

Diffusion coefficients in viscous sodium alginate solutions

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Abstract

Sodium alginate solution, being viscous hydrocolloid, was examined voltammetrically in the context of viscous effects by use of a ferrocenyl compound as a redox probe. Voltammograms were almost independent of concentrations of sodium alginate even in a solid-like state. Diffusion coefficients of the ferrocenyl compound did not vary with viscosity evaluated by a viscometer. Ionic conductivity of sodium alginate was also independent of the viscosity. In contrast, diffusion coefficients of the latex particle 0.84 μm in diameter decreased with an increase in the viscosity. The intrinsic viscosity was evaluated. The value is equivalent to the volume as large as 3 m^3 of water in which one mole of the unit of sodium alginate polymer generates the viscosity. Consequently, redox species diffuse through water portions circumventing the alginate network. As an application, sodium alginate solutions were used for long-time chronoamperometry. The current was decayed with the time even of 1500 s without any effect of natural convection, whereas that in the aqueous solution was irreproducible for times longer than 20 s. The other application was electroplating of silver. The silver surface deposited in sodium alginate had no morphology by the SEM image, while the surface plated without sodium alginate showed morphology even on an optical microscopy scale.

key words, cyclic voltammetry in viscous sodium alginate; diffusion coefficients; intrinsic viscosity; network polymer structure; uniformly electroplating metal films;

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1. Introduction

Sodium alginate is a water-soluble, natural occurring linear polysaccharide [1,2]. It takes a form of viscous hydrocolloid, dispersions or gels by crosslinking. It has been widely applied to safety food additives, pharmaceutical materials, textile, thickeners, emulsifiers, and stabilizers [3]. The extensive applications lie in modifiable scaffold of functional species in films or gel [4-7] under biocompatible circumstances [6,8-11]. Viscous sodium alginate solutions decrease in general mass transfer rates owing to the frictional resistance. For example, the detection time of oxygen at the Clark-type chip was prolonged 1.5 times when the chip contained sodium alginate [4]. The higher was the viscosity of sodium alginate, the lower was the separation sensitivity of pervaporation [12]. Some opposite data have been reported [5,7,13-15], in which mass transfer rates are independence of viscosity. The concept of the independence is based on the prediction that molecules can transfer through a large network of sodium alginate [13,15-18].

Electrochemical measurements in viscous solutions are complicated by poor conductance of solution due not only to retarded ion transport but also to limited ionic solubility. The poor conductance deforms voltammetric waves as if sluggish electrode kinetics were to be involved in reactions [19,20]. The decrease in ionic solubility enhances adsorption of redox species, e.g., ferricenium ion as an oxidation product [21]. Strong temperature-dependence of viscosity causes poor reproducibility of data. Despite these complications, some fundamental features proper to viscosity have been reported; slip effects which deviates the proportionality of shear stress to velocity [22], deviation from Levich's equation at Reynolds number less than 30 [23], inhomogeneity of redox sites in polymer giving rise to a delay of diffusion currents [24], dependence of diffusion coefficients on concentrations of redox species [25], estimation of solvent-solute interaction [26], and deviation from the inverse proportion of diffusion

coefficients to viscosity [27,28].

Mass transport rates in viscous sodium alginate are controversial because of few data reported on size of the network [5]. The data required for the discussion are a diffusion coefficient, D , and viscosity, η , which are generally related through the Stokes-Einstein equation [29]

$$D = k_B T / 6\pi\eta r_0 \quad (1)$$

where r_0 is the hydrodynamic radius of spherical diffusing particle, and k_B is the Boltzmann constant. Eq. (1) has been obtained from the concept that thermal motion of a particle is compensated with the viscous friction. If the macroscopic viscosity obtained by a viscometer is different from the microscopic viscosity which the particle experiences, Eq. (1) does not hold. Difference between the two viscosities may reflect polymer structure of sodium alginate. This work is devoted to examining Eq. (1) in sodium alginate solutions containing a redox species by combining voltammetry and measurements of viscosity.

2. Experimental

Powder of sodium alginate (Wako), of which molecular weight corresponded to 500-600 mPa s in 10 g dm⁻³ solution, was used as received. It was stored in a refrigerator. The electroactive species, ferrocenyl tetramethylammonium hexafluorophosphate (FcTMA), was synthesized in house. FcTMA contained salt, mainly ammonium iodide, which was formed when iodide in ferrocenyl tetramethylammonium iodide was substituted for hexafluorophosphate. Therefore, it was not easy to prepare accurate concentrations of FcTMA. Water was deionized and distilled.

