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Diffusion-controlled currents in viscous solutions of polyethylene glycols

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Abstract

Voltammetry of ferrocenyl derivative, known as a reversible redox species, was made in viscous solutions of polyethylene glycols in order to find effects of the viscosity on voltammograms, especially deviation from the ordinary diffusion-controlled behavior. Voltammetric peak currents at high scan rates and in high viscous solutions were deviated lower from the proportionality to the square-root of the scan rates. The deviation could not be explained in terms of participation of sluggish electron transfer reactions or solution resistance, because the peak potential difference corrected by the solution resistance were close to 60 mV. The deviation was similar to the memory effect of diffusion. Diffusion coefficients and the solution resistance were evaluated from the proportionality of the peak current and peak potential shits, respectively. These values obeyed Stokes-Einstein equation for the viscosity less than 0.3 Pa s. Dilatancy was observed at viscosity more than 0.3 Pa s.

key words: voltammetry in viscous solutions; polyethylene glycols; Stokes-Einstein equation; memory diffusion; fast potential scan

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1. Introduction

Mass transport in electrochemical processes depends strongly on viscosity of solution [1,2] not only in hydrodynamic voltammetry but also in cyclic voltammetry through diffusion coefficients [3]. Effects of voltammetric responses on high viscosity are classical subjects on mass transport [4-6]. Viscous media frequently employed are sucrose [7-9], polyethylene glycols [10-12], guar gum solutions [13], ethylene carbonate [14], carboxy- methylcellulose [15,16], supermolecules with polyethylene chains coordinated with redox couples [17,18], polyacryl acids incorporated by alkali-metal counterions [19], and conventional organic solvents [20]. Recently, viscous effects on voltammetry have been reported on ionic liquids as new high viscous solvents and ions [21-25] as well as on supercritical liquids [26-32] in context of very small viscosity. Viscous effects are still an important subject for solidification of electrochemical liquid materials as practical use.

Measurements of electrochemical responses in viscous solutions are complicated by poor conductance of solution due to limited solubility of ions or formation of ion pairs. The poor conductance deforms voltammetric waves so largely that potential difference between an anodic and a cathodic peak looks due to sluggish electrode kinetics [10,33]. The decrease in ionic solubility enhances also adsorption of redox species, e.g., ferricenium ion as an oxidation product [34]. Voltammograms of viscous solutions sometimes show poor reproducibility because of sensitive variations of viscosity with temperature. Despite these complications and experimental artifacts, some fundamental features proper to viscous solutions have been reported; slip effects at high viscosity which deviates the proportionality of shear stress to velocity [35], deviation from Levich's equation at Reynolds number less than 30 [13], inhomogeneity of redox sites in polymer leading to delay of diffusion currents [36], dependence of diffusion coefficients on concentrations of redox species [37], and estimation of solvent-solute interaction [38].

A diffusion-controlled current of voltammetric peak is generally proportional to the square-root of the diffusion coefficient and thus is inversely proportional to the square-root of the viscosity. We have a question about whether an increase in viscosity depresses the current in accord with this rule until solutions get close to a solid. This question is inspired by the difference in diffusion mechanisms in solution and in solid; the former being due to continuous flow of entropy, the latter being due to an activation process stepping between sites. The answer requires overcoming the difficulties of (a) accurate subtraction of voltage by solution resistance from peak potentials, (b) sufficient control of temperature against fluctuation during voltammetry, (c) preparation of homogeneous solutions, and (d) confirmation of a delay of a potentiostat against high impedance. A long time voltammetric response in high viscous solution resembles a short time response in low viscous solution. Therefore, variations of both viscosity and scan rates are expected to provide voltammetric data in an actually wide domain of viscosity. This paper deals with voltammetric measurements of a ferrocenyl derivative in polyethylene glycols (PEG) with various viscosities at high scan rates. The aim is to find if voltammetric behavior obeys the simple diffusion-controlled equation in viscous solution at fast scan rates.

2. Experiments

Polyethylene glycols (Wako) with molecular weight, 200, 400, 1000 and 4000 were used for solvents as received. (Ferrocenylmethyl)trimethylammonium bromide (FcTMA) was synthesized according to the bibliography [39], and was purified by re-crystallization. Sodium tetrafluoroborate (Wako), of analytical grade, was used as received. Aqueous solutions were prepared with deionized and twice-distilled water.

Solutions were prepared by heating PEGs at 70°C to liquid, mixing a PEG of low viscosity with a highly viscous PEG, dissolving FcTMA and salt in the mixture, and cooling the mixture to room temperature.

