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Author(s)	Ozaki, Ryotaro; Takagi, Taichiro; Kadowaki, Kazunori et al.
Citation	電気材料技術雑誌. 2015, 24(1), p. 10-15
Version Type	VoR
URL	<a href="https://hdl.handle.net/11094/76094">https://hdl.handle.net/11094/76094</a>
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## Observation of Electroviscous Effect of Ionic Liquid by Capillary Filling

Ryotaro OZAKI<sup>1)</sup>, Taichiro TAKAGI<sup>1)</sup>, Kazunori KADOWAKI<sup>1)</sup>,  
Hiroshi MORITAKE<sup>2)</sup>, and Katsumi YOSHINO<sup>3)</sup>

- 1) Graduate School of Science and Engineering, Ehime University, 3 Bunkyo-cho, Matsuyama, Ehime 790-8577, Japan
- 2) Department of Electrical and Electronic Engineering, National Defense Academy, 1-10-20 Hashirimizu, Yokosuka, Kanagawa 239-8686, Japan
- 3) Shimane Institute for Industrial Technology, 1 Hokuryo-cho, Matsue, Shimane 690-0816, Japan

Electroviscous effect of an ionic liquid (1-methyl-3propyl imidazolium iodide) in ethylisopropylsulfone is measured using capillary action in which the capillary filling speed is depend on viscosity of the sample. Rectangular capillary cells are prepared with two indium-tin oxide coated glasses and polyimide film spacers. The electrodes allow us to measure the electroviscous effect of the sample. The results of electroviscous measurements clearly show voltage dependence in which the application of voltage slows the capillary filling speed. The theoretical analysis of the capillary action is also performed. The calculated results show a well agreement with the experimental results.

**KEYWORDS:** Ionic liquid, Electroviscous effect, Capillary action, Viscosity

## キャピラリー構造を利用したイオン液体の電気粘性効果の観察

尾崎 良太郎<sup>1)</sup>、高木 泰知郎<sup>1)</sup>、門脇 一則<sup>1)</sup>、森武 洋<sup>2)</sup>、吉野 勝美<sup>3)</sup>

- 1) 愛媛大学大学院理工学研究科電子情報工学専攻、〒790-8577 愛媛県松山市文京町3
- 2) 防衛大学校電気情報学群電気電子工学科、〒239-8686 神奈川県横須賀市走水1-10-20
- 3) 島根県産業技術センター、〒690-0816 島根県松江市北陵町1

イオン液体は高いイオン電導性から、電気二重層キャパシタ、色素増感太陽電池、燃料電池、リチウムイオン電池などへの応用が期待されている。また、イオン液体は、優れた電気特性だけでなく、難燃性・不揮発性も有するため、安全性も同時に兼ね備えた材料である。本論文では、イオン液体 1-methyl-3propyl imidazolium iodide と ethylisopropylsulfone の混合溶液の電気粘性効果を調べている。電気粘性効果は、ITO ガラス 2 枚からなるセルを作製し、溶液を注入したときの液先端速度の電圧依存から測定している。また、理論解析による矩形断面をもつキャピラリー構造における溶液注入時の液先端速度および液先端位置の検討も行っている。

キーワード：イオン液体、電気粘性効果、毛細管現象、粘度

## 1. Introduction

Viscosity plays a significant role in the performance of electronic devices and electrical equipments such as electric double layer capacitor and electrolytic capacitor. Electrolyte solutions and ionic liquids have recently attracted much attention because of the possibility for a breakthrough of electrochemical devices [1-9]. Ionic liquids are liquids composed of only ions at room-temperature [2]. They are expected to lead development of high performance of capacitors, fuel cells, Li-ion batteries, and dye-sensitized solar cells, because they have high ionic conductivity and wide voltage potential window. In particular, as the ion conductivity depends on viscosity, the viscosity measurements of electrolyte solutions and ionic liquids are important for fundamental and application researches [10-12].

