

Diffusion-controlled behavior of ferrocenyl derivative in viscous solutions

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The reversible redox species ferrocenyl derivative was dissolved in high viscous solution of polyethylene glycols and was taken the cyclic voltammetry with the aim of finding the effects of viscosity on voltammograms, and determining whether it is similar with the behavior of ferrocenyl derivative in aqueous solution¹. Voltammetric peaks at low scan rates appeared at potential similar to those in the aqueous solution and with an increase in the scan rates the waves became broad and both peaks were separated. The plots of the peak current without background-correction against the peak potential fell on each line and with common slopes indicated the effect of solution resistance. The difference between the anodic and the cathodic peak potentials was close to 60 mV. Peak current at high scan rates were deviated lower from the proportionality to the square-root of the scan rates but for $\nu < 0.3 \text{ V s}^{-1}$ the anodic and the cathodic peak currents showed a proportional relationship suggesting the diffusion-controlled process. The deviation could not be described by reason of participation of sluggish electron transfer reactions or solution resistance but was similar to the memory effect of diffusion². Solution resistance and diffusion coefficients were evaluated and these values obeyed Stokes-Einstein equation³ for the viscosity less than 0.3 Pa s. Dilatancy was observed at viscosity more than 0.3 Pa s. We defined the critical scan rate, ν_c , as the average of the scan rate of the onset of the deviation of the anodic current and that of the cathodic one. An invariant relation can be found when the viscosity more than 0.3 Pa s and the part less 0.3 Pa s can be described by

$$\nu_c \eta F/RT = 1.2 \text{ Pa}$$

The stress, 1.2 Pa, is independent of viscosity.

¹ K. Aoki, C. Xian, *J. Phys. Chem. C*, 111 (2007) 15433.

² Aoki, K. *J. Electroanal. Chem.* 592 (2006) 31.

³ P. W. Atkins, *Physical Chemistry*, 6th ed., Oxford University Press, Oxford, 1998, p.749.