Cyclic voltammetry was carried out with a potentiostat, Compactstat (Ivium Tech., Netherlands), in the viscous mixture. A Pt disk 1.6 mm in diameter (BAS, Tokyo) was used as a voltammetric working electrode. The surface of the working electrode was polished with alumina paste on wet cotton, and was rinsed with distilled water in an ultrasonic bath. The electrode was dried before mounting it in the cell. A platinum wire and an Ag|Ag_xO electrode were used as the counter-electrode and the reference electrode, respectively. The Ag|Ag_xO reference electrode was made by immersing a polished silver wire into concentrated nitric acid until its surface turned to grey (normally in 10 min). Voltammetric runs were made from the lowest scan rate successively to the highest one, and returned back to the lowest one. We confirmed that the first voltammogram was almost identical with the last one in the successive run. The reproducibility was confirmed by carrying out the opposite scan sequence.

Viscosity was determined with a rotational viscometer, Visco (Viscoteck, Tokyo), at room temperature after each voltammetric measurement. We tried to control temperature of the viscous mixture in order to get a variety of viscosities. However, an increase in temperature provided poor reproducibility of the viscosity values, probably because of difficulty of uniform temperature control, especially a loss of temperature control of the rotator. Digital optical photomicrographs were obtained with a video microscope, VMS-1900 (Scalar).

3. Results and Discussion

More viscous solvents generally have less ionic solubility. We tried to dissolve some inorganic and organic salts in PEG, and found that ca. 40 mM sodium tetrafluoroborate in PEG could be prepared over a wide domain of the viscosity. The salt and FcTMA were dissolved in mixed PEGs on a heater so that the mixture was clear and uniform. Homogeneity of the mixture was confirmed by the view a microscope at which no solid or no mirage was detected in the mixture. Water was not dissolved in the solution at all.

Voltammograms of 1 mM FcTMA in 40 mM $NaBF_4$ aqueous solution (0.89 mPa s) shows the oxidation and the reduction peaks at 0.57 and 0.50 V, respectively. These peak potentials were independent of the scan rates less than 9 V s^{-1}. The background-corrected currents of both peaks were proportional to the square-roots of the scan rates less than 9 V s^{-1}. Scan rates higher than 20 V s^{-1} deviated the current lower from the proportionality. The deviation is due to a delay of the potentiostat, which was confirmed through an equivalent electric circuit composed of electric resistors corresponding to solution resistances.

Figure 1 shows voltammograms of FcTMA in the viscous solution with 95 mPa s at various scan rates. The anodic and the cathodic peaks at low scan rates (Fig. 1(A)) appeared at potentials similar to those in the aqueous solution. With an increase in the scan rates, the waves became broad (Fig. 1(B)) and both peaks were separated. Even if peaks were vague at high scan rates, peak potentials were determined unequivocally with the conventional background correction by use of a flat portion of the voltammogram before the peak. The shift of peak potentials may be ascribed to solution resistance. In order to confirm this prediction, we plotted the peak current without background-correction, I_p, against the peak potential, E_p, in Fig. 2. The plots of the anodic and the cathodic peak currents fell on each line, the slopes of which were common. The linear variations indicate that the potential shift should not be due to electrode kinetics but should be ascribed to ohmic drop by solution resistance. The peak potential corrected by the ohmic drop is expressed by

$$(E_p)_{\mathrm{crrct}} = E_p - I_p\, r \qquad (1)$$

where r is the solution resistance. Values of r for the anodic peak should be the same as those of the cathodic one, as is consistent with the common value of the slopes in Fig. 2. Solution resistance sometimes deforms voltammetric shape when redox ions caused by a Faradaic process vary solution resistance during electrolysis. The deformation has been observed in microelectrode voltammetry without deliberately added supporting electrolyte. The present voltammograms were obtained in the presence of 40 mM electrolyte, and hence they are not predicted to be deformed.

We tried to use a positive feedback IR compensation technique. The difference between the anodic and the cathodic peak potentials was sometimes much less than 60 mV at a large compensation resistance. In other words, peak potentials corrected by the positive feedback could not be determined unequivocally.

We measured voltammograms of FcTMA in PEG solutions for various values of the viscosity, and obtained the linear plots similar to in Fig. 2. Since $(E_\mathrm{p})_\mathrm{crrct}$ is the diffusion-controlled peak potential, the difference between the anodic and the cathodic potential

$$(\Delta E_\mathrm{p})_\mathrm{crrct} = (E_\mathrm{p,a})_\mathrm{crrct} - (E_\mathrm{p,c})_\mathrm{crrct} \qquad (2)$$

should be equal to $2.3F/RT$. Figure 3 shows variations of $(\Delta E_\mathrm{p})_\mathrm{crrct}$ with the viscosity, η, on the logarithmic scale. These values were close to $2.3RT/F$ (59 mV), irrespective of the viscosity. Consequently, the peaks can be regarded as diffusion-controlled currents although voltammograms were deformed by the solution resistance. Zhou and Dong attributed the potential shifts in PEG to sluggish electrode kinetics [10].

