}

Results and Discussion

OTTLE electrolysis

The spectra of C₆₀⁻, C₆₀²⁻ and C₆₀³⁻ observed over wavelengths of 0.6 to 1.1 μm in the OTTLE electrolysis cell were similar to those observed in various solvents and at different temperatures in references.^{19-24,26-29} The relative concentrations of C₆₀⁻, C₆₀²⁻ and C₆₀³⁻ in the OTTLE cell produced by electrolysis were determined by the prominent absorption peaks at 1.08 μm, 0.95 μm and 0.79 μm, respectively, on the bases of these spectra. When C₆₀ was electrolyzed at $E_1^{(1)}$, the spectrum of C₆₀⁻ increased its intensity by the electrolysis time, and no other significant spectrum appeared. When the potential was stepped to E_2 , the absorbance decreased reflecting the reoxidation of C₆₀⁻ to C₆₀. Also when the electric circuit was cut off after the electrolysis at $E_1^{(1)}$, the absorbance remained almost constant. The C₆₀⁻ produced by the electrolysis at the first potential step can be regarded as stable for the period of the DPS-chronoamperometric measurement, *i.e.* less than 10 s. We can conclude that $D_{C_{60}}$ and $D_{C_{60}^-}$ can be determined by SPS-chronoamperometry of the potential step E_0 - $E_1^{(1)}$ and DPS-chronoamperometry of E_0 - $E_1^{(1)}$ - E_2 , respectively.

On the other hand, the electrolysis products of the double potential step, E_0 - $E_1^{(2)}$ - E_2 , were complicated, as would be expected for two successive electrochemical reactions. The concentration changes of C₆₀⁻ and C₆₀²⁻ during the OTTLE electrolysis are shown in Fig. 2(a). At the first potential step $E_1^{(2)}$, C₆₀⁻ was produced as well as C₆₀²⁻, and at the second

Fig. 2 Concentration changes of C₆₀²⁻ and C₆₀⁻ in the thin layer of the OTTLE cell during (a) electrolysis at -1000 mV and successive electrolysis at 0 V, (b) electrolysis at -1000 mV and successive open circuit. Solution: 0.145 mM C₆₀ in 0.1 M TBAP/BZ.

potential step E_2 , C₆₀²⁻ was reduced to C₆₀⁻ as well as to C₆₀. When the electric circuit was cut off after the electrolysis at $E_1^{(2)}$, the spectrum of C₆₀²⁻ gradually shifted to that of C₆₀⁻, showing an isosbestic point at 0.99 μm. An example of this concentration change is shown in Fig. 2(b). We could see that one mole of C₆₀²⁻ was oxidized by some oxidizing agent and produced one mole of C₆₀⁻, though the oxidizing agent could not be identified. When C₆₀ was electrolyzed at the potential $E_1^{(3)}$, C₆₀⁻, C₆₀²⁻ and C₆₀³⁻ were produced simultaneously and the chemical reactions between them were complicated. Similar electrochemical reactions were also observed in (TBA)BF₄/BN and TBAP/DM solutions. We have to conclude that the determination of $D_{C_{60}^-}$ by DPS-chronoamperometry is impossible when n is larger than one. We also have to be aware of this complication when we determine the diffusion coefficient of C₆₀^{*n*-} ($n \geq 2$) by any other electrochemical methods.

One might expect that $D_{C_{60}^{2-}}$ can be determined by chronoamperometry, of which the potential sequence would be $E_1^{(1)}$ - $E_1^{(2)}$ - $E_1^{(1)'$, where the potentials correspond to those shown in Fig. 1, and $E_1^{(1)'}$ is the same potential with $E_1^{(1)}$. If the reduction current of C₆₀ can be decreased to zero and the concentration of C₆₀⁻ is made uniform in the diffusion layer by the electrolysis at $E_1^{(1)}$, the potential sequence would become virtually the same as that of the double potential step, and $D_{C_{60}^{2-}}$ could be determined simply. However, the situation can not be so, because the current at $E_1^{(1)}$ does not become zero, but approaches to $4FamcD$, as can be seen in Eq. (1), when the potential is kept at $E_1^{(1)}$ for a very long time. The concentration profiles of C₆₀ and its anions in the diffusion layer become much more complicated than was expected. The potential sequence, $E_1^{(1)}$ - $E_1^{(2)}$ - $E_1^{(1)'}$, has to be regarded as the triple potential step of E_0 - $E_1^{(1)}$ - $E_1^{(2)}$ - $E_1^{(1)'}$. The theoretical problems of the triple potential step chronoamperometry at a small disk electrode have not yet been solved. We can not calculate $D_{C_{60}^{2-}}$ from the observed chronoamperograms.

Table 2 D_{C60} and D_{C60}/D_{C60^-} in DM and BN solutions containing 0.1 M TBAP at 25°C

Solvent	$c_{\text{obsd}}/c_{\text{anal}}$	$D_{C60}/10^{-10} \text{ m}^2 \text{ s}^{-1}$	$\eta/\text{g s}^{-1} \text{ m}^{-2}$	$\gamma/10^{-10} \text{ m}$	D_{C60^-}/D_{C60}
DM	1.06(15)	14(3)	0.473(5)	3.4	1.0(3)
BN	1.00(9)	4.1(3)	1.388(5)	3.9	1.2(2)

The figures in the parentheses are the 95% confidence limits in the last significant digits.