A homogeneous solution of sodium alginate was prepared by dissolving sodium alginate powder in distilled water at 60°C and mixing slowly. Viscous solution

contained air bubbles coming from the powder. Bubbles were removed by ultrasonication for 30 min. The sodium alginate solution was mixed with the solution including 0.1 M (= mol dm⁻³) KCl and ca. 1 mM FcTMA. Mixing of very viscous solution was made by squeezing the mixture in a polyethylene bag.

Accurate concentrations of FcTMA solution were determined by the combinational use of voltammetric peak currents at the platinum electrodes 1.6 mm and 0.1 mm in diameters [30]. This technique included the following steps; carrying out voltammetry at the two electrodes for the potential scan rates, ν , in the range from 10 to 100 mV s⁻¹, evaluating the proportionality constant of the peak current, I_p , vs. $\nu^{1/2}$ at the 1.6 mm electrode, evaluating the extrapolated limiting current, I_L , to $\nu^{1/2} \rightarrow 0$ at the 0.1 mm electrode in the I_L' , vs. $\nu^{1/2}$ plot, and taking the ratio of the $(I_p \nu^{-1/2})^2 / I_L$. In contrast the ratio $(I_p \nu^{-1/2}) / I_L$ provided values of the diffusion coefficient of FcTMA without knowing accurate concentrations.

A conductometer was home-made by arranging two platinum disk electrodes flush with a polytetrafluoroethylene plate. The separation of two electrodes was 5.5 mm. Alternating voltage with 1 kHz and 10 mV amplitude was applied to the electrodes. The in-phase component of the responding current was collected through a potentiostat. It was calibrated with several concentrations of KCl solution ranging from 0.01 to 0.1 M to determine the cell constant.

Cyclic voltammetry was carried out with a potentiostat, Compactstat (Ivium Tech., Netherlands), in viscous mixtures. Platinum disks 1.6 mm and 0.1 mm in diameter (BAS, Tokyo) were used as voltammetric working electrodes. The surface of the working electrode was polished with alumina paste on wet cotton, and was rinsed with distilled water in an ultrasonic bath.

Viscosity was determined with a vibration viscometer, SV-10 (A&D, Tokyo), at room temperature after each voltammetric measurement. Viscosity was also obtained under the temperature control from 0 to 73°C.

Polystyrene latex was synthesized in house [31]. Uniformity of size of the latex in aqueous suspension was confirmed by an optical microscope, VH-5000 (Keyence, Osaka). The size distribution of latex particles was determined by a dynamic light scattering (DLS) instrument (Malvern Zetasizer Nano-ZS, UK). Diameters by a scanning microscope and DLS were identical within experimental errors.

3. Results and Discussion

3.1 Relation of diffusion coefficient with viscosity

Voltammetry of FcTMA was made in solutions including 0.1 M KCl and several concentrations of sodium alginate. Figure 1 shows voltammograms (a) without and (b) with sodium alginate at Pt electrodes (A) 1.6 mm and (B) 0.1 mm in diameter. The voltammograms in (A) at an ordinary sized electrode showed peaked shape, whereas those in (B) at a microelectrode-like small electrode exhibited steady-state like shape. The sodium alginate solution for (b) was almost in such a solid state that the solution|air boundary did not move when the boundary was turned vertically to the gravity. With an increase in concentrations of sodium alginate, voltammograms were slightly shifted in the negative direction. The maximum shift was 20 mV, as is shown in Fig. 1. The shift may be caused by stabilization of the reduced ferrocenyl moiety, $\text{Fe}^{2+}(\text{C}_5\text{H}_5)^-(\text{C}_5\text{H}_4^-)$, with the hydrophobic backbone of sodium alginate. Values of the peak currents at similar concentration of FcTMA in Fig. 1(A) did not vary largely with the viscosity although viscosity was quite different in (a) and (b). Voltammetric peak currents controlled by diffusion at an ordinary sized electrode are proportional to square-roots of the scan rate, ν , whereas those at a ultramicroelectrode do not vary with ν . Figure 2 shows variations of the peak currents with $\nu^{1/2}$ at the electrodes (A) 1.6 mm and (B) 0.1 mm in diameter. The former variations exhibited the proportionality, while the latter

variations were not constant but increased linearly with $v^{1/2}$. Thus, voltammograms at the 0.1 mm electrode show the intermediate property at a large electrode and at a microelectrode. A measure of the peaked current or the steady-state current is the variable $p^2 = a^2Fv/RTD$ [32], where D is the diffusion coefficient of an electroactive species. This variation should also be observed when the diffusion coefficient becomes small in viscous media [28]. However, the voltammetric shape at the electrode 0.1 mm in diameter (Fig. 1B(a)) was independent of viscosity. If a value of D were to get small in the sodium alginate solution, the plot for (b) in Fig. 2(B) should show a slope steeper than that for (a). Consequently, viscosity of sodium alginate seems to have qualitatively no effect on diffusion coefficients of FcTMA.

