Electrochemical hydrogen evolution by catalyst membrane composed of platinum, alkyl viologen and Nafion: consideration of the kinetically dominant factor based on understanding of electron-mediating ability of the viologen molecule

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Abstract

Electrocatalytic H_2 formation was carried out by using a Nafion membrane (Nf) embedding a Pt catalyst as well as an alkyl viologen (denoted as RV^{2+}; alkyl group (R): methyl, ethyl, propyl, heptyl, or dodecyl group). The H^+ reduction catalyzed by the Pt via the electrogenerated $RV^{\bullet+}$ was investigated. In order to understand the electron-mediating characteristic of the RV^{2+} on kinetic aspect, turnover numbers (TON) of the RV^{2+} for H_2 formation as well as electron transport kinetics (represented by the apparent diffusion coefficient of electron, D_{app}) of the mediator were studied with respect to RV^{2+} concentration. In any RV^{2+} system, both the TON and the D_{app} exhibited a similar dependence on the concentration, showing that the overall kinetics is dominated by the electroreduction process of the mediator. When applying both the tetrachloroplatinate(II) (Pt^0 in catalytically active state) and the viologen mediator to the H_2 formation system, the TON was found to be controlled by the D_{app}.
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1. Introduction

Water photolysis, an artificial solar energy conversion and storage system, has been attracting a great attention as one of the most promising candidates for creating renewable energy resource in the near future [1–4]. However, such an artificial photosynthetic system has not been achieved yet. As one of the approaches to realize an artificial photosynthetic system, photochemical H^+ reduction has been most extensively studied, where the system was often composed of a photosensitizer (P) (e.g. $Ru(bpy)_3{}^{2+}$; bpy: 2,2′-bipyridine), an electron relay (R) (e.g. methyl viologen (MV^{2+})), a catalyst (e.g. a colloidal Pt), and a sacrificial electron donor (e.g. alcohol, and amine, etc.) [5–8]. As for a typical example, photochemically generated $MV^{\bullet+}$ reacts with H^+ to give H_2 catalyzed by Pt. However, the H_2 formation takes place only in the presence of a sacrificial donor. Water photolysis is a series of redox reaction involving multi-electron transfer processes at oxidation/reduction sites, so that it is essential to develop active and efficient catalysts capable of H_2 and O_2 formations by means of catalysis. In our recent examples for the H^+ reduction site, highly active molecule-based catalysts

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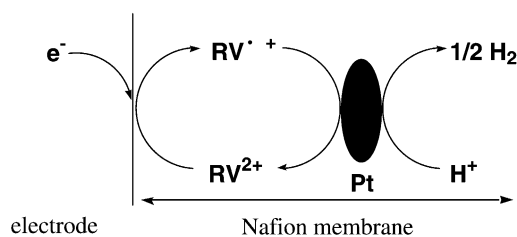
Scheme 1.

composed of a metal complex and a polymer membrane have been found by an electrocatalytic method [9–11]. Considering that the photosynthetic system should involve an efficient charge separation system to form P^+ and R^- in a photochemical primary process, and that H^+ is then reduced on a catalyst by reductive power of the R^- (at that time, water oxidation should simultaneously be induced by P^+), fabrication of a catalyst site coupled with an electron relay is an essential and promising approach. In this point of view, it is of importance to understand the intrinsic characteristics of the electron mediator for forming H_2.

In the present work, electrocatalytic H_2 evolution was carried out by using a Nafion membrane (Nf) embedding both a Pt catalyst and an alkyl viologen (denoted as RV^{2+}; alkyl group: methyl, ethyl, propyl, heptyl, or dodecyl group), according to Scheme 1. The H^+ reduction catalyzed by the Pt via the electrogenerated $RV^{\bullet+}$ was investigated in terms of kinetics. Viologen molecule is the most typical electron acceptor capable of electron mediation, as used in a photoinduced electron transfer system up to now [12–14]. By using several kinds of mediator, the electrocatalytic H_2 formation as well as electron transport by the $RV^{\bullet+}$ were investigated especially with respect to the mediator concentration. Based on these results, the dominant factor that affects the overall kinetics in the present catalytic system will be discussed.