Conductivity is proportional to the ionic charge, $z_i e$, and inversely proportional to viscosity because flux of the charge carrier, $z_i e$, with ionic sphere a in radius is suppressed by viscous friction of the medium [40]. It is expressed by

$$\sigma = F\sum_i |z_i| e / 6\pi\eta\, a_i \qquad (3)$$

Since the configuration of the electrodes and the cell were common to all the voltammetric experiments, the cell resistance should be inversely proportional to σ. Figure 4 shows logarithmic plot of r against η. According to Eq. (3), the resistance is proportional to η, or unity slope of the plot of $\log(r)$ against $\log(\eta)$. This holds for $\eta <$ 0.3 Pa s ($\log(\eta) < -0.5$) in Fig.4. However, the resistance did not increase for $\log(\eta) >$ -0.5. This fact corresponds to an over-enhancement of the viscous resistance against higher diffusing velocity of FcTMA. This behavior is similar to the dilatant effect, i.e. solidification by extra stress.

Background currents increased with an increase in the scan rates parallel with x-axis in Fig. 1(A). The background-corrected peak currents, $I_{\mathrm{p,crrct}}$, were plotted against the square-roots of the scan rates in Fig. 5. Both the anodic and the cathodic peak currents showed a proportional relationship for $v < 0.3$ V s^{-1}, suggesting the diffusion-controlled process. We evaluated the diffusion coefficient, D, of FcTMA in various media from the slope of the proportionality. Figure 6 shows variations of D with η on the logarithmic scale. According to the Stokes-Einstein relation [3]

$$D = k_{\mathrm{B}}T / 6\pi\eta a \qquad (4)$$

the plot of $\log(D)$ against $\log(\eta)$ should have a linear relation with slope -1. A line was drawn in Fig. 6 so that some points at lower values of η fell on a line with slope -1, including the D-value of FcTMA in the aqueous solution (square mark in Fig. 6). The domain of $\log(\eta$ /Pa s$) < -0.5$ exhibiting the slope -1 is in accord with that of the variation of the resistance (Fig. 4) for $\log(\eta$ /Pa s$) < -0.5$. Equation (4) tells us that the intercept should be $\log(k_{\mathrm{B}}T/6\pi a)$, which equals 7.1×10^{-14} N from the line in Fig.6. Then we have a reasonable value, $a = 0.3$ nm, or 0.6 nm in diameter of FcTMA. The points in $\log(\eta$ / Pa s$) > -0.5$ are deviated upward from the line, which fell on another line with slope -0.5. This value has been reported in the mixture of polypropylene glycol and polyethylene glycol [10,13]. Similar deviation has been observed in the variation of the resistance (Fig. 4), like the dilatancy. However, a kind of room temperature ionic liquids has not exhibited the deviation [22].

The plots of the peak currents against $v^{1/2}$ for $v > 0.3$ V s^{-1} deviated to smaller values from the proportionality, as has been shown in Fig. 5. The deviation was found in both the anodic and the cathodic currents. The lower deviation from the proportionality implies that the current or the mass transport should be blocked at high scan rates. This is opposite to the deviation in Fig. 4 and 6 at which mass transport of the electrolyte (in Fig. 4) and FcTMA (in Fig. 6) were facilitated in higher viscous solutions (dilatancy). We define the critical scan rate, v_c, as the average of the scan rate of the onset of the deviation of the anodic current and that of the cathodic one. Values of v_c decreased with an increase in the viscosity. We have no *a priori* prediction of variation of v_c with η. We attempted to make a logarithmic plot of the variation in Fig. 7. The points for log(η / Pa s) < -0.5 fell on a line with a slope -1, e.g., $v_c\eta = 0.03(=10^{-1.5})$ V Pa, as is similar to the variations in Fig. 4 and 6. The upward deviation from the line or scattering for log(η / Pa s) > -0.5 was also similar to the deviations for the lines in Fig. 4 and 6. Conclusively, the v vs. η plane can be divided into three domains (in Fig. 7); the ordinary diffusion-controlled domain ($|I_p| = kv^{1/2}$) for $v < v_c$, the diffusion-controlled domain with lower peak currents $|I_p| < kv^{1/2}$) for $v > v_c$, and current-facilitated domain for log(η / Pa s) > -0.5.