Evaluation of diffusion coefficients from voltammetric currents needs accurate values of concentrations. Unfortunately, it is not easy to control concentrations of FcTMA in viscous solutions because of no confirmed evidence of uniform mixing, as can be seen from the difference in current values between (a) and (b) in Fig. 1 and 2. We determined diffusion coefficients of FcTMA by taking the ratio of the peak currents at the electrode 1.6 mm in diameter to that at 0.1 mm without knowing concentrations of FcTMA, as was presented in the experimental section. Immediately after voltammetry, viscosity was determined with the viscometer. Figure 3 shows the variation of the diffusion coefficient with the viscosity, η , in logarithmic axes. Values of D did not vary with η . The Stokes-Einstein equation (Eq. (1)) mentions that the slope of the plot of $\log(D)$ vs. $\log(\eta)$ is -1 (dotted line in Fig. (3)). Disagreement of the experimental data with Eq. (1) indicates that the viscosity experienced by the FcTMA molecule should be smaller than that by the viscometer. The data points are rather scattered at high viscosity, because of possibility of inhomogeneous mixing or fluctuation of temperature.

The variation of the viscosity with temperature, as is shown in Fig. 4, is much smaller than the variation in Fig. 3. Therefore the scattering is ascribed to insufficient

mixing.

Figure 5 shows temperature-variations of the viscosity of sodium alginate and the diffusion coefficient of FcTMA. With an increase in the temperature, the viscosity decreased and the diffusion coefficient increased. According to the Stokes-Einstein equation, the product, $D\eta$, should increase slightly with temperature. However, it decreased because the diffusion coefficient was less influenced by temperature than the viscosity was.

Values of diffusion coefficients by electrochemical measurements necessarily include complications due to change in redox charge. Therefore, the invariance of D to η in Fig. 3 does not always come from a simple hydrodynamic effect. As an example of variation of diffusion coefficients without change in ionic charge, we paid attention to ionic conductance, which is proportional to the diffusion coefficient [29]. Conductance of Na^+ in sodium alginate was determined with the home-made calibrated conductometer in various concentrations of sodium alginate. Variation of conductivity, κ , vs. the viscosity is shown in Fig. 3 on the right axis. The variation was similar to that of D vs. η for FcTMA. Therefore the independence of D from η is not relevant to redox species, but is a property of sodium alginate.

The invariance of D with η might be caused by voltammetric unknown problems in viscous solutions. In order to confirm the invariance, we estimated approximate values of D in sodium alginate by use of time-evolution of diffusing dye in the following way. A viscous solution of sodium alginate was prepared on a petri dish, onto which a small amount of methylene blue-included aqueous solution was dropped. The methylene blue zone was expanded concentrically on the sodium alginate surface, as shown in Fig. 6. Although the boundary of the zone was not well-defined, we read outer and inner diameters of the blue circle zone at some periods after the drop. Figure 7 shows variations of the radii with the square-root of the time, on the concept of the thickness of a diffusion layer approximately given by $r = (Dt)^{1/2}$. As predicted, the radii

had linear variations with $t^{1/2}$. The slope provided $D = 0.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, being common for two viscosity values (6030 and 386 mPa s). This value is not only independent on the viscosity of sodium alginate but also is close to D -values of organic molecules in water.

In order to grasp a molecular image of the independence, we discuss intrinsic viscosity [33] here. We measured the viscosity at several low concentrations of sodium alginate solutions, c . The viscosity increased with the concentration. Letting the viscosity of water be η^* , we obtained a linear relation of $(\eta/\eta^* - 1)/c$ with c , as is shown in Fig. 8. The intercept is the intrinsic viscosity, $[\eta] = 15 \text{ dm}^3 \text{ g}^{-1}$. Multiplying $[\eta]$ by the molecular weight (198 g/mol) of the unit of sodium alginate ($\text{NaC}_6\text{H}_7\text{O}_6$) yields the volume, 3.0 m^3 , for the viscosity per unit of sodium alginate. This volume contains 1.7×10^5 moles of water, whereas it does one molecule of a unit of sodium alginate. Consequently, a conventional molecule such as FcTMA diffuses through water portion without colliding with the network of sodium alginate.