2. Experimental

1,1′-Dimethyl-4,4′-bipyridinium dichloride (MV^{2+}) was purchased from ACROS ORGANICS. 1,1′-Diethyl-4,4′-bipyridinium dibromide (ethyl viologen,

EV^{2+}), 1,1′-diheptyl-4,4′-bipyridinium dibromide (heptyl viologen, HV^{2+}) and Nafion alcoholic solution were from Aldrich. Potassium tetrachloroplatinate(II) was from KANTO CHEMICAL CO. INC., and glassy carbon (GC) (RA5-100) from Tokai Carbon Co. Ltd. Other alkyl viologens (propyl viologen (PV^{2+}) and dodecyl viologen (DV^{2+})) were synthesized according to the previous procedure [15]: a mixture of 4,4′-bipyridine and 1-bromoalkane in *N,N*-dimethyl formamide (DMF) was heated under reflux for 8 h, and then the product was purified by recrystallization from methanol. The purest grade reagents were used without further purification.

Electrode modification was carried out as follows. Firstly, equal volume of 5 wt.% Nf, 1.3×10^{-4} mol dm^{-3} K_2PtCl_4/DMF, and a known concentration of alkyl viologen (RV^{2+})/methanol ([RV^{2+}] = 1.5×10^{-4} to 1.0×10^{-3} mol dm^{-3}) was mixed (the density of this mixture solution is 0.87 g cm^{-3}). A 9.8 μl of this solution was cast onto a GC electrode (effective area, ∼0.2 cm^2), followed by solvent evaporation under air. The membrane thickness was estimated as ca. 3.6 μm by considering the density of the Nf membrane (2 g cm^{-3}) [16]. The modified GC was dipped into deionized water for 30 min prior to electrochemical study. As a reference, the modified electrode was prepared by another procedure. Six microliter of 5 wt.% Nf alcoholic solution (the density of this solution, 0.87 g cm^{-3}) was cast onto a GC electrode (effective area, ∼0.2 cm^2), followed by solvent evaporation under air (the thickness was estimated as ca. 6.6 μm). The Nf-coated GC was dipped into deionized water for 30 min to improve cation exchange ability of the membrane, and subsequently, the introduction of RV^{2+} into the Nf was carried out by dipping the GC electrode into an aqueous solution containing a known concentration of the RV^{2+}. The adsorbed amount was estimated by the UV absorption spectral change before and after the adsorption.

An electrochemical cell was equipped with the modified working electrode, a spiral Pt counter and a silver/silver chloride (Ag|*b*AgCl|*b*KCl (sat)) reference electrode. Electrochemical study was carried out by using a potentiostat (HOKUTO DENKO, HA-301) equipped with a function generator (HOKUTO DENKO, HB-104), a coulomb meter (HOKUTO

DENKO, HF-201) and a recorder (GRAPHTEC, WX-4000). All of the electrochemical study was run in a pH ~3.1 aqueous phosphate buffer solution. Typical potentiostatic electrolysis for H^+ reduction was run for 1 h under argon atmosphere. The H_2 produced during electrolysis was analyzed by a gas chromatograph (Shimadzu, GC-8A) with a molecular sieve 5 Å column and Ar carrier gas. Faradaic efficiency (%) for the H_2 formation in the electrolysis always exceeded 80%.