The behavior at fast scans, especially for $v > v_c$, has not been reported in PEG solution yet, to our knowledge. There are few publications on the plot of peak currents vs. $v^{1/2}$ at fast scans even in conventional solvents. Some reports have showed plots of peak currents vs. $v^{1/2}$ to be proportional for ferrocene in acetonitrile at Pt and carbon electrodes up to 400 V s^{-1} [41], to be proportional for ferroceneacetic acid in aqueous solution up to 1 V s^{-1} and be deviated to lower values at higher scan rates [42], and to be proportional for hexamminecobalt in aqueous solution up to 300 V s^{-1} [43]. The deviation of the proportionality seems to depend on redox species and solvents, and thus values of v_c should also depend on. The value of v_c, extrapolated to viscosity of water (0.89 mPa s) along the line $v_c\eta = 0.03$ V Pa becomes $v_{c,water} = 34$ V s^{-1}. Peak currents in aqueous solution over 34 V s^{-1} might be deviated lower from the conventional expression if a delay of the potentiostat were to be corrected accurately, and if the electrochemical reaction of FcTMA in PEG were to be the same as that in water. However, the reaction depends strongly on solvents, and hence this prediction is simplistic. This scan rate corresponds to 0.8 ms of $RT/F\ v_{\mathrm{c,water}}$, which is close to the delay time of diffusion (ca. 1 ms) in the aqueous solution [44] when diffusion is complicated with memory effects [45]. The memory effects are caused by a delay of transport of a diffusing molecule from the onset of concentration gradients through the relation $J(t+\tau) = -D(\partial c(t)/\partial x)$ instead of $J(t) = -D(\partial c(t)/\partial x)$ of the Fick's first law, where J is the flux and τ is the delay period. The delay period may be equivalent to $v_{\mathrm{c}}F/RT$ in cyclic voltammetry. The effects have been examined with measurements of the propagation time at the pair electrode [45] and Monte Carlo molecular simulation [46]. The empirical relation of $v_{\mathrm{c}}\eta = 0.03$ V Pa can be rewritten as

$$v_{\mathrm{c}}\eta\, F/RT = 1.2 \text{ Pa} \qquad (5)$$

The stress, 1.2 Pa, is independent of viscosity, and thus it represents transport properties of redox species (FcTMA) rather than of the solvent. It makes the force $1.2(\pi a^2) = 8.5\times10^{-20}$ N act on one redox particle, which is equivalent to the force 51 N acting on 1 mM FcTMA in 1 dm^3. This force is large enough for 1 kg materials to move spontaneously. Therefore, the observation of the stress is not surprising.

4. Conclusion

All the voltammograms of FcTMA were reversible and had no participation in electrode kinetics in the domain of the viscosity, $0.85 < \eta < 2800$ mPa s at $v < 9$ V s^{-1}, according to the criterion of peak potential difference. However, they showed broader waveforms with an increase in viscosity because of the solution resistance. Essential voltammetric features relevant to viscosity was exhibited in the dependence of the peak currents on the scan rates rather than peak potentials.

The PEG solutions containing 40 mM $NaBF_4$ had such low solubility that the peak potentials were always shifted by the solution resistance. The plot of the peak currents against the peak potentials showed the linear variation, the inverse slope of which was equivalent to solution resistance. The resistance was inversely proportional to the viscosity for $\eta < 0.3$ Pa s. The deviation of the resistance from the proportionality suggests dilatancy, which may be proper to PEG.

The dependence of the peak currents on the scan rates can be classified into two groups across the boundary, $v\eta = 0.03$ V Pa on the basis of the proportionality of the peak currents to $v^{1/2}$. We defined the scan rate at the boundary as the critical scan rate, which was equivalent to 34 V s^{-1} or 0.8 ms in water. These values are close to the relaxation time of memory diffusion.

The peak currents for $v\eta < 0.03$ V Pa were proportional to $v^{1/2}$, and obey the conventional equation of diffusion-controlled currents. The values of the diffusion coefficient calculated from the slope of the proportional line were in accord with the Stokes-Einstein equation for $\eta < 0.3$ Pa s, whereas they were deviated from the equation for $\eta > 0.3$ Pa s probably owing to the dilatancy. In contrast, the peak currents for $v\eta >$ 0.03 V Pa were deviated lower from the proportional line, and hence do not obey the conventional equation. The deviation cannot be explained in terms of the dilatancy because of $\eta < 0.3$ Pa s but suggest a delay such as memory diffusion.