Viscosity of a liquid is generally measured with a rotational viscosity meter, which requires a large amount of sample. Therefore, it is not suited for a small amount of sample or quite expensive materials. We have proposed a method for viscosity measurement of a liquid crystal by using shear horizontal (SH) wave propagation [13-17]. The viscosity meter using a SH wave device has a thin cell structure composed of two glass plates in which an orientation treatment can be prepared for the viscosity anisotropy measurement of a liquid crystal. Moreover, when electrodes are prepared on the glass plates, an electroviscosity effect can be measured by applying a voltage to the electrodes. Using this technique, we have measured the electric field dependence of viscosity of ionic liquids [18]. The viscosities of the ionic liquid solutions monotonously increased with increasing applied electric field, and the electroviscous effects did not depend on the polarity of the electric field.

In this study, viscosity of an ionic liquid in a solvent is measured using simple capillary action. The results of electroviscous measurements show the capillary

filling speed depending on voltage. To quantitatively investigate the electroviscous effect, the theoretical analysis of capillary action is also performed.

## 2. Basics of capillary action

In this section, we will discuss the basics of capillary action for viscous liquid. We here consider liquid flow in a rectangular capillary, as shown in Fig. 1. The long and short sides of the rectangular capillary are  $a$  and  $b$ , respectively, and  $x$  is the length of the liquid filled into the capillary.

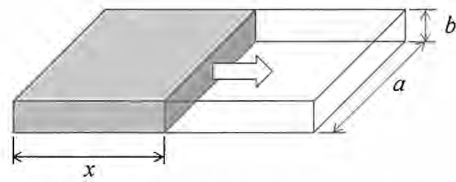


Fig. 1 Flow in a rectangular capillary.  
図1 矩形管内の流れ

The total mass of the liquid moving in the capillary is,

$$m = abx\rho \quad (2)$$

where  $\rho$  is the mass density of the liquid. The velocity of the liquid in the capillary is

$$v = \frac{dx}{dt} \quad (3)$$

The equation of motion for the moving liquid in the capillary is given by,

$$\frac{d}{dt} \left( abx\rho \frac{dx}{dt} \right) = -\frac{12a\mu}{b} x \frac{dx}{dt} + 2(a+b)\sigma \cos\theta \quad (4)$$

where  $\mu$  is viscosity of the liquid,  $\sigma$  is surface tension, and  $\theta$  is contact angle. The first term of the right-hand side of eq.(4) represents viscous friction, while the second term is a driving force for the motion of the liquid which is caused by surface tension. Since  $a$ ,  $b$ , and  $\rho$  do not depend on time, eq.(4) can be written as

$$\frac{d}{dt} \left( x \frac{dx}{dt} \right) = -\frac{12\mu}{b^2\rho} x \frac{dx}{dt} + \frac{2(a+b)\sigma \cos\theta}{ab\rho} \quad (5)$$

To simplify eq.(5), we use the following expression

$$A = \frac{2(a+b)\sigma \cos\theta}{ab\rho} \quad (6)$$

$$B = \frac{12\mu}{b^2\rho} \quad (7)$$

$$X = x \frac{dx}{dt} \quad (8)$$

Now, eq.(5) is written as

$$\frac{dX}{dt} = -BX + A \quad (9)$$

This equation can be easily solved. The solution of the differential equation is,

$$X = \frac{1}{B} \exp(-Bt + C_1) + \frac{A}{B} \quad (10)$$

where  $C_1$  is a constant of integration. When  $0^\circ < \theta < 90^\circ$ , we can obtain,

$$x = \sqrt{-\frac{2}{B} \exp(-Bt + C_1) + \frac{2A}{B} + C_2} \quad (11)$$

where  $C_2$  is a constant of integration. The velocity of the liquid in the capillary is also easily obtained as

$$v = \frac{dx}{dt} = \frac{\frac{1}{B} \exp(-Bt + C_1) + \frac{A}{B}}{x} \quad (12)$$