Molecules bigger than this volume should exhibit viscous effects by blocking diffusion with the network of sodium alginate. This prediction was examined by dependence of diffusion coefficients of polystyrene latex particles $0.84 \text{ }\mu\text{m}$ in diameter on viscosity of sodium alginate. The diffusion coefficients were estimated with DLS for a given viscosity value. Their values were decreased with an increase in the viscosity, as is shown in Fig. 9. They are close to the linearity (solid line) by the Stokes-Einstein equation for $r_0 = 0.42 \text{ }\mu\text{m}$.

3.2 Applications

Long-term chronoamperometry often provides irreproducible currents owing to the buildup of density gradients and stray vibrations [34]. Currents for times longer than 30 s include convective effects, and those for times longer than 300 s are not controlled by

diffusion any more [35]. Viscous sodium alginate is predicted to suppress natural convection. Figure 10 shows chronoamperometric curves of FcTMA in (a) 1 M KCl in viscous sodium alginate solution and (b) 1 M KCl aqueous solution. The currents in the alginate solution were decayed smoothly and were reproducible. They did not vary with angles of the electrode surface against the horizon ((i) 0 degree or (ii) 60 degree). In contrast, the currents in the aqueous solution for times longer than 100 s were irreproducible and larger than those in the sodium alginate solution. They include convection effects. Consequently, sodium alginate works as stabilization of diffusion currents by preventing convection.

The property of uniformizing current distributions may be applied to formation of electroplating films. Figure 11 shows voltammograms of silver ions (a) with and (b) without of sodium alginate. Both voltammetric shapes were similar but the current values in sodium alginate were smaller than those in solutions without sodium alginate at the identical concentration of Ag^+ . The difference in values of the cathodic current does not seem to be consistent with the result in Fig. 1. Since sodium alginate includes carboxylic moiety, silver ion forms silver carboxylate complexes. Consequently the net concentration of silver ion to be deposited is decreased in the bulk by chelate. The charge of the reduction current in the sodium alginate solution (Fig. 11(a)) was close to that for a half concentration of Ag^+ (12.5 mM AgNO_3) in KNO_3 without sodium alginate. Therefore a half Ag^+ was stabilized with sodium alginate.

Silver ion was deposited on the Pt electrode at -0.3 V in 25 mM AgNO_3 + 1 M KNO_3 solution and in 25 mM AgNO_3 + 1 M KNO_3 + 9 g dm^{-3} sodium alginate solution, respectively, for 15 s and 60 s so that the cathodic charge was common (ca. 1.5 mC). The electrode was rinsed gently with water, and was observed by the optical microscope, as shown in Fig. 12. The photograph without sodium alginate shows a pattern (B), whereas that with sodium alginate has little morphology (A). The former is composed of basically two types of morphology; grains less than 10 μm , and domains larger than

0.1 mm. When the effective concentration of Ag^+ , that is, a half the concentration was used for deposition without sodium alginate, the deposit surface (Fig. 12(C)) was similar to the pattern in Fig. 12(B). The SEM photograph (Fig. 13(B)) without sodium alginate shows fish-shaped grains with various sizes, whereas that (Fig. 13(A)) with sodium alginate exhibits no pattern. The difference is ascribed to the chronoamperometric result (Fig. 10) that sodium alginate prevents natural convection of silver ion.

4. Conclusions

With an increase in concentrations of sodium alginate, the viscosity of ionic solution increases up to actually solid states. Diffusion coefficients of ions, however, do not vary with the viscosity as if the ions were in water. The value of the intrinsic viscosity is so large that one mole of the unit of sodium alginate polymer can make 3 m³ aqueous solution viscous. Consequently ions diffuse in the domain of the aqueous solution without collision with the network of sodium alginate. Sodium alginate is extremely efficient in generating viscosity.

Sodium alginate solution is useful to keep ideal concentration profiles by diffusion long (a half hour) without effects of natural convection and/or of stray vibrations. The property of retaining ideal mass transport can be applied to metal plating. The silver metal cathodically deposited in sodium alginate solution has no morphology.