5. Acknowledgement

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6. References

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Figure Captions

Fig. 1 Cyclic voltammograms of 1 mM FcTMA in PEG of 94.6 mPa s in viscosity including 40 mM $NaBF_4$ for (A) v = 0.01, 0.03, 0.05, 0.07, 0.1, 0.3, 0.5, 0.7 V s^{-1} and (B) v=1, 2, 3, 4, 5, 6, 7, 8 V s^{-1}.

Fig. 2. Plots of peak currents against peak potentials in the PEG of 94.6 mPa s when scan rates were varied. The slope is equivalent to the conductance. The intercept of the line at $I_p = 0$ gives the peak potential without involving solution resistance.

Fig. 3. Variations of ΔE_p with the logarithm of the viscosity, η, of PEG, where ΔE_p was evaluated from the difference in the two intercepts of Fig.2.

Fig. 4. Logarithmic plot of the resistance against the viscosity of PEG, where r was evaluated from the slopes in Fig. 2. The line has a slope 1.

Fig. 5. Variations of the background-corrected peak currents with square-roots of scan rates for voltammograms in PEG of 770 mPa s.

Fig. 6. Logarithmic plot (circles) of the diffusion coefficient against the viscosity of PEG, where D was evaluated from the slopes of the proportional part in Fig. 5. The square denotes the diffusion coefficient of FcTMA in water. The line has a slope -1.

Fig. 7 Logarithmic plot of v_c against the viscosity, and the three domains of v-η plane, where the line has a slope -1.

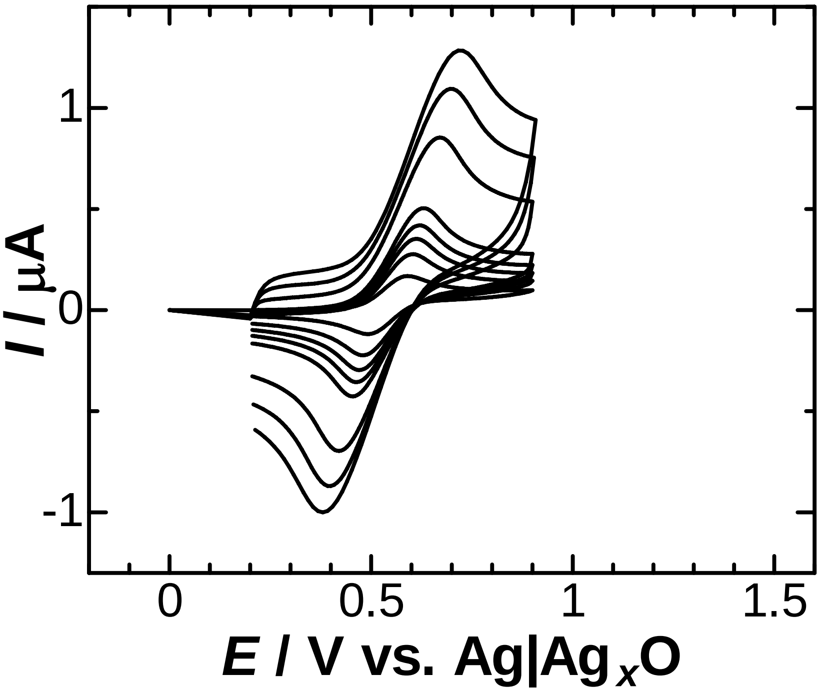


Fig. 1(A)