Since  $v(0) = 0$  and  $x(0) = 0$ ,  $C_1$  and  $C_2$  are determined as

$$C_1 = \ln A \quad (13)$$

$$C_2 = \frac{2}{B} \exp C_1 \quad (14)$$

Figure 2 shows the capillary filling speed and time graph and the length of the viscous liquid in the rectangular capillary. Here, we calculated it using the following experimental parameters:  $a$  of 8.8 mm,  $b$  of

15  $\mu\text{m}$ ,  $\rho$  of 1170  $\text{kg/m}^3$ ,  $\sigma \cos\theta$  of 40  $\text{mN/m}$ , and  $\mu$  of 32  $\text{mPa}\cdot\text{s}$ . The velocity rapidly decreases at the moment when the liquid poured into the capillary, and then the velocity gradually decreases with increasing time. The reason is easily explained: viscous friction is proportional to the length of the liquid and the capillary filling speed, as shown in eq.(4). That is, when the time variation of  $x$  is small, the time variation of viscous friction is also small. As the result, the capillary filling speed changes, as shown in Fig. 2(a).

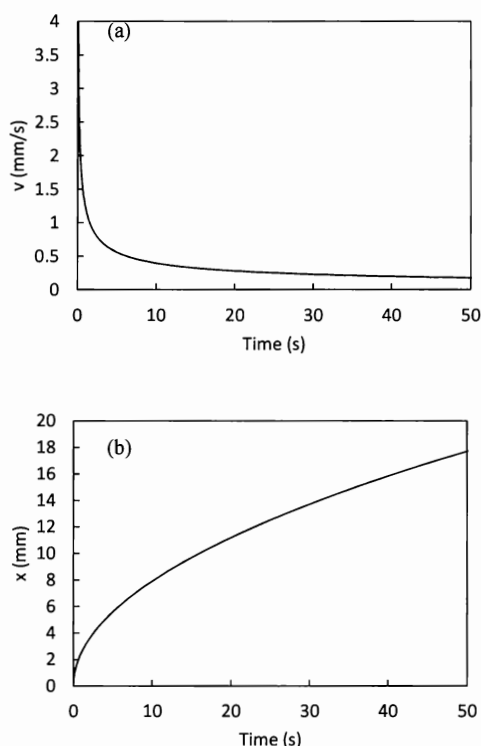


Fig. 2 (a) The velocity of viscous liquid in a rectangular capillary. (b) The length of the viscous liquid in the capillary.

図2 (a) 矩形断面キャピラリー中の粘性流体の液先端速度、(b) 矩形断面キャピラリー中の粘性流体の液先端位置

### 3. Experiment

The test sample was 1.5 mol/L 1-methyl-3propyl imidazolium iodide (MPII) in ethylisopropylsulfone (EiPS). The densities of mass of MPII and EiPS are 1540 and 1000  $\text{kg/m}^3$ , and the molar mass of MPII and EiPS are 252.1, and 136.2 g/mol. This ionic liquid MPII has widely been investigated in the

dye-sensitized solar cells because of its low viscosity (865 mPa·s) [19], and the viscosity of EiPS is 5.6 mPa·s [20]. These molecular structures are shown in Fig. 3.

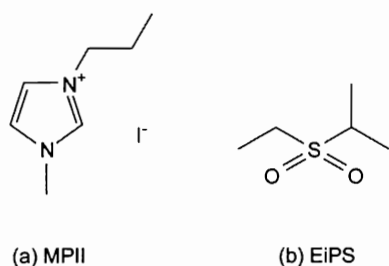


Fig. 3 Molecular structures of  
 (a) 1-methyl-3propyl imidazolium iodide (MPII) and  
 (b) ethylisopropylsulfone (EiPS)  
 図 3 イオン液体と溶媒の分子構造  
 (a) 1-methyl-3propyl imidazolium iodide (MPII),  
 (b) ethylisopropylsulfone (EiPS)