3. Results and discussion

Redox characteristics of RV^{2+} confined in a Nf membrane coated on a GC electrode (denoted as GC/Nf[RV^{2+}]) were studied, and the results are shown in Fig. 1 (denoted as a). A couple of peaks for $MV^{2+/\bullet+}$ appeared at -0.67 V (versus Ag|bAgCl|bKCl (sat)), while it was found that the redox potential for other $RV^{2+/\bullet+}$ couples is present
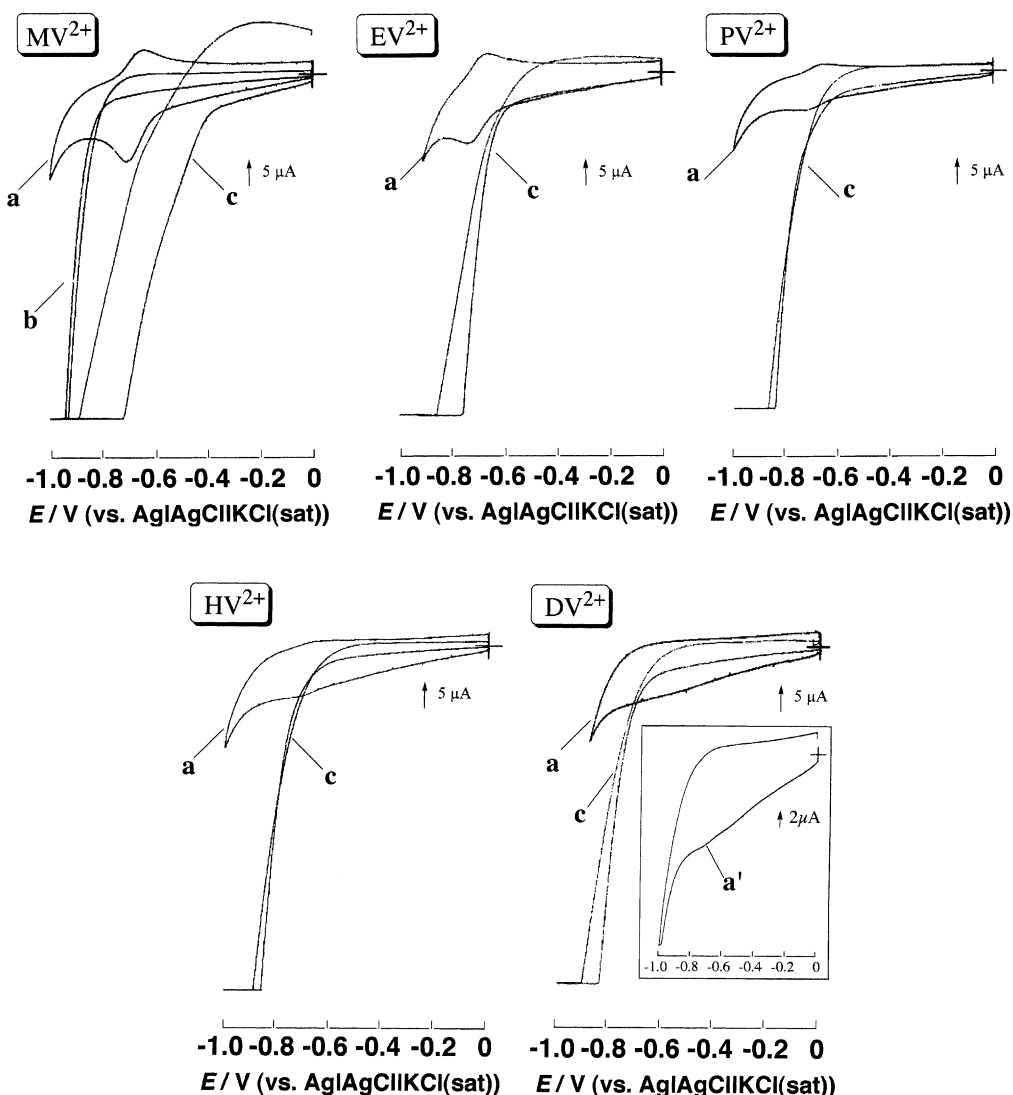

Fig. 1. Typical cyclic voltammograms at GC/Nf[RV^{2+}] (a), GC/Nf[Pt] (b) and GC/[RV^{2+} + Pt] (c) in a pH 3.1 aqueous electrolyte solution. As for GC/Nf[HV^{2+}] (a′), the magnified voltammogram is shown in inset. Scan rate: 20 mV s^{-1}; RV^{2+} amounts, 1.9×10^{-9} mol (RV^{2+} concentration: ~2.5×10^{-2} mol dm^{-3}); Pt amounts: 4.2×10^{-10} mol.