Chronoamperometry

The SPS-chronoamperograms of C_{60} in 0.1 M TBAP/DM and in 0.1 M TBAP/BN solutions could be well fitted to the theoretical equation, Eq. (2). The values of D_{C60} obtained are shown in Table 2 along with the ratio, $c_{\text{obsd}}/c_{\text{anal}}$. The concentrations calculated from the chronoamperograms c_{obsd} agreed well with the spectroscopically determined values c_{anal} ; thus, the D_{C60} s obtained from the same chronoamperograms are regarded as reliable in the confidence limits of $c_{\text{obsd}}/c_{\text{anal}}$. The confidence limits of $c_{\text{obsd}}/c_{\text{anal}}$ shown in Table 2 are rather large because the c_{anal} s themselves have an analytical uncertainty of 3%. The poor solubility⁴² of C_{60} in these solvents also made the precisions of $c_{\text{obsd}}/c_{\text{anal}}$ and D_{C60} smaller. The concentration of C_{60} had to be kept much lower than the solubility, because aggregation of C_{60} seldom occurred in solutions of high concentrations. Such unusual aggregation could be detected by the opaqueness of the solution, by the absorption spectrum, by the shape of the CV, or by the chronoamperogram.

The value of D in this work in DM solution is close to that obtained by Jung and Kwak by their careful measurements,⁶ though the supporting electrolyte is different (see Table 1). The values by Dubois *et al.*¹ are small beyond the experimental errors in both solvents.

To compare with other data in solvents of different viscosities, we calculated the Stokes radii (r_s) of C_{60} using the Stokes-Einstein equation, Eq. (3), for the no-slip boundary condition:

$$D = k_B T / 6\pi\eta r_s. \quad (3)$$

The viscosity (η) values used for the calculation were those measured for the 0.1 M TBAP solutions at 25°C in this work. The symbols k_B and T mean the Boltzmann constant and the absolute temperature, respectively. The values given in Table 2 are similar to each other, even though the values of D_{C60} greatly differ. One can see that the diffusion coefficients are controlled mainly by the viscosity of the medium. The Van der Waals radii determined by single crystal X-ray diffraction analysis are from 0.501 to 0.505 nm.⁴³⁻⁵⁰ The radii of C_{60} in Langmuir-Blodgett film were estimated to be in the range from 0.52 to 0.56 nm,^{51,52} and those calculated from partial molar volumes in 12 aprotic solvents are from 0.518 to 0.558 nm.⁵³ The values of hydrodynamic radius r_s obtained in this work are smaller than all these geometrical sizes.

The Stokes-Einstein equation, Eq. (3), has often been used for analyzing the transport phenomena in solutions, while many research workers have discussed this equation both theoretically^{54,55} and experimentally.^{56,57} Generally, when the size of the solute molecule of symmetrical shape is not large enough compared with the solvent one, the D value becomes smaller than the geometrical size.^{56,57} Most r_s values of C_{60} in various solvents with and without indifferent electrolytes are comparable with or smaller than the Van der Waals radius,³⁻¹⁷ though a few exceptions have been reported.^{1-3,5,16} The molecule C_{60} has a perfect spherical shape, but its size is not large enough

Fig. 3 (a) DPS-chronoamperogram (·····) and its residual current (·····) by a Pt-disk electrode of 0.101 mm radius, $\tau = 3.64$ s at 25°C. (b) Fitting of the observed $I_2(t)/I_1(t - \tau)$ vs. $\{t/(t - \tau)\}^{-1/2}$ curve (+) to the theoretical curves (—). Solution: 0.106 mM C_{60} in 0.1 M TBAP/BZ solution.

to fulfill the basic condition of the Stokes-Einstein equation, that is, “hard-sphere in continuum incompressible fluid, and no-slip boundary condition”.

Examples of the DPS-chronoamperogram and the $I_2(t)/I_1(t - \tau)$ vs. $\{t/(t - \tau)\}^{-1/2}$ curve calculated from the chronoamperogram superimposed on the theoretical curves are shown in Figs. 3(a) and (b), respectively. The observed curve ran along one of the theoretical curves. The experimental values of D_2/D_1 were determined by interpolating the theoretical curves at several points of $\{t/(t - \tau)\}^{-1/2}$, where D_1 and D_2 are the diffusion coefficients of the species electrolyzed at the first and the second potential steps, respectively. The observed curve did not run along the theoretical curves but crossed them if the τ value was set on the bases of an incorrect value of D_{C60} , or if some experimental accident occurs. The curve shown in Fig. 3 is an example of a chronoamperogram that proceeded successfully. The ratios of obtained D_{C60^-} to D_{C60} are listed in Table 2. Unexpectedly, the value of D_{C60^-} is almost the same as or larger than D_{C60} in both solutions. The delocalized negative charge over the surface of the large molecule, such as C_{60} , seems to have no significant effect on the interaction with the solvent molecule or the indifferent electrolyte ions.

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