We prepared a cell as a rectangular capillary as shown in Fig. 1. The length, width, and thickness of the capillary were about 20 mm, 10 mm, and 15  $\mu\text{m}$ , respectively. The cell consisted of two indium-tin oxide (ITO)-coated glass substrates sandwiching two polyimide films as a spacer. The application of electric field to the ITO electrodes allows us to measure the electroviscous effect of the sample. The ITO electrode was covered with thin polyvinyl-alcohol film to prevent electrolysis of the ionic liquid on the electrode. A DC voltage was applied to the electrodes in all experiment. We recorded the capillary action after pouring the sample with a video camera.

#### 4. Experimental results and discussion

The voltage dependence of the capillary filling speed is investigated by pouring the MPII/EiPS solution into the cell. A DC voltage was applied to the ITO electrodes during the measurement. The capillary filling speed decreased with increasing voltage. We easily observed that the application of voltage slowed the capillary filling speed. Figure 4 shows the snapshots of the video recorded during the infiltration of the MPII/EiPS solution into the cell. In this

experiment, we measured the capillary filling speeds with 0 and 2 V. Thicknesses of both cells were about 15  $\mu\text{m}$ , which were determined by optical interference method before pouring the sample. Figure 4(a) shows that the MPII/EiPS solution is poured into the cell with the application of a voltage of 2 V. The figure caption of 6 sec means that we started to pour the sample into the cell at 6 seconds after recording a video. After 10 seconds from the first pouring, i.e. 16 sec in the video, we poured the same ionic liquid solvent into the other cell without voltage, as shown in Fig. 4(b). At that point, the front of the MPII/EiPS solution in the 2 V cell was reached to about 1/3 of the capillary length. Figure 4(c) shows the snapshot after 8 seconds from the second pouring. Since the capillary filling speed of 0 V was faster than that of 2 V, the front of the MPII/EiPS solution at 0 V caught up that of 2 V. Finally, the front of the MPII/EiPS solution of 0 V went in advance of that of 2 V, as shown in Fig. 4(d). As is evident from Fig. 4, the electroviscous effect of the MPII/EiPS solution is easily observed by capillary filling.

To quantitatively investigate the capillary action, we plotted the front position of the MPII/EiPS solution versus time by measuring them from the video. Figure 5 shows the plot of the front position  $x$  of the MPII/EiPS solution in the cell for 0, 1, and 2 V. We read the data of  $x$  from the front position at the center of width.  $x$  rapidly increases at the moment when the MPII/EiPS solution poured into the cell, and then  $x$  gradually increases with increasing time. This characteristic is quite similar to the theoretical curve, as shown in Fig. 2(b). It is clear from Fig. 5 that the time of arrival to the end of the capillary strongly depends on voltage. This indicates that we can control liquid flow by the external voltage of a few V.

We performed a curve fitting analysis for these experimental results. Figure 6 shows the measured and calculated results. The calculated results show good agreement with the measured results. On the other



(a) 6 sec



(b) 16 sec



(c) 24 sec



(d) 35 sec

Fig. 4 Snapshots of the video recorded during the infiltration of the MPII/EiPS solution into the cell.  
 図4 電圧無印加時と2V印加時における矩形断面キャピラリー中のMPII/EiPSの液面先端位置の比較

