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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 shifts, 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.

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 [10,11,5], guar gum solutions [12], ethylene carbonate [13], carboxy-methylcellulose [14,15], supermolecules with polyethylene chains coordinated with redox couples [16,17], polyacryl acids incorporated by alkali-metal counterions [18], and conventional organic solvents [19]. Recently, viscous effects on voltammetry have been reported on ionic liquids as new high viscous solvents and ions [20–24] as well as on supercritical liquids [25–31] 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 [10,32]. The decrease in ionic solubility enhances also adsorption of redox species, e.g., ferricenium ion as an oxidation product [33]. 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 [34], deviation from Levich's equation at Reynolds number less than 30 [12], inhomogeneity of redox sites in polymer leading to delay of diffusion currents [35], dependence of diffusion coefficients on concentrations of redox species [36], and estimation of solvent–solute interaction [37].

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.

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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 [38], 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$_x$O electrode were used as the counter-electrode and the reference electrode, respectively. The Ag|Ag$_x$O 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 of 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.

Fig. 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. 1A) appeared at potentials similar to those in the aqueous solution. With an increase in the scan rates, the waves became broad (Fig. 1B) 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

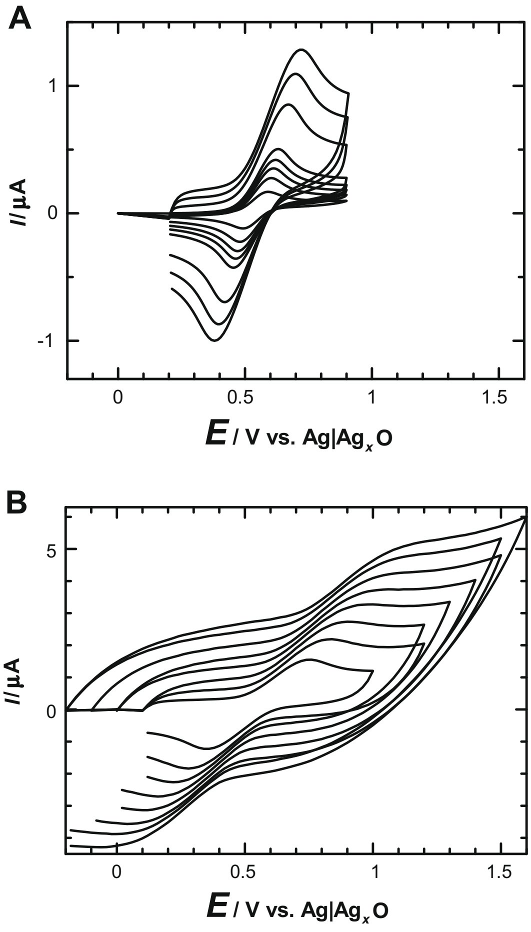

Fig. 1. Cyclic voltammograms of 1 mM FcTMA in PEG of 94.6 mPa s in viscosity including 40 mM NaBF$_4$ for: (A) v = 0.01, 0.03, 0.05, 0.07, 0.1, 0.3, 0.5, 0.7 V s^{-1} and (B) v = 1, 2, 3, 4, 5, 6, 7, 8 V s^{-1}.

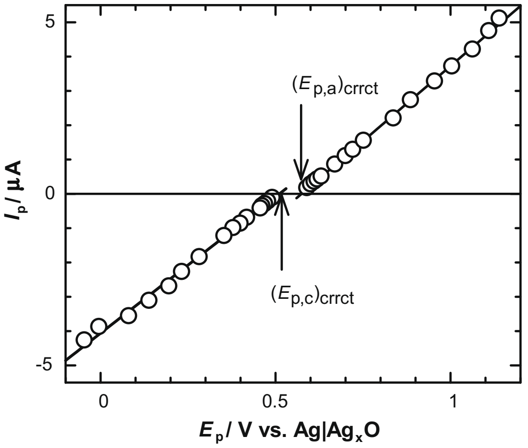

Fig. 2. Plots of peak currents against peak potentials in the PEG of 94.6 mPa s when scan rates were varied. The slope is equivalent to the conductance. The intercept of the line at I_p = 0 gives the peak potential without involving solution resistance.