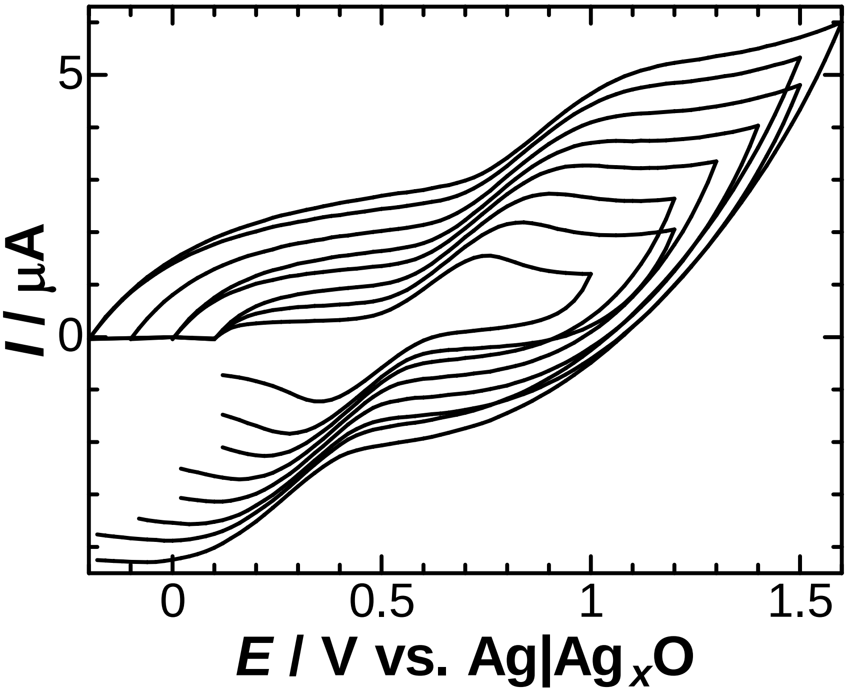
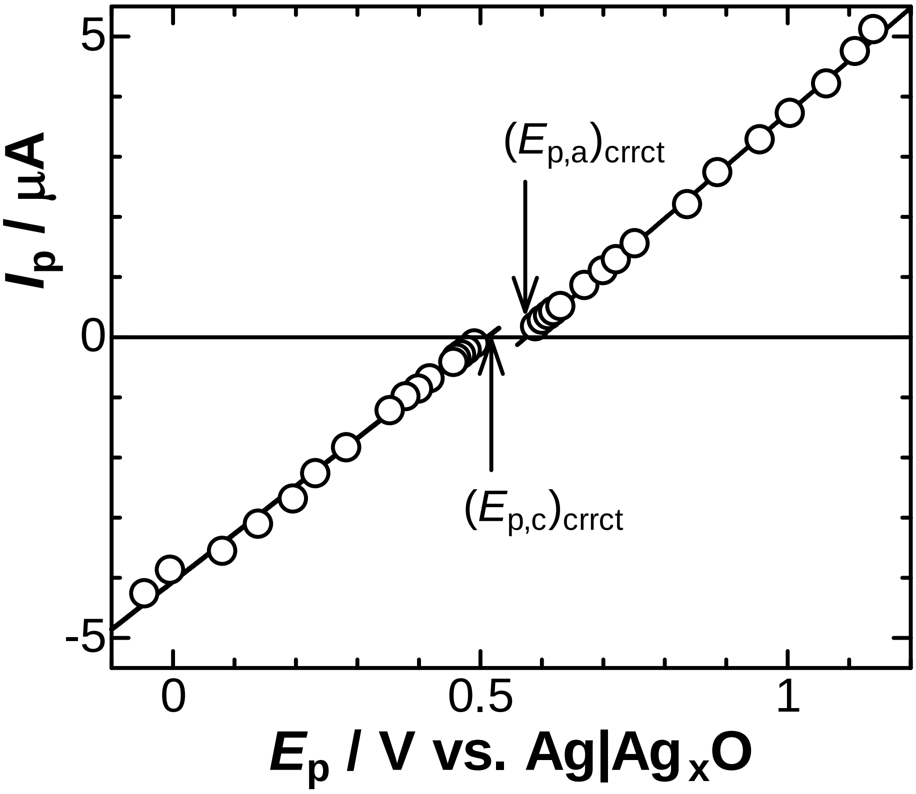
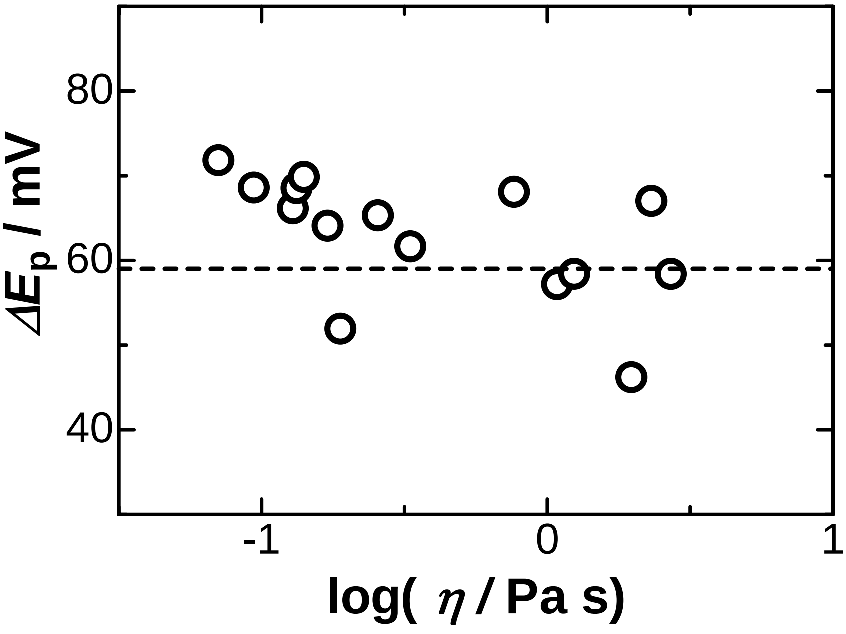