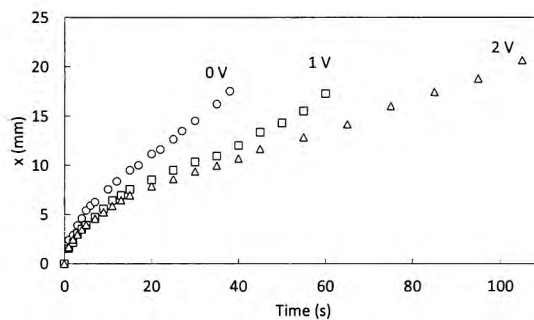
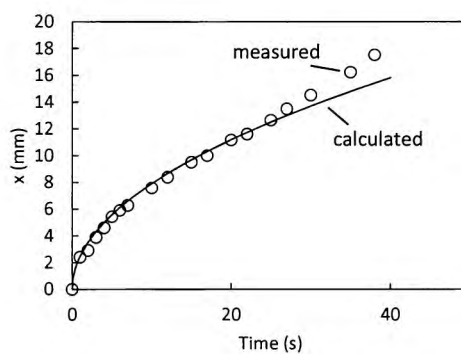
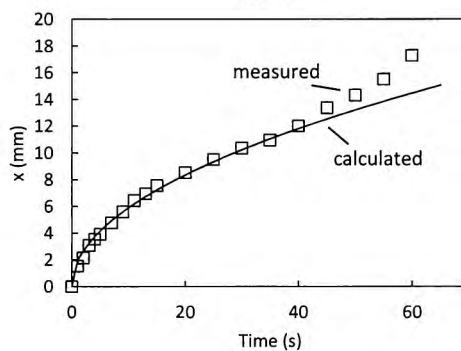


Fig. 5 Front position of the MPII/EiPS solution in the rectangular capillary with the application of a voltage of 0, 1, and 2 V.

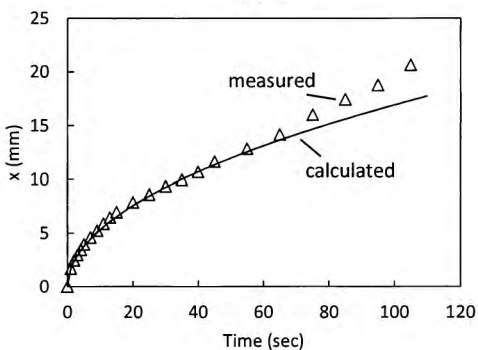
図5 矩形断面キャピラリー中のMPII/EiPSの液面先端位置の電圧依存



(a) 0 V



(b) 1 V



(c) 2 V

Fig. 6 Measured and calculated capillary-filling speed and time graph with the application of a voltage of 0, 1, and 2 V.

図6 矩形断面キャピラリー中のMPII/EiPSの液面先端位置の計算値と実験値の比較

Table 1. Physical parameters used for calculations

表 1 計算に用いた物理パラメータ値		0 V	1 V	2V
$a$	(mm)	8.8	8.8	8.8
$b$	( $\mu\text{m}$ )	15	11.5	15
$\rho$	( $\text{kg}/\text{m}^3$ )	1170	1170	1170
$\mu$	( $\text{mPa}\cdot\text{s}$ )	32	44	70
$\sigma\cos\theta$	( $\text{mN}/\text{m}$ )	40	40	40

hand, at near the end of the experimental results, the calculated results do not show a good match with the measured results. This is because the end of capillary is not taken into account in our calculation. Physical parameters used for the calculations are summarized in Table. 1. In the parameters, the viscosities for 0, 1, 2 V are estimated values in the previous study [16]. We performed curve fitting by changing  $\sigma\cos\theta$  concerning surface tension. If we independently measure surface tension and contact angle, the viscosity of ionic liquid solution can be determined by the capillary experiment.

## 5. Conclusions

We observed the electroviscous effect of MPII in EiPS by capillary action. The capillary filling speed and position were obtained from the video recorded during the infiltration, which showed a well agreement with theoretical calculations. The increase of a DC voltage to the sample decreased the capillary filling speed. This result indicated that the viscosity of the MPII/EiPS solution increased with increasing electric field. If we independently measure surface tension and contact angle, the viscosity and electroviscous effect of ionic liquid solution can be determined by the capillary experiment. The large electroviscous effect will become important role in development of electric devices using ionic liquids and electrolyte solutions. We believe that this study will contribute to provide a better knowledge for the development of electrochemical application using ionic liquids.

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(November 4, 2015 accepted)