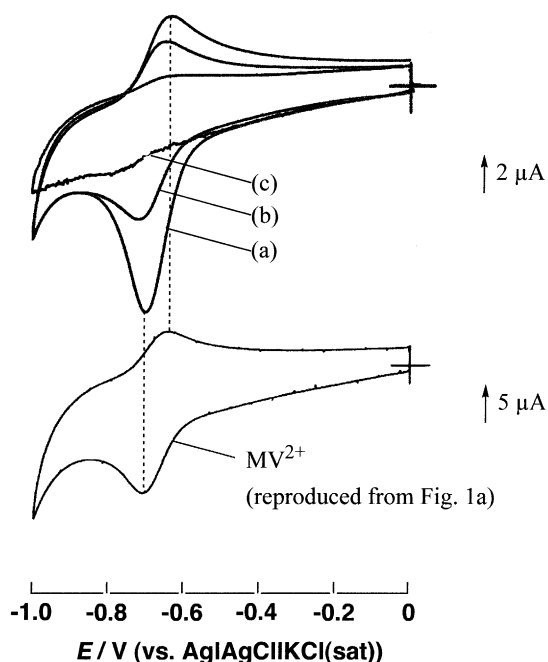Fig. 2. Typical CVs at GC/Nf[MV^{2+}(ad)] (a), GC/Nf[EV^{2+}(ad)] (b) and GC/[HV^{2+}(ad)] (c) in a pH 3.1 aqueous electrolyte solution. The CV at GC/Nf[MV^{2+}] was reproduced from Fig. 1. Scan rate: $20\,mV\,s^{-1}$; RV^{2+} amounts: $\sim3.3 \times 10^{-9}\,mol$ (RV^{2+} concentration: $\sim2.4 \times 10^{-2}\,mol\,dm^{-3}$).

at ca. $-0.70\,V$. Firstly, the general characteristics of the RV^{2+} on the voltammogram are interpreted in the following part. As for the MV^{2+} system, the details will be discussed in combination with Fig. 2.

Fig. 1a showed that the electrochemical response for the RV^{2+} decreases with lengthening of the alkyl chain although the present Nf[RV^{2+}] was uniformly prepared from a non-aqueous solution containing a constant amount of both RV^{2+} and Nf. It is most probable that such a redox characteristic for the $RV^{2+/\bullet+}$ couple is influenced by the property of the Nf membrane employed as the matrix. It is well known that Nf has three distinct physico-chemical regions [17,18], i.e. a hydrophilic column around sulfonic groups on the polymer side chain, a hydrophobic column composed of the fluorocarbon polymer chain, and an interfacial region between hydrophilic and hydrophobic columns. Therefore, it is inferred that in the mixture solution the alkyl substituent in the RV^{2+} interacts with the polymer backbone and/or an alkyl side chain

of the Nf, and consequently, the RV^{2+} is surrounded by the hydrophobic region and/or the interfacial one in the membrane. Buttry and Anson [19] have previously exhibited that a macrocyclic complex confined in the hydrophobic column of the Nf cannot take part in electrochemical redox reaction. The data from Fig. 1a suggests that the longer is the chain length, the more is the amount of the RV^{2+} in the hydrophobic column where the viologen is electrochemically inactive. These results could also lead to an interpretation that the electrochemical response most probably originates from the RV^{2+} (except MV^{2+}) located in the interfacial region. It has been previously reported that in an acetonitrile solution the redox potential of the RV^{2+} was almost independent of the alkyl substituents when the substituent was varied from methyl group to heptyl one [20], which could support the present redox reactions of RV^{2+} (except MV^{2+}) taking place in a hydrophobic phase (i.e. interfacial region).

In order to obtain further knowledge of the voltammetric characteristics in the Nf[RV^{2+}] system, cyclic voltammetric (CV) measurement was carried out using Nf[RV^{2+}] prepared by an adsorption method for which Nf-coated electrode is dipped into an aqueous RV^{2+} solution (denoted as Nf[RV^{2+}(ad)]). In that system, RV^{2+} can be expected to occupy a hydrophilic column of the Nf due to an electrostatic interaction between a sulfonic group (anion) and divalent cation. CVs measured for MV^{2+}, EV^{2+}, and HV^{2+} by employing a constant concentration are shown in Fig. 2. Especially for the Nf[MV^{2+}(ad)], the CV was compared with that of the Nf[MV^{2+}] reproduced from Fig. 1a. Irrespective of the preparation procedures, a constant redox potential for the $MV^{2+/\bullet+}$ couple was found to appear at $-0.67\,V$. Even when preparing the MV^{2+}-incorporating membrane from a mixture solution of each component, it might suggest that the electroactive MV^{2+} can be present in the hydrophilic column of the Nf. In addition, similar to the Nf[RV^{2+}] system, a series of the voltammograms exhibited that the electroactive amount of the RV^{2+} decreases with increase in the length of the alkyl chain, and then the redox potential of the RV^{2+} was observed to shift to negative regions. The potential was almost independent of the preparation procedures especially in RV^{2+} of a long alkyl substituent (EV^{2+} (Fig. 2), $-0.68\,V$; HV^{2+} (Fig. 2), ca. $-0.70\,V$; EV^{2+}–DV^{2+} (in Fig. 1a), ca. $-0.70\,V$).