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References

- [1] A. Haug, B. Larsen, O. Smidsrod, *Acta Chem. Scand.* 20 (1966) 183.
- [2] Z.Y. Wang, Q. Z. Zhang, M. Konno, S. Saito, *Biopolym.* 34 (1994) 737.
- [3] A. Regand, H.D. Goff, *Food Hydrocolloids* 17 (2003) 95.
- [4] C.-C. Wu, H.-N. Luk, Y.-T. T. Lin, C.-Y. Yuan, *Talanta* 81 (2010) 228.
- [5] A. Kikuchi, M. Kawabuchi, A. Watanabe, M. Sugihara, Y. Sakurai, T. Okano, *J. Control. Rel.* 58 (1999) 21.
- [6] G. Zhao, X. Zhan, W. Dou, *Anal. Biochem.* 408 (2011) 53.
- [7] A.C.F. Ribeiro, A.J.F.N. Sobral, S.M.N. Simoes, M.C.F. Barros, V.M.M. Lobo, A. M.T.D.P.V. Cabral, F.J.B. Veiga, C.I.A.V. Santos, M.A. Estesio, *Food Chem.* 125 (2011) 1213.
- [8] S. Wei, W. Dandan, G. Ruifang, J. Kui, *Electrochem. Commun.* 9 (2007) 1159.
- [9] T. Zhan, M. Xi, Y. Wang, W. Sun, W. Hou, *J. Colloid Interface Sci.* 346 (2010) 188.
- [10] X. Wang, M. Han, J. Bao, W. Tu, Z. Dai, *Anal. Chim. Acta* 717 (2012) 61.
- [11] Y. Hu, N. Hu, *J. Phys. Chem. B* 112 (2008) 9523.
- [12] U.S. Toti, T.M. Aminabhavi, *J. Membr. Sci.* 228 (2004) 199.
- [13] M. Grassi, I. Colombo, R. Lapasin, *J. Control. Rel.* 76 (2001) 93.
- [14] W. Lubas, P. Ander, *Macromolecules* 13 (1980) 318.
- [15] Y. Li, X. Zhao, Q. Xu, Q. Zhang, D. Chen, *Langmuir* 27 (2011) 6458.
- [16] A. Mohanan, B. Vishalakshi, *Int. J. Polym. Mat.* 58 (2009) 561.
- [17] A.R. Kulkarni, K.S. Soppimath, T.M. Aminabhavi, W.E. Rudzinski, *Eur. J. Pharm. Biopharm.* 51 (2001) 127.
- [18] D. Şolpan, M. Torun, *J. Appl. Polym. Sci.* 100(2006) 335.
- [19] H. Zhou, S. Dong, *Electrochim. Acta* 42 (1997) 1801.
- [20] H. Zhou, N. Gu, S. Dong, *J. Electroanal. Chem.* 441 (1998) 153.
- [21] I. Svorstøl, T. Sigvartsen, J. Songstad, *J. Acta Chem. Scand.* B42 (1988) 133.
- [22] R.A. Mashelkar, A. Dutta, *Chem. Eng. Sci.* 37 (1982) 969.

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- [23] J. Legrand, E. Dumont, J. Comiti, F. Fayolle, *Electrochim. Acta* 45 (2000) 1791.
- [24] K. Aoki, K. Tokuda, H. Matsuda, N. Oyama, *J. Electroanal. Chem.* 176 (1984) 139.
- [25] P. Daum, J. R. Lenhard, D. Rolison, R. W. Murray, *J. Am. Chem. Soc.* 102 (1980) 4649.
- [26] P. Zuman, D. Rozbroj, J. Ludvík, M. Aleksic, L. Camaione, H. Celik, *J. Electroanal. Chem.* 553 (2003) 135.
- [27] K. Aoki, Y. Guo, J. Chen, *J. Electroanal. Chem.* 629 (2009) 73.
- [28] Y. Guo, K. Aoki, J. Chen, T. Nishiumi, *Electrochim. Acta*, 56 (2011) 3727.
- [29] P.W. Atkins, *Physical Chemistry*, Sixth edition, Oxford University Press, Oxford, 1998, p. 479
- [30] H. Zhang, K. Aoki, J. Chen, T. Nishiumi, H. Toda, E. Torita, *Electroanalysis* 23 (2011) 947.
- [31] H. Chen, J. Chen, K. Aoki, T. Nishiumi, *Electrochim. Acta*, 53 (2008) 7100.
- [32] K. Aoki, K. Akimoto, K. Tokuda, H. Matsuda, J. Osteryoung, *J. Electroanal. Chem.* 171 (1984) 219.
- [33] P.W. Atkins, *Physical Chemistry*, Sixth edition, Oxford University Press, Oxford, 1998, pp. 690-691.
- [34] H.A. Latinen, *Trans. Electrochem. Soc.* 82 (1942) 289.
- [35] A. J. Bard, L.R. Faulkner, *Electrochemical Methods, Fundamentals and Applications*, Second edition, 2001, John Wiley & Sons, New York. p. 163.