Fig. 1(B)



5
0
-5
0
0.5
1
I_p / μA
E_p / V vs. Ag|Ag$_x$O
$(E_{p,a})_{crrct}$
$(E_{p,c})_{crrct}$

Fig. 2



80
60
40
-1
0
1
ΔE_p / mV
log(η / Pa s)

Fig. 3

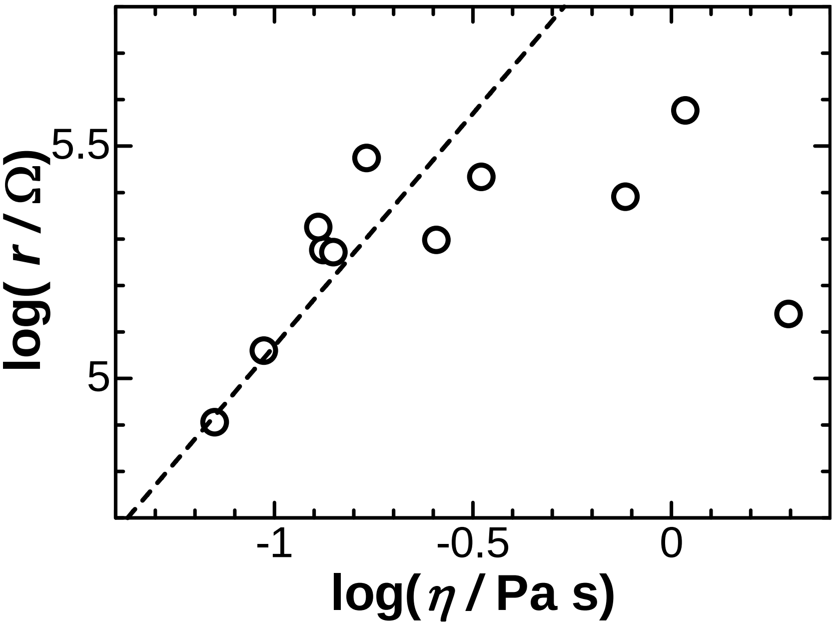


Fig. 4

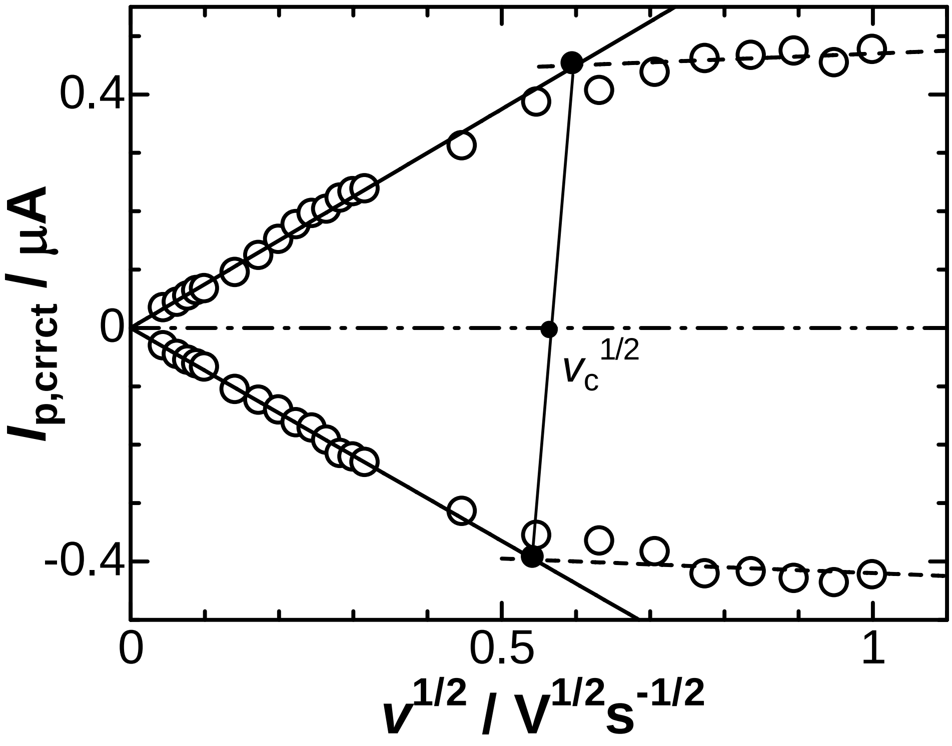


Fig. 5