Those voltammetric characteristics probably show that, also in the Nf[RV^{2+}(ad)] system, RV^{2+} is preferably present in the hydrophobic/interfacial region of the Nf rather than in the hydrophilic one as alkyl chain becomes longer. Although it is most probable that the electrochemical response for the Nf[EV^{2+}(ad)] is from the viologen molecule present not only in the interfacial region but also in the hydrophilic one when comparing the voltammetric characteristics of the Nf[EV^{2+}(ad)] with the Nf[EV^{2+}], the present voltammetric results could suggest that the surroundings of the RV^{2+} capable of electrochemical response in the polymer matrix do not almost change with the preparation procedures of the membrane.

A modified GC electrode coated with a Nf membrane incorporating $PtCl_4{}^{2-}$ (catalyst) as well as RV^{2+} was prepared (denoted as GC/Nf[RV^{2+} + Pt]), and the voltammetric characteristics were studied (Fig. 1c). A blank modified electrode, on which only the $PtCl_4{}^{2-}$ is confined in the membrane, was also prepared (denoted as GC/Nf[Pt] (Fig. 1b)) to compare with GC/Nf[RV^{2+} + Pt]. In the GC/Nf[Pt] system (Fig. 1b), the growth of cathodic current due to the H_2 evolution started to take place below -0.8 V (versus Ag/AgCl) (the electrolysis date will be shown later). Although $PtCl_4{}^{2-}$ was used as a starting catalyst material for the H_2 evolution, the Pt complex would exhibit the catalysis after in situ formation of a metallic species (Pt^0) (ca. $\sim$0.76 V versus NHE for $PtCl_4{}^{2-}$/Pt couple [21]) since the Pt(II) complex itself has no reductive power for H_2 formation. Also in a photochemical H_2 formation system (as stated in Section 1), it has been indicated that a catalytic H_2 formation starts to take place after forming colloidal Pt when the polychloroplatinate was applied to the system [22]. In the GC/Nf[RV^{2+} + Pt] system, the voltammetric study was carried out in varying the RV^{2+} species. In every case (Fig. 1c), it appeared that the catalytic current is grown on reducing the RV^{2+}, showing that the electrocatalytic H_2 evolution is enhanced by electron mediation of RV^{2+} between electrode and Pt catalyst. Furthermore, it was found that the potential at which the catalytic current is grown is the most positive in the GC/Nf[MV^{2+} + Pt] system, indicating that the electron-mediating ability of the RV^{2+} changes with the alkyl chain length.

Potentiostatic electrolysis at the GC/Nf[RV^{2+} + Pt] was carried out. Table 1 shows the typical results.

Table 1
Turnover numbers (TON) of RV^{2+} for H_2 formation[a]

RV^{2+}	TON (h^{-1})[b]	Alkyl chain
MV^{2+}	110	Short
EV^{2+}	86	↑
PV^{2+}	78	
HV^{2+}	63	
DV^{2+}	51	Long

[a] Potentiostatic electrolysis in GC/Nf[RV^{2+} + Pt] system was run at applying potential of -0.90 V for 1 h. [RV^{2+}] = 8.3 × 10^{-3} mol dm^{-3}; [Pt] = 8.3 × 10^{-3} mol dm^{-3}.
[b] The TON was calculated by subtracting the amounts of H_2 evolved in the absence of RV^{2+} (GC/Nf[Pt]).

The turnover numbers (TON) of the RV^{2+} for H_2 formation was calculated by subtracting the amounts of H_2 evolved in the absence of RV^{2+} (i.e. GC/Nf[Pt]). The TON therefore represents the degree of the RV^{2+} molecule participating in the H_2 formation on the Pt catalyst. It was evidently confirmed that the electrocatalytic H_2 formation is enhanced by the presence of the RV^{2+}. However, the TON was found to decrease with lengthening the chain of the alkyl substituent, following the above voltammetric characteristics (Fig. 1c).