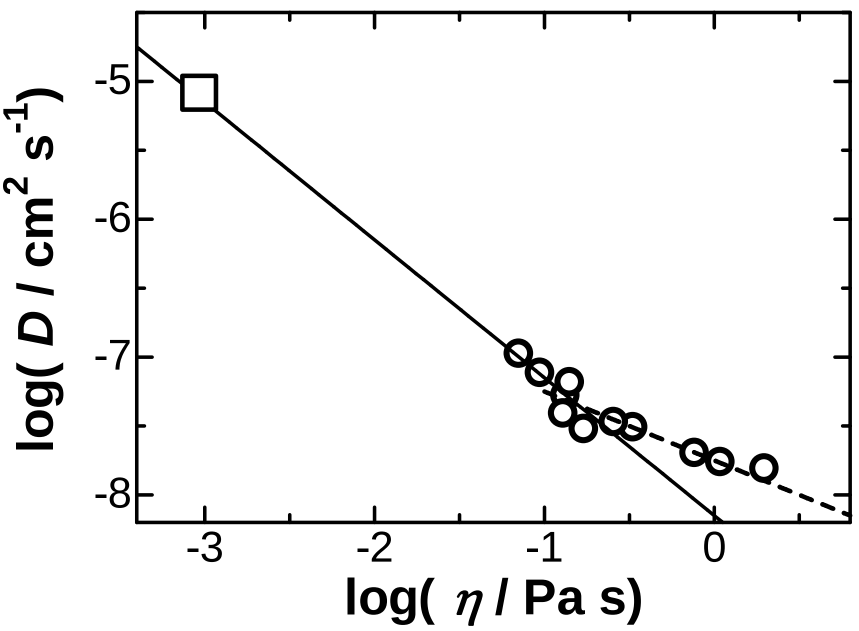

log(D / cm^2 s^{-1})
-5
-6
-7
-8
-3
-2
-1
0
log(η / Pa s)

Fig. 6

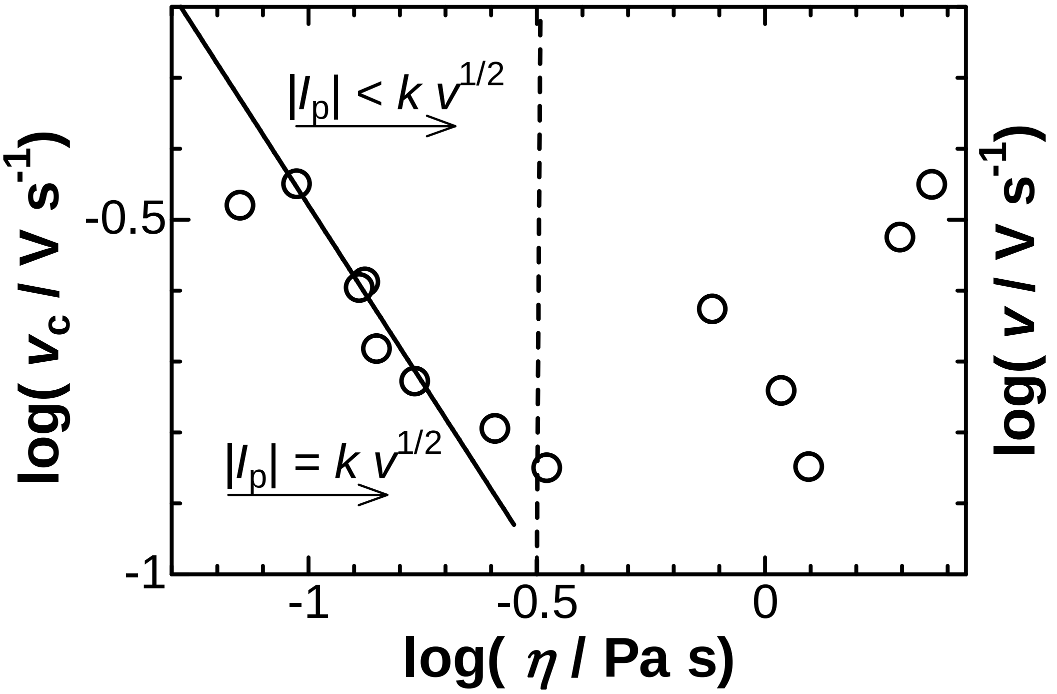

log(v_c / V s^{-1})
log(v / V s^{-1})
$|I_p| < k\, v^{1/2}$
$|I_p| = k\, v^{1/2}$
-0.5
-1
-1
-0.5
0
log(η / Pa s)

Fig. 7