The potentiostatic electrolysis was carried out by changing the concentration of the RV^{2+} in the Nf membrane (Pt amount is constant ($\sim$6.3×10^{-10} mol)). Three kinds of the RV^{2+}, i.e. MV^{2+}, PV^{2+}, and HV^{2+}, were used. Fig. 3a shows the relationship between the TON for H_2 formation and the RV^{2+} concentration. The order of the TON of the RV^{2+} followed the results of Table 1 over the whole RV^{2+} concentrations. In addition, in every case the TON decreased with the increase of the concentration, which showed that the electron-mediating ability of a RV^{2+} for the H_2 formation is apparently lowered by increasing the concentration. In Fig. 3b, dependence of the amount of H_2 (ΔV) on the RV^{2+} concentration is shown (Pt amount: $\sim$6.3 × 10^{-10} mol). The ΔV represents the net amount of H_2 catalyzed by Pt via electron mediation of the RV^{2+}, and the value is used also in calculating the TON (vide supra). In every system, it was
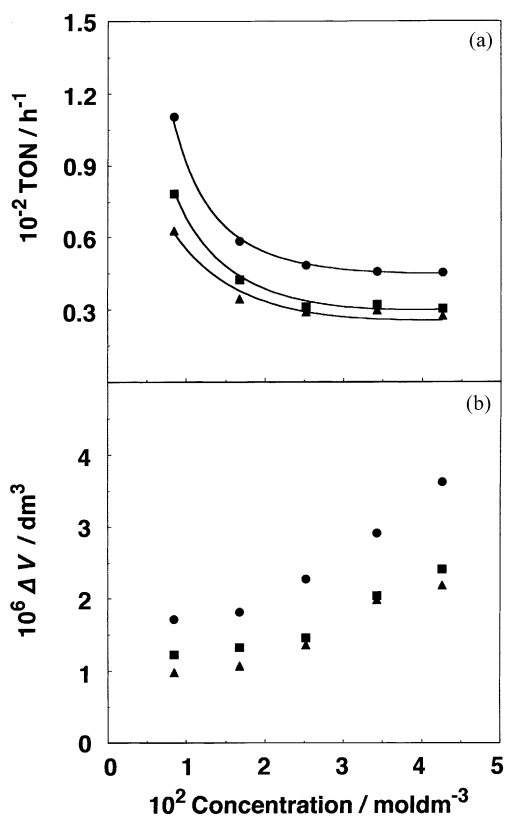
Fig. 3. (a) Relationship between TON of RV^{2+} for H_2 formation and RV^{2+} concentration. The potentiostatic electrolysis for H_2 formation was carried out at -0.90 V, and turnover number (TON) of a RV^{2+} for the H_2 formation was calculated by subtracting the amount of H_2 produced at a GC/Nf[Pt] (blank). (●) GC/[MV^{2+} + Pt]; (■) GC/[PV^{2+} + Pt]; (▲) GC/[HV^{2+} + Pt]. (b) Dependence of the amount of H_2 produced (ΔV) on the RV^{2+} concentration. The ΔV represents the net amount of H_2 catalyzed by Pt via the electron mediation of the RV^{2+}, and the value is calculated by subtracting the amounts of H_2 evolved in the absence of RV^{2+} (i.e. GC/Nf[Pt]). (●) GC/[MV^{2+} + Pt]; (■) GC/[PV^{2+} + Pt]; (▲) GC/[HV^{2+} + Pt].

found that the H_2 production is gradually enhanced with the RV^{2+} concentration, and that the electroactive amount of the RV^{2+} actually increases not only with increasing the total concentration but also with shortening the alkyl chain. This can also mean that the effective concentration of the RV^{2+} increases with the concentration since a constant volume of the Nf is always employed. When considering both the Fig. 3a and b, the inverse dependence of the TON on the total concentration most probably means that the ratio of

the electroactive amount to the total one decreases not only with increasing the total concentration but also with lengthening the alkyl chain.

As for the H_2 formation in the Nf[RV^{2+} + Pt] system, there is a possibility that the overall kinetics is affected by electron propagation via the RV^{2+} through the matrix. Therefore, heterogeneous electrocatalysis was discussed in combination with the electron transfer process of the RV^{2+}. Potential-step chronoamperometry was carried out to analyze the electron transfer process at GC/Nf[RV^{2+}] according to Cottrell's equation (Eq. (1)) [23,24] based on a semi-infinite diffusion process,

$$j = \frac{nFc(D_{app})^{1/2}}{(\pi t)^{1/2}} \tag{1}$$

where D_{app} ($cm^2 s^{-1}$) is the apparent diffusion coefficient of the electron, j (A cm^{-2}) the current density, n the number of electrons concerned in the process (the present case, 1), F the Faraday's constant (9.65×10^4 coulombs mol^{-1}), and c (mol cm^{-3}) the total concentration of the RV^{2+} in the Nf membrane. The electron propagation was studied by potential step from 0 to -0.8 V. The relationship between j and $t^{-1/2}$ was linear and applicable to Cottrell's equation. From the slope, D_{app} was estimated as shown in Fig. 4.

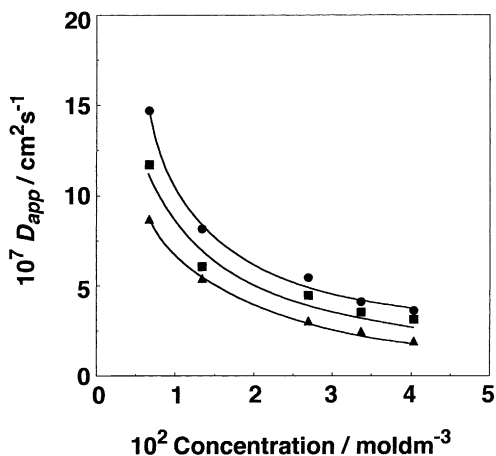Fig. 4. Dependence of D_{app} on RV^{2+} concentration in a pH 3.1 aqueous electrolyte solution. The chronoamperometry to obtain the j–$t^{-1/2}$ plot was carried out by stepping the potential from 0 to -0.8 V. (●) GC/[MV^{2+} + Pt]; (■) GC/[PV^{2+} + Pt]; (▲) GC/[HV^{2+} + Pt].

The D_{app} of the electron propagation decreased not only with increasing the RV^{2+} concentration but also with lengthening of the alkyl substituent. At first, the mechanism for the electron transport by the RV^{2+} will be discussed. The D_{app} value is usually represented by the sum of an intrinsic diffusion coefficient (D_p) in the absence of any electron self-exchange reaction and a contribution of electron self-exchange (D_{et}; this includes a term of concentration as a function) [25–27]. If the electron transport by the RV^{2+} takes place by a hopping mechanism, the D_{app} value should increase with the concentration. However, this is not the case. Therefore, these results show that the present electron transport occurs by physical diffusion of the redox center. We have previously studied electron transport process for the $Nf[MV^{2+}(ad)]$ system by means of the potential-step chronoamperospectrometry [28], in which the electron transport mechanism was in agreement with the present $Nf[MV^{2+}]$ system. However, the apparent electron transport kinetics (corresponding to the present D_{app}) for the $Nf[MV^{2+}(ad)]$ system was independent of the total concentration, indicating that all the MV^{2+} adsorbed most probably in the hydrophilic column is capable of electron transport. Difference between the $Nf[MV^{2+}(ad)]$ and the $Nf[MV^{2+}]$ systems on the kinetic aspect must be ascribed to the preparation procedures of the membrane. Although, also in the latter system, the MV^{2+} responsible for the electron transport is expected to be present in a hydrophilic region of the Nf (Figs. 1 and 2), the amount of electrochemically inactive species could markedly increase (due to the hydrophobic interaction between the methyl group and the polymer backbone) as the total concentration is higher, which would consequently lead to the downward dependence of the D_{app} on the total concentration. Since the dependence of the D_{app} on the total concentration is consistent with the TON, this is most reasonable explanation. Furthermore, this interpretation is also applicable to other RV^{2+} ($Nf[RV^{2+}]$) systems although such a contribution of the hydrophobic interaction must be considered to increase with lengthening the alkyl chain.

In conclusion, both the TON (Fig. 3) and the D_{app} (Fig. 4) exhibited a similar dependence not only on the alkyl chain length but also on the RV^{2+} concentration. Therefore, when applying both Pt catalyst and viologen mediator to the H_2 formation system,

it was found that the overall kinetics is dominated by the electroreduction of the RV^{2+}, i.e. the TON is controlled by the D_{app}.

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